



# Coordination chemistry and catalysis with mixed ligands associating iminophosphorane to thiolate or phenolate

Thi-Phuong-Anh Cao

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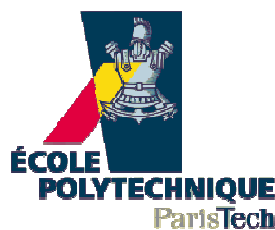
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## THESE

Présentée pour obtenir le titre de

**Docteur de l'Ecole Polytechnique,**

Spécialité Chimie

Par **Thi Phuong Anh CAO**

### **COORDINATION CHEMISTRY AND CATALYSIS WITH MIXED LIGANDS ASSOCIATING IMINOPHOSPHORANE TO THIOLATE OR PHENOLATE**

Thèse soutenue le lundi 24 septembre 2012 à 14h00

à Ecole Polytechnique 91128 Palaiseau Cedex FRANCE

#### Composition du jury

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## ***Publications and notable communications***

[1] Clare M. Bakewell, Thi-Phuong-Anh Cao, Nicholas Long, Xavier F. Le Goff, Audrey Auffrant and Charlotte K. Williams, “*Yttrium Phosphasalen Initiators for rac-Lactide Polymerization: Excellent Rates and High iso-Selectivities*”, **Journal of the American Chemical Society**, **2012** (DOI: 10.1021/ja310003v).

[2] Thi-Phuong-Anh Cao, Antoine Buchard, Xavier F. Le Goff, Audrey Auffrant and Charlotte K. Williams, “*PhosphaSalen Yttrium Complexes: Highly Active and Stereoselective Initiators for Lactide Polymerization*”, **Inorganic Chemistry**, **2012**, 51(4), 2157-2169.

[3] Thi-Phuong-Anh Cao, Stéphanie Labouille, Audrey Auffrant, Yves Jean, Xavier F. Le Goff and Pascal Le Floch, “*Pd(II) and Ni(II) Complexes Featuring a “Phosphasalen” Ligand: Synthesis and DFT Study*”, **Dalton Transactions**, **2011**, 40, 10029-10037.

[4] Thi-Phuong-Anh Cao, Elina Payet, Audrey Auffrant, Xavier F. Le Goff and Pascal Le Floch “*Facile Synthesis of Bifunctional Ligands Using LiCH<sub>2</sub>PPh<sub>2</sub>=NPh Obtained From [PhNH-PPh<sub>3</sub>]<sup>+</sup>[Br<sup>-</sup>]*”, **Organometallics**, **2010**, 29, 3991-3996.

[5] Clare M. Bakewell, Thi-Phuong-Anh Cao, Nicholas Long, Xavier F. Le Goff, Audrey Auffrant and Charlotte K. Williams, “*Yttrium Phosphasalen Initiators for rac-Lactide Polymerization*”, submitted to **Organometallics**.

[6] Thi-Phuong-Anh Cao, Xavier F. Le Goff, Gregory Nocton, Audrey Auffrant, “*Tuning of Oxidation Locus on Metal Complex: the Geometric and Electronic Structure of One-Electron Oxidated Nickel Phosphasalen Complex*”, working paper.

[7] Thi-Phuong-Anh Cao, Thibault Cheisson, Xavier F. Le Goff, Pascal Le Floch and Audrey Auffrant, “*Nickel Complexes as Highly Active Catalysts for the Dimerisation of Ethylene*”, working paper.

[8] Thi-Phuong-Anh Cao, Stéphanie Labouille, Antoine Buchard, Xavier F. Le Goff, Duncan Carmichael, Jean Yves, Audrey Auffrant, Pascal Le Floch and Charlotte K. Williams, “*Phosphasalen complexes: what phosphorus changes*”, Oral Communication (20 min), Congress “*European Workshop in Phosphorus Chemistry*”, 22-23 March **2012**, Rennes.

[9] Thi-Phuong-Anh Cao, Stéphanie Labouille, Audrey Auffrant, Yves Jean, Xavier F. Le Goff and Pascal Le Floch, “*Synthesis and Coordination of a Phosphasalen ligand*”, Oral Communication (20 min), Congress: “*Journées de chimie de coordination de la Société Chimique de France*”, 3-4 February **2011**, Angers.



# Guide to the reading

## Compound numbering

Synthesised compounds are numbered as **1,2,3**, etc. Reference compounds existing in the literature are named using a letter and a number. The letter refers to the metal if the compounds are metal complexes (e.g. **Al1**, **Ni2**, **Y3**, etc.), and is **X** if not (e.g. **X1**).

## List of abbreviations

**COD**: 1,5-cyclooctadiene

**DABCO**: 1,4-diazabicyclo[2,2,2]octane

**DFT**: Density Functional Theory

**DME**: Dimethoxyethane

**EPR**: Electron Paramagnetic Resonance

**Et**: Ethyl

**Fc**: Ferrocene

**GPC**: Gel Permeation Chromatography

**HOMO**: Highest Occupied Molecular Orbital

**iPA**: isoPropanol

**iPr**: isoPropyl

**KHMDS**: Potassium bis(trimethylsilyl)amide

**LA**: Lactide

**LUMO**: Lowest Occupied Molecular Orbital

**M**: mol/L

**MALDI-ToF**: Matrix Assisted Laser Desorption Ionisation-Time of Flight

**MAO**: Methylaluminoxane

**Me**: Methyl

**NBO**: Natural Bond Orbital

**nBu**: n-Butyl

**NMR**: Nuclear Magnetic Resonance

**ORTEP**: Oak Ridge Thermal-Ellipsoid Plot Program

**PCM**: Polarisable Continuum Model

**PDI**: Polydispersity Index

**Ph**: Phenyl

**PLA**: Polylactic Acid

**rac-**: racemic mixture

**ROP**: Ring Opening Polymerisation

**SOMO**: Singly Occupied Molecular Orbital

**tBu**: *tert*-Butyl

**THF**: Tetrahydrofuran

**TMS**: Trimethylsilyl

**TOF**: Turn Over Frequency

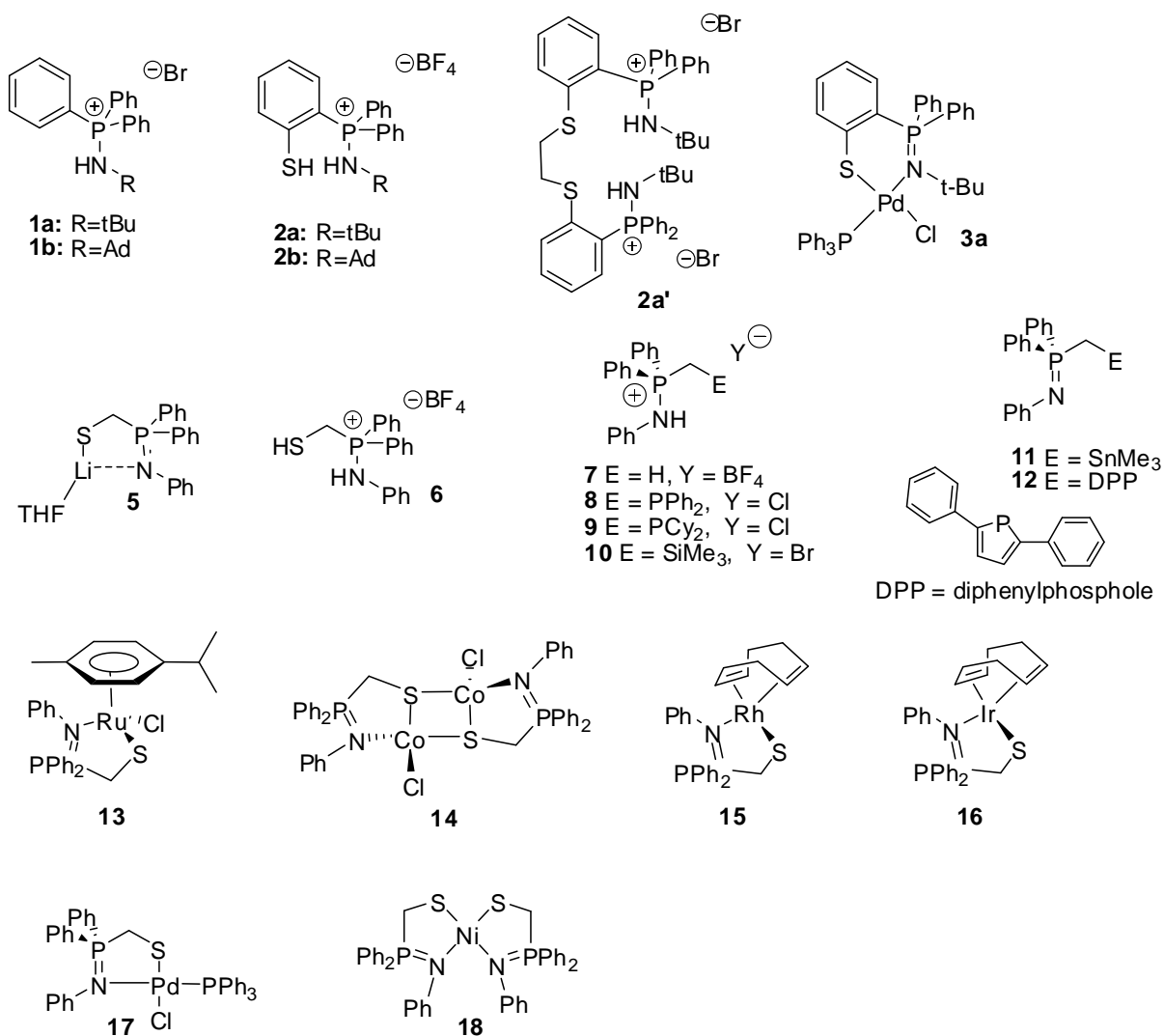
**TON**: Turn Over Number

**TS**: Transition State

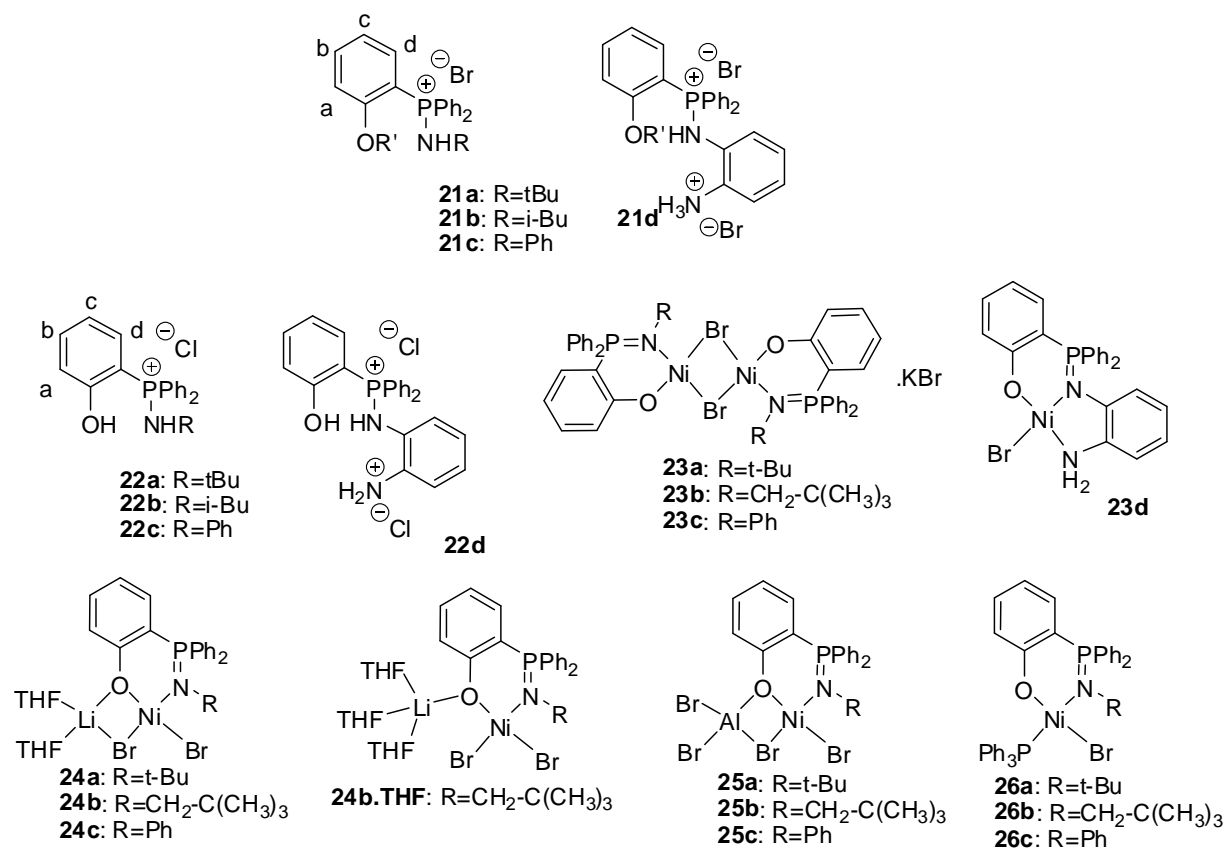


# List of Synthesised Compounds

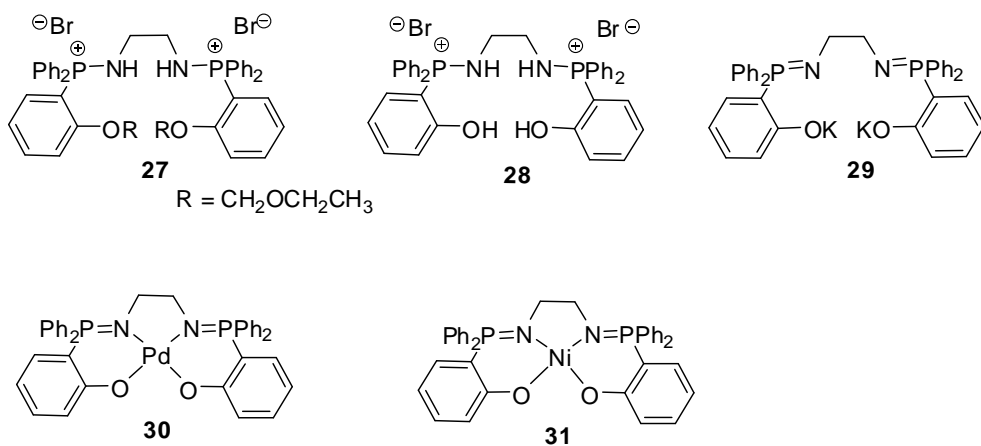
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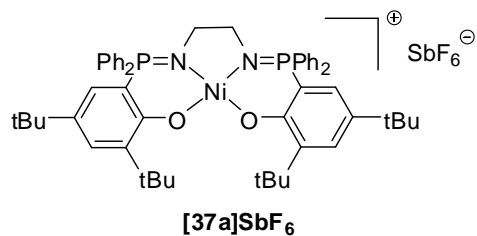
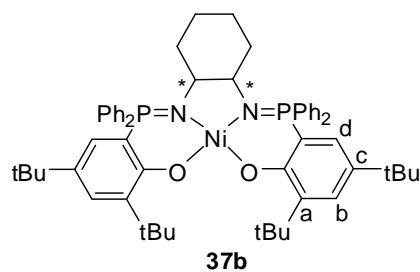
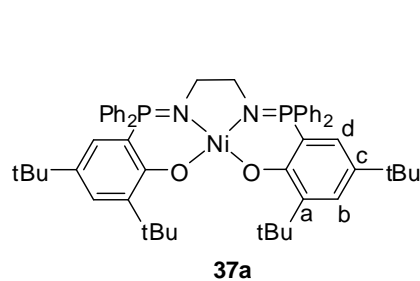
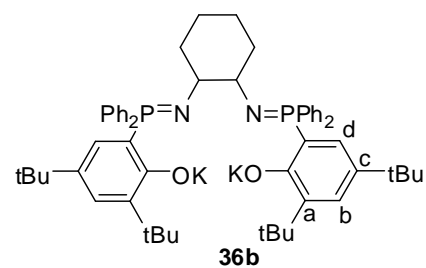
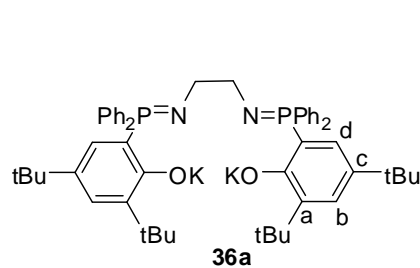
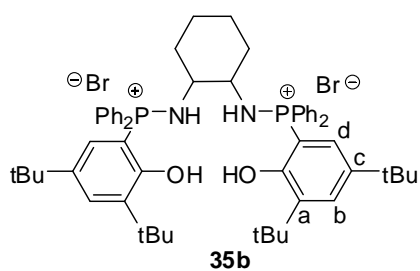
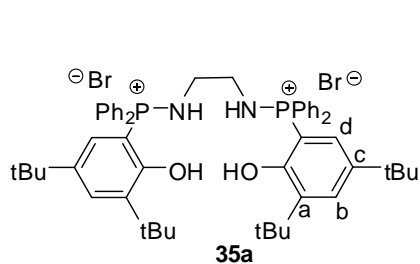
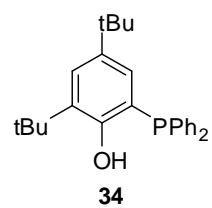
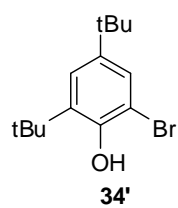
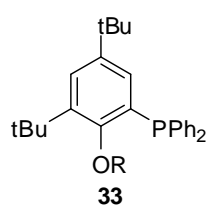
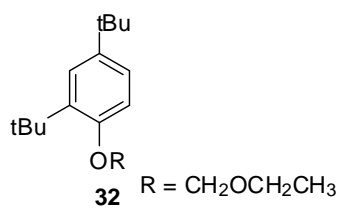
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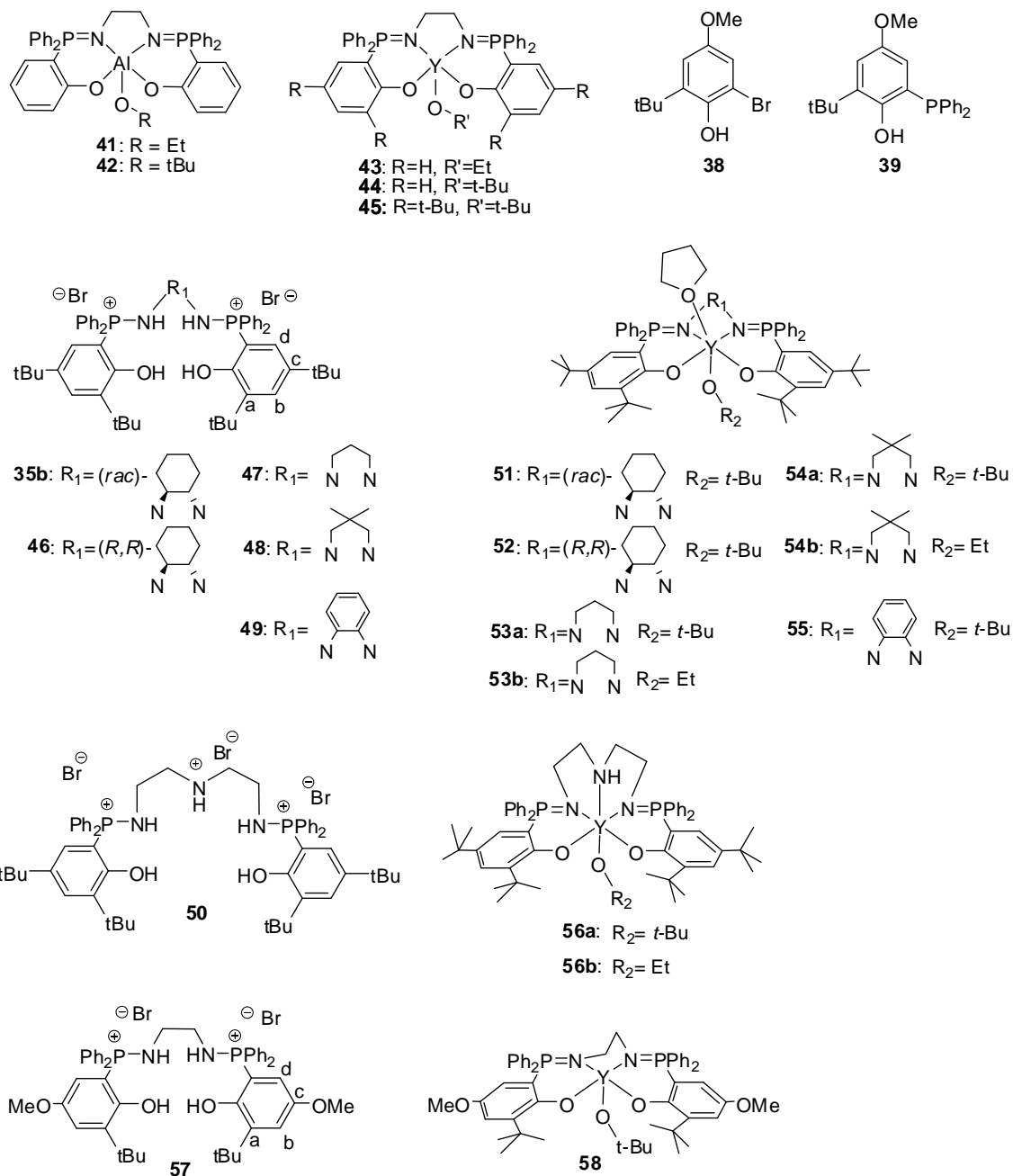
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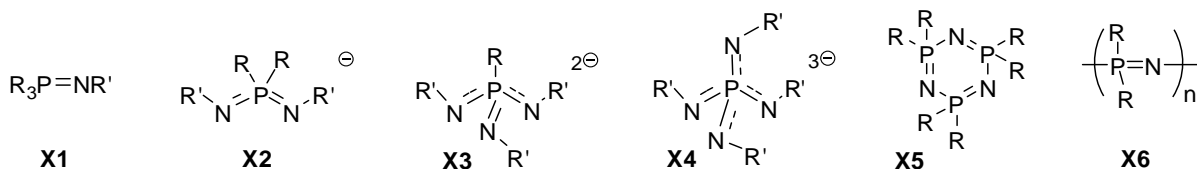
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# Introduction

## The Iminophosphoranes

### I . Introduction to Iminophosphorane

The class of iminophosphoranes, compounds with formal P-N double bonds, is a well established, yet still not thoroughly explored class of compounds in coordination chemistry and synthesis. The first iminophosphoranes were synthesized by Staudinger and Meyer in 1919,<sup>1</sup> they exist under various nomenclatures: iminophosphorane, phosphazene, phosphinimine. Successive replacement of R group at the phosphorus atom in simple neutral iminophosphoranes **X1** (Scheme 1) leads to monoanionic diiminophosphinate **X2**, dianionic triiminophosphonate **X3** and trianionic tetraiminophosphate **X4**.<sup>2</sup> These compounds could also exist in polymeric or cyclic forms (**X5** and **X6** respectively). Cyclic and polymeric forms of neutral iminophosphorane are commonly called cyclophosphazene and polyphosphazene. They are interesting agents in biochemistry, especially in drug design and drug delivery,<sup>3</sup> as their metabolisms yield only ammonium and phosphate, ions already largely involved in the cellular functioning.



*Scheme 1. Different forms of iminophosphorane compounds*

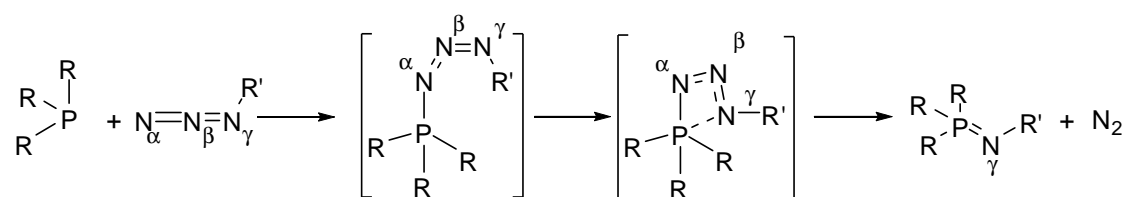
The work presented here focuses on simple neutral iminophosphoranes of the form **X1**.

## 1. Synthesis

Whereas a great number of synthetic approaches exist for the preparation of iminophosphoranes, only the three most used methods are presented here, which are the Staudinger reaction (first reported in 1919), the Kirsanov reactions (discovered in 1950), which was modified by Horner and Oediger in 1959, and more recently, the aza-Mitsunobu reaction.

### *Staudinger Reaction*

The Staudinger reaction, discovered in 1919,<sup>1</sup> is the oldest synthetic approach to iminophosphoranes, yet it is still by far the most commonly used method.<sup>4</sup> The reaction involves an nucleophilic addition of an azide  $R'N_3$  to a  $P^{III}$  centre (e.g. a phosphine  $R_3P$ ), followed by nitrogen elimination (Scheme 2). The Staudinger mechanism has been studied by DFT calculations by the group of Wang.<sup>5</sup> Experimentally, since 1968, by the use of  $^{15}N$ , Bock and coworkers have identified that the nitrogen in the iminophosphorane function is indeed the  $N^\gamma$  atom. The phosphazide intermediate was also isolated in some case by using factors inhibiting the formation of the four-membered ring, such as steric effects (bulky substituents on phosphorus or nitrogen atoms),<sup>6</sup> or electronic effect (increasing electron density on the phosphorus atom and decreasing the one on the  $N^\gamma$  atom).<sup>7</sup> A review about stabilized phosphazide intermediates was published by Bourissou and coworkers in 2009.<sup>8</sup>

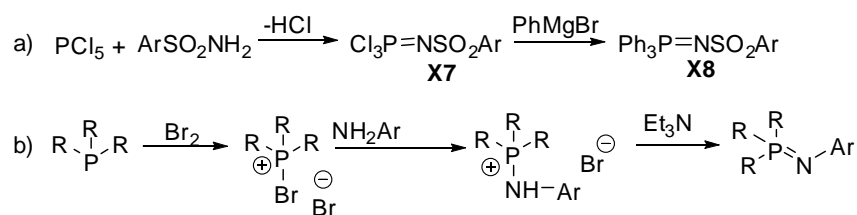


*Scheme 2. Staudinger reaction*

The advantages of the Staudinger method may in part be ascribed to the fact that during this reaction, nitrogen ( $N_2$ ) is released as the only side product, thus rendering unnecessary further purification of the iminophosphorane product. Furthermore, the reaction could be applied to a wide range of  $P^{III}$  centres containing different types of substituents. However, the major inconvenience of this method is the risk of explosion associated with most azide derivatives. This is a major drawback to the variation of the nitrogen substituent  $R'$ , as well as for large-scale synthesis.

### *Kirsanov Reaction*

The Kirsanov method for the synthesis of iminophosphoranes originated from a reaction discovered by Kirsanov in 1950 (Scheme 3a).<sup>9</sup> Reaction of  $PCl_5$  with phenylsulfonamide resulted in the formation of compound **X7** by nucleophilic substitution on two chlorides. This compound **X7** in turn was transformed into P,P,P-triphenyl iminophosphorane **X8** by nucleophilic substitution of the three remaining chlorides with phenyl magnesium bromide.



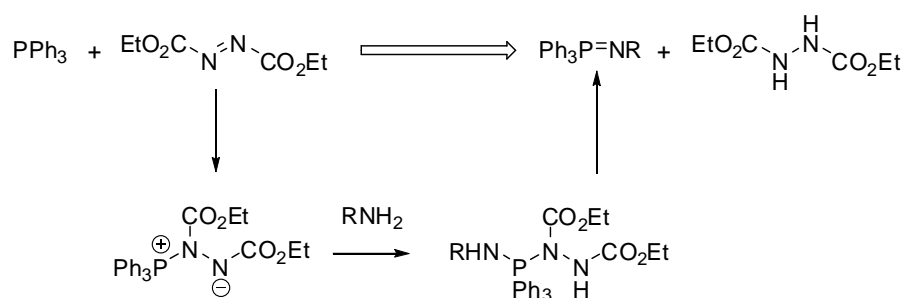
Scheme 3. Kirsanov reaction (a) and Horner/Oedinger variation (b).

In 1959, Horner and Oedinger developed the modern version of the Kirsanov reaction by using in situ generated  $\text{PR}_3\text{Br}_2$  compounds, obtained from the bromination of a tertiary phosphine, instead of  $\text{PCl}_5$  (Scheme 3b).<sup>10</sup> The bromination product underwent a nucleophilic substitution with aromatic amine in the presence of two equiv. of triethylamine, to give the corresponding iminophosphoranes in high yields.

Several years later, Zimmer and Singh applied this method to alkylamines and found that the reaction got stuck at the formation of the aminophosphonium bromide salt  $[\text{R}_3\text{PNHR}']^+[\text{Br}]^-$ .<sup>11</sup> Likely, triethylamine is not strong enough to deprotonate these salts. A second step, employing stronger bases such as MeLi, KHMDS is required to generate the corresponding iminophosphoranes. This necessity of a second step is not a drawback, but quite the opposite: aminophosphonium salts, as opposed to their iminophosphorane analogues, are air- and water stable, and thus easy to manipulate and in most cases easy to isolate from the reaction mixture. They can be prepared in big quantities.

Another advantage of this method over the Staudinger reaction is the variability brought to the nitrogen residue  $\text{R}'$ , as virtually any primary amine may be employed in this reaction. This opens the route towards a great variety of derivatives, including chiral iminophosphoranes, which is important notably for catalysis. Furthermore, the scope of applications of this reaction does not involve solely amines (aromatic and aliphatic), but also hydrazines ( $\text{H}_2\text{NNXY}$ ),<sup>12</sup> hydrazones ( $\text{H}_2\text{NN}=\text{CXY}$ ),<sup>13</sup> hydrazide ( $\text{RC(O)-NHNH}_2$ ),<sup>14</sup> etc.

### Aza-Mitsunobu Reaction



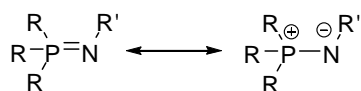
Scheme 4. Aza-Mitsunobu reaction

The aza-Mitsunobu method for the synthesis of iminophosphorane was developed in the 1970s. It is based on the reaction of triphenylphosphine with diethylazodicarboxylate (DEAD) and a primary amine  $\text{R}'\text{NH}_2$  (Scheme 4). Even though this one-pot reaction proceeds with excellent

yields, its scope is limited to amines with electron withdrawing groups, with a proton sufficiently acidic to allow its abstraction by the azodicarboxylate.

## 2. Structural Data and Electronic Properties: DFT Calculations

Two electronic configurations are conceivable for an iminophosphorane: a compound with double bond P-N or a zwitterion.



*Scheme 5. Two descriptions of an iminophosphorane*

Based on literature data, the bond length of an iminophosphorane in the solid state is comprised between 1.54 Å and 1.64 Å. Taking into account the fact that the sum of the covalent radii of nitrogen and phosphorus is 1.84 Å for a single bond and 1.62 Å for a double bond,<sup>15</sup> these two limiting values indicate that structurally, the P-N bond in iminophosphoranes is closer to a double bond.

According to the Valence Shell Electron Pair Repulsion (VSEPR), the angle P-N-R in iminophosphorane would be around 109° if the P-N bond is single bond (in zwitterionic structure), and around 120° if it is a double bond. Experimentally, this angle is measured between 119° and 143°. Thus, this observation also points towards a double bond P-N in iminophosphorane.

However, the hypothesis of the double bond P-N is inconsistent with calculated energy required for the free rotation around the P-N bond, which is very low (2.1 kcal/mol). Theoretical studies have been carried out in order to understand the electronic nature of this P-N bond.<sup>16</sup> Another study was done by NBO (natural bonding orbital) calculations<sup>17</sup> on model compound PH<sub>3</sub>NH, using density functional theory (DFT) with b3lyp functional and 6-31G\* basis set for all atoms. Calculations for model compound of imines were also carried out for the sake of comparisons.

|                     |   |   |
|---------------------|---|---|
|                     | $  \begin{array}{c}  \text{qP } +1.07 \\  \text{H} \quad \text{qN } -1.32 \\  \diagdown \quad \diagup \\  \text{H}-\text{P}=\text{N} \\  \diagup \quad \diagdown \\  \text{H} \quad \uparrow \quad \text{H}  \end{array}  $ | $  \begin{array}{c}  \text{qC } -0.10 \\  \text{H} \quad \text{qN } -0.63 \\  \diagdown \quad \diagup \\  \text{H}-\text{C}=\text{N} \\  \diagup \quad \diagdown \\  \text{H} \quad \uparrow \quad \text{H}  \end{array}  $ |
| Wiberg index        | 1.34  | 2.03  |
| π orbital occupancy | 1.76  | 1.99  |

q<sub>x</sub>: NBO charge at atom X

*Scheme 6. NBO analysis for model compounds of iminophosphorane and imine*

In fact, NBO analysis tends to neglect the delocalisation of the systems and tries to localise the electrons in 1-centre and 2-centre regions of the molecules. Thus, NBO analysis gives a vision

very close to the Lewis model. The results obtained for the model compounds were in favour of a single bond P-N in iminophosphorane. Whereas the Wiberg index of the imine model is 2.03, indicative of a double bond, the one for the iminophosphorane model is close to 1 (1.34 vs 2.03 in imine). Furthermore, the charges at N and P atoms fit perfectly to the dipolar description of the P-N bond. Thus according to these results, for iminophosphoranes, the zwitterionic form seems to be more suitable than a double bond model.

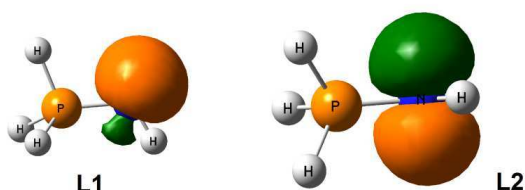


Figure 1. Two lone pairs on Nitrogen atom

According to the zwitterionic form, two lone pairs of electron should be present on nitrogen. Indeed, the NBO analysis supports the existence of these two free electron pairs, which are of highest energies among the occupied orbitals in the molecule (Figure 1). The first one is a hybrid  $sp^x$  (47%*s*, 53%*p*, occupancy 1.88) and the second one a pure *p* orbital (occupancy 1.75). These values of occupancies less than 2 imply a certain degree of delocalisation of electrons on to other atoms. Indeed, as would be seen later, the electron delocalisation from these two orbitals to the unoccupied  $\sigma^*(P-H)$  and Rydberg *d*-orbitals of the phosphorus atom is significant. It is responsible for the negative hyper-conjugation which reinforce the P-N bond, hence the shortening of the P-N bond (Figure 2 and 3) .

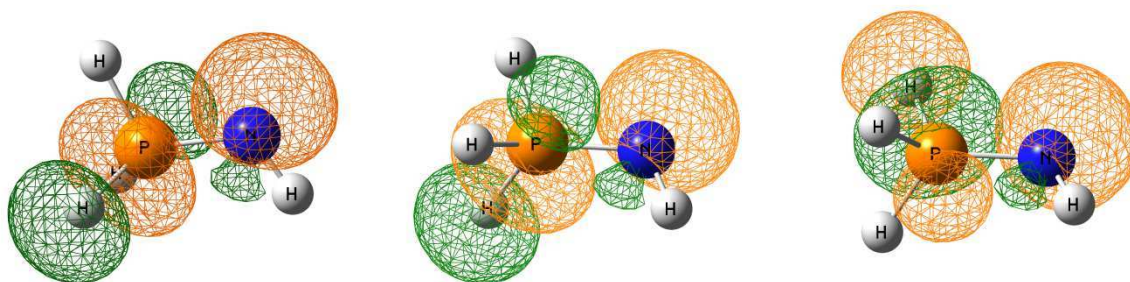


Figure 2. Stabilising interactions between the first lone pair **L1** of nitrogen and three  $\sigma^*(P-H)$ . Stabilisation energy ~17.3 kcal/mol

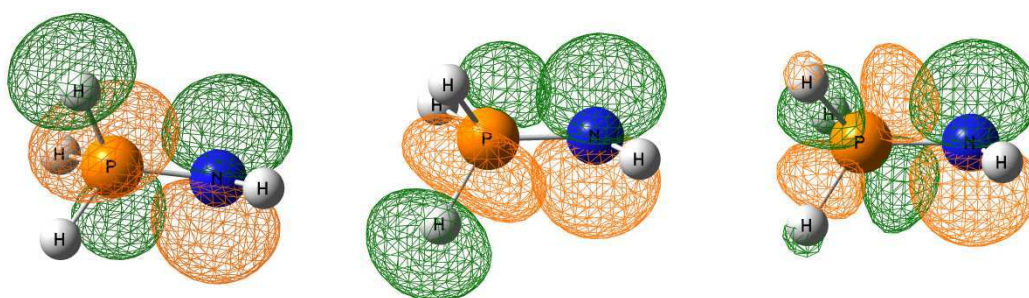


Figure 3. Stabilising interactions between the second lone pair **L2** of nitrogen and two  $\sigma^*(\text{P-H})$  ( $\sim 16.5$  kcal/mol each), and d-orbital of the phosphorus atom ( $\sim 9.0$  kcal).

Both lone pairs L1 and L2 participate in  $\pi$ -interactions with  $\sigma^*(\text{P-H})$  orbitals or Rydberg orbitals on P of appropriate symmetry. As these orbitals are of higher energy, these interactions are stabilising for L1 and L2. In total, such hyper-conjugations bring stabilisation energy of approximately 18 kcal/mol to L1 and 45 kcal/mol to L2.

The real molecular orbitals are obviously different from these natural orbitals described above. But the difference is not huge: the corresponding Kohn-Sham orbitals from DFT calculations on the model compound of iminophosphorane are presented in Figure 4. They sensibly have the same forms as L1 and L2. Just as L1 and L2, they are the two highest occupied orbitals of the molecule and their relative energies do not change.

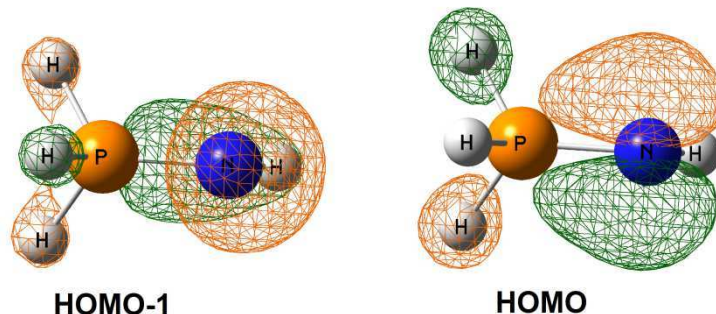


Figure 4. HOMO and HOMO-1 in the real DFT description.

Thus from the calculational analysis, it is clear that the P-N bond in iminophosphorane is in reality a single bond, reinforced with negative hyper-conjugations from the lone pairs of the nitrogen onto other orbitals on the phosphorus atoms. The zwitterionic form correctly represents the nature of the bond, as well as the charge at P and N atoms, but could not describe these hyper-conjugations which are responsible for the strong bond P-N (hence the shortening of P-N bond, for example). The official representation  $\text{P}=\text{N}$  double bond, even though less correct, is adopted for the sake of simplicity and the coherence with the literature.

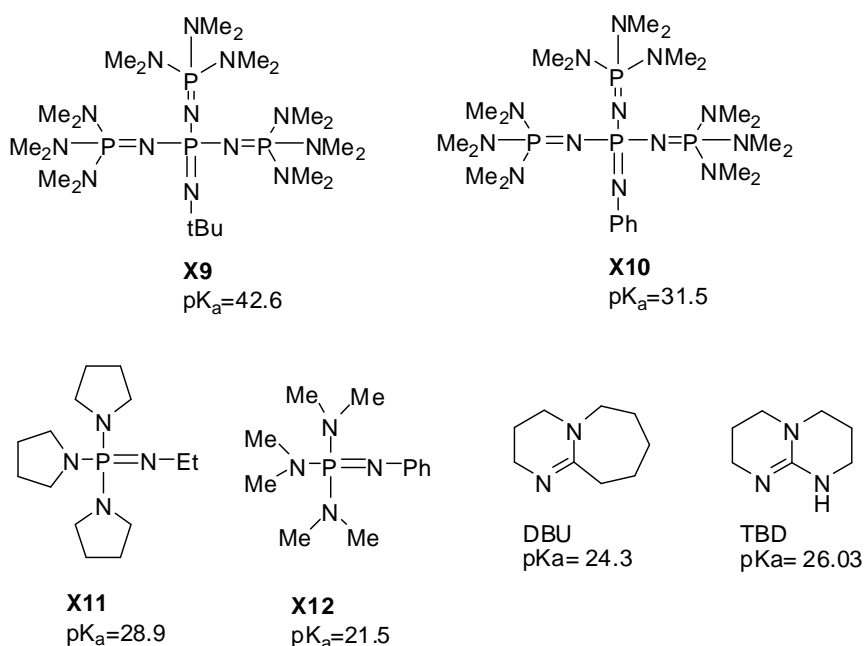


### 3. Reactivities

The reactivities of iminophosphoranes revolve around the positive charge on the phosphorus atom and the negative charge on the nitrogen atom. They could be seen as to resemble a lot to those of phosphorus ylides and amides.

#### Basicity

Thanks to the important negative charge at nitrogen, iminophosphoranes behave as strong bases. The first representative of iminophosphorane bases was prepared in the 1970s by Lischewski and co-workers.<sup>18</sup> In 1987, Schwesinger and co-workers synthesised the iminophosphorane **X9**, which is the strongest neutral base that has been developed to date. Since then, the design of superbases from iminophosphoranes has been thoroughly studied, especially by the Koppel group, both theoretically and experimentally.<sup>19</sup> The basicity of the iminophosphoranes increases with the donating ability of substituents. On going from simple iminophosphoranes, to amino-, and then phosphazo-substituted iminophosphoranes, significant enhancements in basicity have been observed. By careful selection of substituents, various iminophosphorane-containing superbases have been prepared, which are among the strongest ever to exist. Fine tuning of basicity on these systems is also possible. Indeed, bases of  $pK_a$  ranging from 10 to 42 (in acetonitrile) have been obtained.<sup>19b, 20</sup> Examples of these systems are presented in Scheme 7, along with several other bases for comparison.

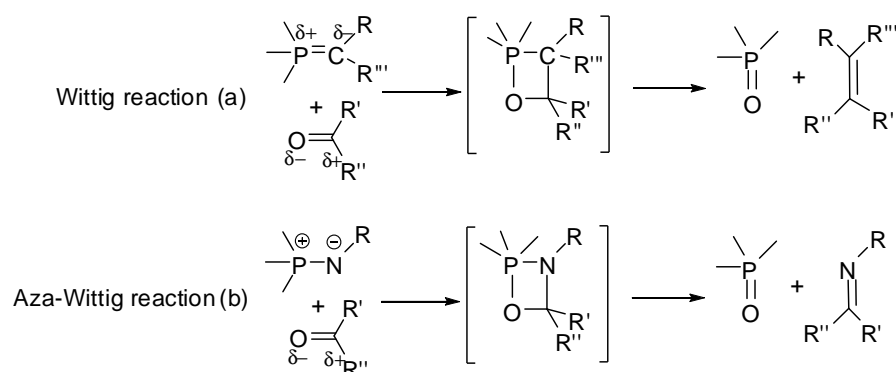


Scheme 7. Examples of iminophosphorane bases and some common non-iminophosphorane bases.

These bases present various advantages for utilities in organic chemistry. Firstly, thanks to their common bulkiness, their nucleophilicity is greatly reduced. Thus, they could give excellent

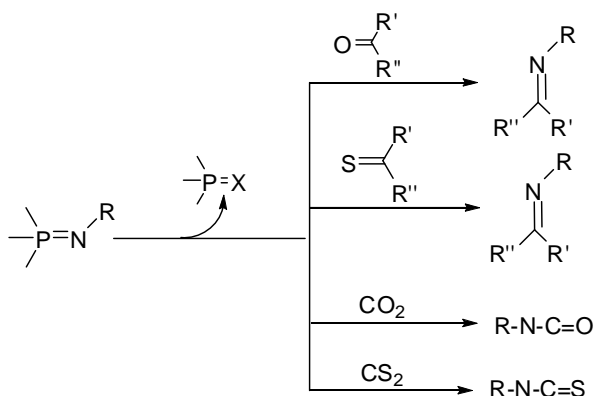
selectivity in reactions requiring activation by basicity, but not nucleophilicity (e.g. enolate and peptide alkylations, catalytic aldol reactions, desilylations, and even aromatic and alkynyl deprotonations). Secondly, as they act without metallic cations and due to their bulkiness, the anions obtained from the deprotonation by these bases are often “naked”, and thus highly reactive. Thirdly, as they are generally soluble in organic solvents and exist in solid form at room temperature, their handling is generally easy.

### Aza-Wittig Reaction



Scheme 8. Wittig and Aza-Wittig reaction

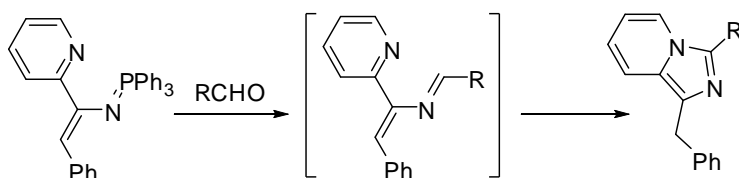
The Aza-Wittig reaction is the most common applications of iminophosphoranes, as has been evidenced by many reviews from different groups.<sup>21</sup> First discovered by Staudinger in 1921 (two years after he synthesised the first iminophosphorane), the reaction is an analogue of Wittig reaction, applied for phosphorus ylides.<sup>22</sup> When an iminophosphorane reacts with a carbonyl or thiocarbonyl, an imine is formed along with the elimination of one phosphinoyl molecule. The mechanism of the reaction is supposed to be similar to the one of the Wittig reaction. Several theoretical studies have been carried out, confirming this hypothesis.<sup>23</sup> In some cases, intermediates were also isolated.<sup>24</sup>



Scheme 9. Aza-Wittig reaction

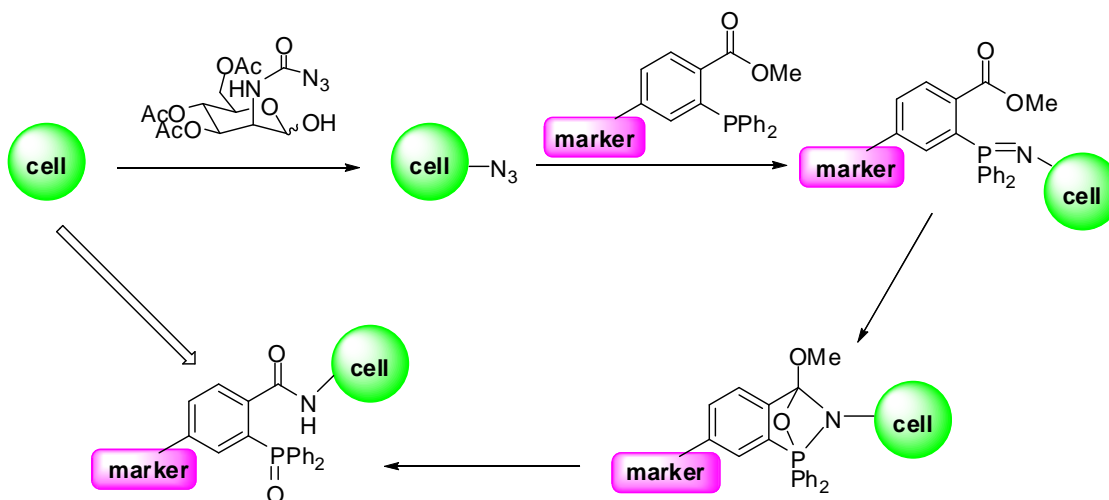
The reaction is not limited only to carbonyl or thiocarbonyl, but could be applied to isocyanates ( $R'N=C=O$ ), or thiocyanates ( $R'N=C=S$ ), giving hetero-disubstituted carbodiimides ( $R-N=C=N-R'$ ). On the other hand, using  $CO_2$  and  $CS_2$  allows the synthesis of isocyanates and thiocyanates.

The Aza-Wittig reaction is often used for the synthesis of heterocycles in organic chemistry. This application has been the subject of various reviews in the literature.<sup>25</sup> An example of one of those syntheses is presented in Scheme 10.



*Scheme 10. Example of Aza-Wittig reaction in heterocycles synthesis.*<sup>26</sup>

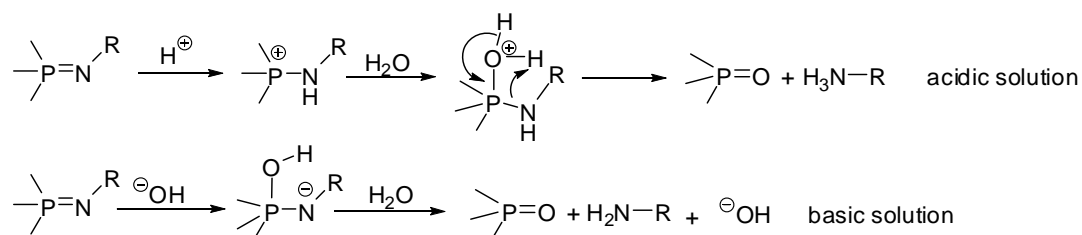
This reaction could be coupled to a Staudinger reaction, and the total process is called a Staudinger ligation.<sup>27</sup> The advantage of such process lies in the highly selectivity of the reactions and the absence of water in the final mixture, which is helpful in some cases. The reaction is mostly used in biochemistry for the grafting of phosphorus-containing marker to the glycoside on the cellular surface. The phosphine, bearing the marker, and the azide, grafted on to the cell's surface, react quickly and selectively in aqueous environment to give iminophosphorane. This latter is however not stable in water, but is trapped quickly by an intramolecular Aza-Wittig reaction with an ester in close proximity to give a stable amide. The marker is thus linked to the cell's surface by this amide bond.



*Scheme 11. Staudinger ligation in cell surface engineering.*

## Hydrolysis

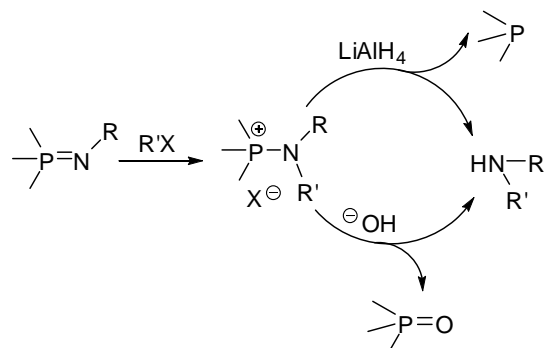
Because of the zwitterionic structure, iminophosphoranes are generally decomposed by water. This involves either the attack of proton on the negatively charged nitrogen, or the nucleophilic attack of hydroxide on the positively charged phosphorus, depending on the pH. This decomposition explains the instability of iminophosphoranes in water and the facile hydrolysis of alkyliminophosphoranes (with better basicity) in air.



Scheme 12. Hydrolysis of iminophosphorane.

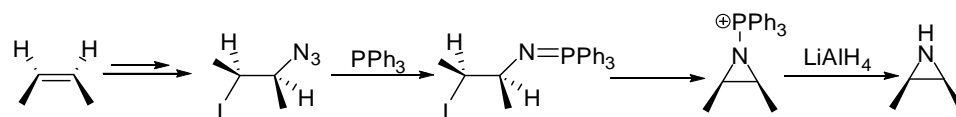
## Alkylation

The negatively charged nitrogen could be alkylated by nucleophilic substitution with alkylhalide. The resulting phosphonium salt could be converted into secondary amine by hydrolyse (with hydroxide, for example) or by reduction with  $\text{LiAlH}_4$ .



Scheme 13. Alkylation of iminophosphorane

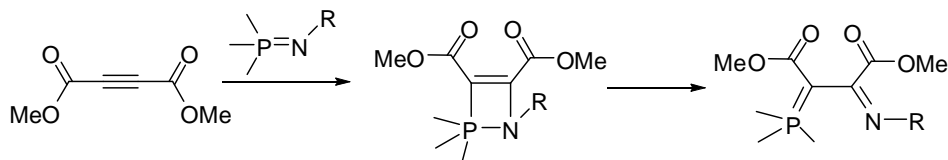
This reaction has been exploited by Hassner and co-workers since 1970 for the synthesis of arizidines.<sup>28</sup>



Scheme 14. Synthesis of arizidines by alkylation of iminophosphorane.

### Insertion

Iminophosphoranes could insert into triple bonds, a mechanism which closely resembles to the Aza-Wittig reaction. A four-membered intermediate is obtained directly from the insertion. The ring-opening of this intermediate gives compounds containing imine and phosphorus ylide functions in the  $\alpha$  position.



Scheme 15. Insertion of iminophosphorane into alkynes.

## 4. Applications in Coordination Chemistry: Overview

The NBO analysis on model compound of iminophosphorane clearly shows the presence of two lone pairs on the nitrogen atom, which are the HOMO and HOMO-1 orbitals, and the absence of a real  $\pi$ -system. The ability of iminophosphorane to coordinate to metal centres lies in these two lone pairs. In fact, iminophosphoranes act as strong  $\sigma$  and  $\pi$  donors (thanks to the HOMO-1 and HOMO respectively), and does not have  $\pi$ -accepting ability. These ligands thus preferably coordinate to “hard” metal centres, as “soft” centres are more stabilised by  $\pi$ -interaction from metal to ligand.

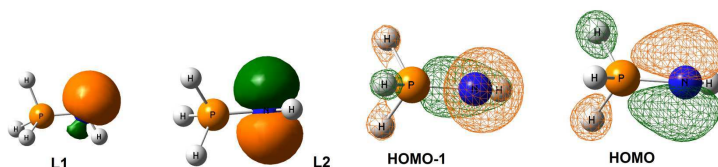
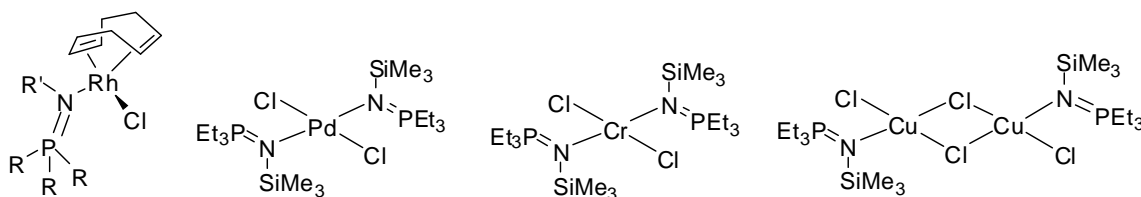


Figure 5. Two lone pairs at the nitrogen atom (NBO analysis) and their respective form (Kohn-Sham orbitals) in real system.

A simple search in the CCDC database shows that in complexes the angle P-N-M has a median value of  $115^\circ$ , and centred around  $120^\circ$ , and the values for P-N-R angle have a median of  $122^\circ$  and centred around  $120^\circ$ . In almost all complexes, the nitrogen atom is in the same plane as R, P, and M. These data clearly indicate that coordination is done by the HOMO-1, and involves the  $\sigma$ -donation from the ligand to the metal.

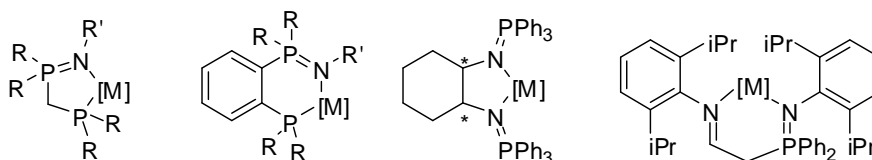
Complexes of simple iminophosphoranes are known, with metals such as magnesium,<sup>29</sup> copper, zinc, chromium(II), palladium or rhodium, etc.<sup>30</sup> It is however worth reminding that because of the lack of  $\pi$ -accepting ability, the coordination of iminophosphoranes with “soft” metal centres are not very strong. The coordinated iminophosphoranes are easily exchanged with other ligands. For example, the rhodium complexes  $[\text{RhL}_2\text{Cl}(\text{R}'\text{N}=\text{PR}_3)]$  ( $\text{L}_2 = \text{COD}$ ) exist in

equilibrium with the parent compounds  $[\text{RhL}_2\text{Cl}]_2$  and  $\text{R}'\text{N}=\text{PR}_3$ , this equilibrium being dependent on substituents on N and P, temperature, and the ratio  $\text{Rh}/\text{R}'\text{N}=\text{PR}_3$ .



*Scheme 16. Examples for complexes of simple iminophosphorane ligands.*

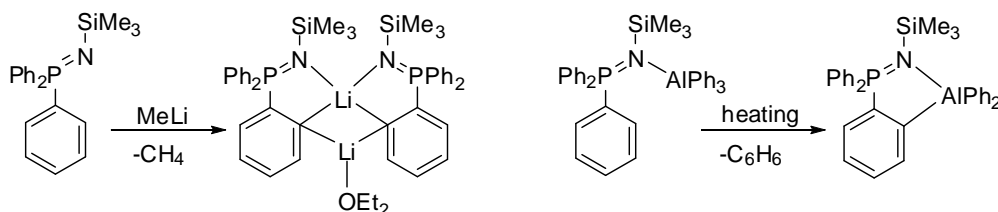
In order to circumvent this limitation, iminophosphoranes are often combined with other donors to obtain multidentate ligands, very often hetero-multidentate ligands. These ligands offer a much larger scope of coordination and could give more stable complexes. Scheme 17 shows examples of such systems: phosphino-iminophosphoranes reported by Cavell and co-workers,<sup>31</sup> chiral bis-iminophosphoranes elaborated by Reetz and co-workers,<sup>32</sup> imine-iminophosphorane ligand by Stephan and coworkers<sup>33</sup>.



*Scheme 17. Examples of multidentate ligands containing iminophosphorane group(s).*

Among the most interesting ligands based on iminophosphorane function are those containing carbanions. In fact, the particular dipolar structure of iminophosphorane allows the stabilisation of carbanions in close proximity by different effects.

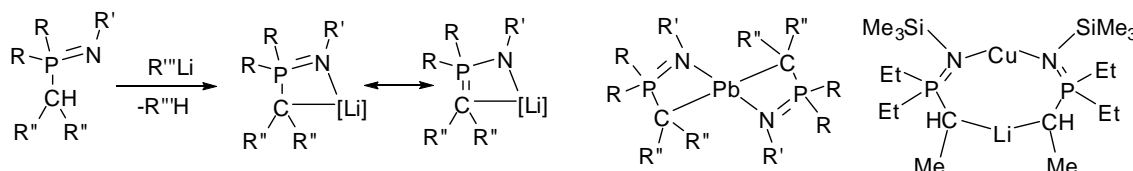
Firstly, the iminophosphorane function could direct the ortho-deprotonation reaction and stabilise the product. Many complexes of this family have been elaborated, either from the reaction of metal precursors with an iminophosphorane-carbanion ligand (such as the lithium compounds in Scheme 18),<sup>34</sup> or from the intramolecular ortho-deprotonation of an already-existed metal-iminophosphorane complex (second reaction, Scheme 18).<sup>35</sup>



*Scheme 18. Ortho-deprotonation reactions*

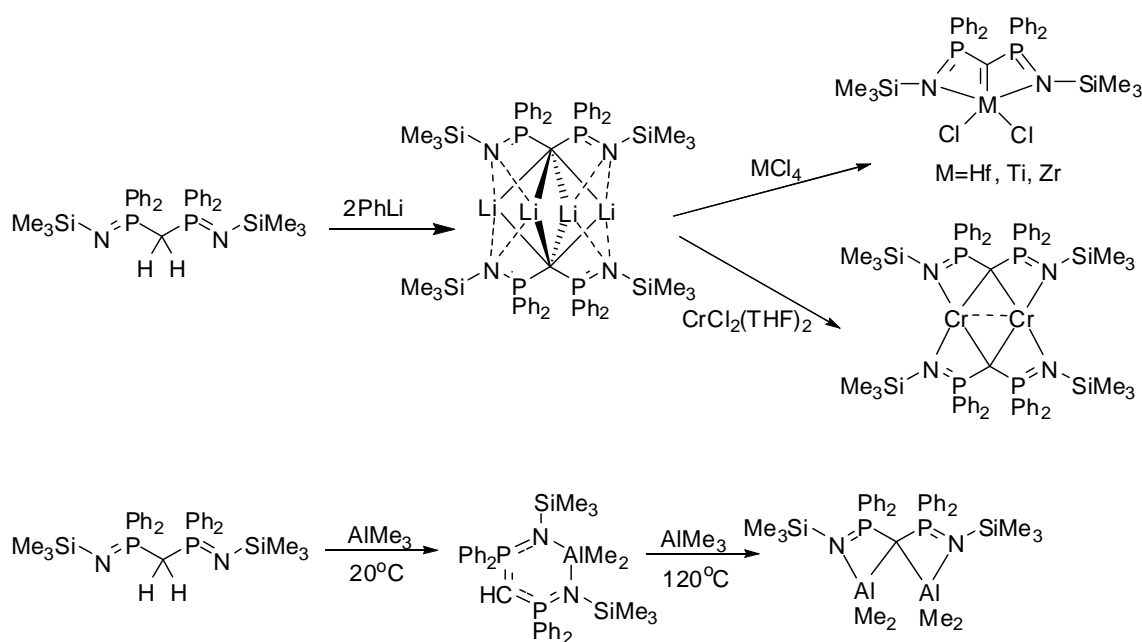
Secondly, the important positive charge at the phosphorus atom opens the possibility of functionalising  $\alpha$  C-H bond by deprotonation reaction. Indeed, monoanions and geminal

dianions of P-alkyl iminophosphorane have been the subjects pursued by many groups. By reacting with organolithiums, P-alkyl iminophosphoranes are deprotonated at the  $\alpha$  positions, yielding lithium complexes in which the lithium centres are chelated in a bidentate fashion by C and N centres.<sup>36</sup> The negative charge on the ligand is delocalised on both C and N atoms, due to resonance structures (Scheme 19).



Scheme 19. Monocarbanion from iminophosphorane and several complexes.

These lithium complexes exist in oligomeric form, the extent of which depends on steric bulk of the ligand(s) and the nature of coordinating solvent ( $\text{Et}_2\text{O}$ , THF, etc.) By reacting with metal precursors, they give iminophosphorane complexes of the corresponding metals. Several complexes of the iminophosphorane- monocarbanion ligands with metals other than lithium are presented on Scheme 19.



Scheme 20. Examples for the synthesis of complexes of bis(iminophosphorane)methandiide ligand.

Of particular interests are geminal dianions generated from the bis(iminophosphorane)methane and derivatives (e.g.  $\text{H}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$ ). In fact, both methylene protons of these compounds are sufficiently acidic to be displaced directly by organolithium. In 1999, the Stephan<sup>37</sup> and Cavell<sup>38</sup> groups independently reported the first dilithio-methandiide complex by deprotonation of  $\text{H}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$  with two equiv. of PhLi or with excess of MeLi (Scheme 20).

Complexes of the corresponding ligands can be generated either by direct reaction of such dianions with metal precursors, or by reaction of the corresponding monoanion with alkyl or amide metal precursors (to yield intramolecular deprotonation) (Scheme 20). The interest of such ligands lie in the various possible coordination modes, the formation of clusters, and in particular the formation of carbene complexes. Various reviews have been dedicated to the chemistry of these species.<sup>36c, 39a, 2, 39b, c</sup>

## II. Objectives

The objective of the work is to develop new iminophosphorane-based systems and to evaluate their applications in coordination chemistry and catalysis. They involve thus three important tasks 1) Organic synthesis of targeted ligands; 2) Coordination chemistry of such ligands and studies on properties/activities of the corresponding complexes; 3) Studies of the complexes in catalysis.

We are interested in developing new ligands combining iminophosphorane with an anionic coordinating group, which has been chosen to be thiolate or phenoxide. The synthesis of such ligands is targeted to be simple, easy to scale-up and based on inexpensive, commercially available starting materials.

Once synthesised, the ligands would be studied in coordination chemistry with different metal centres. Studies of such complexes sometimes leads to modifying existing ligands and re-synthesising the desired complexes. Theoretical studies are carried out in some cases in order to better understand the electronic properties of the ligand in coordination.

The activities of selected complexes in catalysis are then tested. Just like at the coordination step, study on catalytic activities sometimes leads to the developing of new appropriate ligands for “tuning” of the activity. Also, DFT calculations are used in some cases to clarify some aspects of the catalysis when possible.



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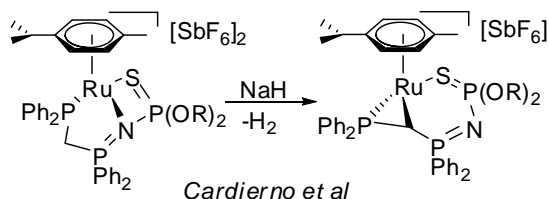
## Chapter 1

# Sulfur Containing Iminophosphoranes

### I. Sulfur-Containing Ligands in Coordination Chemistry

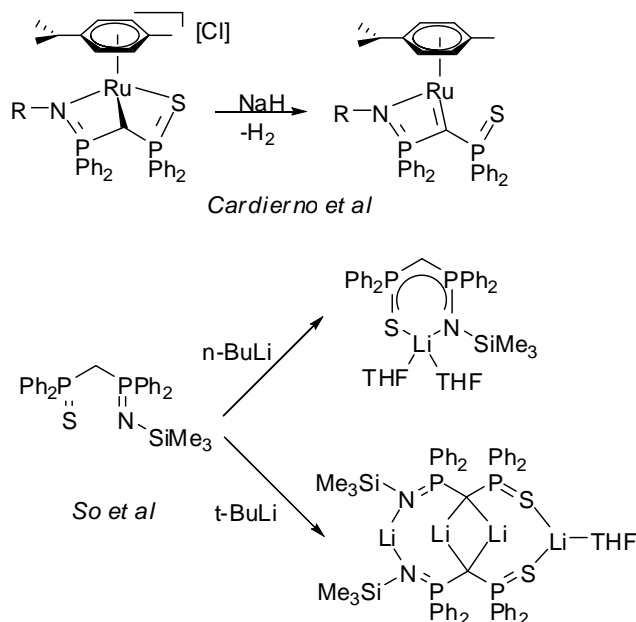
Sulfur containing ligands are of great importance in coordination and catalysis. This might be directly related to the occurrence of sulfur in many enzymatic systems. Of notable examples are iron-sulfur clusters in nitrogenases<sup>1</sup> and aconitase<sup>2</sup> (enzyme catalysing the transformation citrate-isocitrate). The importance of sulfur is also shown by the roles of cysteinyl residues in enzymes such as zinc-fingers<sup>3</sup>, alcohol dehydrogenases,<sup>4</sup> which facilitate the interconversion of alcohols and aldehyde/ketones, thus serving to breakdown alcohols that are otherwise toxic, and recover helpful aldehyde, ketones and alcohols in human and animals. The occurrence of sulfur-containing groups as ligands is also evidenced in blue copper proteins<sup>5</sup> (cupredoxins, for example, are characterized by a single copper atom coordinated by two histidine residues and a cysteine residue in a trigonal planar structure, and a variable axial ligand, function as electron transfer shuttles between proteins), or in hydrogenases<sup>6</sup> (enzymes enabling cells to use molecular hydrogen), etc. Many efforts have been made in order to develop biomimetic models with the aim of elucidating the mechanisms of enzymes and constructing catalytic systems.<sup>7</sup>

Despite the abundance of sulfur containing ligands, systems having both a sulfur-containing group and iminophosphorane (P=N) are still rare. Most of them employ sulfur in thiophosphinate function (P=S, also called thiophosphorane), sometimes as a substituent at the nitrogen atom of P=N group. Examples include the hetero-trifunctional ligand  $\text{Ph}_2\text{PCH}_2\text{P}\{=\text{NP}(=\text{X})(\text{OR})_2\}\text{Ph}_2$  developed by Cardierno and coworkers (Scheme 1).<sup>8</sup> These ligands were synthesized by a direct Staudinger reaction of diphenylphosphinomethane (dppm) with the corresponding thiophosphorylated azide. These compounds acted as versatile ligands in coordination to ruthenium centre, generating unusual systems containing Ru-C bond after selective transformation.



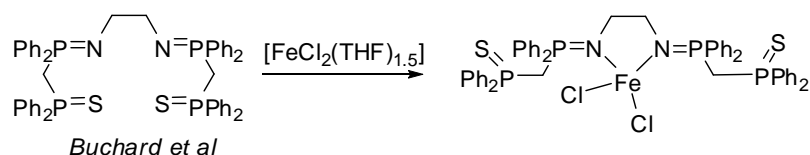
Scheme 1. Example of  $\text{P}=\text{S}$  function as a substituent at the iminophosphorane group.

The same group, following their interest in the iminophosphorane-ruthenium chemistry, developed mixed iminophosphoranyl thiophosphoranyl methane ligands for the preparation of new ruthenium carbene species (Scheme 2).<sup>9</sup> These carbene species, however, do not include a  $\text{P}=\text{S}$ -metal coordination bond. Later, the same molecular structure (iminophosphoranyl thiophosphoranyl methane) was adopted by So and coworkers to successfully obtain methanide dianionic lithium complexes,<sup>10</sup> this time the metal centre is coordinated by the  $\text{P}=\text{S}$  group (Scheme 2).



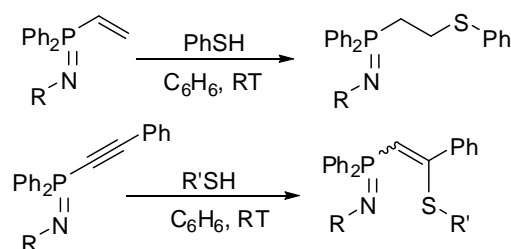
Scheme 2. Iminophosphoranyl thiophosphoranyl methane ligands

In addition to all these reports, our laboratory has developed iron complex of iminophosphorane-thiophosphorane ligand as active catalyst in transfer-hydrogenation of ketones (Scheme 3).<sup>11</sup> The coordination ability of  $\text{P}=\text{S}$  group is limited, as has been shown by the fact that in these iron species, no  $\text{P}=\text{S}$ -metal coordination bond existed in solution or in solid state.

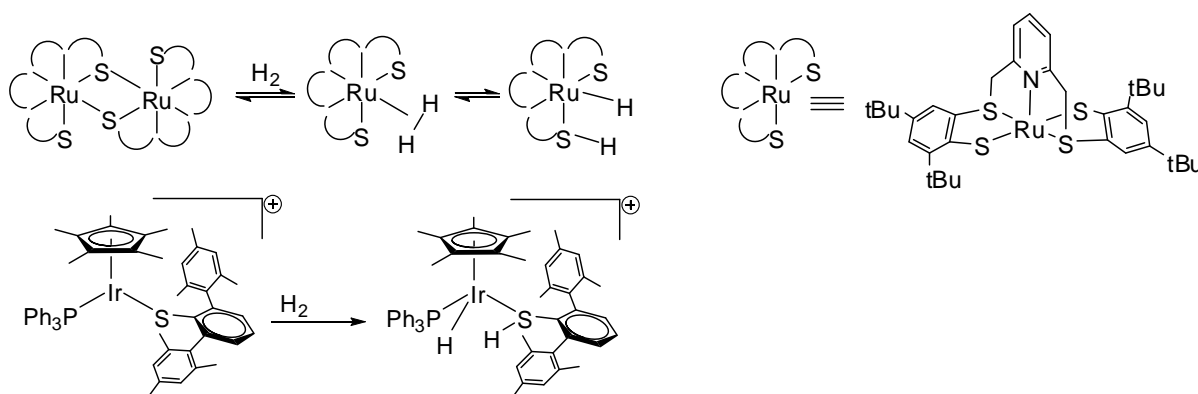


Scheme 3. Tetradentate ( $\text{P}=\text{S}$ ,  $\text{P}=\text{N}$ ) ligand developed in the laboratory.

Examples of iminophosphoranes incorporating the thioether or the thiolate function are much rarer in the literature. Thioether-iminophosphoranes were prepared first by Alajarin and coworkers using Michael-type addition reaction of thiol to diphenylvinyl iminophosphorane (Scheme 4).<sup>12</sup> This method could also be applied to alkynyl iminophosphorane.<sup>13</sup>



Scheme 4. Synthesis of thioether-iminophosphoranes by Michael addition.



Scheme 5. Examples of molecular hydrogen activation by thiolate complexes, from Sellmann group<sup>14</sup> (top) and from Ohki group<sup>15</sup> (bottom).

On the other hand, no ligand associating thiolate and iminophosphorane has been reported. These ligands could be of interest as the electronic properties of thiolates, thioethers and thiophosphinates ( $\text{P}=\text{S}$ ) are very different. Even after coordination, the sulfur of the thiolate function with its diffused orbitals can participate in other chemical transformation such as S-metallation or S-alkylation. Furthermore, the presence of thiolate function give to many complexes the ability to activate molecular hydrogen,<sup>16a-h, 15, 16i</sup> an activity relevant to hydrogenases.

Indeed, the Sellmann group has reported various studies of heterolytic activation of dihydrogen using ruthenium or rhodium complex of mixed tetradentate thioether-thiolate ligand “S4” (1,2-bis((2-mercaptophenyl)thio)ethane) and derivatives (Scheme 5).<sup>7g, 16b, 14</sup> In approaching the M-S

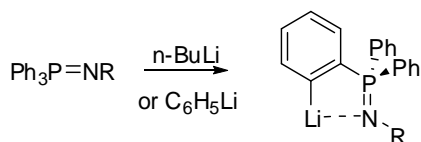
bond, the molecular hydrogen is cleaved into a proton that goes to the thiolate and a hydride that is coordinated to the metal centre. Thus the thiolate acts as a base to trap the formed proton and facilitate the cleavage reaction. In the same manner, the thiolate ligand (2,6-dimesitylphenyl thiolate) reported by Ohki and coworkers, in the rhodium or iridium complexes, is protonated upon exposition to hydrogen to become a thiol which is subsequently decoordinated from the metal centre (Scheme 5).<sup>15</sup> The group has then successfully exploited this activation for the catalytic hydrogenation of C=N and C=O bond with molecular hydrogen.<sup>16f</sup>

Taking into account all these information, and our interest in developing new iminophosphorane ligands incorporating different heteroatoms, we work on the synthesis of thiolate-iminophosphorane ligands through different but simple routes.

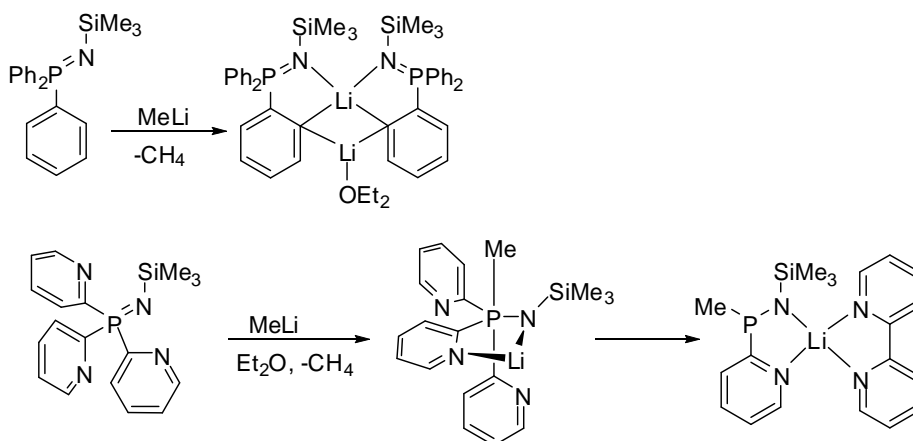
## II. Bidentate PN-S Ligands by Ortho-Lithiation Reaction

### 1. Bidentate PN-S Ligand Synthesis by Ortho-Lithiation Reaction

Selective ortho-lithiation of iminophosphorane derivatives is a valuable synthetic way to the introduction of other donors group giving access to iminophosphorane containing bidentate ligands. The possibility of P=N to favor the  $\alpha$ -deprotonation of a phenyl group at P atom has been reported for the first time in 1976 by C. G. Stuckwisch.<sup>17</sup> They found that the reaction of  $\text{Ph}_3\text{P}=\text{NPh}$  with phenyllithium or n-butyllithium gives primarily a metallation product (Scheme 6).



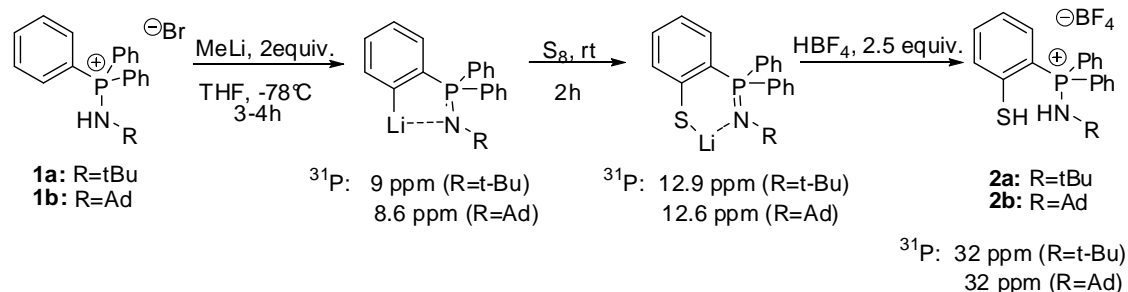
Scheme 6. Ortholithiation reaction



Scheme 7. Substituents-controlled reactions of iminophosphoranes with  $\text{MeLi}$ .

Later, Steiner and Stalke reported the clean formation of the anionic salt  $[(\text{Ph}_2(\text{C}_6\text{H}_4\text{-Li})\text{P}=\text{NTMS})_2(\text{Et}_2\text{O})]$  over the reaction of  $[\text{Ph}_3\text{P}=\text{NTMS}]$  with methyllithium<sup>18</sup>. This reaction is however very sensitive to substituents on the phosphorus atom, as has been shown by a totally different behavior for the reaction between  $[\text{Py}_3\text{P}=\text{NTMS}]$  with methyllithium. Instead of the product from the ortho-lithiation or the exchange reaction, a monomeric amide was immediately formed at  $-78^\circ\text{C}$  along with the reduction of  $\text{P}^{\text{V}}$  to  $\text{P}^{\text{III}}$  (Scheme 7).

The coordination ability of the ortho-lithiation products of different triphenylphosphinimines has been investigated with different metals by the groups of D. W. Stephan<sup>19</sup> and of Stalke.<sup>20</sup> Furthermore, the trapping of this ortho-lithiation product with chlorophosphine was demonstrated in our laboratory to be an efficient route to mixed phosphine-iminophosphorane ligands.<sup>21</sup> Adopting the strategy of the ortho-lithiation reaction, we developed a route to novel thiolate-iminophosphorane ligands.



Scheme 8. Synthesis of thiol-aminophosphonium ligands from ortholithiation reaction.

The aminophosphonium salts **1a-b** were directly reacted with 2 equiv. of MeLi to yield the ortholithiated product (R=tBu, Ad). In the case of R=tBu, the addition of MeLi (2eq) led to the formation of various products as evidenced by  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra. After one night, only one product remained exhibiting a singlet at 9 ppm. For R=Ad, the deprotonation reaction was completed after several hours, a unique product was formed showing a chemical shift of 8.6 ppm in  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum. All these values of chemical shifts are indicative for the formation of ortho-lithiation products where the iminophosphorane function is in weak coordination with lithium cation. Both these two solutions presented a red wine color, which faded rapidly upon addition of solid  $\text{S}_8$ . In  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra, both the obtained solutions exhibited a unique singlet with lower field shift at 12.9 ppm for R=tBu and 12.6 ppm for R=Ad, indicating the completion of the reactions with sulfur.

The resulting solution could be used directly for complexation test. Nevertheless, the ligands were isolated and fully characterised as aminophosphonium salts **2a,b** after protonation with two equivalents of  $\text{HBF}_4$ . The X-ray structure of the product **2a** is shown in Figure 1.



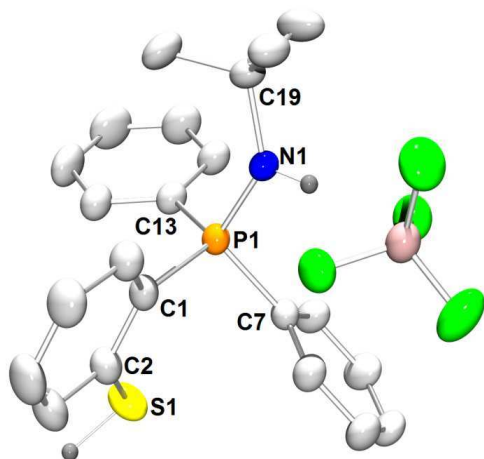


Figure 1. ORTEP view of complex **2a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): S1-C2 1.781 (2), P1-N1 1.623 (1), P1-C1 1.807 (2), P1-C7 1.797 (2), P1-C13 1.791 (2), N1-C19 1.505 (2), P1-N1-C19 134.1 (1).

## 2. Reactivities and Coordination Test of the Thiolate-Iminophosphorane Ligand.

### 2.1 Basicity of the P=N Function

One particular behavior of compound **2a** is that its mono-deprotonation yielded a zwitterion combining a thiolate and an aminophosphonium function. Indeed, addition of one equiv. of MeLi into a slurry of the thiol-aminophosphonium salt in THF gave a pale orange-red solution which presents a unique singlet at +36.2 ppm in  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum, characteristic of the aminophosphonium function. Furthermore, X-ray diffraction experiments on single crystals obtained from slow diffusion of petroleum ether on THF solution of the product shows no presence of counter ion. Importantly, the P-N bond (1.631(1) Å) of the product is slightly longer than the one in the corresponding fully protonated compound (1.623(1) Å), and is significantly longer than P=N bonds found on other iminophosphorane compounds based on the data retrieved from the Cambridge database (1.605). Thus, it is not a P=N bond of an iminophosphorane. On the other hand, the S1-C2 bond (1.741(2) Å) is significantly shortened compared to the one in the fully protonated salt (1.781(2) Å), which could be explained by the stabilisation of the thiolate anionic charge by the phenyl ring.

This result is in perfect agreement with DFT calculations carried out on the possible product(s) from the protonation of the ligand with one equiv. of acid. Optimisation on three possible structures: (1) the proton attached to S, (2) the proton attached to N, (3) the proton located between S and N, all led to a unique stable geometry in which the proton is attached to N.

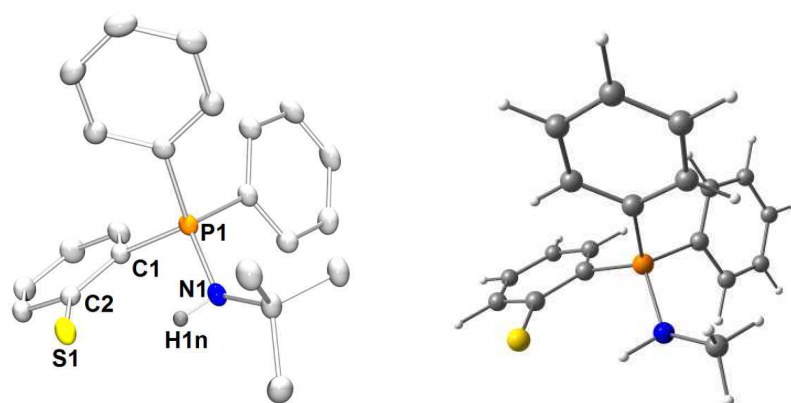
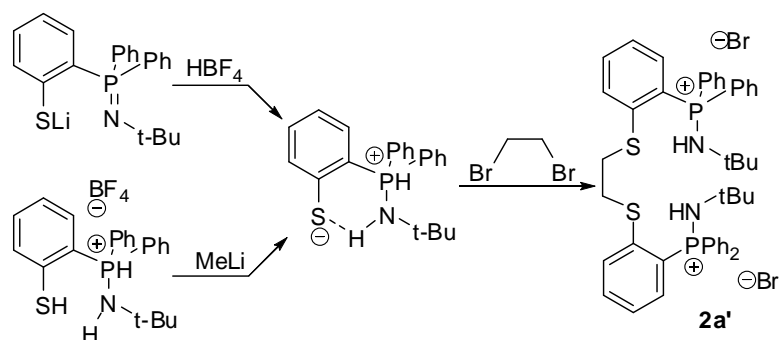


Figure 2. (a) X-ray structure of the monoprotonated compound. Hydrogen atoms have been omitted for clarity (except the one attached to N atom). Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): P1-N1 1.631 (1), P1-C1 1.797 (1), C2-S1 1.741 (2), C1-C2 1.428 (2). (b) optimised model compound. Tert-butyl group has been replaced with Me in order to simplify the calculations. Selected distances (Å) and angles (°): P1-N1 1.674, P1-C1 1.786, C2-S1 1.733, C1-C2 1.430.

This behavior could be explained by the greater basicity of the iminophosphorane compared to the thiolate function. Many of the powerful bases are indeed designed based on iminophosphorane function, as indicated in the introduction.

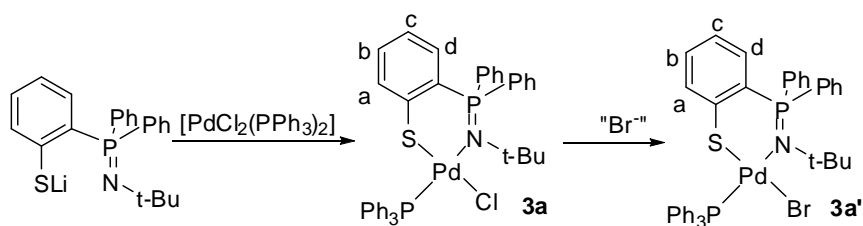
This property of thiolate-iminophosphorane function has been exploited to selectively functionalise the thiolate. The compound reacted with  $\frac{1}{2}$  equiv. of dibromoethane to give the bis(thioether) bis(aminophosphonium) salt as a result of nucleophilic substitution (Scheme 9). This product, upon deprotonation, could give tetradentate ligand incorporating thioether and iminophosphorane groups. Thus, the reaction could be a versatile method of synthesising tetradentate ligands of this type. However, this strategy and chemistry of the possible so-formed species was not exploited further as we concentrated on other ligands which seemed to be more interesting in coordination and catalysis.



Scheme 9. Functionalisation of S in thiolate-aminophosphonium compound.

## 2.2 Coordination Test

Preliminary coordination study of the thiolate-iminophosphorane ligand resulted from **2a** has been done with a palladium precursor. The thiol-aminophosphonium salt was first deprotonated with 2 equiv. of MeLi. Addition of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  into the obtained solution induced a rapid color change from deep red wine to bright orange-red. Completeness of the reaction after one day was monitored in  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum. The signal of the free ligand at +12.9 ppm disappeared, and two doublets at +31.8 ppm ( $J_{\text{P,P}}=3.5$  Hz) and + 15.4 ppm ( $J_{\text{P,P}}=3.5$  Hz) were observed, corresponding to the coordinated iminophosphorane group and  $\text{PPh}_3$  group, respectively. This indicated the clean formation of the palladium complex **3a** (Scheme 10).



Scheme 10. Coordination of **2a'** with palladium(II) and exchange reaction.

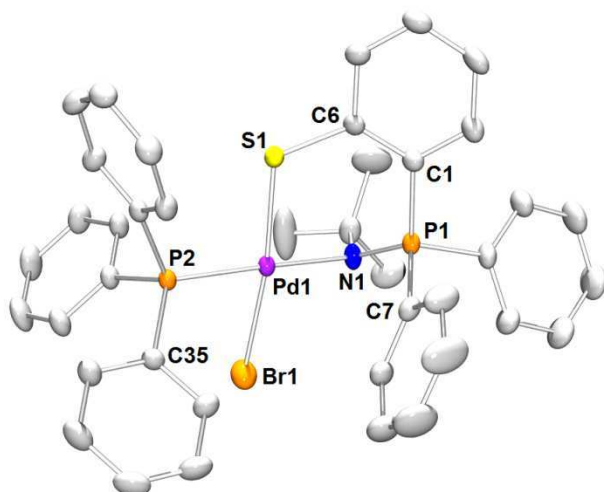
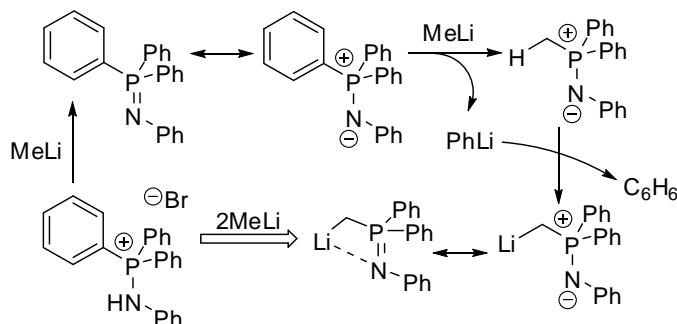


Figure 3. ORTEP view of complex **3a'**. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°):  $\text{Pd1-N1}$  2.116(2),  $\text{S1-Pd1}$  2.283(1),  $\text{Pd1-P2}$  2.2676(8),  $\text{Pd1-Br1}$  2.4781(6),  $\text{N1-P1}$  1.608(3),  $\text{P1-C1}$  1.809(3),  $\text{P1-C7}$  1.803(3),  $\text{C6-S1}$  1.757(3),  $\text{P2-C35}$  1.825(3),  $\text{N1-Pd1-S1}$  92.53(8),  $\text{P2-Pd1-S1}$  90.51(3),  $\text{N1-Pd1-Br1}$  91.97(8),  $\text{P2-Pd1-Br1}$  84.65(3),  $\text{C6-S1-Pd1}$  115.4(1).

Interestingly, when coordination test was done directly on in situ prepared thiolate-iminophosphorane ligand by the ortho-lithiation reaction, two set of doublets were found in the final reactional medium: the two as described above, and two other doublets at +31.3 ppm ( $J_{\text{P,P}}=3.5$  Hz) and + 15.5 ppm ( $J_{\text{P,P}}=3.5$  Hz). These two latters increased in intensity when excess LiBr was added, along with the total disappearance of the first set of doublets corresponding to



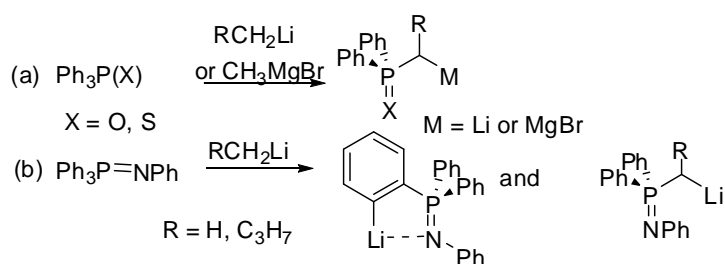
observation, conditions for the clean formation of the anion **4** were found. Indeed, adding two equivalents of MeLi (1.6 M in diethyl ether) to a suspension of N-phenyl triphenylaminophosphonium bromide in THF induced a marked color change, the white suspension disappeared giving an orange-red solution.



Scheme 12. Mechanism of the nucleophilic substitution on iminophosphorane

$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the crude mixture showed a singlet at  $\delta(\text{THF}) = 24.2$  ppm, which is in the range of the chemical shift observed for ortholithiated derivatives obtained from  $\text{Ph}_3\text{P}=\text{NR}$  ( $\text{R} = \text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ ,  $\text{CH}_2^t\text{Bu}$ ,  $i\text{-Pr}$ )<sup>21</sup> in diethyl ether, but is too high compared to the ortho-lithiation products of N-*t*Bu and N-Ad compounds **1a-b** in THF (Scheme 8).  $^1\text{H}$  NMR spectrum of the crude mixture in  $\text{d}_8\text{-THF}$  showed a broad singlet at  $\delta(\text{THF}) = -0.11$  ppm integrating for 2 protons, and the presence of only two phenyl rings on the phosphorus atom.

These observations were strongly in favor of the formation of a methanide substituent on the phosphorus atom which results from the displacement of one phenyl substituent by methyl lithium, followed by the deprotonation of the so-formed species by the released phenyl lithium. Indeed, NMR characterisation of the compound in THF presented data very similar to those described by Davidson and Lopez-Ortiz group, who synthesized this anion from  $\text{CH}_3\text{PPh}_2=\text{NPh}$  and characterized it in solution and in the solid state.<sup>22</sup>



Scheme 13. Metallation of  $\text{PPh}_3(\text{X})$  derivatives

This reaction resembles the reactivity of thiophosphines and phosphine oxides towards alkyl lithium or Grignard reagents reported by D. Seyferth *et al.* in the early 60ies.<sup>23</sup> Indeed, as described in Scheme 13, they have showed that such reaction lead to the formation of diphenylphosphinylalkyl organometallic reagent  $(\text{MCH}_2)\text{P}(\text{X})\text{Ph}_2$  ( $\text{M} = \text{MgBr}$ ,  $\text{Li}$ ;  $\text{X} = \text{O}$ ,  $\text{S}$ ). However, no report has been found for a clean exchange reaction in the case of

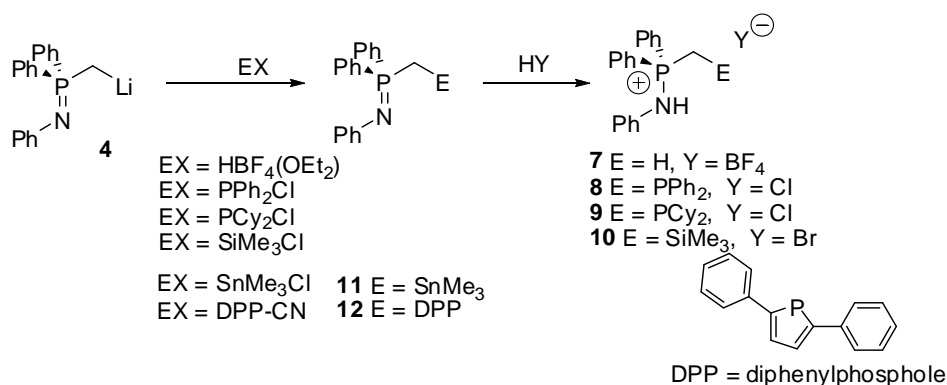
iminophosphoranes. In fact, for  $\text{PPh}_3=\text{NPh}$ , C. G. Stuckwisch<sup>17</sup> mentioned that a competitive reaction takes place when performing the ortho-lithiation, metalated diphenylalkylphosphine N-phenylimide was indeed observed as by-product.

The formation of **4** from  $\text{PPh}_3=\text{NPh}$  was found to depend highly on the reaction conditions. When using *n*-BuLi instead of MeLi in THF two different products were obtained, one coming from ortho-lithiation and the other from a phenyl displacement followed by  $\alpha$ -metallation. Moreover, the lithiation carried out with MeLi (1.6 M in diethyl ether) in toluene leads also to a mixture of two product: **4** and the ortho-lithiated derivative corresponding to a singlet at  $\delta(\text{toluene}) = 16.9$  ppm in  $^{31}\text{P}\{\text{H}\}$  NMR spectrum. The latter can also be obtained as the sole product by using *n*-BuLi in toluene.

The reaction is also very sensitive to the nature of the nitrogen substituent. Indeed, with alkyl substituent at the nitrogen, whatever the nature of the base or solvent used, only ortho-lithiation was observed as we described earlier (Scheme 6)<sup>21</sup>.

## 2. Synthesis of Mixed Ligand Containing Iminophosphorane and other Heteroatoms-Based Groups by Substitution Reactions.

After having determined the experimental conditions enabling a clean preparation of **4**, this anion was trapped with various electrophiles (Scheme 14). These reactions were carried out not only to test the reactivity of **4**, but also to test the possibility to prepare ligands containing iminophosphoranes and heteroatoms. Contrary to bidentate iminophosphorane-phosphine ligands which are quite well-known, the combination of iminophosphorane with other donating groups containing heteroatoms still remains scarce, not least because of the synthesis difficulty.



Scheme 14. Electrophilic trapping of **4**

Protonation of **4** with  $\text{HBF}_4$  results immediately in a colorless solution. In  $^{31}\text{P}\{\text{H}\}$  NMR spectrum, the phosphorus signal is strongly deshielded ( $\delta(\text{THF}) = +36.6$  ppm). The aminophosphonium salt **7** was isolated in 70% yield as a white solid. The presence of the

methyl group is attested by a doublet at  $\delta(\text{THF}) = 2.44$  ppm ( $^2J_{\text{P,H}} = 69.5$  Hz) in the  $^1\text{H}$  NMR spectrum.

Reaction of **4** with one equivalent of  $\text{PPh}_2\text{Cl}$  induced the formation of the (P, P=N) adduct as evidenced by the presence of two doublet at  $\delta(\text{THF}) = 0.80$  ppm and  $-26.6$  ppm ( $^2J_{\text{P,P}} = 51.5$  Hz) in the  $^{31}\text{P}\{\text{H}\}$  NMR of the crude mixture, corresponding respectively to  $\text{P}^{\text{III}}$  and  $\text{P}^{\text{V}}$ . After protonation the aminophosphonium salt **8** can be isolated. NMR spectra of **8** correspond exactly to the ones reported for this compound earlier.<sup>21</sup>

In fact, compound **8** has already been prepared in the lab using Kirsavov reaction on bis(diphenylphosphine)methane (dppm,  $\text{CH}_2(\text{PPh}_2)_2$ ). However, this previous method could not be used to prepare mixed phosphine-iminophosphorane ligands, in which the two phosphorus atoms do not bear the same substituents. With the new synthesis strategy using **4**, the preparation of such compounds is possible. For example the reaction of **4** with  $\text{PCy}_2\text{PCl}$ , followed by acidic work-up gave compound **9** in good yield. In  $^{31}\text{P}\{\text{H}\}$  NMR spectroscopy two doublet at  $\delta(\text{CD}_2\text{Cl}_2) = -22.2$  ppm and  $34.80$  ( $^2J_{\text{P,P}} = 87.5$  Hz) were observed corresponding respectively to the  $\text{P}^{\text{III}}$  and  $\text{P}^{\text{V}}$  atoms. The bridging methylene appears as doublet at  $\delta(\text{CD}_2\text{Cl}_2) = 3.22$  ppm ( $^2J_{\text{P,H}} = 16.5$  Hz) and a doublet of doublet at  $\delta(\text{CD}_2\text{Cl}_2) = 18.7$  ppm ( $^2J_{\text{P,C}} = 39.0$  Hz and  $68.0$  Hz) in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra respectively.

In the same manner, reaction of **4** with trimethylsilylchloride also proceeded cleanly, giving after acidic work up the aminophosphonium salt **10** in high yield. The methylene group gave rise to a doublet at  $\delta(\text{CDCl}_3) = 2.71$  ppm ( $^2J_{\text{P,H}} = 18.0$  Hz) in  $^1\text{H}$ -NMR spectrum and a doublet at  $\delta(\text{CDCl}_3) = 14.5$  ppm ( $^2J_{\text{P,C}} = 58.5$  Hz) in  $^{13}\text{C}$  NMR spectrum.

Reaction of anion **4** with trimethyltin chloride gave **11** as a white solid in 75% yield. In  $^{31}\text{P}\{\text{H}\}$  NMR spectroscopy **11** exhibited a singlet at  $\delta(\text{C}_6\text{D}_6) = 7.40$  ppm and satellites due to tin isotope ( $^2J_{\text{P,Sn}} = 60.0$  Hz). In  $^1\text{H}$  NMR the methylene protons appears as a doublet with tin satellites centered at  $\delta(\text{C}_6\text{D}_6) = 2.71$  ppm ( $^2J_{\text{Sn,H}} = 52.0$  Hz,  $^2J_{\text{P,H}} = 11.0$  Hz).

Finally, reaction of **4** with 1-cyano-2,5-diphenylphosphole gave access to **12** in 85 % yield. The formation of **12** was ascertained by NMR spectroscopy.  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of the compound showed a doublet at  $\delta(\text{C}_6\text{D}_6) = -23.7$  ppm for the phosphole P-atom and another doublet at  $0.8$  ppm for the  $\text{P}^{\text{V}}$  atom. This mixed bidentate ligand is very promising since it features coordination sites with very different electronic properties iminophosphorane as a strong  $\sigma$  and  $\pi$  donor and the phosphole ring as a phosphine with greater accepting ability.

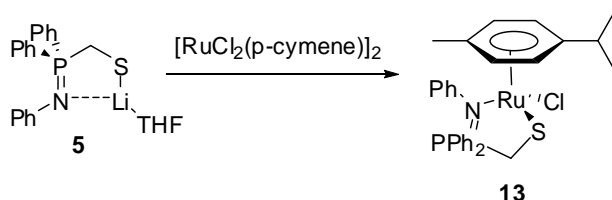
As we focused in the development and reactivities of sulfur-containing iminophosphorane ligands, the coordination chemistry and reactivities of these compounds have not been studied. However, taking into account the differences in electronic and steric properties of these groups, they could make interesting ligands for other studies.

### 3. Coordination Chemistry of the Thiolate-Iminophosphorane **5**

As first coordination experiments, the thiolate-iminophosphorane anion **5** was coordinated to metals of group 8, 9, 10 (Ru, Co, Rh, Ir, Pd and Ni). Some of these metals are chosen also for their potential applications related to thiolate ligands: many thiolate complexes of Ru(II), Rh(I) and Ir(I) give high activity for hydrogen activation.

#### 3.1 Coordination of PN-S Ligand with a Group VIII-Metal Centre: Ru(II)

The iminophosphorane-thiolate anion **5** was easily coordinated to Ru(II) centre. Addition of THF to a mixture of **5** and dichloro(p-cymene)ruthenium(II) dimer in the solid state led rapidly to a red solution. The disappearance of the precipitated anion was a good sign of coordination which was confirmed by  $^{31}\text{P}\{\text{H}\}$  NMR of the crude mixture showing the formation of a unique product exhibiting a singlet at  $\delta(\text{THF}) = 36.9$  ppm. After 3h at room temperature, the solvent was evaporated, the lithium salt was filtered-off after precipitation in dichloromethane and **13** was isolated as a red solid in 76% yield.



Scheme 15. Coordination of the thiolate-iminophosphorane ligand with Ru(II)

In the  $^1\text{H}$  NMR spectrum the methylene protons appear as two doublets at 2.67 and 4.12 ppm, this accounts for the chirality of the Ru centre which bears four different substituents. In the same manner the protons of the coordinated p-cymene ring are differentiated giving three doublets at 4.64, 4.76, and 4.90 ppm integrating respectively for 1, 2, and 1 protons. In the aromatic area, the differentiation of the protons of the phenyl rings on the phosphorus atom can also be seen. In the  $^{13}\text{C}$  spectrum most of the carbons of both the p-cymene and phenyl rings (on P) are differentiated. All these data suggest the structure depicted in Scheme 15 for complex **13**.

#### 3.2 Coordination of PN-S Ligand with Group IX-Metal Centres: Co(II), Rh(I), Ir(I)

Reaction of the ligand with one equivalent of  $\text{CoCl}_2$  in THF gives first a green solution, from which a green solid precipitated out after 3 hours. If stirring is stopped just after the introduction of the ligand and the solution was allowed to stay for one day, green crystals are formed. X-ray diffraction experiment carried out on these crystals showed a dimeric  $[(\text{o-C}_6\text{H}_4(\text{S})\text{P}(\text{Ph}_2)=\text{N}(\text{Ph}))\text{CoCl}]$  complex (Figure 4), the sulfur atoms serving as bridges forming a planar four-membered ring  $\text{Co}_2\text{S}_2$ .



The complex is symmetric with an inversion point at the centre of this ring. The metals adopt distorted tetrahedral geometry, the values of P=N and other bonds on the ligand are in the usual range as in other complexes. The distance Co-Co (2.87 Å) is larger than the sum of covalent radii of the two Co atoms (1.26 Å each) and significantly longer than the average value of Co-Co distances (2.50 Å) in all compounds containing any type of Co-Co bond (from the CCDC database). The complex **14** is thus a simple dimeric complex and does not contain any special metal-metal bond. (Indeed, DFT calculations performed on this complex do not show any special metal-metal interaction).

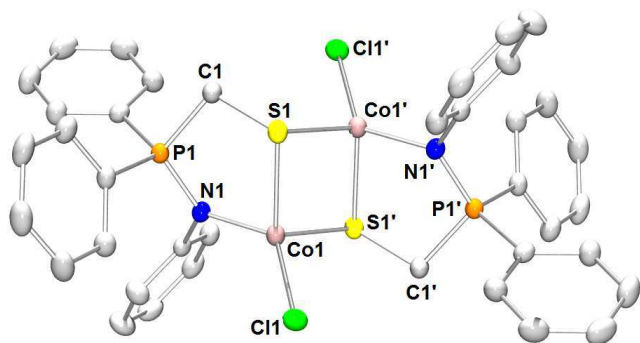
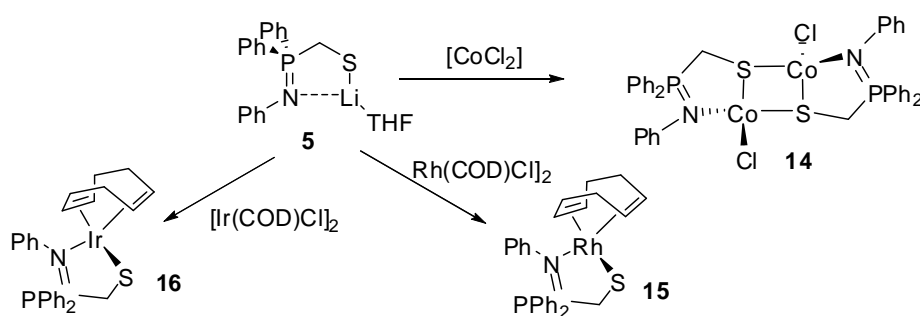


Figure 4. ORTEP view of complex **14**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. The molecule has an inversion point at the centre of the 4-membered ring Co2S2. Selected distances (Å) and angles (°): Co1-N1 1.977 (2), Co1-Cl1 2.2501 (7), Co1-S1 2.3643 (8), Co1-S1' 2.3465 (7), Co1-Co1' 2.8689 (7), N1-P1 1.613 (2), N1-Co1-S1' 105.4 (6), Cl1-Co1-S1 109.14 (3), S1-Co1-S1' 104.97 (2), Co1-S1-Co1' 75.04 (2), S1-Co1-S1'-Co1' 0.



Scheme 16. Coordination of the thiolate-iminophosphorane ligand with Co(II), Rh(I), Ir(I)

Addition of **5** to a solution of [Rh(COD)Cl]<sub>2</sub> or [Ir(COD)Cl]<sub>2</sub> in toluene at room temperature immediately resulted in the change of color from yellow to light orange. <sup>31</sup>P{H} NMR of the crude mixture showed a unique product exhibiting a singlet at δ(THF) = 63.0 ppm for the reaction with iridium precursor. In the case of reaction with rhodium precursor, a unique doublet was observed at δ(THF) = 47.7 ppm with a coupling constant of 5.0 Hz, clearly showing the formation of the rhodium complex of iminophosphorane ligand. After removal of lithium salts and evaporation of solvent, rhodium and iridium complexes (**15** and **16**) could be obtained as

orange solids. Single crystals of **15** suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether over a solution in  $\text{CH}_2\text{Cl}_2$  (Figure 5). The complex adopts a square-planar geometry, the rhodium centre being coordinated by the thiolate and iminophosphorane from the ligand, and two double bonds from the cyclooctadiene. No special effect has been found on the structure of the complex.

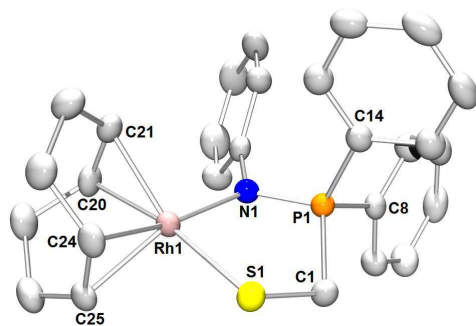
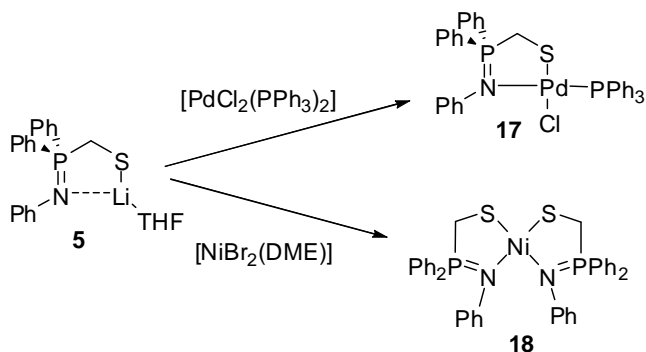


Figure 5. ORTEP view of complex **15**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Rh1-N1 2.118 (2), Rh1-S1 2.3291 (8), Rh1-C21 2.118 (3), Rh1-C20 2.157 (3), Rh1-C24 2.133 (3), Rh1-C25 2.138 (3), S1-C1 1.821 (3), P1-N1 1.613 (2), P1-C1 1.788 (3), P1-C14 1.808 (3), P1-C8 1.812 (3), N1-Rh1-S1 88.32 (7), N1-Rh1-C21 93.9 (1), N1-Rh1-C20 94.7 (1), S1-Rh1-C24 89.5 (1), S1-Rh1-C25 91.1 (1), N1-P1-C1 107.2 (1), P1-C1-S1 106.8 (2), C1-S1-Rh1 103.4 (1).

### 3.3 Coordination of PN-S Ligand with Group X-Metal Centres: Pd(II) and Ni(II)



Scheme 17. Coordination of the thiolate-iminophosphorane ligand with Pd(II), Ni(II)

Due to the low solubility of **5** in THF, complexation reactions were carried out by addition of THF onto a mixture of isolated **5** and the appropriate metal precursor. With [*trans*- $\text{PdCl}_2(\text{PPh}_3)_2$ ], after 4h hours at room temperature, the yellow slurry had turned to an orange solution. Compared with the analog thiolate-iminophosphorane **2a'**, the coordination of **5** is thus much faster, probably due to the more important donating ability of the thiolate attached to an alkyl group, and the greater flexibility of the ligand.

The  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of the crude mixture showed the presence of one equivalent of free triphenylphosphine ( $\delta(\text{THF}) = -5.1$  ppm) and an AB signal pattern evidencing the coordination of the ligand to the palladium centre. The complex  $[(\text{PhNPPH}_2\text{CH}_2\text{S})\text{Pd}(\text{PPh}_3)\text{Cl}]$  **17** exhibited two doublets ( $^3J_{\text{P,P}} = 6.5$  Hz) at  $\delta(\text{THF}) = 34.2$  ppm and  $\delta(\text{THF}) = 45.0$  ppm corresponding respectively to the coordinated triphenylphosphine and iminophosphorane function. This complex was isolated in 87% yield and was characterized by multinuclear NMR, elemental analysis and X-Ray diffraction analysis.

Single crystals were obtained by slow diffusion of petroleum ether into a concentrated  $\text{CH}_2\text{Cl}_2$  solution of **17**. An Ortep plot of **17** is depicted in Figure 6 together with the most relevant structural data. The complex adopts a slightly distorted square-planar geometry, the iminophosphorane and the phosphine being located *trans* to each other. This *trans*-configuration is probably due to the initial configuration of the palladium precursor.

The deviation from planarity was measured at  $16.70(9)^\circ$ . The P-N bond distance is normal at  $1.597(3)$  Å, the P3-C1 bond is shortened compared to the P-C bond in  $[(\text{PhNCH}_2\text{PPh}_2)\text{PdCl}_2]$  featuring bidentate phosphine-iminophosphorane ligand ( $1.801(3)$  Å vs  $1.842(2)$  Å). On the contrary both the N-Pd ( $2.100(2)$  Å) and the Pd-Cl ( $2.3869(7)$  Å) are elongated compared to the same reference (N-Pd =  $2.076(2)$  Å and Pd-Cl =  $2.3668(5)$  Å,  $2.3035(6)$  Å). Compared with complex **3a'**  $[(o\text{-C}_6\text{H}_4(\text{S})\text{P}(\text{Ph}_2)=\text{N}(\text{t-Bu}))\text{Pd}(\text{PPh}_3)\text{Cl}]$  of another thiolate-iminophosphorane ligand resulted from the ortho-lithiation reaction, the Pd-S, Pd-N and Pd-PPh<sub>3</sub> bonds are almost of the same values

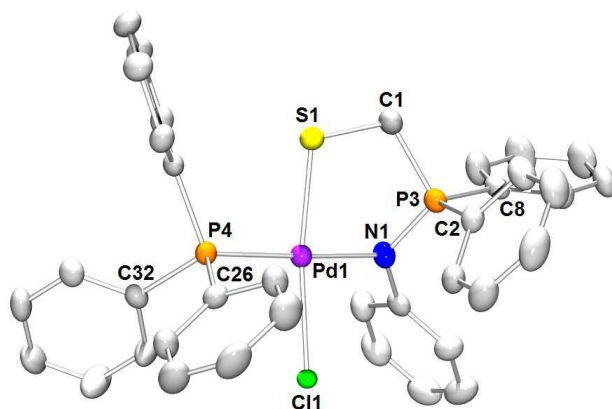
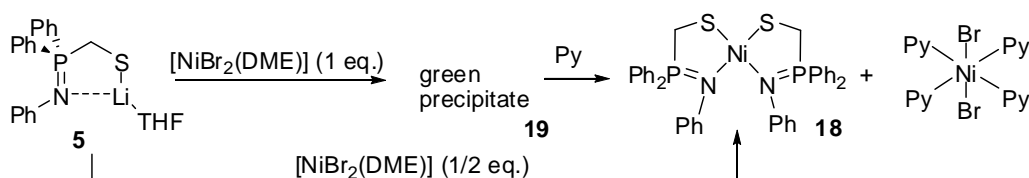


Figure 6. ORTEP view of complex **17**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles ( $^\circ$ ): Pd1–N1  $2.100(2)$ , S1–Pd1  $2.289(1)$ , Pd1–P4  $2.2528(8)$ , Pd1–Cl1  $2.3869(7)$ , N1–P3  $1.597(3)$ , P3–C1  $1.801(3)$ , P3–C2  $1.799(3)$ , P3–C8  $1.808(3)$ , C1–S1  $1.824(3)$ , P4–C32  $1.829(3)$ , P4–C26  $1.818(3)$ , N1–Pd1–S1  $88.52(7)^\circ$ , P4–Pd1–S  $89.87(3)^\circ$ , N1–Pd1–Cl1  $92.45(7)^\circ$ , P4–Pd1–Cl1  $89.73(3)^\circ$ , P3–C1–S1  $109.5(2)^\circ$ , N1–P3–C1  $104.9(2)^\circ$ , C1–S1–Pd1  $103.6(1)^\circ$ , S1–Pd1–N1–Cl1  $16.70(9)^\circ$ .

Along with the Pd complex described above, nickel complex of the thiolate-iminophosphorane ligand **5** was synthesised with the aim of studying the coordination chemistry of the ligand, because tetracoordinated  $\text{Ni}^{\text{II}}$  complexes, in difference from Pd complexes, could adopt

tetrahedral or square-planar geometry, and exist in singlet or triplet state, depending on the rigidity of ligand and its field-strength.

Reaction of the iminophosphorane-thiolate ligand with one equivalent of  $[\text{NiBr}_2(\text{DME})]$  gives a deep green solution, from which a green precipitate appears after 1h. Elemental analysis of this product shows that it corresponds to the formula  $[(\text{CH}_2(\text{S})\text{P}(\text{Ph}_2)=\text{N}(\text{Ph}))\text{NiBr}]$ . SQUID measurement showed that only half of the nickel centres are in triplet state. Attempts to obtain single crystals suitable for X-ray diffraction measurement have been carried out. However, due to the very limited solubility of the complex in common solvents, no crystals have been obtained. The complex is soluble in pyridine, but in this solvent, crystallisation yields two types of crystals:  $[\text{NiBr}_2(\text{Py})_4]$  (pale green) and deep green crystals corresponding to a complex in which the nickel centre is coordinated by two iminophosphorane groups in *cis*-position, forming a distorted square planar geometry (**18**, deep green crystals).



Scheme 18. Reaction of **5** with  $[\text{NiBr}_2(\text{DME})]$ .

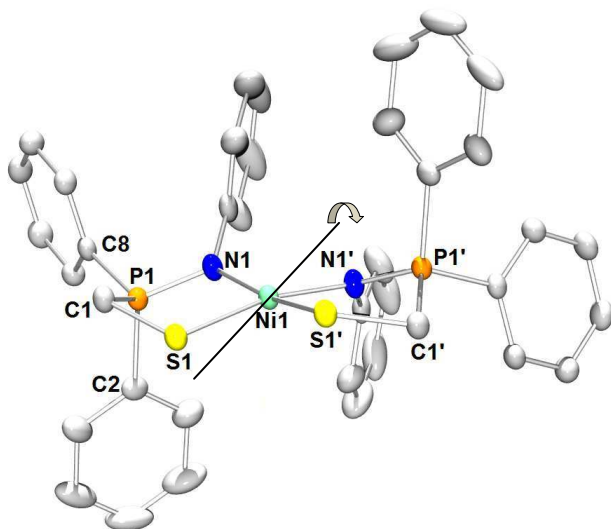


Figure 7. ORTEP view of complex **18**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. The molecule has a  $C_2$  axis passing through Ni1. Selected distances (Å) and angles (°): Ni1-Ni1.961 (1), Ni1-S1 2.1996 (5), S1-C1 1.834 (2), P1-Ni1 1.612 (1), P1-C1 1.787 (2), P1-C8 1.800 (2), Ni1-Ni1-S1 91.38 (4), Ni1-Ni1-Ni1' 94.61 (8), S1-Ni1-S1' 84.62 (2), Ni1-Ni1-S1' 168.2 (4), C1-S1-Ni1 104.35 (5), P1-Ni1-Ni1 115.35 (8).

Intrigued by this result, we tested the coordination to Ni(II) using 2 equiv. of the thiolate ligand **5**. Reaction of two equivalents of ligand **5** with  $[\text{NiBr}_2(\text{DME})]$  in THF yielded immediately a bright green solution, from which a green slurry was formed after 4h. After removal of lithium

salts by dissolving the solid in  $\text{CH}_2\text{Cl}_2$  and evaporation of solvent,  $[(\text{CH}_2(\text{S})\text{P}(\text{Ph}_2)=\text{N}(\text{Ph}))_2\text{Ni}]$  was isolated as green solid at high yield. X-ray diffraction experiment carried out on monocrystals of the complex obtained from slow diffusion of petroleum ether over  $\text{CH}_2\text{Cl}_2$  solution showed the same complex **18**.

The complex, even though having a geometry close to square-planar in solid state, is paramagnetic in solution. Magnetic measurement with Evans method on a solution of this complex in  $\text{CH}_2\text{Cl}_2$  showed a magnetic moment of  $2.3 \mu_{\text{B}}$ , suggesting that the majority of the complex molecules in solution are high-spin. DFT calculations has been carried out to rationalise this behavior. Nickel was represented by the relativistic effective core potential of Hay and Wadt<sup>24</sup> and the associated triple zeta quality basis set<sup>25</sup>, augmented by a f polarization function as proposed by Frenking<sup>26</sup> (lanl2tz(f)). S was described with 6-31+G\* basis set. All other atoms were described with the 6-31G\* Pople basis set<sup>27</sup>. Optimisations were done in nonsymmetric condition. It was then found that the triplet state which is in tetrahedral geometry is much more stable than the singlet state, which adopts a distorted-square planar geometry very close to the structure resolved with X-ray diffraction experiment. The difference in free energy is 9.0 kcal/mol. This result explains paramagnetic behavior of the complex in solution.

In solid state, however,  $\pi$ -stacking interactions between phenyl rings of neighboring molecules were detected from the X-ray crystal structure (the distances between these phenyl rings, i.e centroid perpendicular distances, being approximately 3.35-3.39 Å). These interactions, along with weak hydrogen bonds between H(phenyl) and Sulfur atoms ( $d(\text{H}-\text{S})$  being approximately 2.90-2.94 Å), are stabilising for the square-planar geometry in the singlet state.

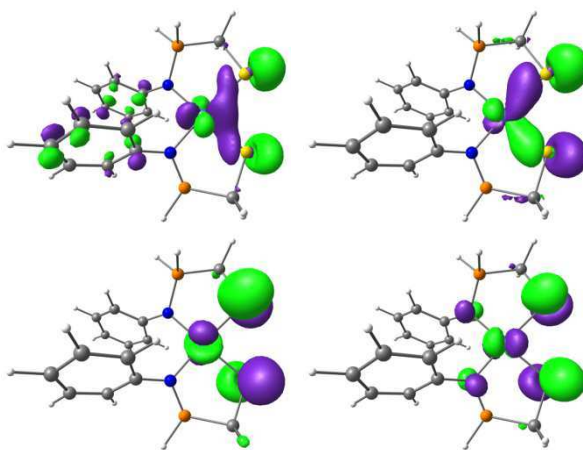
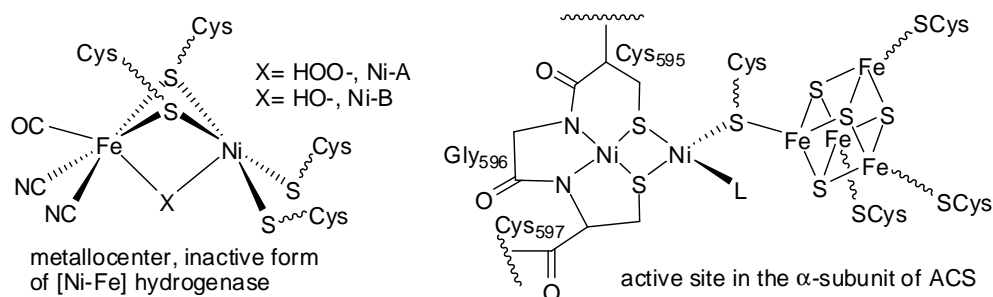


Figure 8. Orbitals in singlet *cis*-complex for in  $\sigma$ - and  $\pi$ -donating interaction.

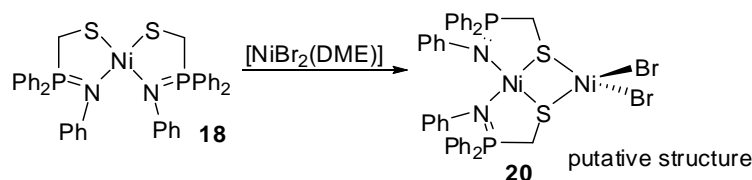
One interesting finding for the *cis*-complex in square-planar geometry is that, the HOMO, HOMO-1 and two other occupied molecular orbitals resulted essentially from orbitals p of S in antibonding/ bonding interaction with d-block orbitals of Ni are in good steric and electronic conditions to enter in  $\sigma$ -and  $\pi$ -interaction with other d-orbitals of a second metal. Thus, this species can behave as a bidentate ligand.

Indeed, multinuclear complexes having discrete  $[\text{NiS}_2]$  units, and in particular  $[\text{Ni}_2\text{S}_2]$  units serving as S-donor ligand are common in coordination chemistry, because of the tendency of mercapto groups to form bridge between metals. Most of them are synthesised as structural mimics of biological species such as the  $\alpha$ -subunit of the acetyl CoA synthase<sup>28</sup>, or  $[\text{Ni-Fe}]$  hydrogenase<sup>6b, 29</sup>, whose active site are presented in Scheme 19.



Scheme 19. active site of acetyl CoA synthase<sup>28a, b</sup>, or  $[\text{Ni-Fe}]$  hydrogenase<sup>6b</sup>.

Reaction of complex **18** with  $[\text{NiBr}_2(\text{DME})]$  in  $\text{CH}_2\text{Cl}_2$  gave a green suspension after 2 hours. After solvent removal, a deep green solid was obtained which also corresponds to the formula  $[(\text{CH}_2(\text{S})\text{P}(\text{Ph}_2)=\text{N}(\text{Ph}))\text{NiBr}]$  as **19** as attested by elemental analysis. SQUID measurement of this species also showed that one half of the nickel centre is in triplet state. This suggest the formation of dinuclear complex **20**, as shown in scheme 17. The first nickel centre is in square-planar geometry ( $S \approx 0$ ) and the second in tetrahedral geometry ( $S \approx 3$ ). From experimental results, this complex might also be the same species as **19** (Scheme 18). However, no definite evidence was obtained as this product is hardly soluble in common solvents, just like the case with **19**.



Scheme 20. Reaction of **18** with  $[\text{NiBr}_2(\text{DME})]$ .

Complex **18** was reacted with other metal precursor, especially  $[\text{Fe}(\text{CO})_4\text{Br}_2]$ . However, as the products are all insoluble in common solvents, their characterisations would not be carried out. Nevertheless, the well controlled formation of **18** and its stability, as well as the electronic properties conferred by iminophosphorane function which differ largely from amines or imines make this species an interesting ligand in synthesizing multinuclear complexes.

## IV. Conclusion

Taking into account the importance of sulfur-containing ligands in nature and in coordination chemistry, we were interested in developing new systems combining iminophosphorane and

different sulfur-containing functions. In particular, different bidentate thiolate-iminophosphorane ligands have been synthesised using the ortho-lithiation reaction or nucleophilic substitution. This second synthetic route is in fact based on the first report on a clean nucleophilic substitution on iminophosphorane. Other mixed bidentate ligands combining iminophosphorane and different heteroatoms-containing groups (phosphine, phosphole, silane, borane, etc) have been developed thanks to this reaction. Though coordination chemistry has not been further studied for these ligand precursors, this demonstrated a versatile route to a series of possible bidentate ligands combining iminophosphorane and other donating groups that are very different in steric and electronic properties.

Among the bidentate thiolate iminophosphorane ligands, coordination study has been done extensively on the more flexible ligand **5**. This latter has been coordinated with different transition metal precursors of groups 8, 9, 10. In particular, discrete  $[\text{NiN}_2\text{S}_2]$  complex resulted from the reaction of **5** with 2 equiv. of  $[\text{NiBr}_2(\text{DME})]$  could act as bidentate ligand through electron pairs on sulfur atoms, leading to bimetallic complexes. Although definite evidence of the coordination ability of this species was not established due to the insolubility of the complexes, along with other ligands synthesised, it enlarges greatly the library of iminophosphorane with sulfur-containing group, in particular, and hetero-atom containing group in general, for further studies in coordination chemistry and catalysis.

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## Chapter 2

# Iminophosphorane-Phenoxide Bidentate Ligands & Applications in Oligomerisation of Ethylene

## I. Introduction

### 1. Oligomerisation of Ethylene

Linear alpha olefins (LAOs) are important chemicals in industry, with important applications in various domains. The main uses of alpha molecules are represented in the table 1.<sup>1</sup> The low carbon numbered compounds (C4-C8) are mainly used as co-monomer in polyethylene production because the addition of alpha olefines co-monomers creates branches and renders the polymer more flexible. It's also thanks to the presence of these branches that many polyalphaolefines, from the polymerisation of alpha olefine (C12 and more) do not easily crystallise or solidify and remain oily even at low temperature and thus could serve as lubricants in a wide temperature range. LAOs (mainly C4-C8) are also used for the production of linear aldehydes by hydroformylation (addition of CO and H<sub>2</sub>) for latter production of short-chain fatty acids or alcohols (used as plasticizers). C10-C14 linear alpha olefines are used to make surfactants for aqueous detergent formulations, the higher C16-C16 LAOS are used as the hydrophobes in oil soluble surfactants, etc.

Table 1. Main use of LAOs, from Forestiere et al<sup>1</sup>

| Polyethylene comonomer<br>C4-C8 | Oxo alcohols<br>C6-C16 | Poly alpha olefins<br>C10-C14 | others |
|---------------------------------|------------------------|-------------------------------|--------|
| 40%                             | 19%                    | 14%                           | 27%    |

The main route to LAOs is the oligomerisation of ethylene. A remarkable catalytic system for the selective production of linear alpha olefins is the Shell Higher Olefin Process (SHOP), developed by Keim and coworkers<sup>2</sup>, using  $[\text{Ni}(\text{P},\text{O})(\text{PR}_3)\text{R}']$  system. Alpha olefins C6-C18 could be obtained from the process following a geometric Schulz-Flory distribution.

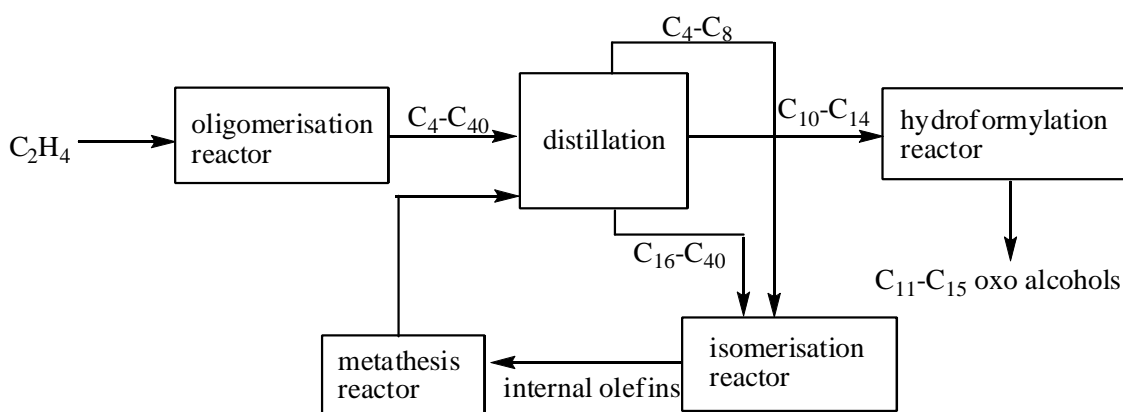


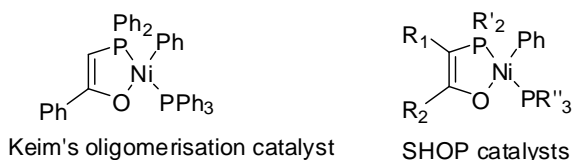
Figure 1. SHOP process<sup>3a, 2b, 3b</sup>

The two important industrial processes allowing the selective production of hexene and butene are the Philips trimerisation process, based on the work of Morgan and co-workers<sup>4</sup> and employed by Chevron-Philips,<sup>5, 1</sup> and the Alphabutol process, developed by Chauvin and coworkers at IFP.<sup>6</sup> The latter utilises titanium alkoxide complexes along with alkyl aluminum as co-catalyst, accounts for nearly 25% of 1-butene serving as co-monomer in PE units. The selectivity of 1-butene could be up to 93% in optimised condition. The modified process, called AlphaSelect, using a different catalyst, produces C4-C10 alpha olefins with high selectivity and the ability of adjusting the olefins distribution.

## 2. Nickel Catalysts for Dimerisation of Ethylene.

The use of nickel complexes in homogenous catalysis and in particular, in olefin oligomerisation dated back to the 50s from a discovery of Karl Ziegler and co-workers, latter called the “nickel effect”. They found that the presence of nickel salt in catalytic system for the polymerisation of ethylene by titanium complexes and alkyl aluminum compounds changed the product nature: instead of polymers, they obtained 1-butene.

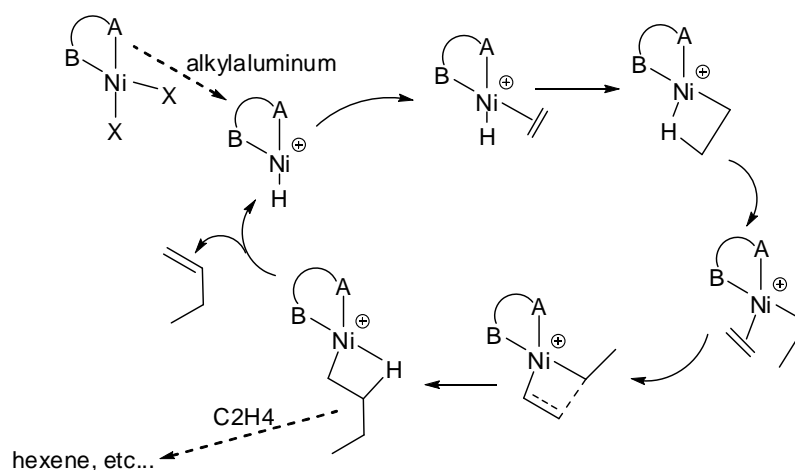
The SHOP process described above used nickel complexes (Scheme 1). Following its success, many other nickel complexes have been made in order to obtain highly active and selective catalysts for the oligomerisation of ethylene, and in particular the di- or tri-merisation of this compound, as the commercial demands for alpha olefins C4-C10 is high and has increased these years. Variations for the ligand close to the ones in SHOP process would not be detailed here and could be found in publications by Keim and coworkers.<sup>2a, 7</sup> Notable systems using nickel complexes for the oligomerisation/polymerisation of ethylene will be briefly discussed.



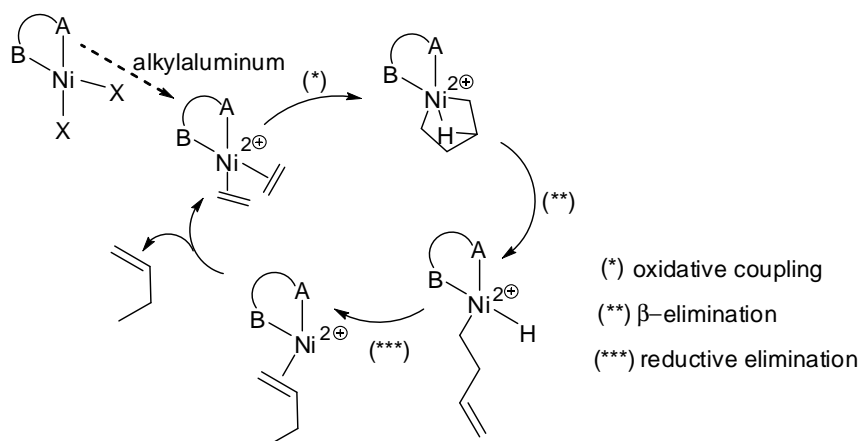
Scheme 1. Nickel complexes for the oligomerisation of ethylene: SHOP complexes and Keim's complexes.

## 2.1 Mechanism of the Oligomerisation and Polymerisation of Ethylene using Ni Complexes

The oligomerisation/polymerisation of ethylene using nickel complexes is often assumed to go through a Cossee mechanism (Scheme 2),<sup>8</sup> although a metallacyclic mechanism<sup>9, 1</sup> (Scheme 3) as in the case of the titanium catalysts involved in the Alphabutol process and the chromium catalysts in the Phillips trimerisation process is also conceivable. In our laboratory, full DFT calculations on the two possible mechanisms have shown that the Cossee mechanism is the more suitable one.<sup>10</sup>



Scheme 2. Simplified representative Cossee mechanism of the dimerisation of ethylene with nickel complex



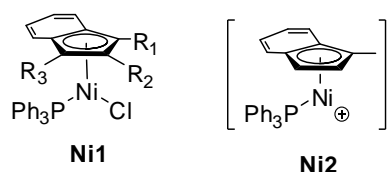
Scheme 3. Simplified representative metallacyclic mechanism of the dimerisation of ethylene with nickel complex

## 2.2 Catalysts

Nickel complexes tested in oligomerisation and polymerisation of ethylene often include a bi/tri-dentate ligand, as multidentate ligands could offer better control of the intermediate configurations and thus better control over the catalytic reaction of ethylene. Except several examples of indenyl nickel complexes where the multidentate ligands is aromatic ring, other ligands for nickel complexes could be divided into several groups based on the atoms coordinated to Ni: (P,P), (N,N), (N, P), (O,N), (O, P)

### Indenyl Nickel Complexes

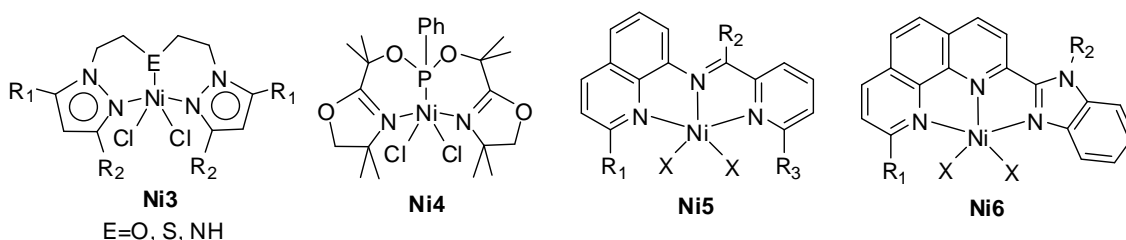
The phosphine nickel indenyl complexes have been used successfully. The neutral complex **Ni1** synthesized by Collins et al acts along with MAO as catalysts for the polymerisation of ethylene,<sup>11</sup> giving PE with PDI from 1.7-2.0. On the other hand, the cationic complex **Ni2** arising from the abstraction of the chloride, described by the same group,<sup>12</sup> gives only 1-butene, as shown by GC/MS analyses with an ethylene consumption rate of *ca.* 390 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h. The species was not isolated but has been trapped with several agents which allowed the isolation of more stable complexes.



Scheme 4. Nickel indenyl complexes

### Nickel Complexes of Tridentate Ligands

The coordination of tridentate N,X,N ligands to  $\text{NiCl}_2$  gave penta-coordinated Ni complexes which are efficient for the oligomerisation of ethylene. The best example is given by Carpentier et al. Their nickel complexes with tridentate pyrazolyl ligands<sup>13</sup> (general structure **Ni3**, Scheme 5) can achieve performance up to  $\text{TOF}=80\,000\text{ mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$ . The selectivity of these systems could be up to 93% in 1-butene, all in maintaining a very high TOF ( $60\,000\text{ mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$ ). A very similar system of penta-coordinated Ni with bidentate ligand developed by Braunstein<sup>14</sup> (**Ni4**, Scheme 5) gave a TOF of 31 400 during 35 min, with 70% selection in C4, using a very low loading of co-catalyst  $\text{Al}/\text{Ni}=6/1$ . The content in alpha-olefin in the product was not high, however.

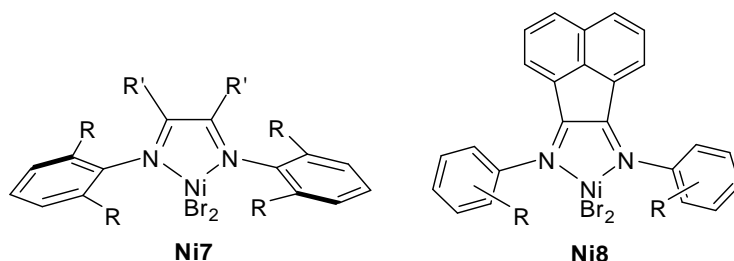


Scheme 5. Nickel complexes with tridentate ligands

A more rigid system as the one reported by Sun<sup>15</sup> based on N-((pyridin-2-yl)methylene)quinolin-8-amine (general structure **Ni5**, Scheme 5) could give generally high TOFs, and in the same time achieve high selectivity in butane and 1-butene. When  $\text{R}_1=i\text{-Pr}$ ,  $\text{R}_3=\text{Me}$ ,  $\text{X}=\text{Cl}$ , the TOF of the oligomersation was up to  $120\,000\text{ mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$  during 20 min, with 92.9% of C4 and 91.2% 1-C4. These systems use however a very important amount of  $\text{Et}_2\text{AlCl}$  as co-catalyst ( $\text{Al}/\text{Ni}=500/1$ ). A similar systems, based on the more rigid and less-donor ligands (2-(benzimidazol-2-yl)-1,10-phenanthrolines), reported by Lu<sup>16</sup> and coworkers are also highly active (general structure **Ni6**, Scheme 5). One of the most active complex, with  $\text{R}_1=\text{R}_2=\text{H}$ ,  $\text{X}=\text{Cl}$ , gave a TOF of up to  $314\,000\text{ mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$  during 20 min with 89.9% C4 (66% in 1-C4). However, just like complexes **Ni5**, these systems use very high charge of co-catalyst ( $\text{Et}_2\text{AlCl}/\text{Ni}=1000/1$ ).

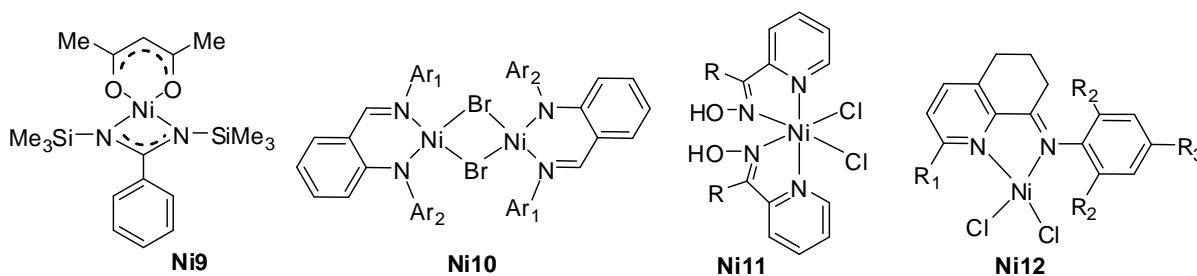
### Nickel Complexes of Bidentate Ligands (N,N), (N,P), (P,P)

Bidentate (N,N) and (N,P) ligands based one amine, imine, amide and phosphine functions are very often used and fine tuning of the steric and electronic properties of these ligands could provide strong catalysts. Among the notable systems are  $\alpha$ -diimine nickel(II) complexes, studied by Brookhart and coworkers.<sup>17</sup> They could catalyse either the polymerization (Complexes **Ni8**, Scheme 6) or the oligomersation of ethylene (Complexes **Ni7**, Scheme 6), depending on the steric bulk of the  $\alpha$ -diimine ligands. The oligomerisations are however not selective and follow Schulz-Flory distributions just like in the case of SHOP catalysts.



Scheme 6.  $\alpha$ -diimine nickel(II) complex.,

The nickel complexes based on other bidentate (N,N) ligands, but combining imine-amide functions reported by Wu<sup>18</sup> (**Ni10**, Scheme 7) and Eisen<sup>19</sup> (**Ni9**, Scheme 7) are also unselective in the oligomerisation of ethylene. Better selectivities have been observed with systems using imine-pyridine bidentate ligands. For example, Mukerjee<sup>20</sup> and coworkers reported nickel complexes of general structures **Ni11** (Scheme 7) which gave very high values of TOFs (around 130 000-170 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h) over a period of 30 min, along with a selectivity of 92% in butane. A reasonable amount of Et<sub>2</sub>AlCl as co-catalysts (Al/Ni=100/1) is needed for the oligomerisation. Same order of activity has been observed for other complexes with imine-pyridine ligand reported by Sun and coworkers (general structure **Ni12**, Scheme 7).<sup>21</sup> The group also claimed that changes of co-catalyst from Et<sub>2</sub>AlCl to ethylenealuminum sesquichloride (ESAC) was beneficial. High TOFs (up to 310 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h over a period of 30 min, when R<sub>1</sub>=Cl, R<sub>2</sub>= i-Pr, R<sub>3</sub>=H) and high selectivities (89.6% in C<sub>4</sub> (of which >99% 1-C<sub>4</sub>)) were obtained. The experiments were done under 10 bar of ethylene. Note that in these examples, the charge in ESAC was very high (Al/Ni=400/1).

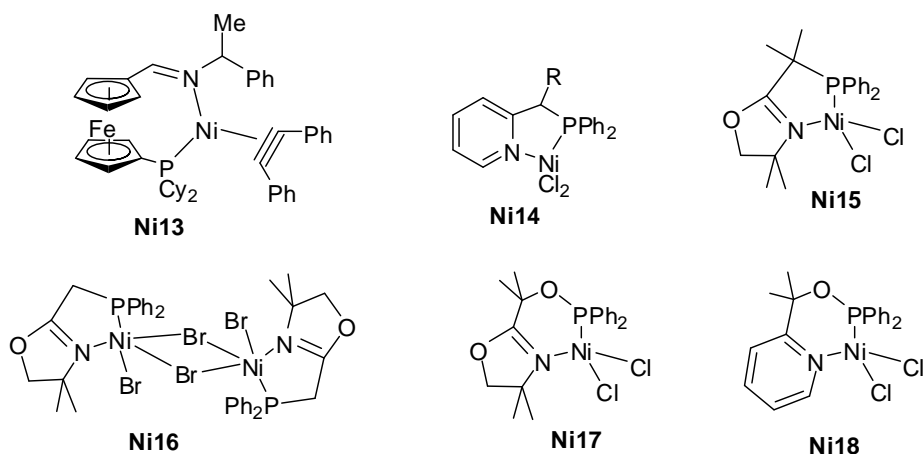


Scheme 7. Nickel complexes of bidentate imine-amide and imine-pyridine ligands

Hor<sup>22</sup> developed complexes of (P,N) ferrocenediyl imine-phosphine bidentate ligands (**Ni13**, Scheme 8) which are very active (TOF up to 91 600 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h during 3h with a reasonable amount of cocatalyst Et<sub>2</sub>AlCl/Ni=146), but not very selective for the oligomerisation of ethylene (69.9% C<sub>4</sub>, 45.9%  $\alpha$  olefins). Other complexes with (P,N) bidentate ligands, such as phosphinopyridine<sup>23</sup> (**Ni14**), phosphino oxazoline<sup>24</sup> (monomer **Ni15**, or dimer **Ni16**), phosphinito oxazoline<sup>25</sup> (**Ni17**), phosphinito (**Ni18**) and phosphonito-pyridine<sup>23b</sup> developed by Braunstein and coworkers also present the same behavior: high activity and limited selectivity in C<sub>4</sub>. For example, with a very low loading of co-catalyst EtAlCl<sub>2</sub>/Ni=6/1, the phosphino

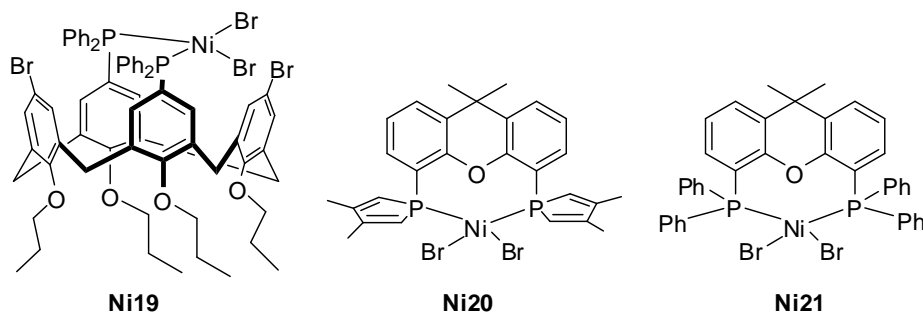


pyridine complexes **Ni14**<sup>23a</sup> with R=Me could give TOF up to 55 200 over 35 min run, under  $p(\text{C}_2\text{H}_4)=10$  bar. The selectivities are however not excellent: for the same cited reference the products contained 66% C4 and 30% C6, selection 11% in  $\alpha$ -C4. Details about (P,N) chelating ligands and dimerisation of ethylene have been the objects of a review by the same group.<sup>26</sup>



Scheme 8. Examples of nickel complexes of (N,P) bidentate ligands

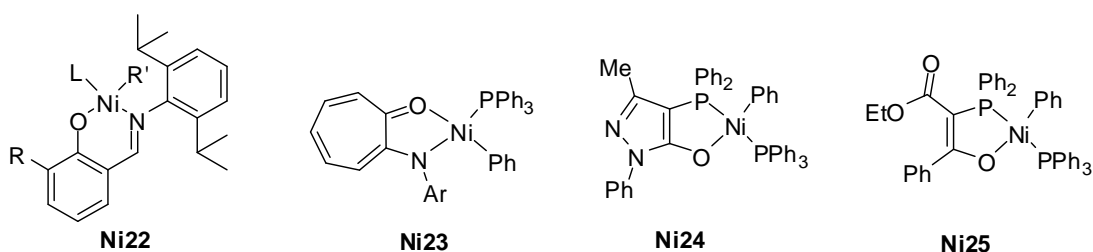
Matt's group suggested that the use of a ligand with large bite angle would facilitate the elimination step terminating the catalytic cycle, thus increase the catalytic activity. They successfully synthesised diphosphinated calix[4]arenes systems which upon coordination to  $\text{Ni}^{\text{II}}$  centres give strongly active complexes for the dimerisation of ethylene (for example, **Ni19**, Scheme 9).<sup>27</sup> Complex **Ni19** could give a TOF of up to 830 000  $\text{mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$  for a run during 15 min at 20 bar ( $\text{C}_2\text{H}_4$ ). The selectivity in 1-butene was limited due to the isomerisation reactions. In the laboratory, other complexes based on diphospholes with large bite angle were synthesized (**Ni20**, **Ni21**, Scheme 9).<sup>28</sup> They act as highly selective catalysts for the dimerisation: oligomerisation catalysed by **Ni20** gave 97% selection in C4 (90% in 1-C4) for a high TOF of 43 000  $\text{mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$ . Complex **Ni21**, however, is less active: under the same conditions, the TOF was of 14 000  $\text{mol}(\text{C}_2\text{H}_4)/\text{mol}(\text{Ni})/\text{h}$ , with 96% selection in C4 (88% in 1-C4).



Scheme 9. Complexes of bidentate (P,P) ligands with large bite angle.

### Nickel Complexes of (N,O) or (P,O) Chelating Ligands.

As the complexes in the SHOP process are based on (P,O) bidentate ligands, many systems employing (N,O) and (P,O) bidentate ligands have been elaborated. However, most of them direct the polymerisation of ethylene and very few are active for the oligomerisation. For example, nickel salicylaldimine complexes **Ni22** (Scheme 10) developed by Grubbs and coworkers<sup>29</sup> or the anilinetropone complexes **Ni23** (Scheme 10) reported by Brookhart and coworkers<sup>30</sup> are highly active in polymerisation. **Ni22** with R=9-anthracene, R'=Ph, L=PPh<sub>3</sub>, catalysed exclusively the polymerization of ethylene with high efficiency (TOF=1.2x10<sup>6</sup> g(PE)/mol(Ni)/h, M<sub>w</sub>= 347 000, PDI=3.0, without co-catalyst). **Ni23** with Ar = C<sub>6</sub>H<sub>3</sub>(iPr)<sub>2</sub> is also highly active in the polymerization of ethylene, with a TOF of 1.34x10<sup>6</sup> g(PE)/mol(Ni)/h, giving polymers with M<sub>n</sub>=104 000 and a rather low polydispersity PDI=1.95.



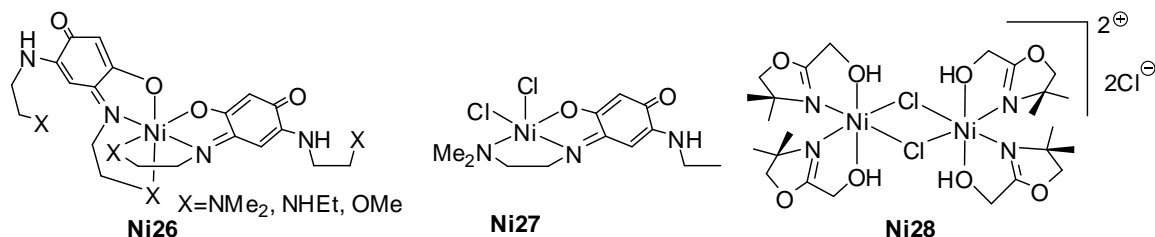
Scheme 10. Complexes of (N,O) and (P,O) bidentate ligands.

When electron poor (P,O) ligands<sup>7</sup> were employed, as those reported by Matt and coworkers, short chain olefins were formed instead of polyethylene. For example, oligomerisation catalysed by **Ni25** (Scheme 10) could attain TOF=68 000 for 1h run, with a selection on C<sub>4</sub>-C<sub>16</sub> equals to 12.3% (in weight), the Schulz–Flory parameter  $\alpha = \text{mol}(\text{C}_{n+2})/\text{mol}(\text{C}_n)$  being 0.93.<sup>7b</sup> Alpha olefins were yielded primarily (wt%=95.8).

Under a constant pressure of ethylene (p=5 bar), in 30 min, **Ni24** catalysed the formation of C<sub>4</sub>-C<sub>16</sub> in 80.2% weight (of which 96.2% weight of alpha olefins), the TOF was of 14 400 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h). The in situ generated complex obtained from **Ni24**, where the coordinated phenyl was replaced by a coordinated ethylene molecule, catalysed the formation of polyethylene.<sup>7a</sup>

The Ni complexes (general structures **Ni26**, **Ni27**, Scheme 11) supported by benzoquinonemonoimine (N,O) chelates developed by Braunstein and coworkers show much better selectivity in oligomerisation of ethylene, with selectivity in C<sub>4</sub> up to 90% with TOF of 24 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h.<sup>31</sup> The amount of  $\alpha$ -olefins is however very limited (9.4%). The same group also developed (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol as (N,O) chelating ligands for Ni complexes (for example, **Ni28**, Scheme 11).<sup>32</sup> These complexes are generally very active and selective in oligomerisation of olefins. Complex **Ni28** offered a TOF of 20 700 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h, with 92% in C<sub>4</sub> (with 62% in 1-C<sub>4</sub>), using a very low co-catalyst charge

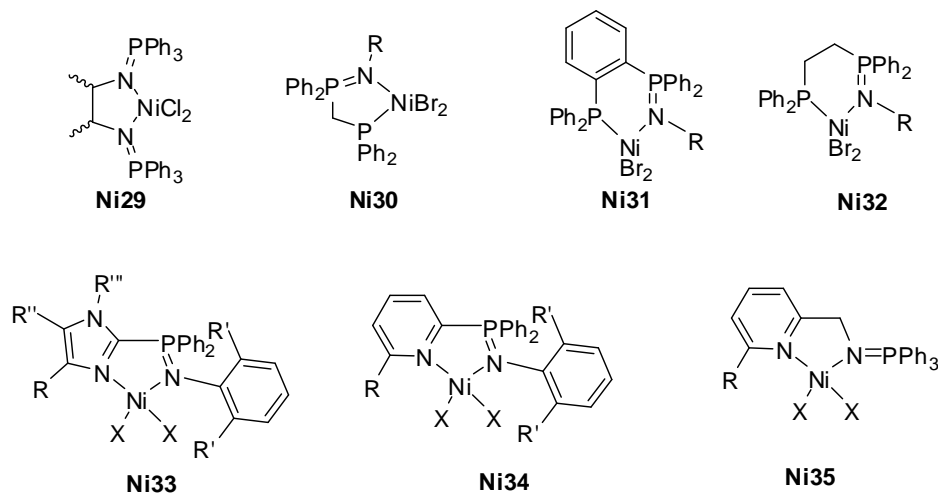
(AlEtCl<sub>2</sub>/Ni=2/1). Activities could be increased with increasing the amount of Al, but this led to a dramatic decrease in C<sub>4</sub>-selectivity.



Scheme 11. Nickel complexes of (N,O) ligands, developed by Braunstein and coworkers.

### Nickel Complexes of Iminophosphoraness

The use of iminophosphoranes for nickel-catalysed oligomerisation has been reported by several groups. All of them are bidentate (N,N) or (N,P) ligands. In 2001, Reau and coworkers reported the synthesis and activities of bis(iminophosphorane) nickel complexes (general structure **Ni29**, Scheme 12).<sup>33</sup> For an 1h run under very low pressure of C<sub>2</sub>H<sub>4</sub> (p(C<sub>2</sub>H<sub>4</sub>)=1.1 bar), the most active catalyst (with phenylene bridge) offered a TOF of 11 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h with 61% selectivity in C<sub>4</sub> (2% of 1-C<sub>4</sub>).

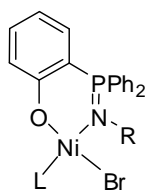


Scheme 12. Nickel-iminophosphorane complexes for the oligomerisation of ethylene.

In 2003, Stephan et coworkers reported on nickel complexes of bidentate ligands combining iminophosphorane and pyridine- or imidazole (**Ni33-35**, Scheme 12).<sup>34</sup> They showed at best an activity of 48 g oligomer/g cat/h/atm, i.e. TOF<1000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h, with very low content in alpha olefins (1-C<sub>4</sub>/2-C<sub>4</sub>=1%/99%). If, however, the iminophosphoranes are associated with a softer donor group (phosphine for example), just as the complexes developed in our laboratory in 2007 (**Ni30-32**, Scheme 12), the resulted complexes offer much better performance in dimerisation of olefins, in terms of both activity and selectivity.<sup>35</sup> As an

example, oligomerisation of ethylene catalysed by **Ni31**, with R=iPr, gave TOF up to 166 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h for a run of 1h under 30 bar of ethylene. The selectivity was 97% in C<sub>4</sub> (73.6% in 1-C<sub>4</sub>).

As the examples of iminophosphorane nickel complexes active in oligomerisation of ethylene remains relatively scarce in comparison with amine or imine functions, and as a continuation of our work in developing bidentate ligands associating one iminophosphorane and one anionic donor group, we were interested in nickel complexes of these types of ligands.



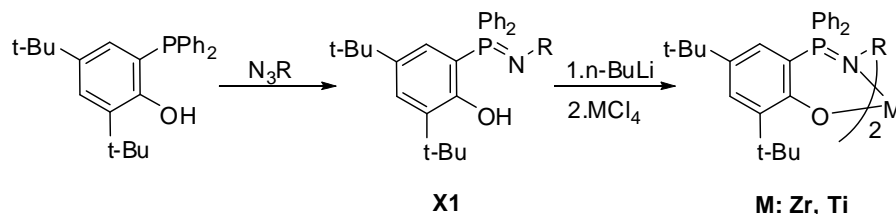
*Scheme 13. Targeted nickel complexes*

Bidentate ligands containing iminophosphorane and phenoxide were chosen to be studied (Scheme 13). In fact, as has been observed above, nickel complexes of (N,O) or (P,O) chelating ligands are not highly active in oligomerisation of ethylene. On the other hand, it seems that the combination of iminophosphorane with a soft, electron-rich donating group is beneficial for the performance of the complexes. It would be thus difficult to predict the performance of such systems in oligomerisation of ethylene.

## II. Synthesis and Activities of Ni-PO Complexes

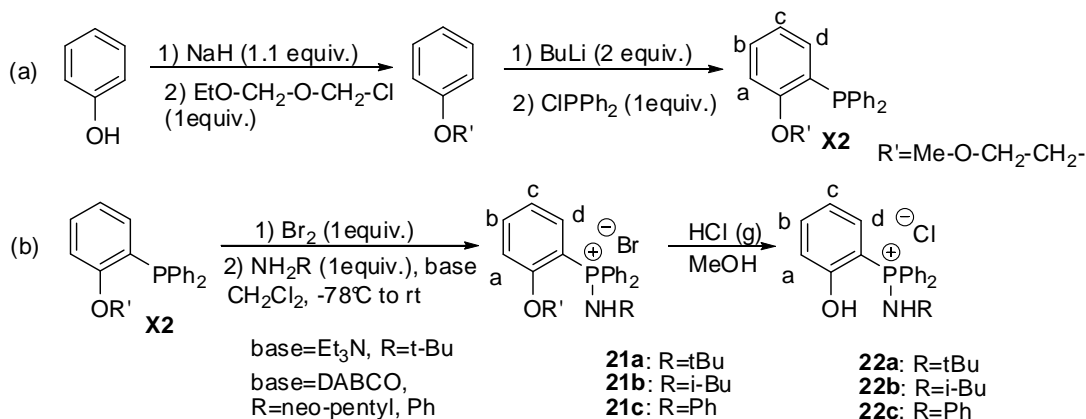
### 1. Ligand Synthesis

In fact, an example of one ligand phenoxide-iminophosphorane already existed in the literature. In 2005, the group of Zhang synthesized the iminophosphorane **X1** by the Staudinger method (Scheme 14).<sup>36</sup> The resulting ligand was coordinated to zirconium and titanium centres. These two complexes showed little activities in polymerization of ethylene: under various activation conditions with MAO (Al/M=2000/1) or i-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (Al/M = 100/1) as co-catalysts, only traces of polymer was obtained.



*Scheme 14. Synthesis of alkolate-iminophosphorane ligands by Zhang and coworkers*

As the use of azides may restrain the possible substitution pattern at the nitrogen atom, another approach was developed using the Kirsanov reaction on the protected phosphinophenol **X2** (Scheme 15). This latter in turn was prepared from phenol according to a procedure described by Bianchi and coworkers (Scheme 15 (a)).<sup>37</sup> After the formation of the aminophosphonium salt, a simple deprotection of the phenol group gave the phenol aminophosphonium salt as colorless crystals or white solid in reasonable yields (60-71% of total yield for the synthesis of **2a-c** from **X2**).



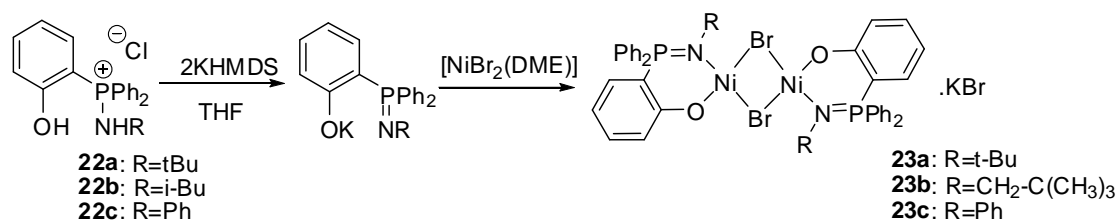
Scheme 15. Synthesis of alcohol-aminophosphonium ligand.

All compounds **22a-c** were fully characterized by NMR multinuclear. In <sup>31</sup>P{<sup>1</sup>H}NMR spectra, each of the three compounds **22a-c** exhibits a unique singlet in the zone (**22a**: 35.2 ppm, **22b**: 36.4 ppm, **22c**: 39.9 ppm), corresponding to the chemical shift of the aminophosphonium groups.

After a double deprotonation with 2 equiv. of KHMDS, colorless solutions were obtained for all three ligands with significant high field chemical shift in <sup>31</sup>P{<sup>1</sup>H} NMR spectra (**22a**: 12 ppm, **22b**: 14.6 ppm, **22c**: 8.4 ppm). These values are much higher than the simple iminophosphorane function in THF (typically from -10 ppm to -20 ppm for the iminophosphorane without a phenoxide function), and differ by the way of deprotonation (when using MeLi, values of chemical shifts are slightly higher). Thus, they are supposed to be the one of the phenoxide iminophosphorane with coordinated potassium (or lithium) cation. However, definitive evidence of this coordination by X-ray diffraction experiments was not obtained due to the difficulty to grow mono-crystal.

As it is unnecessary to isolate the anionic iminophosphorane-phenoxide ligands, coordination tests were carried out on in situ generated ligands from reaction of **22a-c** with KHMDS.

## 2. Complexes Synthesis

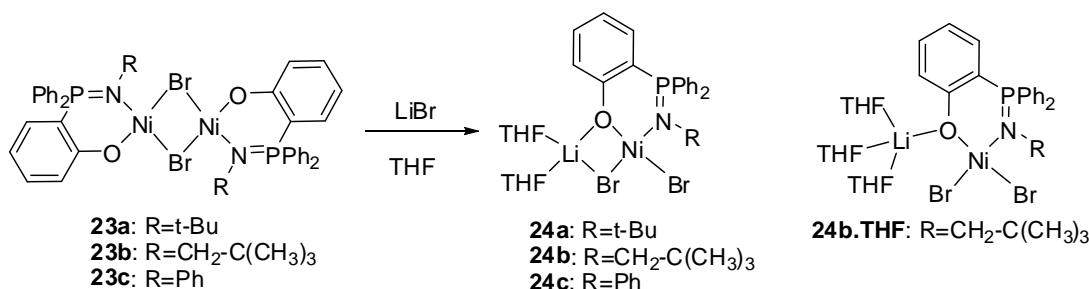


Scheme 16. Coordination of iminophosphorane-phenoxide ligands with [NiBr<sub>2</sub>(DME)]

Addition of [NiBr<sub>2</sub>(DME)] into the solutions issued from the deprotonation of **22a-c** with 2 equiv. of KHMDS in THF immediately yielded pale purple-to-red solutions along with the formation of a white insoluble potassium bromide salt. The complete disappearance of the signal in <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicates the completeness of the coordination reaction and the formation of paramagnetic nickel(II) compounds. After removal of insoluble potassium salts by centrifugation, evaporation of THF and washing of the resulting solid with petroleum ether, nickel complexes **23a-c** were isolated in good yield as pale purple solids for **23a-b**, and a green solid for **23c**.

Elemental analyses correspond to the presence of one molecule of KBr for two Ni centres. This stoichiometry for KBr and the difficulty of complete removal of this molecule suggest that KBr is coordinated to the nickel complex(es), maybe through the interaction with the oxygen of the phenoxides. Structures of complexes **23a-c** as presented in Scheme 16 are just putative simplistic representations. Attempts have been carried out in order to obtain crystals of **23a-c** for X-ray diffraction experiments, using various solvent systems at different temperatures, but no crystal was obtained.

As the coordination of this oxygen with hard cation such as Li is stronger than the one with potassium, lithium could replace the potassium in the above-mentioned complexes. Indeed, the addition of one equivalent of lithium bromide into the solution of **23a-c** in THF results immediately in a change of color from pale purple-blue to deep blue-purple (**24a-b**) or deep green (**24c**). In decreasing the solvent volumes, lithium-nickel complexes precipitated out as purple crystals (**24a-b**) or green crystals (**24c**).



Scheme 17. Formation of bimetallic nickel-lithium complexes.

Single crystals of **24a-c** suitable for X-ray diffraction experiments were obtained by slow diffusion of petroleum ether into a THF solution of the complexes at -40°C. These crystals are extremely sensitive towards the raise of temperature, probably because of the incorporation of many THF molecules in the crystals structures.

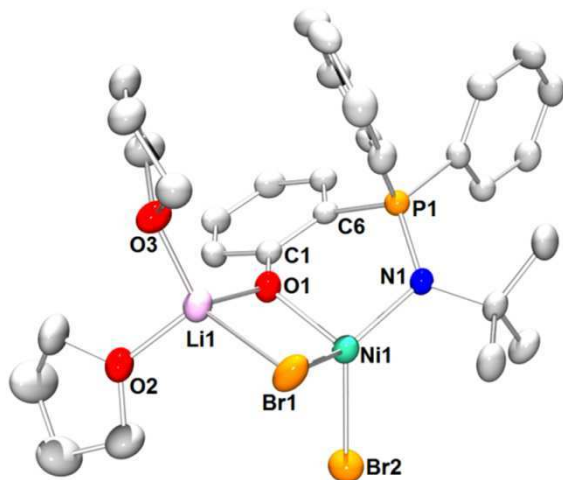


Figure 2. Ortep view of complex **24a**. Hydrogen atoms and non-coordinated THF molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni1-N1 1.977(2), Ni1-O1 1.954(2), Ni1-Br1 2.4526(5), Ni1-Br2 2.3799(5), Li1-Br1 2.535(5), Li1-O1 1.893(5), Li1-O2 1.915(6), Li1-O3 1.915(6), N1-P1 1.602(2), O1-C1 1.332(3), O1-Ni1-N1 98.30 (8), N1-Ni1-Br2 116.17(7), Br2-Ni1-Br1 104.99(2), Br1-Ni1-O1 91.47(6), Li1-O1-Ni1 102.2 (2), Li1-Br1-Ni1 73.8 (1), Br1-Li1-O1 90.4 (2), O1-Li1-O3 117.3 (3), O3-Li1-O2 104.4(3), O2-Li1-Br1 16.5(2),

**24a** is a bimetallic complex (Figure 2). The driving force of the formation of this bimetallic structure is probably the strong interaction between O<sub>phenoxide</sub> and Li atoms. Both the nickel and lithium are in tetrahedral geometry. The two metallic centres Li and Ni are bridged by Br and O-phenoxide atoms, forming a nearly-planar four-membered ring, as shown by the value of the distortion angle O1-Li1-Br1-N1 close to 10°, the two angles at Ni and Li being very close to 90°. Both Li and Ni adopt slightly distorted tetrahedral geometry. The Ni1-Br1 bond (2.4526(5) Å) is slightly longer than Ni1-Br2 (2.3799(5) Å) due to the bridging position of the Br1 atom.

The crystals comprise one non-coordinated THF molecule and is very sensitive to air and temperature. Despite this fragility, the structure described above of the dinuclear complex is maintained in dried solid state, as elemental analysis done on vacuum-dried crystals evidences the presence of LiBr and two molecules of THF.

Elemental analysis results showed the same composition for the two other compounds **24b-c** in the solid state after drying, i.e. the formation of bimetallic complexes with the presence of one LiBr and two molecules of THF. However, X-ray diffraction on single crystals of **24b** obtained from slow diffusion of petroleum ether over a solution in THF shows a different structure (Figure 3). The complex is still binuclear, but this time the Li cation is linked only to the

phenoxide oxygen and surrounded by three THF molecules. Upon drying the solid in vacuum, a four-membered ring similar to the one in **24a** is probably formed along with the release of one coordinated THF, which explains the composition found in elemental analysis.

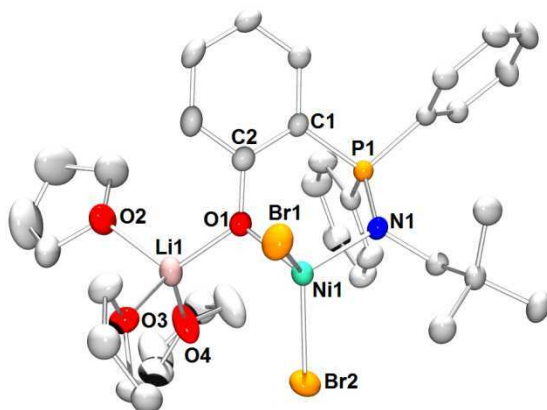


Figure 3. Ortep view of complex **24b-THF**. Hydrogen atoms and non-coordinated THF molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Exchange between Br and Cl anions is observed for the coordinated bromides, probably because of traces of chloride anions from the deprotonation step. Selected distances (Å) and angles (°): Ni1-N1 1.981(3), Ni1-O1 1.975(2), Ni1-Br1 2.4020(8), Ni1-Br2 2.381(2), Li1-O1 1.930(7), Li1-O2 2.006(7), Li1-O3 1.945(7), Li1-O4 1.917(7), N1-P1 1.607(3), O1-C2 1.338(4), O1-Ni1-N1 98.9 (1), N1-Ni1-Br2 107.5(1), Br2-Ni1-Br1 124.39(4).

The solid state structure of **24c** resembles to the one of **24a**. Green crystals of the complexes were obtained by slow diffusion of petroleum ether over a THF solution at -40°C. Though these crystals did not diffract well, X-ray diffraction experiment allowed to establish the connectivity as shown in Figure 4. The two metallic centres Li and Ni are bridged by Br and O-phenoxide atoms, forming a nearly-planar four-membered ring, the lithium being coordinated with two molecules of THF (Figure 4). Elemental analysis on the isolated complex is consistent with the composition in complex **24c**.

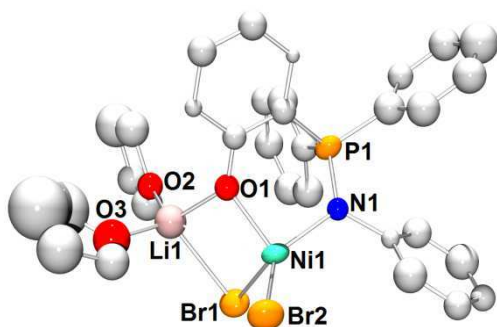
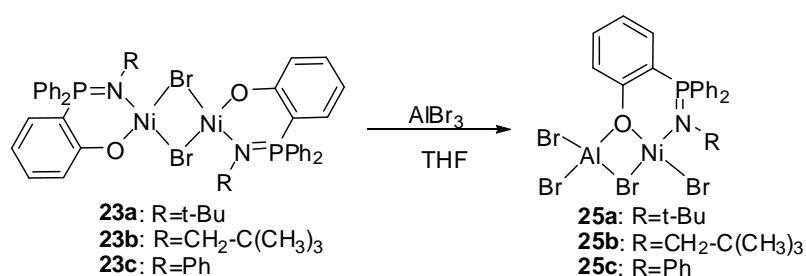


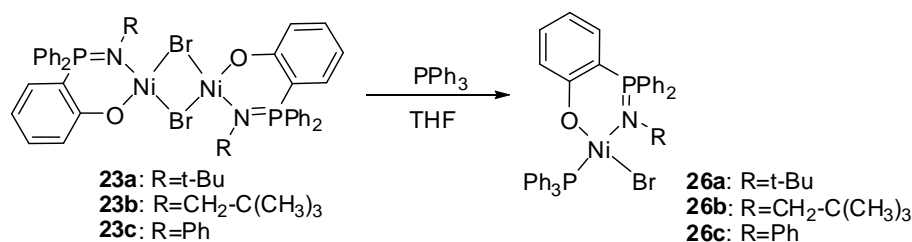
Figure 4. Ortep view of complex **24c**. Hydrogen atoms and non-coordinated THF molecules have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. The poor resolution of the structure does not allow any discussion about distances and angles.





Scheme 18. Formation of bimetallic nickel-aluminum complexes

The formation of binuclear complexes of Ni and Li in **24a-c** demonstrates the strong vocation of the phenoxide oxygen to coordinate to hard Lewis centres. We thus attempted the synthesis of binuclear Al-Ni complexes from **23a-c** (Scheme 18). Indeed, the additions of AlBr<sub>3</sub> into the solutions of **23a-c** in THF yielded blue precipitates after overnight stirring at room temperature. Though X-ray structures for these complexes were not obtained, elemental analysis evidenced the incorporation of AlBr<sub>3</sub> into the nickel complexes and suggested the formation of Al-Ni complexes like the case with Li.



Scheme 19. Formation of nickel-iminophosphorane complex with PPh<sub>3</sub>

In an attempt to break the suspected multimetallic structures in **23a-c**, PPh<sub>3</sub> was added (Scheme 19). The addition of PPh<sub>3</sub> into a solution of **23a-c** in THF resulted in a change of color to deep green in all cases, with the formation of green solid with reduced solubility in THF compared to **23a-c**. These complexes are paramagnetic, suggesting that the nickel centres are still in tetrahedral geometry. These products have been characterised with elemental analysis.

Definite structure of one of these complexes, **26a**, was obtained by X-ray diffraction (Figure 5). Suitable crystals for this experiment have been grown by slow diffusion of petroleum ether over a solution of **26a** in THF at -40°C. The complex adopts tetrahedral geometry, with Ni1-Br1, Ni1-N1, N1-P1 bond lengths having very close values to those observed in **24a,b**. The Ni1-O1 bond length is however significantly shorter (1.921(3) Å in **26a** compared to 1.954(2) Å in **24a** and 1.975(2) Å in **24b**), as a consequence of the fact that the oxygen atom is only coordinated to one metal centre in **26a**, whereas it is coordinated to two metal centres in **24a,b**.

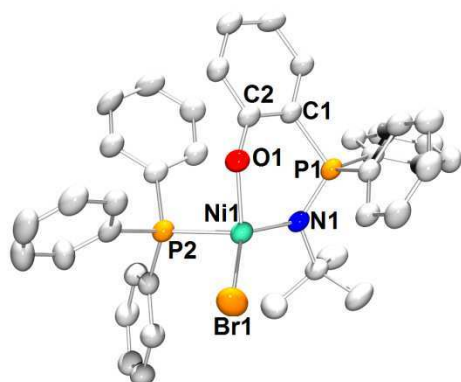
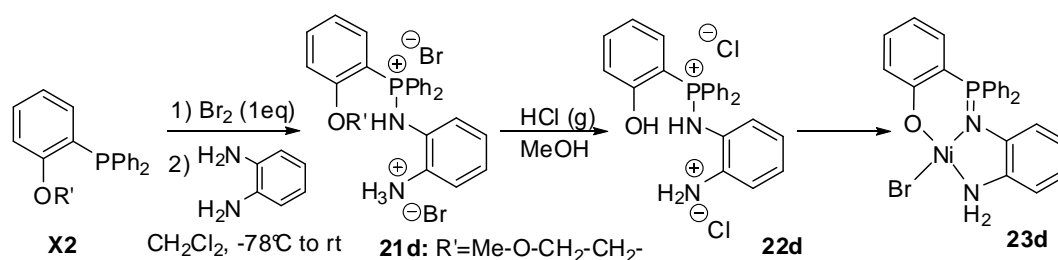


Figure 5. Ortep view of complex **26a**. Hydrogen atoms and non-coordinated THF molecules have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni1-N1 1.971(3), Ni1-O1 1.921(3), Ni1-Br1 2.3712(7), Ni1-P2 2.321(1), N1-P1 1.616(4), O1-C2 1.314(5), O1-Ni1-N1 99.4 (1), N1-Ni1-Br1 127.8(1), Br1-Ni1-O1 109.7(1), P2-Ni1-Br1 102.25(4).

From the results of the described complexes, it has been observed that the nickel completes its coordination sphere with one extra ligand coming from different sources: KBr, LiBr, AlBr<sub>3</sub> or PPh<sub>3</sub>. To circumvent this problem, we have thus developed a tridentate N2O proligand similar to **22a-c**, using *o*-phenylenediamine instead of monoamines. The Kirsanov reaction did not need any additional amine as base, thanks to the presence of another amino group in the diamine. This facilitates greatly the purification step, as the product **21d** was isolated after a simple evaporation of dichloromethane and washing with THF. Deprotection of **21d** was much easier than for **21a-c** and gave the proligands **22d** in high yield (80% starting from **X2**). In <sup>31</sup>P{<sup>1</sup>H}NMR spectrum, **22d** is characterised by a singlet at 39 ppm, a value very close to the ones obtained for **22a-c**.



Scheme 20. Synthesis and coordination to Ni(II) of tridentate iminophosphorane-phenoxide ligand.

Addition of 3 equiv. of KHMDS into a slurry of **22d** in THF yielded a cloudy solution, with the disappearance of the signal of the proligand at 39 ppm and apparition of one unique singlet at 15 ppm, indicating the formation of the anionic phenolate- iminophosphorane ligand. After removal of insoluble potassium salt, addition of [NiBr<sub>2</sub>(DME)] into the obtained solution gave a

deep red solution. Insoluble potassium salt was removed by centrifugation, THF was evaporated and petroleum ether was introduced to wash traces of HMDS. The nickel complex **23d** was isolated as a deep red solid in high yield (73%). This compound however decomposes slowly in solution to give metallic Ni: a mirror could be seen after several weeks on the wall-side of the vial containing **23d** in THF or dichloromethane. This decomposition is likely due to the reductive ability of the amino group on a very-electron donating ligand.

### 3. Catalytic Activities

The synthesized nickel complexes were tested in oligomerisation of ethylene, with  $\text{Et}_2\text{AlCl}$  as co-catalyst (it was found that  $\text{Et}_2\text{AlCl}$  is much more efficient than MAO as co-catalyst, giving higher TOF at much lower Al/Ni ratio). In general, the activities and selectivities of these iminophosphorane-phenoxide complexes are in general significantly higher than complexes of (N,O) and (P,O) ligands existed in the literature. Details of the activities are given in Table 2, as well as the activities of related nickel iminophosphorane complexes reported in the literature for the sake of comparison.

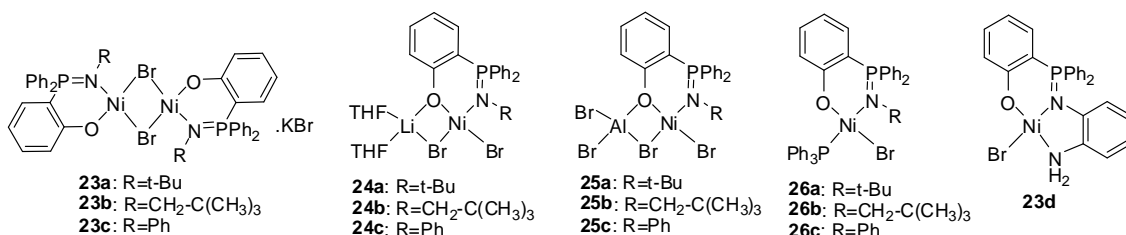


Table 2. Activities of nickel-iminophosphorane complexes in oligomerisation of ethylene.<sup>a</sup>

| entry | complex                   | Co-catalyst          | Al/Ni | Time | TOF (x10 <sup>-3</sup><br>mol(C <sub>2</sub> H <sub>4</sub> )/<br>mol(Ni)/h) | %C4 (% 1-C4) | % 1-C6           |
|-------|---------------------------|----------------------|-------|------|--|--------------|------------------|
|       | [NiBr <sub>2</sub> (DME)] | MAO                  | 300   | 0.5h | 15.0   | 94.0 (85)    | 1.7 <sup>b</sup> |
| 1     | <b>23b</b>                | MAO                  | 300   | 1h   | 20.1   | 98.1 (79.1)  | 1.9              |
| 2     | <b>23b</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 36.9   | 98.4 (73.4)  | 1.6              |
| 3     | <b>23a</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 39.6   | 98.2 (74.3)  | 1.8              |
| 4     | <b>23c</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 68.1   | 98.2 (59.8)  | 1.8              |
| 5     | <b>23c</b>                | AlEt <sub>2</sub> Cl | 22.5  | 0.5h | 67.5   | 97.9 (44.0)  | 2.1              |
| 6     | <b>23c</b>                | AlEt <sub>2</sub> Cl | 45    | 1h   | 72.1   | 97.0 (48.1)  | 3.0              |
| 7     | <b>24a</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 23.7   | 97.6 (73.1)  | 2.4              |
| 8     | <b>24b</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 30.3   | 98.4 (78.1)  | 1.6              |
| 9     | <b>24c</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 14.0   | 98.1 (82.7)  | 1.9              |
| 10    | <b>25a</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 18.5   | 98.7 (85.9)  | 1.3              |
| 11    | <b>25b</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 28.9   | 98.5 (82.4)  | 1.5              |
| 12    | <b>25c</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 7.3  | 98.7 (93.5)  | 1.3              |
| 13    | <b>26a</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   |  |              |                  |
| 14    | <b>26b</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 14.5   | 99.4 (48.9)  | 0.6              |
| 15    | <b>26c</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 15.8   | 99.0 (55.0)  | 1.0              |
| 16    | <b>23d</b>                | AlEt <sub>2</sub> Cl | 22.5  | 1h   | 41.2   | 97.1 (55.6)  | 3.0              |

<sup>a)</sup> experimental conditions: T=25°C, P(C<sub>2</sub>H<sub>4</sub>)=30 bar, 8x10<sup>-3</sup> mmol (Ni), toluene 20 mL. TOF and selectivities are determined by gas-phase chromatography, using n-heptane as internal reference. <sup>b)</sup> other isomers of hexene are formed

The synthesized nickel complexes show high activities (TOF up to 67 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h) and high selectivities in the dimerisation (>97% of C<sub>4</sub> in all cases). No trace of polymer was found.

As stated above, two tendencies were expected concerning the performance of these complexes. Firstly, nickel complexes of (N,O) or (P,O) chelating ligands are not highly active in oligomerisation of ethylene, at least not as active as those featuring (N,N), (N,P), (P,P) ligands. As has been seen in the previous section, they either direct the polymerisation or the oligomerisation of ethylene with a wide product distribution. One the most active and selective systems in the oligomerisation of ethylene (**Ni26-Ni28**), developed by Braunstein and coworkers, offer *ca.* 90-92% selection in C<sub>4</sub> (with at best 62% selection in 1-C<sub>4</sub>), and TOFs between 20 000-24 000 mol(C<sub>2</sub>H<sub>4</sub>)/mol(Ni)/h). Secondly, it seems that the combination of iminophosphorane with a soft, electron-rich donating group is beneficial for the performance of the complexes. Indeed, for the nickel complexes developed in this study, their activities are higher than the nickel complexes of pyridine or oxazoline-iminophosphorane ligands reported by Stephan and coworkers,<sup>34</sup> but not as high as those of phosphine-iminophosphorane ligands previously synthesized in the laboratory.<sup>35</sup>

Inside the series of the synthesized complexes, it clearly appears that with the same iminophosphorane-phenoxide ligand, the more difficultly the auxiliary ligand is removed from the coordination sphere, the lower the activities of the complexes in dimerisation. This is easy to understand, as according to both Cosse and metallacyclic mechanisms, it requires at least two coordination sites in order for the dimerisation/oligomerisation to occur. Thus complexes **26a-b** which have a strongly coordinated PPh<sub>3</sub> as auxiliary ligand are the less active. The bimetallic lithium-nickel complexes are better for the dimerisation, probably because the lithium bromide easily goes away, leaving two possible coordination sites (from two bromides). The most active ones are complexes **23a-b**, as they are supposed to be more exposed in solution (the possible multinuclear structures being easily broken).

The electronic properties probably play an important role. Complex **23c** with phenyl substituent at nitrogen is much more active than complex **23a,b**, which has the same structure but bear alkyl substituents at the nitrogen atom.

The selectivities in alpha olefins vary greatly among the complexes. The formation of 2-C<sub>4</sub> probably results from the capacity of the complexes to catalyse the isomerisation of C<sub>4</sub>. In fact, it has been observed that the longer the systems are kept at low temperature after stopping the C<sub>2</sub>H<sub>4</sub> alimentation and before the quenching of the catalysts with MeOH, the lower the selectivities in 1-C<sub>4</sub> are, and the more 2-C<sub>4</sub> are obtained. Extreme care was thus taken in order to reduce this isomerisation due to the handling conditions, and to represent correctly the state

of the product mixture just after stopping the ethylene alimentation. It is interesting to notice that bimetallic nickel-lithium and nickel-aluminum offer very good selectivities in 1-C4 (more than 70% in all cases and up to 93.5% for **25c**), whereas the complexes with PPh<sub>3</sub> and the complex **23d** of a tridentate ligand are much less selective in terms of 1-C4.

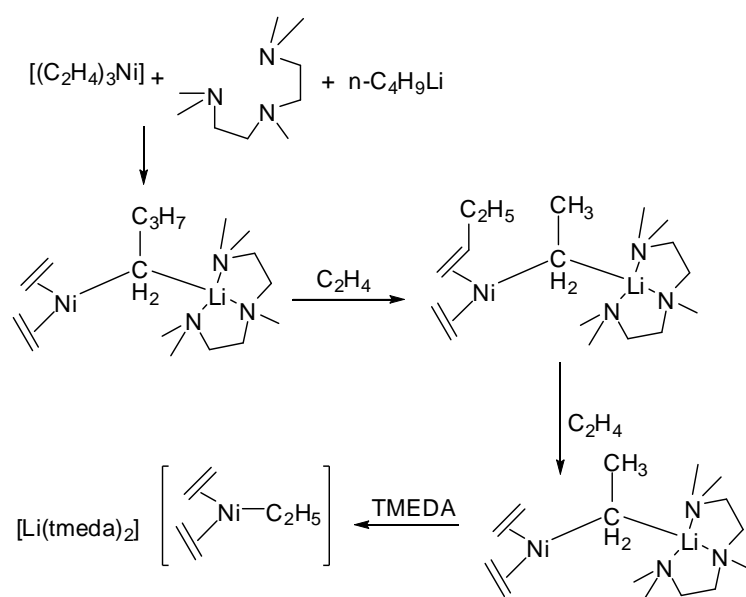
In conclusion, from these results, it could be concluded that during the oligomerisation, the complexes incorporating lithium, aluminum or PPh<sub>3</sub> do not simply act as if these “added” components were removed and left aside, leaving solely the iminophosphorane-phenoxide nickel complexes acting on their own. The formation of bimetallic nickel-lithium and nickel-aluminum complexes **24a-c** and **25a-c** are beneficial for the selectivities of the dimerisation of ethylene, though they are less active than the simple nickel complexes **23a-c**.

### III. Conclusion

A new method for the synthesis of bidentate iminophosphorane-phenoxide ligands have been developed using Kirsanov reaction. This method allows a large variation of substituents on the ligand (in particular at the nitrogen atom), uses inexpensive starting materials and could be applied for large scale synthesis.

The newly synthesized iminophosphorane-phenoxide ligands were coordinated to nickel(II). In particular, the presence of anionic phenoxide group on the ligands allows then coordination of a second metal centre, such as lithium or aluminum. Thus monometallic and bimetallic complexes of nickel-iminophosphorane have been obtained, containing tetrahedral nickel centres. Some of their structures have been evidenced by X-ray diffraction experiments. These nickel complexes were studied in the oligomerisation of ethylene. The activities and selectivities of these iminophosphorane-phenoxide complexes are in general significantly higher than complexes of (N,O) and (P,O) ligands existed in the literature. Their performances in terms of TOF and selectivities (in C4 and in 1-C4) vary greatly in function of the auxiliary ligand or substituents at the nitrogen atoms. The comparisons of performance between the synthesized complexes could be used for the fine design of new nickel complexes efficient for the dimerisation of ethylene.

Furthermore, the formation of bimetallic nickel-lithium and nickel-aluminum complexes is interesting and opens the possibility to develop self-activated bimetallic nickel-aluminum complexes for the oligomerisation of ethylene, based on iminophosphorane ligands. In fact, it has been suggested by many groups (e.g the Wilke and Eisch groups) that one of the key intermediates in the Ziegler nickel effect in polymerization/oligomerisation of olefins are multimetallic complexes of the type Ni( $\mu$ -C)Al or Ni( $\mu$ -C)Li, or the bridging hydride of Ni and Al (Scheme 21, next page).<sup>38</sup> Thus the formation of such self-activated complexes might contribute to the clarification of the mechanism of the Ziegler polymerization/oligomerisation of olefins.



Scheme 21. Model demonstrating the “nickel effect”, from Wilke and coworkers.<sup>38b</sup>

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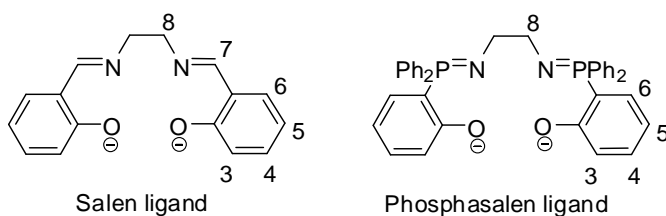


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## Chapter 3

# Phosphasalen Ligand: Synthesis, Coordination and Properties

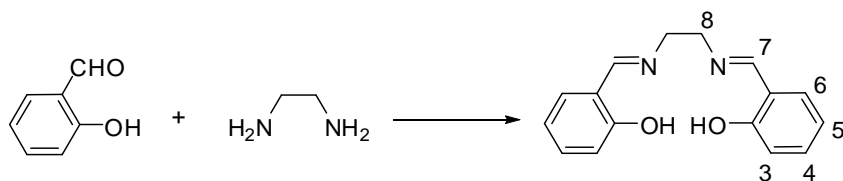
Following our interest in new systems of ligands associating iminophosphorane(s) with anionic donating group, and as a continuation to the work on bidentate iminophosphorane-phenoxide ligands, we developed tetradentate ligands combining two iminophosphorane functions and two phenoxides. These latter, termed “phosphasalen”, are the phosphorus analogues of the well known Salen ligands in chemistry.



## I. Introduction to Salen Ligands

### 1. Synthesis, Coordination and Application of Salens

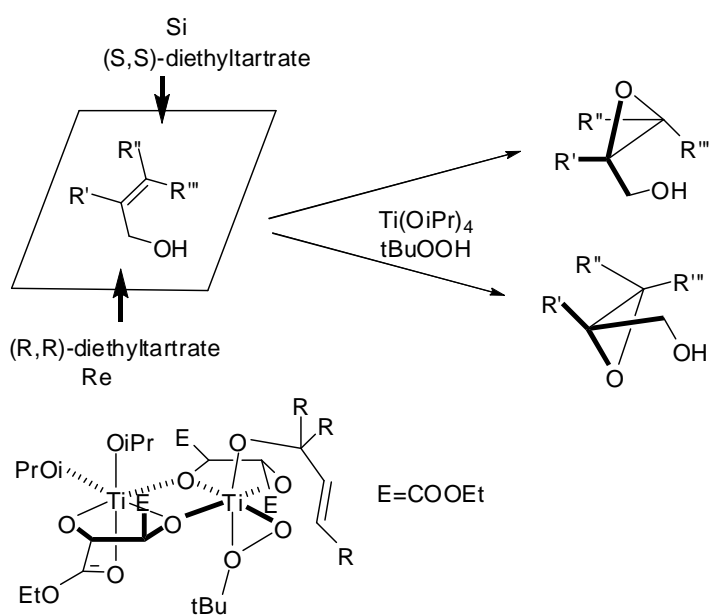
The chemistry of Salen ligands and their complexes, as well as their applications in catalysis is a well elaborated yet still fertilised domain.<sup>1</sup> Strictly speaking the term Salen is reserved to the diimine diphenol product (N,N'-bis(salicylaldehyde)ethylenediamine) from the condensation of two equivalents of salicylaldehyde with one equivalent of ethylenediamine. Variations of substituents on the diamine linker, the phenoxide rings or on the carbon of the imine functions extend largely the Salen ligands class. Recently, the term Salen is even used to describe general tetradentate N<sub>2</sub>O<sub>2</sub> ligands resulting from the condensation of a diamine and two aldehydes.



Scheme 1. Synthesis of unsubstituted Salen ligand and its conventional numbering.

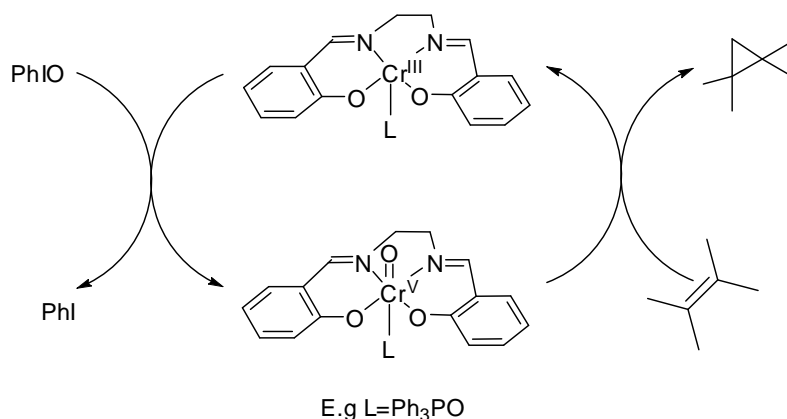
The double deprotonation of Salens gives tetradentate ligands which could bind strongly to metal centers through the phenoxide and imine groups. The ease of synthesis, the large scope of possible variations on ligand structure, and the ease of complex structure control when dealing with tetradentate ligands makes Salens ligands of choice in many studies. Their complexes have been successfully employed in various chemical transformations. The most significant ones being asymmetric epoxidation, epoxide ring-opening and co-polymerisation of carbon dioxide and epoxides.

The major breakthrough in asymmetric epoxidation was reported by Sharpless and Katsuki with titanium systems.<sup>2</sup> This method allows the enantioselective epoxidation of prochiral allylic alcohols. The asymmetric induction is achieved by adding an enantiomerically enriched tartrate derivative (Scheme 2). The catalyst is supposed to be a titanium dimer, and the reaction is thought to happen through a key intermediate in which the hydroperoxide, the allylic alcohol group, and the asymmetric tartrate ligand are bound to the titanium centres via oxygen atoms.<sup>3</sup> This discovery and the development of the reaction has led to what is now called the Sharpless AE (AE: asymmetric epoxidation). In 2001, Sharpless was given the Nobel prize in Chemistry "for his work on chirally catalysed oxidation reactions" together with William S. Knowles and Ryoji Noyori "for their work on chirally catalysed hydrogenation reactions".



Scheme 2. Sharpless asymmetric epoxidation and putative key intermediate.

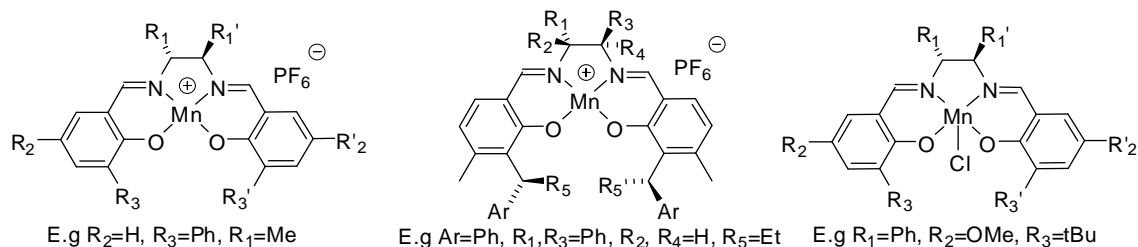
This method is however restricted to functionalised alkenes. On the other hands, in the 80ies, Koichi and co-workers first found that both Cr(Salen) and Mn(Salen) complexes were effective catalysts in epoxidation of unfunctionalised alkenes using PhIO as terminal oxidants.<sup>4</sup> Their studies on the mechanism of the reaction showed the roles of oxo-chromium or oxo-manganese salen complexes as active species in the oxygen transfer.



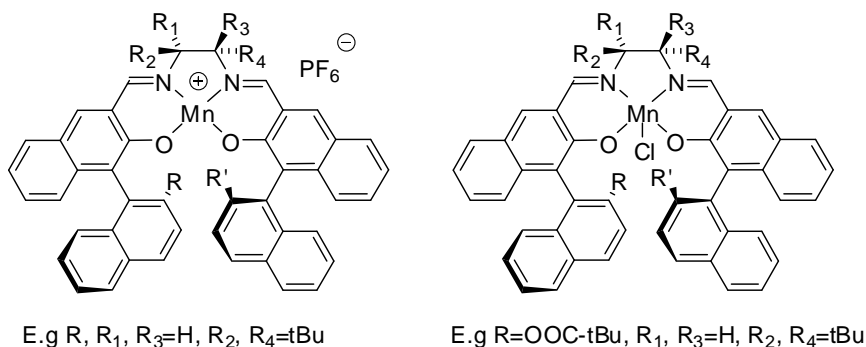
*Scheme 3. Mechanism of the epoxidation of alkenes with PhIO, catalysed by Cr(Salen) complexes.*

The potential of developing asymmetric catalysts on the Kochi catalyst was noticed by Jacobsen and Katsuki, both had worked under Sharpless. Compared to systems of two or three dentate ligands as used in AEs developed by Sharpless et coworkers, Salen complexes do not normally dissociate in solution, thus the control on the composition and geometries of metal complexes in solution becomes easier. As a consequence, the enantiomeric control should also be better.

In 1990, Jacobsen and Katsuki independently reported the AEs of unfunctionalised alkenes with ArIOs as oxidants using manganese salen complexes. Since then the area of metal salen mediated asymmetric reaction in general, and AE in particular has expanded rapidly.<sup>4a, 5</sup> The possible introduction of asymmetric centers at many different places on the salen ligands, and its relative rigid frame offers fine tunings of the salen ligands to better catalytic performances. Scheme 4 and Scheme 5 present examples of Jacobsen's first and second generation catalysts as a small demonstration for these mentioned possibilities.

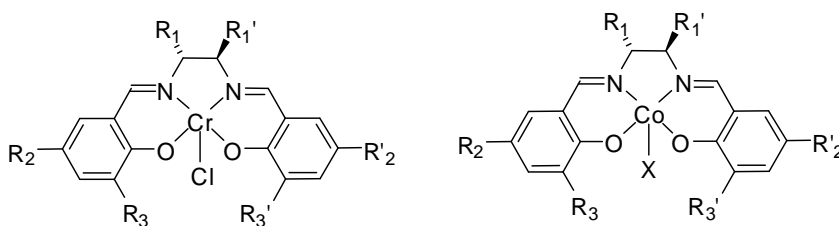
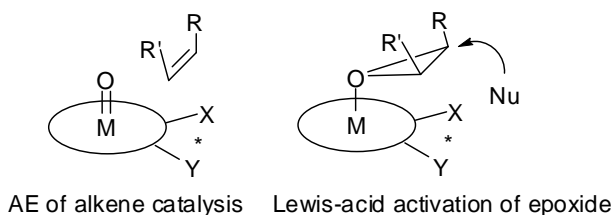


*Scheme 4. Jacobsen's catalysts*



Scheme 5. Katsuki's second generation catalysts.<sup>4a</sup>

From the studies of asymmetric epoxidation, an apparent relationship between the transition state of epoxidation and the ground state of coordinated epoxides was established. This relation led to one question whether the same catalysts which are able to discriminate effectively the two faces of olefins would be able to create an asymmetric environment and thus favor one particular attack on the epoxide (Scheme 6). Following this direction, Jacobsen and coworkers have developed powerful catalysts for the epoxide ring-opening reaction based on chromium and cobalt salen complexes<sup>6</sup> (though the mechanism for ring-opening of epoxides has been shown to be much more complicated and involve in the same time the activation of the epoxide and the nucleophile by two catalyst molecules).

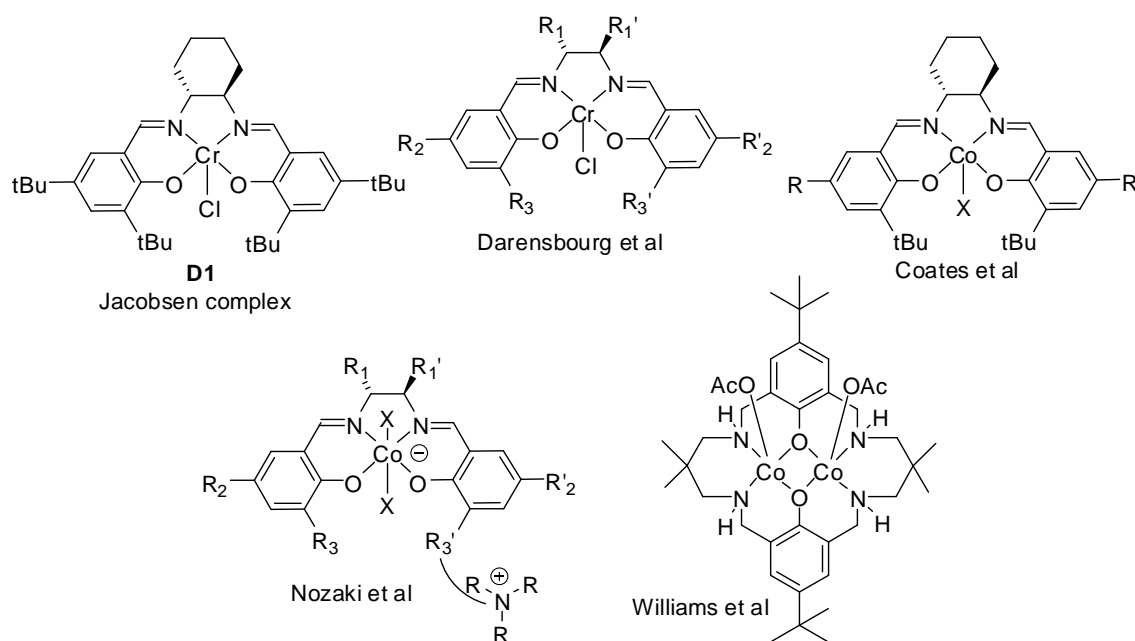


Scheme 6. (top) Side-on approach in AE and possible mode of activation in Asymmetric ring-opening of epoxies by chiral metal catalyst, adopted from Jacobsen *et al*<sup>6c</sup>, (bottom) Jacobsen's catalysts in asymmetric epoxide resolution

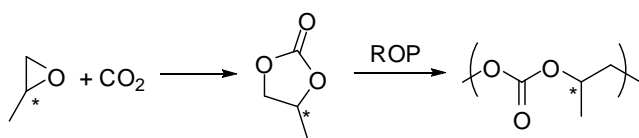
Another important application in catalysis of Salen complexes is the copolymerisation of epoxides and CO<sub>2</sub>. The heterogeneously catalysed reaction of CO<sub>2</sub> and propylene oxide to give polycarbonate was first discovered by Inoue's group in 1969.<sup>7</sup> Following this discovery, many heterogeneous and homogeneous catalytic systems have been developed.

The success of Jacobsen's catalysts in the ring-opening of epoxides suggested that these same compounds could be active in the stereo-regular copolymerization of epoxides and  $\text{CO}_2$ . Indeed, in 2000, Jacobsen and coworkers reported in a patent that the (R,R)-chromium complex **D1** (Scheme 7) catalysed the selective reaction of  $\text{CO}_2$  (1 bar) with the (S)-enantiomer of *rac*-1,2-epoxyhexane to afford polycarbonate.<sup>8</sup> In the same period, Paddock and Nguyen studied the use of various chromium salen complexes for the coupling of epoxides and  $\text{CO}_2$  to give cyclic carbonate.<sup>9</sup>

Since then, the use of salen ligands in designing catalysts for this transformation has expanded. Indeed, cobalt and chromium salen complexes were demonstrated to be among the most effective catalysts up to date for this process.<sup>10</sup> Scheme 7 presents some of these systems.<sup>10c, d</sup> With carefully modification of the substituents on the salen ligand, the catalysts could afford stereo-regular enriched polycarbonate. This subject is actively studied by many groups (mainly Coates', Nozaki's and Lu's).<sup>10d</sup>



Scheme 7. Selective catalysts for the copolymerization of  $\text{CO}_2$  and epoxides, based on Salens and derivatives.



Scheme 8. Polycarbonate production from cyclic carbonate.

One other interesting method, but less direct, for the production of stereo-regular polycarbonate from  $\text{CO}_2$  and epoxides also originated from the studies in asymmetric epoxide ring opening. As mentioned before, the use of salen complex to catalyse the formation of cyclic carbonate from

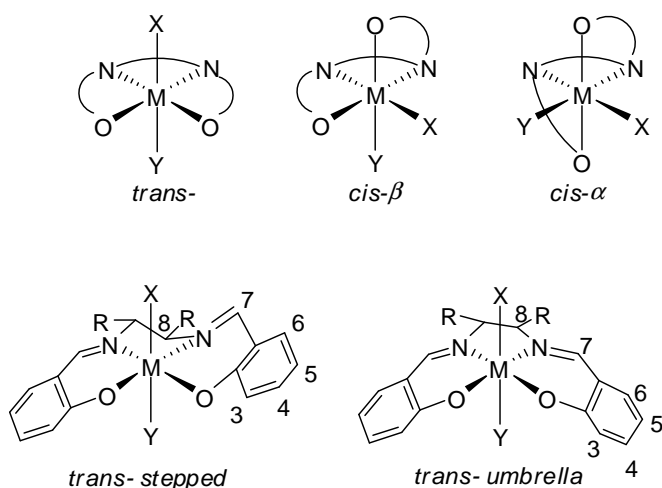
CO<sub>2</sub> and epoxide was first reported by Paddock and Nguyen.<sup>9</sup> The products are however racemic mixtures. Lu and coworkers used chiral Co(Salen) catalysts for the coupling of epoxides and CO<sub>2</sub> to obtain enantiomerically enriched cyclic carbonates,<sup>11</sup> which could then give enantiomerically enriched polycarbonate by ring-opening polymerization.

Applications of Salen ligands in catalysis could be found in many other reactions. For metal-based catalysts for selective asymmetric sulfoxidation, salens and derivatives are ligands of choice and give most of the effective catalysts.<sup>12</sup> Environmentally friendly metals such as titane<sup>13</sup> or iron<sup>14</sup> are the preferred metals for this transformation. Other examples include Nguyen's ruthenium salen complexes for cyclopropanation reaction of alkenes,<sup>15</sup> Salen complexes of titanium and vanadium for the asymmetric cyanosilylation of carbonyl compounds,<sup>16</sup> BINOL-Salen ligands for the asymmetric addition of alkynes to aldehydes with zinc complexes,<sup>17</sup> chromium and cobalt salen complexes for asymmetric hetero Diels-Alder reaction,<sup>18</sup> cobalt and zirconium-salen complexes for the Bayer-Villiger reaction.<sup>19</sup>

## 2. Configuration of Salen Complexes and Importance of *cis*-Complexes

### 2.1 Configurations and Conformations for Salen Complexes

Catalytic activities of Salen complexes strongly depend on the geometry and electronic properties conferred by the ligands. The rigidity of salen ligands due to the presence of the imine functions in conjugation with the phenoxide ring is in the same time an advantage and a drawback. The advantage is that the geometry of the complex is well controlled. The drawback is the limited flexibility, which may be detrimental for many catalytic transformations. However, this rigidity of the imine functions is often overcome by the flexibility endowed by the two C<sub>sp</sub><sup>3</sup> in the diamine backbone.



Scheme 9. Configurations and conformations of salen complexes.

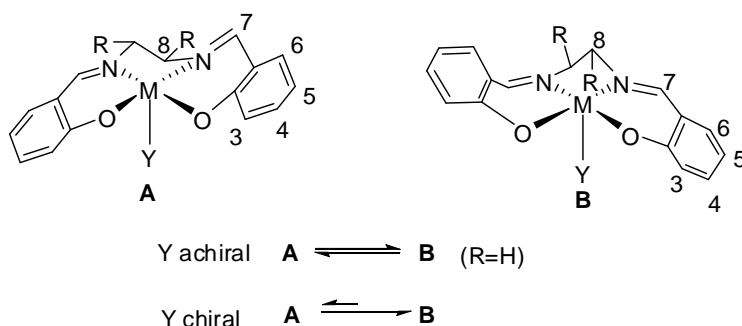
Upon coordination to a metal, the [O,N,N,O] frame can adopt many configurations: *trans*-configuration, in which the [O,N,N,O] occupy all the four equatorial positions and the two

ancillary ligands occupy two apical positions, *cis-β* in which the two ancillary ligands occupy one apical and one equatorial position, and *cis-α* where they take two equatorial positions.

The most usually seen configuration for salen complexes is *trans*-.<sup>1b, 12</sup> A *trans*-metallo-salen complex in its turn could exist in different conformations, due to the flexibility of the diamine backbone. Two typical ones are stepped and umbrella conformations.

The choice of stepped or umbrella conformation is often determined by the substituents on the diamine backbone, which govern the conformation of the five-membered ring formed by the metal center and the diamine (half-chair or envelope), which would in turn govern the conformation of the complex. The chelate ring in *trans*-stepped salen complexes generally exists in half-chair conformer, and that of the *trans*-umbrella complexes exists in envelope conformer. For example, salen complexes with substituents at 8,8' positions often exist in stepped configuration, with the chelate ring in half-chair conformation, so that the two substituents could be in equatorial positions (Scheme 9).

Just as the substituents on the diamine backbone, the steric elements from the ancillary ligands could also be determinant for the conformation of the salen ligands. For example, *trans*-step metallo-salen exist in two possible step conformations which are in equilibrium. The introduction of one chiral element in Y shifts the equilibrium to one side (Scheme 10).



Scheme 10. Influence of ancillary ligands to the conformation of Salen.

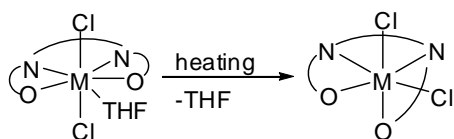
## 2.2 Cis-Complex and Catalytic Activity.

When the ancillary ligand is multidentate, metallo-salen adopt *cis*-configuration. For example, Co(II) salen complexes often adopt *trans*- configuration with stepped or umbrella conformations.<sup>20</sup> When treated with acetylacetonate or oxalate, both bidentate ligands, they change to *cis-β* configuration.<sup>21</sup>

Salen complexes of some metals preferentially adopt *cis*- configuration with or without multidentate ancillary ligand. Zirconium and hafnium salen complexes adopt seven-coordinated pentagonal bipyramidal geometry, in which one solvent molecule (THF) takes an equatorial

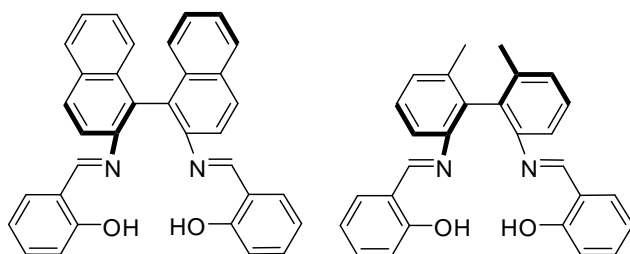


position along with the salen ligands in *trans*-configuration. When heated in toluene, they lose the solvent molecule and adopt octahedral geometry with *cis-β* configuration (Scheme 11).<sup>22</sup>



Scheme 11. Transition *trans-cis* configurations of zirconium and hafnium salen complexes

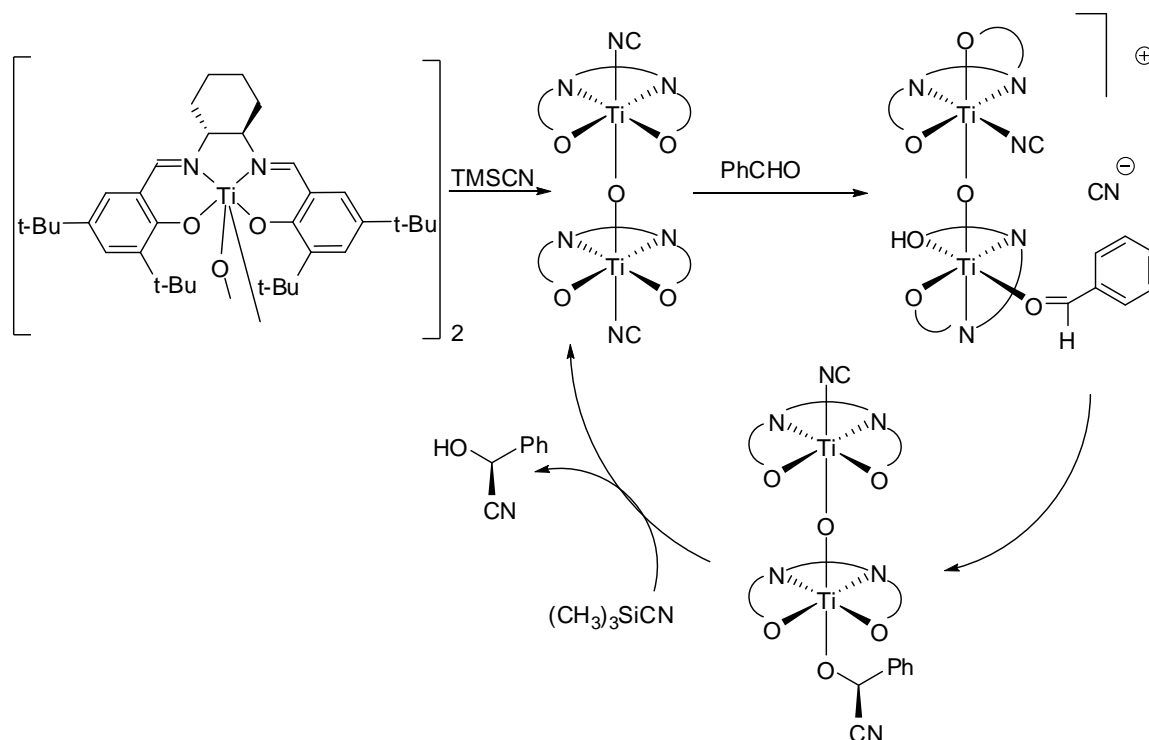
Substituents can also direct the configuration of the ligand: chiral metallosalen complexes of titanium having substituents at C7 and C8 (C7' and C8') adopt *cis-β* configuration to avoid steric repulsions between these substituents,<sup>23</sup> whereas the complex with only substituents at C7 and C7' exists in *trans*-configuration (Scheme 9). Some bulky chiral salen ligands also adopt *cis-β* configuration, such as those derived from 2,2'-diamino-1,1'-binaphthyl or 2,2'-diamino-6,6'-dimethyl-1,1'-biphenyl (Scheme 12).<sup>24</sup>



Scheme 12. Salens derived from 2,2'-diamino-1,1'-binaphthyl (left) or 2,2'-diamino-6,6'-dimethyl-1,1'-biphenyl (right).

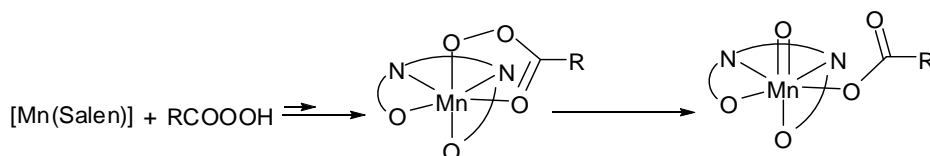
Though *cis*-metallosalen complexes are not as abundant as those for *trans*-configurations, it has been shown that *cis*- configurations offer unique catalytic activities compared to *trans*-configurations.<sup>12</sup> For example, in these complexes interactions between two ancillary ligands could be favored, this aspect being important in catalytic transformations involving two or more agents. In some cases it has been shown that a *trans*-complex isomerises to the *cis*-complex to participate in the catalytic cycle.

The most well-known example is the case of titanium complexes in asymmetric addition of TMSCN to aldehydes (Scheme 13). The active species is considered to be a *cis-β-μ*-oxo titanium complex. Upon treatment with TMSCN, a *trans-μ*-oxo dimer was formed. With the arrival of the aldehyde in equatorial position, an apical CN is displaced by one arm of the ligand, this moiety being in *cis-β* configuration. On the other moiety of the complex, the CN anion changes position from apical to equatorial. In the so formed intermediate, CN ligand and the aldehyde are placed close to each other and could react in an intramolecular fashion.



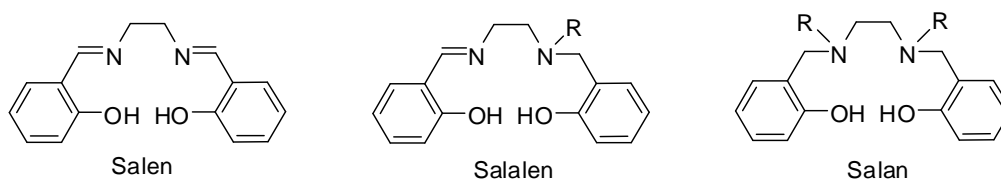
Scheme 13. Mechanism of Ti-catalysed asymmetric addition of TMSCN to aldehydes.

Another example includes Mn-salen complexes in epoxidation reaction using a mixture of molecular oxygen and aldehyde. These complexes are often considered to adopt trans-configuration.<sup>25</sup> But later studies suggested the participation of *cis-β* peroxo complexes in the catalytic cycle (Scheme 14).<sup>26</sup>



Scheme 14. Formation of oxo-complex from  $[Mn(Salen)]$  complex and organic peroxy acid.

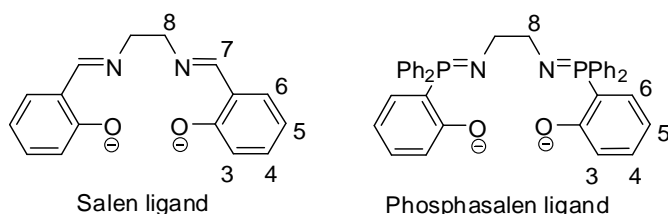
The need for new ligands presenting different electronic environment and especially a more important degree of flexibility has led to a rapid development of Salen ligands, featuring two amine functions instead of imines, and their derivatives as well as the hybrid Salalens (containing an imine and an amine group) recently (Scheme 15).



Scheme 15. Salen, Salalen and Salan ligands

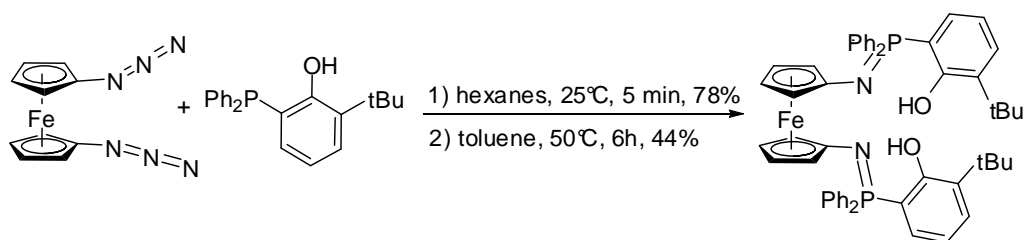
As expected, the change from a double bond C=N in the imine group of Salen to a single one in the amine group of Salan renders the [O,N,N,O] skeleton more flexible, thus in some cases favors the formation of *cis*-complexes.<sup>27</sup> For example Goldberg or Zigler<sup>27b</sup> has reported the formation of *cis-β* complexes of titanium or zirconium<sup>27c</sup> or molybdenum with salalen ligands. Complexes of Salan ligands have shown unique catalytic activities.<sup>27b, 28</sup> The titanium salan complexes<sup>28c, 28a</sup> are efficient catalysts in asymmetric epoxidation. In sulfoxidation with H<sub>2</sub>O<sub>2</sub>, salan complexes of iron or titanium offer high activity.<sup>14a, 29</sup> Other applications of salan or salalen ligands are still to be actively investigated,<sup>30</sup> such as in copolymerisation of epoxide and CO<sub>2</sub><sup>30b</sup> or in aerobic oxidation.<sup>30a</sup>

Following this trend, we noticed that replacing imines by iminophosphoranes in salen ligands could be interesting. As we have seen, the P=N bond in iminophosphorane is not a real double bond and thus could be free to rotations.<sup>31</sup> Furthermore, electronic properties of P=N is very different from imine, amine, or amide. We thus developed a new class of ligand which we called Phosphasalen, whose general structure is presented in Scheme 16.



Scheme 16. Salen ligand and Phosphasalen ligand.

Independently, and unknown to our group, in the same time, the group of Diaconescu developed a new ferrocene diphosphazene ligand based on Staudinger reaction of diazidoferrocene and a phosphinophenol<sup>32</sup> (Scheme 17).

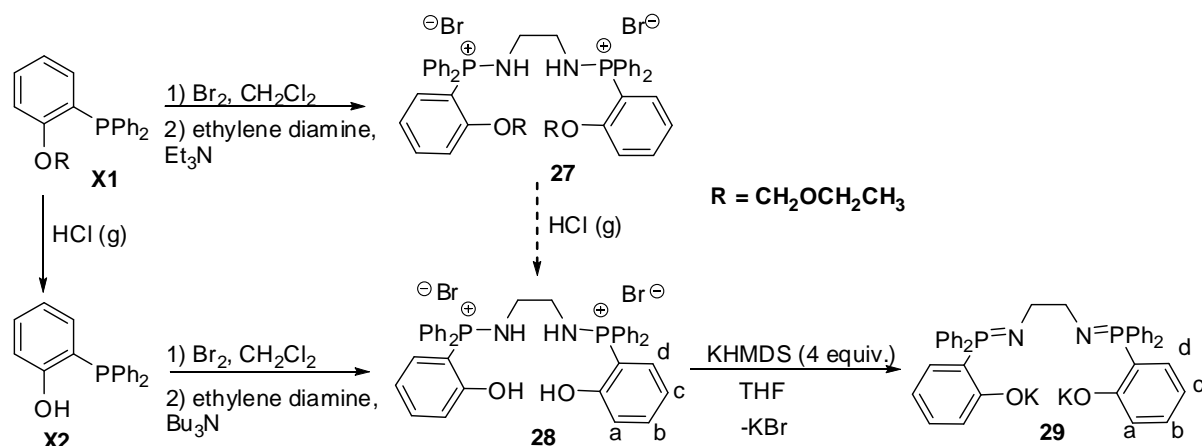


Scheme 17. Synthesis of ferrocene diphosphazene by Diaconescu et al.

The ligand also contain two iminophosphoranes and two phenoxide functions, but the molecule has a ferrocenediyl linker instead of ethylene. Its electronic and steric properties are thus completely different from phosphasalen ligands. Furthermore, the synthesis of phosphasalen ligands was achieved using Kirsanov reaction, thus giving access to a broad, completely different range of compounds.

## II. Phosphasalen Ligand: Synthesis, Coordination and Properties

### 1. Phosphasalen Synthesis



Scheme 18. Synthesis of Phosphasalen ligand.

Following the synthesis of bidentate (PN,O) ligand reported in chapter 2, the synthesis of unsubstituted phosphasalen ligand **29** featuring an ethylene diamine link was first attempted from the protected o-diphenylphosphinophenol **X1** (Scheme 18), which was prepared starting from phenol following a literature procedure reported by Bianchi and coworkers.<sup>33</sup> After oxidation of the phosphine function with bromine, the corresponding phosphonium bromide salt was reacted with ethylenediamine (0.5 equiv.) in presence of triethylamine (1 equiv.) to give the bis-aminophosphonium salt **27** in 70% yield after aqueous work-up. The deprotection of the protected group by HCl-saturated MeOH solution gave the proligand **28** in high yield (81%).

However, contrary to the deprotection leading to bidentate (PN,O) proligand, this reaction was very sensitive to the experimental conditions, and the factors allowing the formation of **28** proved to be difficult to control. We thus modified the synthesis strategy and performed first the deprotection of the phenol functionality and then the Kirsanov reaction. O-diphenylphosphinophenol **X2** was obtained from **X1** by deprotection in HCl-saturated MeOH.<sup>33</sup> Its bromination followed by nucleophilic substitution with ethylenediamine (0.5 equiv.) in presence of tributylamine (1 equiv.) gave the expected bis-aminophosphonium salt **28** in 63% yield (Scheme 18). The compound has limited solubility in dichloromethane and could be isolated by precipitation in THF. For this reason, tributylamine was used in place of triethylamine because of the solubility of its ammonium hydrobromine salt in THF which enabled its easy removal.

**28** was characterised by multinuclear NMR spectroscopies in  $\text{CDCl}_3$ , despite its poor solubility in this solvent. In  $^{31}\text{P}\{^1\text{H}\}$  spectroscopy the equivalent phosphorus atoms of **28** appear as a

singlet at  $\delta(\text{CDCl}_3) = 39.3$  ppm which is in the range of the signals for bidentate phenol-aminophosphonium salts reported in chapter 2. In  $^1\text{H}$  NMR spectrum, the bridging ethylene protons appear as a doublet ( $^3J_{\text{P,H}} = 10.5$  Hz) with a chemical shift ( $\delta(\text{CDCl}_3) = 3.43$  ppm) similar to the one observed for bis(phosphine-aminophosphonium) salts featuring such ethylenediamine linker.<sup>34</sup>

Monocrystals suitable for X-ray diffraction of **28** were obtained by slow evaporation of a solution in chloroform. The structure of **28** is depicted in Figure 1. No hydrogen bonds between O, N and the protons of the phenol or aminophosphonium group has been detected. The two bromide anions stay quite far away from the diaminophosphonium cation and exert only weak hydrogen bonds with the protons of OH and NH groups, and the proton in chloroform (the distance between O, N,  $\text{Cl}_3\text{C}$  and the nearest Br being 3.120, 3.402, 3.592 Å respectively).  $\pi$ -stacking exists for one phenyl ring on each phosphorus atom, the perpendicular distance between two stacked rings being  $\sim 3.37$  Å.

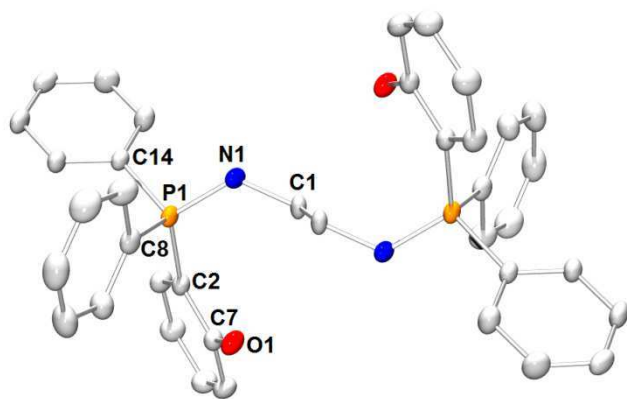


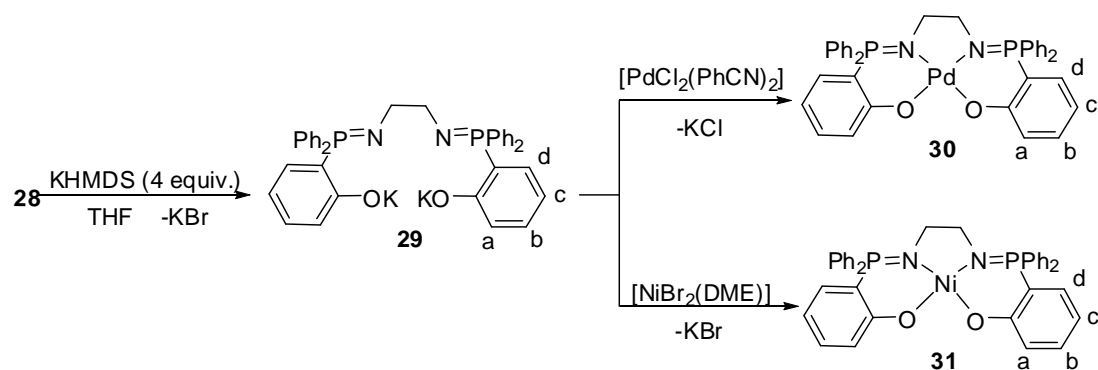
Figure 1. ORTEP view of **28**. Hydrogen atoms, solvent molecules and bromide anions have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): P1-N1 1.623 (2), P1-C2 1.790 (2), P1-C8 1.792 (2), O1-C7 1.355 (3).

The phosphasalen ligand **29** was generated from **28** by deprotonation using potassium hexamethyldisilazane (KHMDs, 4 equiv.) in THF at room temperature (Scheme 18). The formation of **29** was monitored by in situ  $^{31}\text{P}\{^1\text{H}\}$  NMR, the completeness of the reaction was indicated by the presence of one singlet at  $\delta(\text{THF}) = 18.6$  ppm indicating completion of the reaction. After removal of insoluble potassium salts and evaporation of solvent, the obtained residue was washed with petroleum ether to deliver **29** as a white powder in 99% yield. The structure of **29** was unambiguously established by NMR spectroscopy, and elemental analysis.

## 2. Coordination with Group 10 Metals and Studies of the Ligand Properties

### 2.1 Complexes Synthesis and Characterisations

In order to study the coordination properties of the phosphasalen ligand, it was first coordinated to group 10 metals: Pd(II) and Ni(II) (Scheme 19). As it was unnecessary to isolate the free ligand **29**, all coordination experiments were conducted from the bis-aminophosphonium salt **28**.



Scheme 19. Coordination of **29** to Pd(II) and Ni(II) metal centers.

For the synthesis of the palladium complex **30**, deprotonation of **28** was carried out in THF, the potassium bromide salts were removed and  $[\text{PdCl}_2(\text{PhCN})_2]$  was added to the *in situ* generated ligand **29**. The solution turned immediately yellow and after one night stirring at room temperature a brown solid precipitated from the reaction mixture. This solid was dissolved in dichloromethane to eliminate the insoluble potassium salt(s). After evaporation of dichloromethane and washing of the residue with petroleum ether, palladium complex **30** was obtained in 73% yield as a yellow solid. It was characterised by multinuclear NMR spectroscopies and elemental analysis. In  $^{31}\text{P}\{^1\text{H}\}$  NMR, the phosphorus nuclei appear as a singlet at  $\delta(\text{CD}_2\text{Cl}_2) = 33.7$  ppm, thus significantly deshielded compared to the anionic ligand **29**. This indicated the coordination of the iminophosphorane group to the metal center. In contrast, in the  $^1\text{H}$  NMR spectrum little change was seen from the ligand **29** except the resonance of the ethylene protons which are shifted upfield ( $\delta(\text{CD}_2\text{Cl}_2) = 2.54$  ppm vs  $\delta(\text{CDCl}_3) = 3.42$  ppm in **29**).

Note that reactions performed with other palladium precursors failed; with  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  no coordination was observed whereas with  $[\text{Pd}(\text{COD})\text{Cl}_2]$  the reaction was very slow. Importantly whereas the free ligand is sensitive to moisture, the obtained complex proved to be stable on the bench for weeks as already shown for other iminophosphorane complexes.

Definitive evidence concerning the structure of **30** was provided by X-ray crystal analysis of the complex. Suitable crystals were obtained from slow diffusion of petroleum ether over a saturated dichloromethane solution of **30** at room temperature. Ortep view of complex **30** is presented in Figure 2. The complex crystallised with four molecules of dichloromethane. As expected for a diamagnetic  $d^8$  complex **30** adopts a square planar geometry around the metal with almost no deviation from planarity ( $O2-N2-N1-O1$  dihedral angle  $0.05(13)^\circ$ ). The four coordination sites are occupied by the iminophosphorane and phenoxide groups. The  $O_{\text{phenoxide}}-C_{\text{phenyl}}$  bond length is significantly shorter in the complex than in the free proligand **28** ( $1.314(4)$  Å vs  $1.355(3)$  Å in **28**) as a consequence of the charge delocalisation from  $O_{\text{phenoxide}}$  into the phenoxide ring. The  $P-C_{\text{phenoxide}}$  bond does not change much ( $1.777(4)$  Å vs.  $1.790(2)$  Å in **28**).

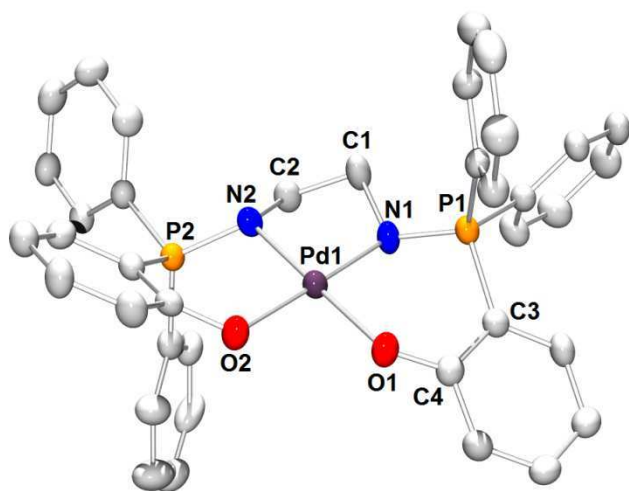


Figure 2. ORTEP view of complex **30**. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles ( $^\circ$ ):  $Pd1-N1$  2.014(3),  $Pd1-N2$  2.017(3),  $N1-P1$  1.620(3),  $N2-P2$  1.623(3),  $Pd1-O1$  2.029(2),  $Pd1-O2$  2.039(2),  $O1-C4$  1.314(4),  $P1-C3$  1.777(4),  $N1-Pd1-O1$   $96.6(1)$ ,  $N1-Pd1-N2$   $82.6(1)$ ,  $N2-Pd1-O2$   $96.1(1)$ ,  $O1-Pd1-O2$   $84.7(2)$ ,  $N1-P1-C3$   $107.4(2)$ ,  $N2-P2-C21$   $106.6(2)$ ,  $N1-C1-C2-N2$   $55.76(29)$ ,  $N1-C4-C3-P1$   $25.64(38)$ ,  $O2-N2-N1-O1$   $0.05(13)$ .

In comparison with the salen complex, the bond lengths of the  $Pd-N$  and  $Pd-O$  were measured at 2.014(3), 2.017(3) and 2.029(2), 2.039(2) Å respectively, which are all longer than the  $Pd-N$  and  $Pd-O$  distances (1.952(2), 1.957(2) and 1.9981(16), 2.0087(16) Å respectively) measured in the corresponding salen complex.<sup>35</sup> Due to the tetrahedral configuration of the phosphorus atoms, the molecule is also much less planar than related  $[Pd(salen)]$ .<sup>35</sup> For example the dihedral angle  $N1-C4-C3-P1$  was measured at  $25.64(38)^\circ$  vs  $-3.02^\circ$  in the imine derivative. In the same manner the flexible ethylene diamine chain is also much more largely deviated from the median plan in **30** than in  $[Pd(salen)]$  ( $N1-C1-C2-N2$ :  $55.76(29)^\circ$  vs  $34.5^\circ$ ), probably because the geometry around the coordinated nitrogen atom in iminophosphorane is not exactly as planar as the one around the coordinated nitrogen in imine function ( $C2-Pd1-P2-N1$   $\sim 25^\circ$  in **30**,  $C1-Pd1-C=N$   $\sim 1.0^\circ$  in  $[Pd(salen)]$ ). Concerning the crystal packing no peculiarity was observed for **30**

whereas the molecules of the salen complex axially packed because of  $\pi$ -stacking interactions between the phenyl rings (the centroid perpendicular distance being  $\sim 3.3\text{\AA}$ ).

A similar procedure was adopted to prepare the phosphasalen nickel complex **31** (Scheme 19).  $[\text{NiBr}_2(\text{DME})_2]$  was added to an *in situ* generated potassium bromide salt free THF solution of **29**, leading to a rapid colour change of the solution from pale yellow to deep purple. After 30 min a purple solid precipitated out of the reaction mixture, the colour of which faded. This solid was isolated by centrifugation and a work-up similar to that described for **30** was carried out. This allowed the isolation of **31** as a purple solid in 82% yield. As for **30**, no decomposition of **31** in air was detected. This complex was characterised by multinuclear NMR spectroscopies and elemental analysis. Interestingly, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum carried out in  $\text{CD}_2\text{Cl}_2$  at room temperature exhibited a broad signal around 33 ppm whereas at  $-80^\circ\text{C}$  the signal sharpened to give a nice singlet at  $\delta(\text{CD}_2\text{Cl}_2) = 32.8$  ppm, confirming the coordination of the iminophosphorane moieties.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR were recorded at room temperature on a concentrated  $\text{CD}_2\text{Cl}_2$  solution. Spectra were very similar to those of complex **30**, except that the resolution of peaks was lower.

Definitive evidence concerning the structure of **31** was brought by X-ray diffraction analysis (Figure 3) realised on single crystals obtained from slow diffusion of petroleum ether over a saturated dichloromethane solution of **31** at room temperature.

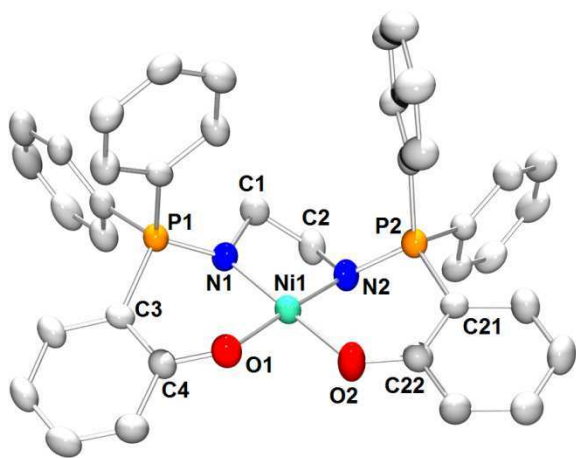


Figure 3. ORTEP view of complex **31**. Hydrogen atoms and solvent molecule have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Ni1-N1}$  1.905(4),  $\text{Ni1-N2}$  1.888(4),  $\text{P1-N1}$  1.613(4),  $\text{P2-N2}$  1.617(4),  $\text{Ni1-O1}$  1.881(3),  $\text{Ni1-O2}$  1.863(4),  $\text{O1-C4}$  1.301 (6),  $\text{O2-C22}$  (1.319 (6),  $\text{C3-P1}$  1.774 (5),  $\text{C21-P2}$  1.771 (5),  $\text{O1-Ni1-N1}$  95.4(2),  $\text{N2-Ni1-N1}$  85.4(2),  $\text{O2-Ni1-N2}$  95.4(2),  $\text{O2-Ni1-O1}$  83.9(2),  $\text{N1-P1-C3}$  108.2(2),  $\text{N2-P2-C21}$  108.1(2),  $\text{N2-C2-C1-N1}$  -45.00(56),  $\text{N1-C4-C3-P1}$  22.57(68),  $\text{N2-N1-O1-O2}$  3.64(35).

The complex crystallised with one molecule of dichloromethane. In the solid state, complex **31** adopts a nearly square planar geometry with a small deviation from planarity ( $\text{N2-N1-O1-O2}$  dihedral angle at  $3.64(35)^\circ$ ). Just like the case with the palladium complex, the  $\text{O}_{\text{phenoxide}}-\text{C}_{\text{phenyl}}$



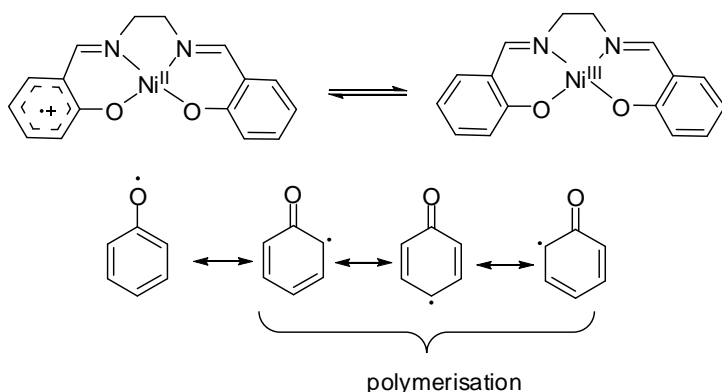
bond length is significantly shorter in **31** than in the free proligand **28** (1.301 (6) and 1.319 (6) vs 1.355 (3)) as a consequence of the charge delocalisation from O<sub>phenoxide</sub> into the phenoxide ring.

The Ni-O bonds are measured at 1.863(4) and 1.881(3) Å while the Ni-N distances are at 1.888(4) and 1.905(4) Å. These bond lengths are on average longer than those recorded for the [Ni(salen)] complex<sup>36</sup> (1.853 and 1.851 Å for the Ni-O bonds and 1.851 and 1.849 Å for the Ni-N bonds). As observed for palladium complex **30**, the overall geometry of the phosphasalén complex is much less planar than the salen counterpart. The dihedral angle N1-C4-C3-P2 was measured at 22.57(68)° vs 3.30° on average in the imine derivative. Moreover, while molecules of [Ni(salen)] complexes axially packed either thanks to  $\pi$ -stacking interactions between the phenyl rings when the carbon of the imine function is unsubstituted<sup>36a</sup> or through weak hydrogen bond when this carbon bears a phenyl group,<sup>37</sup> no particular packing was seen for **31**.

## 2.2 Electrochemical Studies on Nickel and Palladium Complexes.

### 2.2.1. Electrochemistry of Nickel and Palladium Salen Complexes

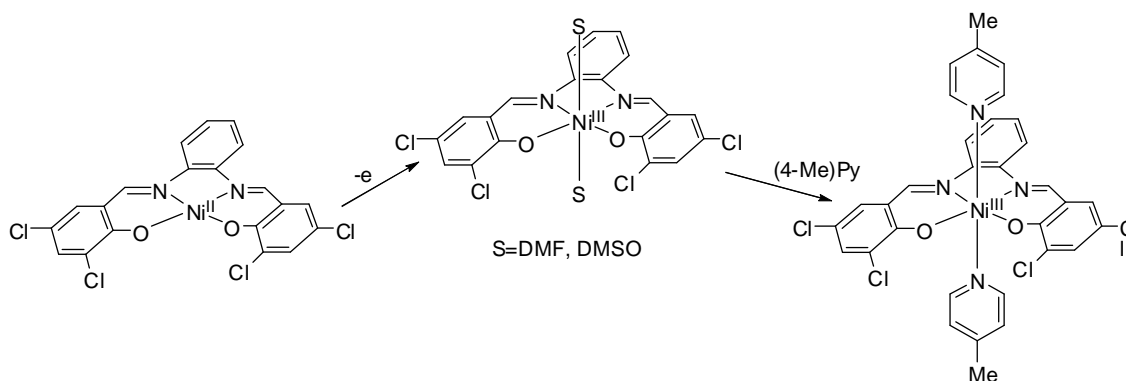
The oxidative chemistry of nickel(II)-Salen complexes and their derivatives has been the subjects of various studies. Two alternatives are imaginable for the oxidation of these complexes: either a ligand-based process (yielding phenoxyl radicals) or metal-based process (yielding high valent Ni(III)). In acetonitrile and other weak donor solvents (with donicity number (DN) inferior to that of acetonitrile (DN=14.1)), they are reversibly reduced to Ni(I) complexes but is oxidatively polymerized at the electrode to generate electroactive film, a process which has been proposed by Goldsby et al. to be ligand-based and probably takes place through a mixture of o- and p-linking of the phenyl ring (Scheme 20).<sup>38</sup>



*Scheme 20. Oxidation of [Ni(Salen)] complexes in weak donor solvents. The canonical forms of phenoxyl radical lead to polymerization of the complexes through o- and p-linking of the phenyl rings.*

In strong coordinating solvent (DN>>14, e.g dimethylformamide, dimethylsulfoxide), these Ni(II) salen complexes are oxidized to hexa-coordinated Ni(III) complexes, as shown by the group of Freire and Castro by electrochemical techniques and EPR spectroscopy of the oxidized

products (Scheme 21).<sup>39</sup> The two coordinated solvents are displaced with the addition of two equiv. of 4-methylpyridine. The explanation for these observations lies in the electronic structure of the square-planar Ni(II) Salen complexes. For these complexes where the  $\pi$  energy levels of the ligand and those of the central Ni(II) ion are very similar, oxidation can be ligand-localized or metal-localized, the final oxidation site depends on the ability of surrounding environment (solvents and other donors) to stabilize the oxidation state of the metal. Axial coordination can shift d-orbitals with z-composant above the filled ligand orbitals, thus making metal oxidation the preferred process.



Scheme 21. Oxidation of  $[Ni(3,5-Cl_2Saloph)]$ , from Freire and coworker

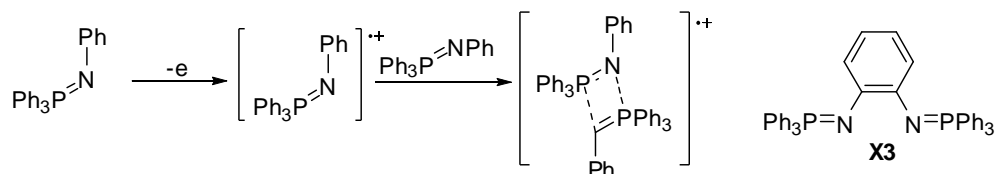
Freire, Castro and coworkers later studied the effects of substituents at the imine bridge on the oxidation of Ni(II) Salen complexes and found that the introduction of substituents not only affects the electronic structure but also imposes steric constraints on the axial coordination.<sup>37</sup> Increasing electron donor ability of the ligand would decrease the half-cell potential  $E^{1/2}$ , but steric constraints may play a more important role. The presence of steric repulsion between the substituents and the ligands at axial positions would destabilise the oxidized Nickel complex and  $E^{1/2}$  of the oxidative process increases as a consequence.

If studies on the comparisons between electronic properties of salen ligands common in the literature, fewer have been done on the comparisons between salens and their analogs, which is partly likely related to the few salen analogs existing in the literature. Elias et al. compared the ligand Salen and tetrahydroSalen (or Salan) through their coordination properties and electrochemistry of their complexes with Ni(II), Co(II) and Cu(II).<sup>40</sup> They found that in contrast to the corresponding Schiff-base complexes  $NiL$ , the  $Ni[H_4]L$  undergo a fast reversible oxidation and irreversible reduction in acetonitrile. Although not stated, the difference of the oxidation process probably lies in the more electron-donor property of the tetrahydroSalen.

### 2.2.2 Electrochemistry of Iminophosphoranes

The oxidation of free iminophosphorane has been studied in the laboratory.<sup>41</sup>  $Ph_3P=NPh$ , for example, presents an irreversible oxidation wave at 0.8 V (vs. SCE) in dichloromethane, using tetrabutylammonium tetrafluoroborate salt as electrolyte. Studies on EPR spectroscopy and DFT

calculations allowed to assert that the oxidation takes place at the nitrogen atom. As a consequence, the spin density is delocalised between the nitrogen atom and the associated phenyl group. The radical cation is not stable and tend to associate with a non-oxidised iminophosphorane through the P=N group (Scheme 22). Bis(iminophosphorane) having two nitrogen atoms being able to communicate with each other through a systems of  $\pi$ -electrons present a first oxidation wave at lower potential (0.3-0.5V vs. SCE), and this oxidation process is often reversible.<sup>42, 41b</sup> As the case with **X3**, the spin density of the oxidised species is delocalized on the two nitrogen atoms and the bridge between them.



Scheme 22. Oxidation of iminophosphoranes

Cyclic voltammetry measurements on the anionic free ligand was carried out in THF. The oxidation wave is very broad, ranging from 0.2 to 0.8 V (vs SCE). The study was thus not conclusive.

### 2.2.3 Electrochemical Study of the Ni- and Pd-Phosphasalen Complexes

The cyclic voltammetry measurements for Ni and Pd phosphasalen complexes were not carried out in DMF or acetonitrile which are the solvents often used for the measurements on Ni-Salen complexes. The reason lie in the limited solubilities of the complexes in these solvents. Thus all measurements were done in a mixture of dichloromethane and DMF or acetonitrile at room temperature. A gold disk was used as working electrode and a Pt gauze as counter electrode. For the sake of comparison with literature data, the potential of ferrocene in the same solvent system is also indicated.

Table 1. Electrochemical data for nickel-phosphasalen complex **31**<sup>a</sup> in MeCN/CH<sub>2</sub>Cl<sub>2</sub> (60/40 volume)

| Complex                | E <sup>a</sup> <sub>1</sub> , V | E <sup>c</sup> <sub>1</sub> , V | E <sup>1/2</sup> <sub>1</sub> | i <sub>pa</sub> /i <sub>pc</sub> |
|------------------------|---------------------------------|---------------------------------|-------------------------------|----------------------------------|
| <b>31</b> <sup>b</sup> | 0.76                            | 0.64                            | 0.70                          | 1.21 <sup>c</sup>                |
| <b>Fc</b>              | 0.50                            | 0.40                            | 0.45                          | 1.01                             |

<sup>a</sup> Tetrabutylammonium tetrafluoroborate salt as electrolyte (c = 0.12 mol L<sup>-1</sup>); scan rate= 100 mV s<sup>-1</sup>; the potential values are relative to SCE; <sup>b</sup> c = 4.5 mmol L<sup>-1</sup>; <sup>c</sup> ratio was observed to change with scan rate with a value of 1.40 at 50 mV s<sup>-1</sup>;

In MeCN/CH<sub>2</sub>Cl<sub>2</sub>, Nickel Phosphasalen complex presents a quasi-reversible oxidation process, whereas Nickel Salen complex presents an irreversible process in MeCN and other solvents of lower coordination donocity, as mentioned before. It is worth noting that the E<sup>1/2</sup> of Nickel Phosphasalen complex in this solvent system is 0.25V higher than E<sup>1/2</sup>(Fc<sup>+</sup>/Fc), a value lower than the difference between E<sup>1/2</sup>([Ni-Salen]<sup>+</sup>/[Ni-Salen]) and E<sup>1/2</sup>(Fc<sup>+</sup>/Fc) in DMF, a better

donor solvent. Thus it clearly shows that either the phosphasalen ligand stabilises better the oxidised Nickel metal center, or this ligand is easier to be oxidated. The anodic-cathodic peak potential separation is larger than expected theoretically for one-electron process (59 mV). However, under similar conditions, peak separation for the couple ferrocenium/ferrocene is about 100mV. This same phenomenon has been reported for Ni-Salen complexes.<sup>39</sup>

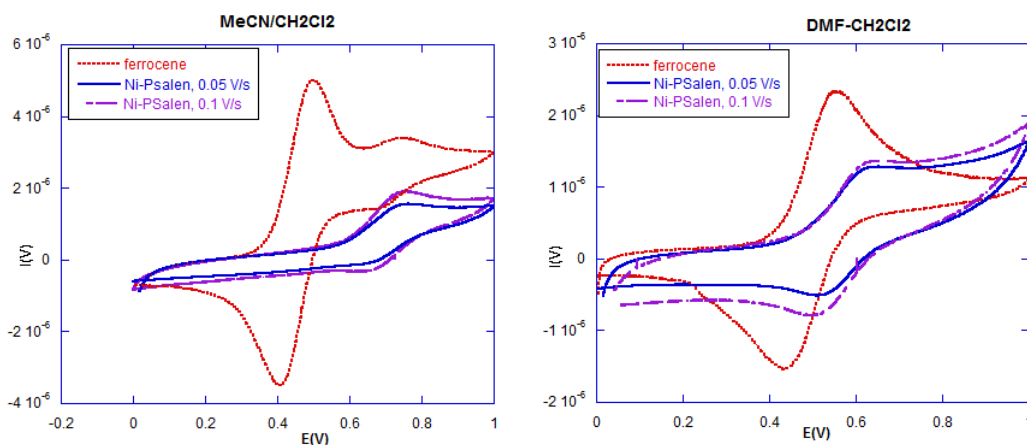


Figure 4. Cyclic voltammetric spectra of Ni-Phosphasalen complex in different systems of solvents.

For the sake of comparison and in order to better stabilise the oxidised species, DMF/CH<sub>2</sub>Cl<sub>2</sub> was employed as system of solvent. In this solvent systems, similar to the case with Nickel (salen) complexes, the oxidized species are likely hexa-coordinated Ni(III) complexes, the coordination sphere of the nickel being completed by two solvent molecules.

Table 2. Electrochemical data for phosphasalen complexes **30** and **31**<sup>a</sup> in DMF/CH<sub>2</sub>Cl<sub>2</sub> (60/40 volume)

| Complex                | E <sup>a</sup> <sub>P1</sub> , V | E <sup>c</sup> <sub>P1</sub> , V | E <sup>1</sup> <sub>1/2</sub> | i <sub>pa</sub> /i <sub>pc</sub> | E <sup>a</sup> <sub>P2</sub> , V | E <sup>c</sup> <sub>P2</sub> , V | E <sup>1</sup> <sub>1/2</sub> | i <sub>pa</sub> /i <sub>pc</sub> |
|------------------------|----------------------------------|----------------------------------|-------------------------------|----------------------------------|----------------------------------|----------------------------------|-------------------------------|----------------------------------|
| <b>31</b> <sup>b</sup> | 0.65                             | 0.51                             | 0.58                          | 1.00 <sup>c</sup>                |                                  |                                  |                               |                                  |
| <b>30</b> <sup>d</sup> | 0.76                             |                                  |                               |                                  | 1.10                             | 1.03                             | 1.06                          | 1.12                             |
| <b>Fc</b>              | 0.55                             | 0.43                             | 0.49                          | 1.01                             |                                  |                                  |                               |                                  |

<sup>a</sup> Tetrabutylammonium tetrafluoroborate salt as electrolyte ( $c = 0.12 \text{ mol L}^{-1}$ ); scan rate =  $100 \text{ mV s}^{-1}$ ; the potential values are relative to SCE; <sup>b</sup>  $c = 3.8 \text{ mmol L}^{-1}$ ; <sup>c</sup> ratio was observed to change with scan rate with a value of 1.46 at  $50 \text{ mV s}^{-1}$ ; <sup>d</sup>  $c = 2.0 \text{ mmol L}^{-1}$ ; <sup>e</sup> ratio was observed to change with scan rate with a value of 1.27 at  $50 \text{ mV s}^{-1}$ .

Indeed the change for a solvent with better donocity reduced the oxidation potential and stabilised even more the oxidised species. For nickel complex **31**, no reduction was observed within the potential window (0 V, -2.0 V) considered, and a reversible one electron oxidation took place at 0.58 V ( $\Delta E_p = 152 \text{ mV}$ ). Interestingly for the salen complex oxidation takes place at  $E_{1/2} = 0.81 \text{ V}$  in DMF, in conditions where oxidation of ferrocene occurs at 0.48 V.<sup>37</sup> Thus,

the oxidation potential of phosphasalen nickel complex **31** is only 0.1 V higher than that of ferrocene, whereas that of the [Ni(salen)] derivative is 0.33 V higher compared to the same reference. This clearly illustrated the better donating ability of the phosphasalen ligand which renders the nickel centre more electron rich and allows an easier oxidation.

For the palladium complex **30**, electrochemical studies were more difficult due to the more limited solubility of this complex in presence of DMF, thus lower concentrations were employed. Similarly to the case of the nickel-phosphasalen complex, no reduction was observed within the potential range explored. Interestingly, two oxidation waves were seen. The first one is irreversible at 0.76 V and the second one at 1.06 V which is pseudo-reversible ( $I_{pc}/I_{pa} \sim 1.12$ ). Thus, the first oxidation of the palladium complex **30** occurred at a higher potential compared to the nickel counterpart **31** which implies a less electron rich metal centre. Nevertheless a second oxidation can only be seen in the case of the palladium derivative which may be related to the increase of the thermodynamic stability of the highest oxidation states of elements within the row Ni-Pd-Pt.<sup>43</sup>

Indeed, for the [Pd(salen)] complex two irreversible oxidation waves were observed<sup>44</sup> at 0.96 and 1.07 V in acetonitrile namely 0.44 and 0.55 V higher than the oxidation potential of ferrocene in the same conditions (0.518 V). The first oxidation is thus easier for the phosphasalen derivative (only 0.27 V higher than the ferrocene oxidation potential) in agreement with the presence of a better electron-donating ligand. However, the second oxidation of the phosphasalen complex occurs at comparable potential as the salen derivative (namely 0.55 and 0.58 V higher than  $E^1_{1/2}(Fc^+/Fc)$ ), but as already established this oxidation in [Pd(salen)] complex corresponds to the electron transfer from a molecular orbital localised predominantly on the ligand and not on the metal centre.<sup>44a</sup>

#### 2.2.4 Magnetic Properties of Nickel phosphasalen Complex and Theoretical Studies

Whereas the palladium phosphasalen complex always give finely resolved NMR spectra, which is quite usual for a diamagnetic compound, it is difficult to obtain nicely resolved spectra for the nickel phosphasalen complex at room temperature. This suggest either a rapid exchange between different conformations of a diamagnetic complex, or the existence of a partial populated triplet state of the complex at room temperature. Indeed, if at room temperature the phosphasalen nickel complex **31** would exist under two different spin states (a singlet and a triplet one), the latter would perturb the NMR measurements. Magnetic moment of phosphasalen complex **31** has been measured using Evans method<sup>45</sup> showing a value of  $1.40 \mu_B$  at room temperature. At first view, this value is very low compared to literature values of 3.0-4.0  $\mu_B$  expected for fully tetrahedral Ni(II) complexes.<sup>46</sup> However, values around 1.3  $\mu_B$  were reported by Braunstein and coworkers for Ni(II) complexes adopting a distorted tetrahedral

geometry in solution.<sup>47</sup> This was attributed to the dependence of magnetic moment on the ligand field, and the occurrence of structural equilibria in solution.<sup>48</sup>

As such observation was neither made for salen Ni(II) complexes we undertook a theoretical study to compare the electronic properties of the [Ni(salen)] and [Ni(phosphasalén)]. Density Functional Theory (DFT) calculations were performed on these two complexes with the Gaussian 03 set of programs<sup>49</sup> in combination with the B3PW91 functional<sup>50</sup>. Nickel was represented by the relativistic effective core potential of Hay and Wadt<sup>51</sup> and the associated triple zeta quality basis set,<sup>52</sup> augmented by a f polarization function as proposed by Frenking<sup>53</sup> (lanl2tz(f)). All other atoms were described with the 6-31G\* Pople basis set.<sup>54</sup>

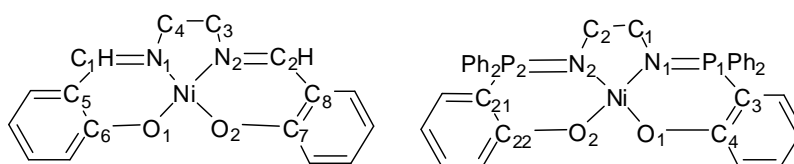


Table 3. Comparison of selected geometric parameters coming from X-ray diffraction analysis and DFT calculations

|             | [Ni(salen)] |                                   |                                   | [Ni(phosphasalén)] |                                   |                                   |
|-------------|-------------|-----------------------------------|-----------------------------------|--------------------|-----------------------------------|-----------------------------------|
|             | X-ray       | Optimised<br>singlet<br>structure | Optimised<br>triplet<br>structure | X-ray              | Optimised<br>singlet<br>structure | Optimised<br>triplet<br>structure |
| N2-Ni1      | 1.851(3)    | 1.857                             | 1.986                             | 1.888(4)           | 1.897                             | 1.966                             |
| N1-Ni1      | 1.849(3)    | 1.856                             | 1.989                             | 1.905(4)           | 1.894                             | 2.011                             |
| Ni-O2       | 1.853(3)    | 1.847                             | 1.900                             | 1.863(4)           | 1.865                             | 1.914                             |
| Ni-O1       | 1.851(5)    | 1.848                             | 1.899                             | 1.881(3)           | 1.883                             | 1.953                             |
| O2-Ni-N2    | 94.1(4)     | 94.31                             | 91.6                              | 95.4(2)            | 94.7                              | 97,5                              |
| O1-Ni-N1    | 94.2(4)     | 93.99                             | 91.5                              | 95.4(2)            | 95.1                              | 96,3                              |
| O1-Ni-O2    | 85.5(4)     | 85.4                              | 105.2                             | 83.9(2)            | 84.4                              | 101.1                             |
| N1-Ni-N2    | 86.3(5)     | 86.4                              | 82.9                              | 85.4(2)            | 85.8                              | 85.8                              |
| N1-Ni-N2-O2 | 178,5       | 177.5                             | 153.4                             | 176.40(35)         | 179.4                             | 127.2                             |
| N2-Ni-N1-O1 | 178.6       | 177.8                             | 151.4                             | 178.68(39)         | 178.8                             | 155.1                             |
| O2-Ni-O1-N1 | 178.7       | 177.5                             | 158.5                             | 176.38(42)         | 179.4                             | 130.6                             |
| O1-Ni-O2-N2 | 178.5       | 177.8                             | 156.1                             | 178.64(39)         | 178.8                             | 162.0                             |

Optimizations of both complexes **31** and [Ni(salen)] were performed in the singlet and triplet states. Table 3 gathers some selected geometric parameters for each optimised structure together with the available experimental data from X-ray diffraction analysis.<sup>13</sup> On the whole there is an excellent agreement between the experimental structure and the theoretical parameters optimised for the singlet state. A nearly square planar geometry was found for both complexes with dihedral angles around the metal centre lying between 176 and 179°. Mean deviations of 0.01 Å were found for the bond lengths and 1° for the bond angles.

In optimized triplet states, both complexes adopt distorted tetrahedral geometry. This change in geometry is illustrated by the dihedral angles given in Table 3 which vary from nearly 180° (the value for an ideal square planar arrangement) in the singlet state to values between 162 and 127° (instead of 120° for an ideal tetrahedral structure) in the triplet state. The phosphasalen ligand seems to be more flexible than the salen one, as demonstrated by the larger geometrical evolution of the phosphasalen complex than the salen one (mean value of 143.7° for the dihedral angles instead of 154.9° for the latter). It's also observed that the metal-ligand bond distances are significantly longer in the triplet than in the singlet state, by 0.094 and 0.076 Å in the salen and the phosphasalen complexes, respectively (mean values).

### *Orbital Analysis for Singlet and Triplet States*

#### *Nickel(Salen) Complex*

To decrypt these observation and have an insight into the low spin-high spin process, orbital analysis has been carried out. In fact, formation of the triplet state in the square planar singlet state involves first removing one electron and then placing it in another orbital. For the Ni-Salen complex, a correlation has been clearly established between different spin states and geometries of the two major orbitals: that from which the electron was removed and that which accepts the removed electron (Figure 5, Figure 6).

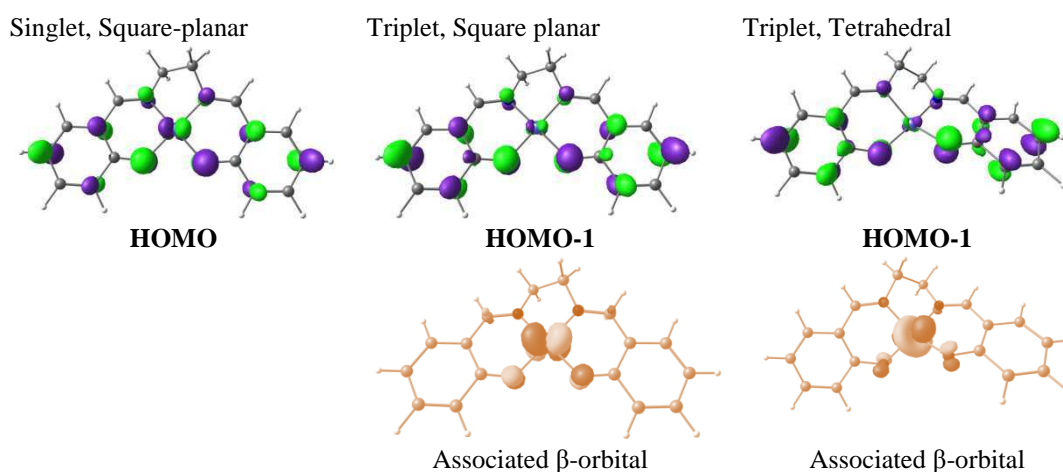


Figure 5. Evolution of MO orbital from which one electron is transferred

The electron is removed from the HOMO, which involves a d orbital in  $\pi$ -antibonding interaction with p- $\pi$  orbitals from O and N. This orbital loses its component in d and becomes essentially ligand-based (the lost d component now resides essentially in the beta-orbital associated, which is unoccupied). The electron is placed in the  $d_{x^2-y^2}$  orbital in strong  $\sigma$ -antibonding interaction with the ligands.

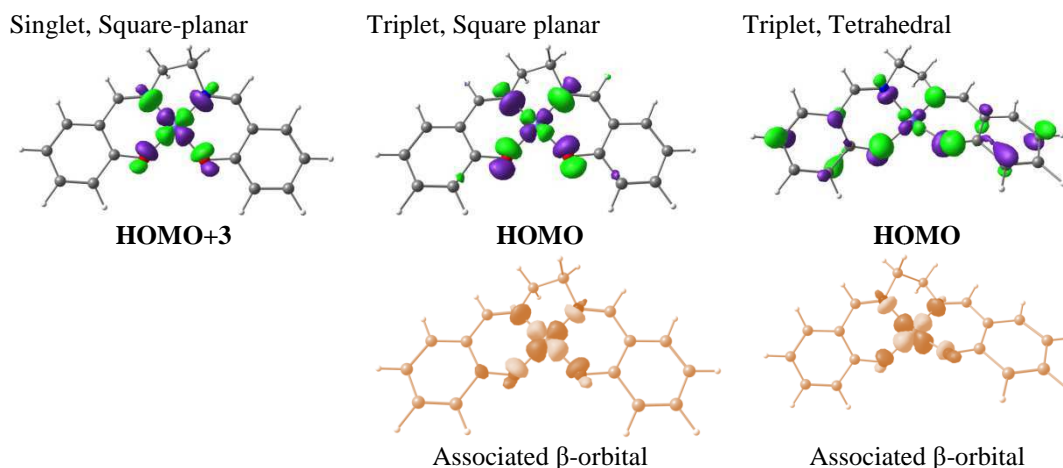


Figure 6. Evolution of MO orbital to which one electron is transferred

According to the metal-ligand  $\pi$  antibonding character of the HOMO orbital of the nickel Salen complex (Figure 5), taking one electron from this should shorten the metal-ligand bond distances. However the electron left from the HOMO now occupies an orbital which was vacant in the singlet state, the fifth d orbital of these  $d^8$  complexes ( $d_{x^2-y^2}$ ). Since it is strongly  $\sigma$ -antibonding between the metal and the ligands (Figure 4), its occupation entails a lengthening of the metal-ligand bonds. So two factors work in opposite direction but the latter dominates (the  $\sigma$  antibonding interactions are stronger than the  $\pi$  ones). A lengthening of the metal-ligand distances thus occurs on going to the triplet spin state, a trend which is preserved upon distortion towards a pseudo-tetrahedral arrangement.

### Nickel(Phosphasalen) Complex

The same reasoning of the elongated M-O and M-N bonds applies for the nickel-phosphasalen complex. Indeed, in the case of Ni-Psalen complex, the electron is also removed from the HOMO and placed in  $d_{x^2-y^2}$ -orbital in strong  $\sigma$ -antibonding interaction with p-orbitals from N and O, which was vacant in the singlet state.

The correlation of orbitals in the singlet, non-relaxed triplet ( $S=3$  PC) and in the relaxed triplet ( $S=3$  Td) states are undoubtful for this  $d_{x^2-y^2}$ -orbital for both the occupied alpha orbital and the associated unoccupied beta-orbital (Figure 7). But it was not obvious for the occupied alpha-orbital which the HOMO has become, as the large molecule has many wave functions with close eigen values, i.e orbitals with close energy, and the singly occupied orbital seems to have



made various combinations with other orbitals which render its identification difficult. However, the associated beta-orbital could be easily identified (Figure 8). This orbital is metal-centered and allows us to conclude that the singly occupied orbital from HOMO has lost most of its component in d-orbital, and that electron is taken from this d-component to placed in the  $d_{x^2-y^2}$  orbital.

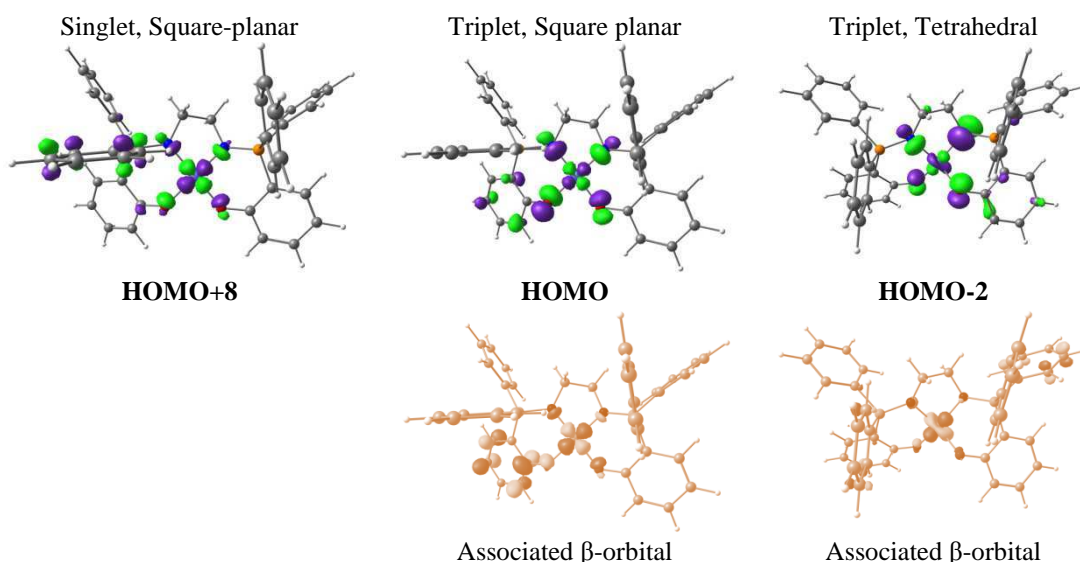


Figure 7. Evolution of MO orbital to which one electron is transferred

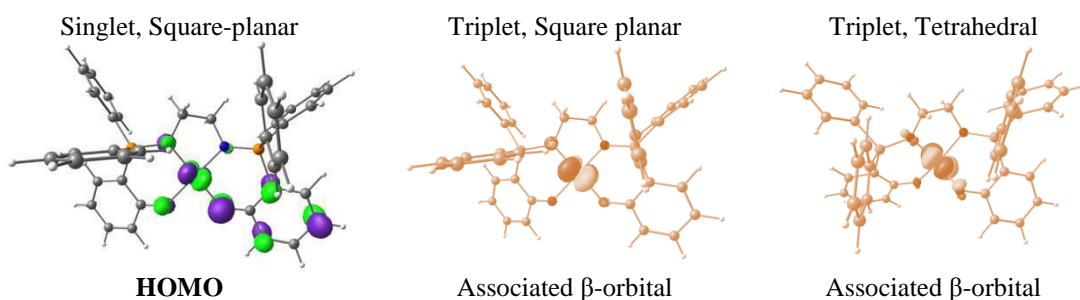


Figure 8. Evolution of MO orbital from which one electron is transferred

Just as the previous case with Ni-Salen complex, the charge at Ni and negative charges at O and N should increase. That is indeed the case: the charge at Ni changes from +0.456 in singlet state to +0.621 in triplet state (square planar), at N from -0.662 and -0.650 to -0.700 and -0.715, at O from -0.580 and -0.571 to -0.605 and -0.599. The spin density is mainly on Ni (+1.59), the rest of spin densities are mainly on N and O atoms. When the geometry is relaxed, the alpha orbital

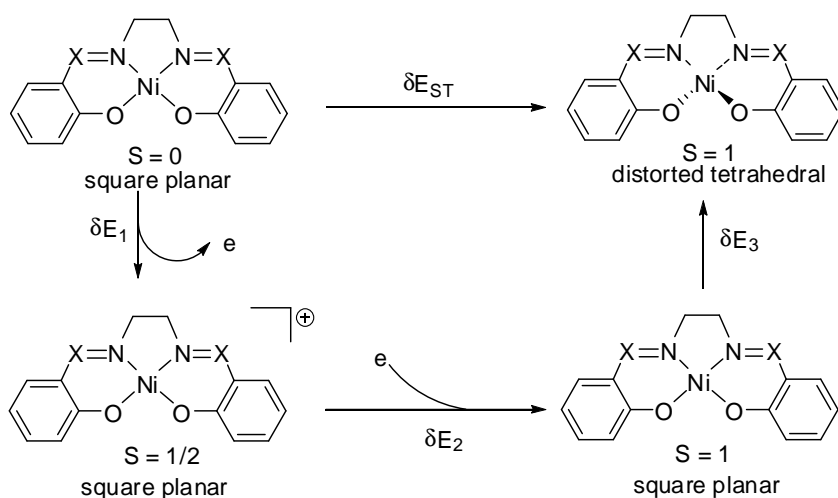
from  $d_{x^2-y^2}$  is more ligand-centered and the associated beta orbital is more metal-centered, so the charge at Ni increases to +0.682, the spin density at Ni is +1.65.

### Magnetic Moment of Ni-Phosphasalén Complex

As could be seen from the orbital analysis before, the HOMO in both complexes involves a d orbital on the metal centre in  $\pi$ -antibonding interaction with the oxygen and nitrogen ligands. However the HOMO of the phosphasalén complex is significantly higher in energy than that of the salen complex (-4.56 instead of -5.12 eV). As a consequence the vertical ionisation energy calculated for the phosphasalén complex (5.73 eV) is lower than that for the salen complex (6.49 eV), a result in agreement with the easier oxidation found experimentally for the former.

From an energetic point of view the singlet state was found 9.0 kcal mol<sup>-1</sup> more stable than the triplet state for the salen complex in agreement with the experimental evidence for a low spin complex in solution.<sup>55</sup> A strikingly different situation was found for the phosphasalén complex with a triplet state slightly more stable than the singlet state ( $\Delta E = -1.4$  kcal mol<sup>-1</sup>). A triplet ground state in solution as well as a small singlet-triplet energy difference (which suggests that both spin configurations could coexist in solution), are in agreement with the experimental measure of the magnetic moment of complex **31**.

In order to rationalise the singlet-triplet energy difference ( $\delta E_{ST}$ ), we made use of the thermodynamical cycle as described in Scheme 23. Starting from the optimised square planar singlet state, one electron is removed from the HOMO keeping the geometry of the complex unchanged ( $\delta E_1$ ). This removed electron is then placed in the antibonding d orbital leading to a triplet state in the square planar geometry ( $\delta E_2$ ). Finally, the geometry is relaxed to reach the optimised geometry for the triplet state ( $\delta E_3$ ).



Scheme 23. Thermodynamical cycle to determine the singlet-triplet energy difference ( $\delta E_{ST}$ )

The values of  $\delta E_1$ ,  $\delta E_2$ ,  $\delta E_3$  and  $\delta E_{ST}$  are reported in Table 4 for both salen and phosphasalen complexes. It clearly appears that the electronic factor responsible for the difference of  $\delta E_{ST}$  between salen and phosphasalen complex (by  $10.4 \text{ kcal mol}^{-1}$ ) is the major lowering (by  $17.5 \text{ kcal mol}^{-1}$ ) of the ionisation energy in going from the salen to the phosphasalen complex. Thus it could be said that the low-lying triplet state of the nickel phosphasalen complex is due to the better donating ability of phosphasalen ligand.

*Table 4. Energy decomposition ( $\text{kcal mol}^{-1}$ ), according to Scheme 4, of the singlet-triplet energy difference for salen and phosphasalen complexes.*

|  | $\delta E_1$ | $\delta E_2$ | $\delta E_3$ | $\delta E_{ST}$ |
|--|--------------|--------------|--------------|-----------------|
| [Ni(salen)]  | 149.6        | -129.6       | -11.0        | +9.0            |
| [Ni(phosphasalen)]   | 132.1        | -122.0       | -11.5        | -1.4            |
| $\Delta E([\text{Ni}(\text{salen})] - [\text{Ni}(\text{phosphasalen})])$ | -17.5        | +7.0         | -0.5         | -10.4           |

### III. Conclusion

Taken into account the importance of salen ligands in coordination chemistry and catalysis, as well as the need to develop salen-like ligands with different electronic properties and improved flexibility, phosphasalen ligands have been developed in the laboratory. This new class of ligand combines two iminophosphorane and two phenoxide groups. The proligand (bis(aminophosphonium) salt) was synthesized by a Kirsanov reaction between ethylene diamine and phosphinophenol in good yield. Although only the unsubstituted proligand has been synthesized, it is well conceivable that this simple method could be apply to the synthesis of other ligands with variations on the phenoxide rings, as well as on the diamine linker. These possibilities would be developed further.

The phosphasalen ligand was easily and cleanly coordinated with nickel(II) and palladium(II) metal centers, giving stable complexes. Chemical study by cyclic voltammetry showed that all these two complexes present oxidation waves at lower potential than the salen analogs, clearly demonstrating the better donating ability of the phosphasalen ligand compared to salen.

In particular, the nickel phosphasalen complex presents a non-negligible magnetic moment in solution, whereas in the solid state it is diamagnetic and adopts square-planar geometry. This behavior is very different from the nickel salen complex and suggest the existence of a low-lying triplet state. DFT calculations carried out on nickel salen and phosphasalen complexes in singlet and triplet states not only elucidate the orbitals involved in the singlet-triplet transition for both complexes, but also explain the origin of this “strange” behavior of the phosphasalen complex. It has been found that the triplet state of phosphasalen complex is slightly lower in

energy than the singlet state, whereas for the salen complex, the triplet state is much higher in energy than the singlet state. The small difference in energy in singlet-triplet state for phosphasalen complex explains the magnetic moment measured in solution for this compound. And this small difference in energy is a direct consequence of the better donating ability of phosphasalen ligand.

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## Chapter 4

# Oxidised Ni(II) Phosphasalen Complexes

From our study on Nickel phosphasalen complex, it has been shown that the phosphasalen ligand is a better donor than the salen one and that the complex is oxidized at lower potential than the salen analog. Furthermore, by cyclic voltammetry study, it was observed that the oxidised species is quite stable, even in solvent with low-coordinating ability such as acetonitrile. Following this direction, and taken into account the interest in Ni(III) and in studying oxidized phenoxide complexes of nickel which has been manifested through Ni-Salen, we carried out the preparation and study of oxidised nickel-phosphasalen complex.

## I. Introduction

### 1. Phenoxyl Radical Complexes

The chemistry of oxidized metal-phenoxide complexes has attracted much attention in the last decade. This might be attributed to the direct relation to the phenoxyl radical in galactose oxidase,<sup>1</sup> a mononuclear copper enzyme catalyzing the oxidation of primary alcohols to aldehydes along with the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. The enzyme functions as a two electron redox unit during the catalytic cycle, and the overall catalytic reaction in fact involves two separable half-reaction: oxidation of a primary alcohol and reduction of oxygen to hydrogen peroxide. The active site of the enzyme is composed of a copper center coordinated by four aminoacid side chains (from Tyr272, Tyr495, His496, His581), along with a solvent molecule, forming a five-coordinated metal complex (Figure 1).

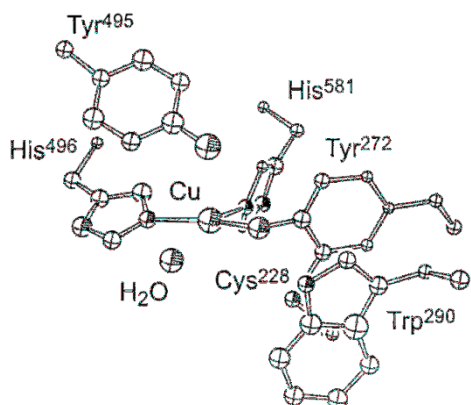
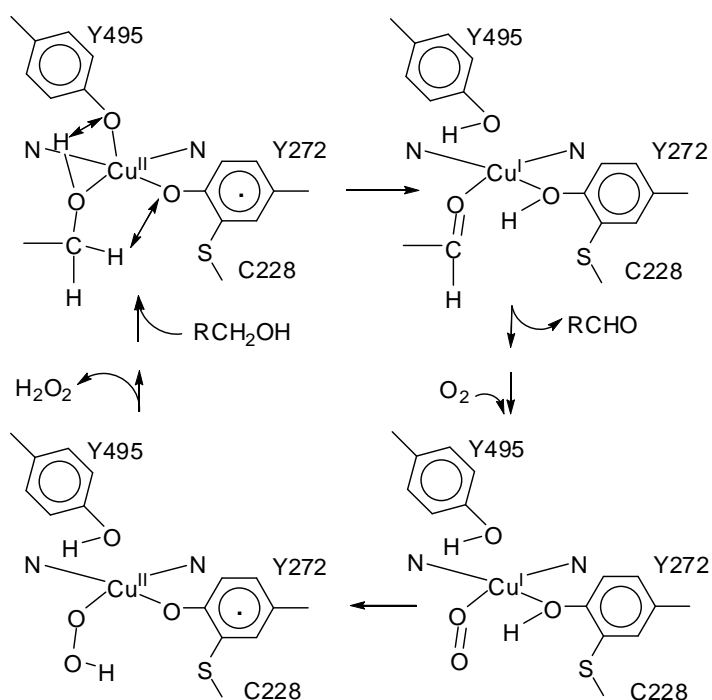


Figure 1. X-ray structure of the active site of galactose oxidase.

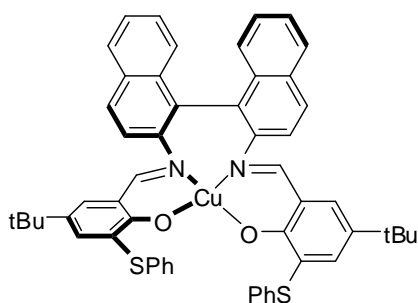
The role of Tyr495 is supposed to act as a general base during the proton transfer. The electron transfer is ensured by the copper ion and Tyr272, which is a modified one and is covalently cross-linked to a cysteine (Cys228) through the sulfur atom. This cross-link has been shown to be redox-active and identified as the protein free radical site in galactose oxidase (Scheme 1). What is important in the mechanism of activity of galactose oxidase is the cooperative and alternative action of the metal center and tyrosine in redox reactions: the copper taking oxidation states of I or II and the tyrosine ligand exists sometimes as a neutral one, sometimes as a radical cation.



Scheme 1. Active site and catalytic mechanism of galactose oxidase (from Whittaker et al)<sup>1a</sup>

The recognition of free radical role in the activity of galactose oxidase has shed insight into the understanding of many other metalloenzyme systems which also contain a redox active metal

center coordinated or adjacent to pro-radical ligand.<sup>2</sup> In catalysis, the cooperative effect between the metal center and the ligand in these systems have inspired the design of many synthetic system of catalyst<sup>3</sup>. The group of Stack, for example, developed copper salen complexes (one of which is presented in Scheme 2, named [Cu(II)BST]) which are able to catalyse the oxidation of primary alcohols by O<sub>2</sub> (1 atm), with turnover numbers up to 1300.<sup>3a</sup> During the catalytic cycles, the complex is oxidized to [Cu(II)BST]<sup>+</sup>, in which the ligand is oxidized to a radical cation.



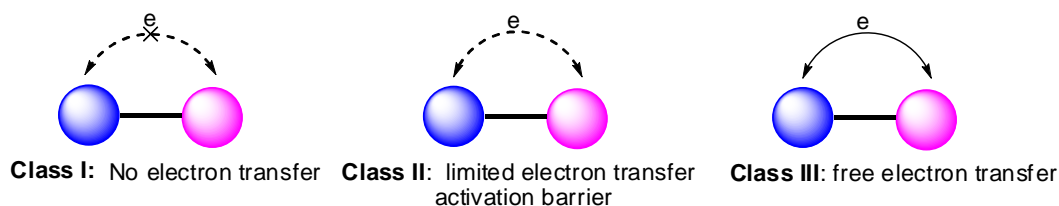
*Scheme 2. Copper salen complex [Cu(II)BST]*

For the importance of understanding the role of phenoxyl radical in biochemistry and the potential applications of these species in catalysis, phenoxide metal complexes have attracted much attention in the last decade. Salen is likely the most important phenoxide-containing ligand in chemistry, and salen complexes have found numerous applications in catalysis (epoxidation, epoxide resolution, copolymerization of epoxides and CO<sub>2</sub>, sulfoxidation, etc). Thus, it's easy to understand that a large part of studies on design and electronic structure of oxidized metal-phenoxide species have evolved around the salen complexes. The use of salen ligands constitutes other advantages: they could be easily synthesized from readily available starting material, and the introduction of various types of substituents on different positions on the ligand is possible, allowing the fine tuning of electronic properties of salen complexes and their oxidized species.

## 2. Mixed-Valence Compounds and Oxidized Nickel Salen Complexes

The oxidized species of a salen complex could not be attributed as phenoxyl radical, or high valent metal complex at first sight. What happens inside the oxidized complex is more complicated.

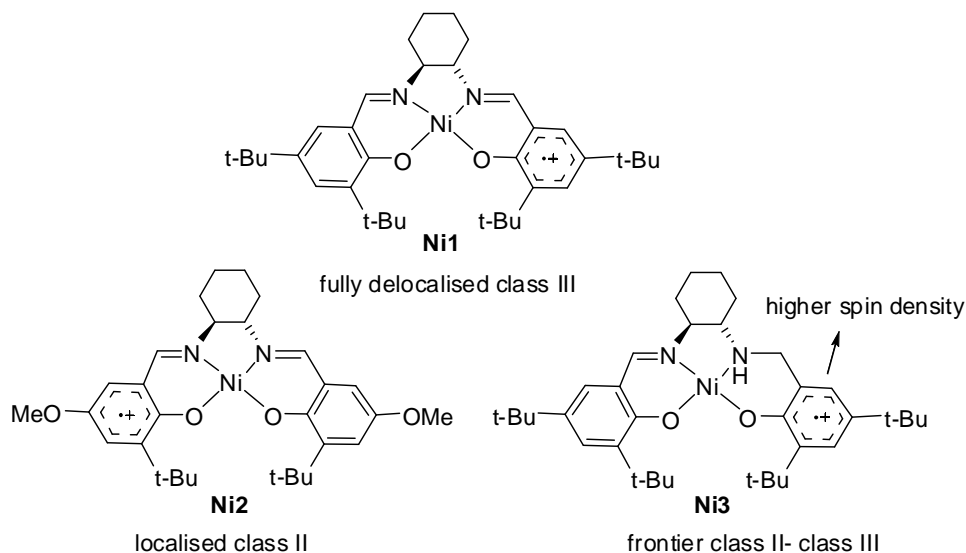
Taking the case of one oxidized metal complexes with a proradical ligand: they could exist in two limiting descriptions: a high valent metal complex [M<sup>(n+1)+</sup>-L<sup>-</sup>], or a metal-ligand radical [M<sup>n+</sup>-L<sup>•</sup>]. These complexes are special case of mixed-valence compounds. The unpaired electron, or the “hole”, could “jump” between the two redox centers which are the metal and the ligand. According to the facility this process, mixed-valence compounds containing two redox centers are divided in three classes (Scheme 3).



*Scheme 3. Three classes of mixed-valence compounds.*

In class I, no electron transfer occurs between the two centers because they are far apart or because their interaction is symmetry or spin forbidden. In class II, electronic interaction between the two centers exists and thus the electron transfer between these two centers. In class III, the two centers have such strong electronic interaction that there's not activation barrier for electron transfer, leading to free spin delocalisation and an average charge on the two centers (Scheme 3).<sup>4</sup>

Oxidised salen complexes of manganese, iron, cobalt, copper and group 10 metals (Ni, Pd, Pt) have been isolated and studied exclusively. Oxidized nickel salen complexes have been found to be of class III mixed valence complexes, the radical being delocalized over the ligand through the metal bridge, the spin density on the metal center is often low (<20%).<sup>5</sup> Three directions to tune the electronic configuration of the complexes have been envisaged: 1) localize the spin density on one of the two phenoxide moiety, 2) increase the activation barrier of electron transfer, 3) change the locus of electron density from ligand to metal (Scheme 4). Needless to say, the first and second options often come together.



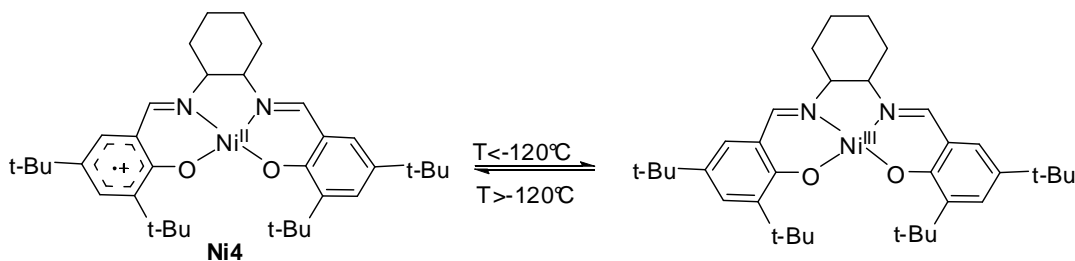
*Scheme 4. Nickel salen complexes*

The first option has been done for example by using nonsymmetrical salen ligand. Oxidised nickel salen complex **Ni1**, realized by Shimazaki and coworkers<sup>5b</sup> has equal spin densities on each phenoxide moiety, with 12% contribution from Ni center. By changing the imine functional group by an amine which is more electron donor, the same group obtained the radical

complex **Ni3** with a more localized spin density on the phenoxide ring linked to the amine function, as has been demonstrated by X-ray diffraction experiment and DFT calculations.<sup>6</sup> The calculations also suggested that the electron transfer between the two phenoxide, presumable mediated through Ni center (orbital  $d_{yz}$ ), is significantly reduced. The complex is at the frontier class II-class III mixed-valence compounds.

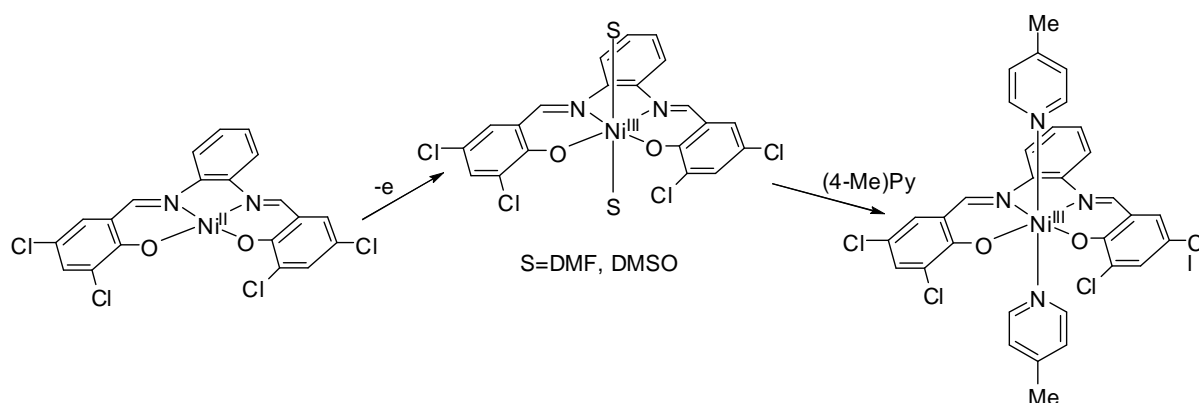
If the activation barrier for the electron transfer is increased, then the spin density can be localized even for complexes of symmetrical ligand. In 2010 Thomas and coworkers reported the complex **Ni2** [Ni(L-OMe)](SbF<sub>6</sub>), featuring OMe at the *para*- position of the phenoxide rings, which shows the unsymmetrical structure containing one quinoid and one phenoxide ring (Scheme 4). This has been explained by the interaction of the fluorides on one phenyl ring which render the molecules non-symmetrical. Later, Kurahashi and co workers examined the intervalence charge transfer band (IVTC) of the same complex in solution and found that the complex is a class II mixed valence compound. They explained this by the change of redox potential induced by OMe groups, which modifies the activation barrier for electron transfer.<sup>4</sup>

The third option, changing the locus of oxidation from ligand to metal, has been realized up to now only with the intervention of external factors: the temperature, the nature of solvent or the presence of exogenous ligands. The effect of the temperature has been investigated by Shimazaki and coworkers, who discovered the tautomerism between the two forms of complex **Ni4** (ligand radical or high valent Ni(III)) by increasing or lowering the temperature.<sup>7</sup> The Ni(III) complex exists under -120°C. (Scheme 5)



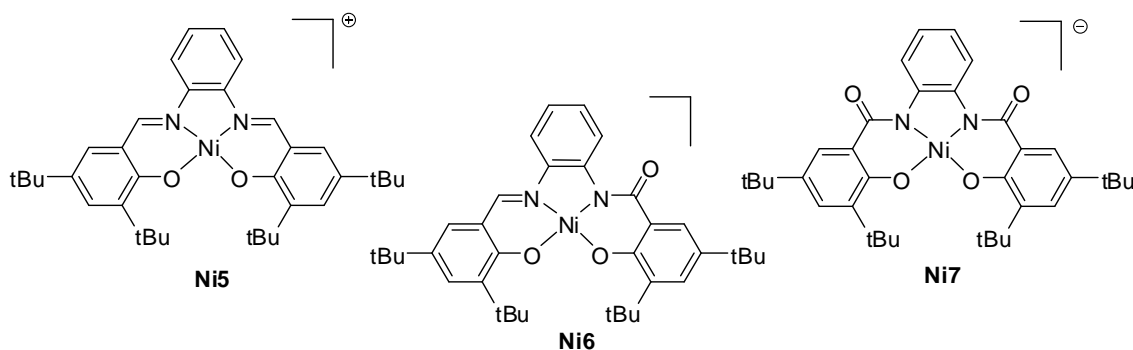
Scheme 5. Tautomerism of oxidized Nickel-salen complex.

The effect of the addition of axial ligands on the stability of oxidised nickel salen complex has been long known in chemistry. Earlier to the studies of nickel-phenoxyl radical complexes and electronic structures of oxidized nickel salens, in 1990, Freire and coworkers studied the oxidation of [Ni(3,5-Cl<sub>2</sub>Saloph)] in DMF and (CH<sub>3</sub>)<sub>2</sub>SO by electrochemistry and formulated the oxidized species as [Ni(3,5-Cl<sub>2</sub>Saloph).S<sub>2</sub>]<sup>+</sup> (S=solvent molecule) (Scheme 6).<sup>8</sup> The products have a large  $g_{iso}$  values at room temperature which suggest that the oxidation is metal-based. The EPR spectra of frozen solutions displayed highly anisotropic, large  $g$  tensor, typical of Ni(III). Upon addition of 4-methylpyridine, the base replaces the two solvent molecules at the axial position, leading to the apparition of a hyperfin coupling in EPR spectrum of the oxidized species, due to the interaction of the unpaired electron and two equivalent nitrogen atoms.



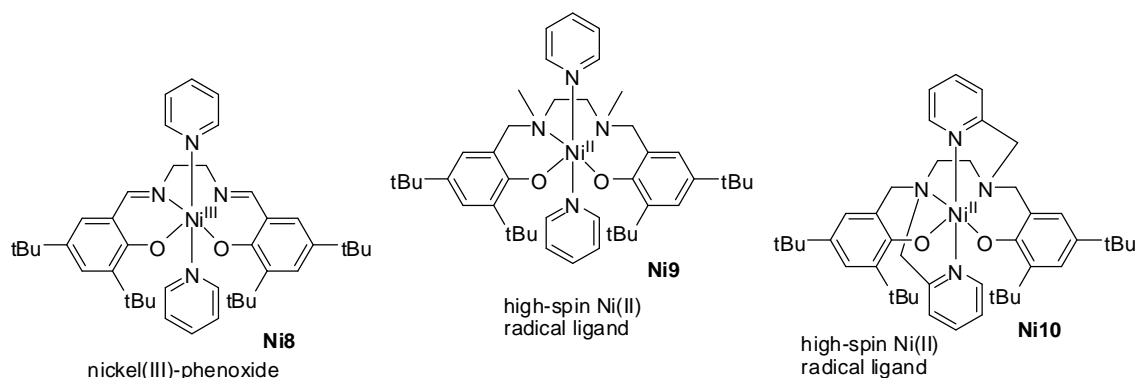
Scheme 6. Oxidation of  $[Ni(3,5-Cl_2Saloph)]$ , from Freire and coworker.<sup>8</sup>

The role of the axial ligand(s) was more deeply investigated by F. Thomas and coworkers.<sup>9</sup> They observed that addition of pyridine into electrochemically generated complexes **Ni5-7** (Scheme 7) in  $CH_2Cl_2$  led to the existence of six-coordinated Ni(III) adducts that has been evidenced by EPR spectra.<sup>9b</sup> This is in contrast to the situation when no pyridine is added: EPR spectra of the oxidized complexes **Ni5-7** in  $CH_2Cl_2$  pointed towards the phenoxyl radical complexes.



Scheme 7. Oxidated nickel salen complexes, from Thomas *et al.*<sup>9b</sup>

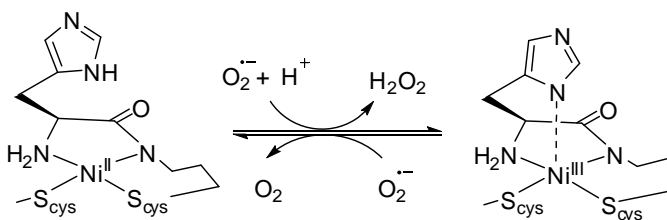
In fact, in square planar nickel salen complexes, the energy level of the d orbitals from the metal and the  $\pi$ -orbitals from the ligands are very close. By changing the relative energies between these orbitals, a metal-based or ligand-based process could be favored, leading to high valent Ni(III) or ligand radical. In those above-cited examples, on going from a square planar to an octahedral geometry, the presence of axial ligands increases the energies of  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$  orbitals, probably makes them higher than the energy of  $\pi$ -orbitals from the ligand. This resulted in the formation of a Ni(III) complex. This “tuning” is however very delicate, and adding axial ligand does not systematically leads to a metal-based oxidation process. For examples, in Scheme 8, all the three oxidized nickel complexes adopt octahedral geometries. But whereas **Ni8** is a high valent Ni(III) complex, **Ni9-10** featuring salen ligands are radical complexes of high spin Ni(II).<sup>9c</sup> For all these three complexes, two-electron oxidations afford bis (phenoxyl) radical species, regardless of the hybridization of the coordinating nitrogen.



Scheme 8. Oxidised nickel complexes of salen-type ligands, from Thomas and coworkers

### 3. Nickel (III) Complexes

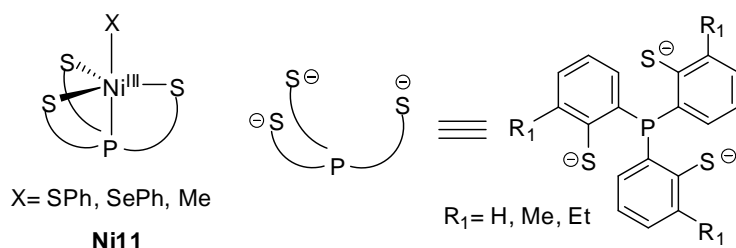
In the discussion about oxidized nickel-salen complexes, it has been demonstrated that the formation of Ni(III) complex could only be obtained in the presence of axial ligands leading to an octahedral geometry. Indeed, most of Ni(III) complexes reported in the literature are hexa-coordinated. However, it's the coordinatively unsaturated complexes that could have attractive applications in catalysis, as there's still place to coordinate the substrate(s). Catalytic applications of Ni(III) in nature are known. The Ni-containing superoxide dismutase (NiSOD) is able to catalyse the disproportionation of  $\text{O}_2^-$  to  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ .<sup>10</sup> The active site of the enzyme features an Ni(II) and a square planar N2S2 ligand set in its first coordination sphere. The oxidation form has N2S2 ligand set in equatorial plane, and an imidazole in axial position, giving a Ni(III) complex in square pyramidal geometry. (Scheme 9)



Scheme 9. Active site of Ni-containing superoxide dismutase.

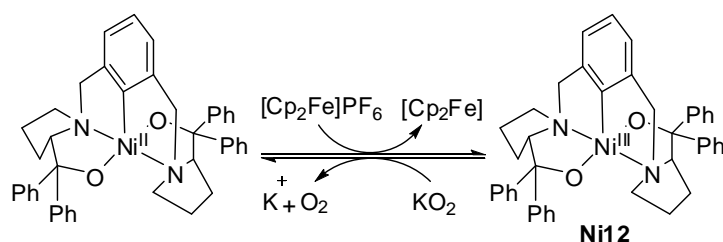
Penta-coordinated Ni(III) complexes are less common than hexa-coordinated Ni(III), but not too rare. For example, Lee C. M. and coworkers synthesised alkyl, thiolate and selenonate penta-coordinated Ni(III) complexes supported by tris(thiolate) phosphine ligand.<sup>11</sup> (Scheme 10) The average g value of the alkyl complex at 77K is 2.13, significantly higher than 2.00, indicating that the unpaired electron is primarily located at Ni. SQUID measurement of the same complex in the solid state gave a magnetic moment of  $1.85 \mu_B$ , which has been judged as “consistent with the  $\text{Ni}^{\text{III}}$  having a low-spin  $d^7$  electron configuration in a distorted trigonal bipyramidal ligand field”.





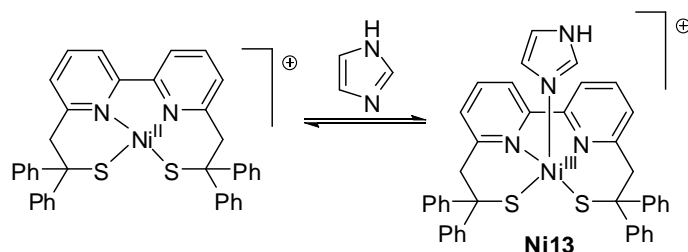
Scheme 10. Penta-dentate nickel(III) complexes, from Lee and coworkers.<sup>11</sup>

More recently, in 2012, W. Z. Lee and coworkers reported the formation of Ni(III) complex with a penta-dentate N3O2 ligand, which resembles the oxidized form of the active site of Nickel-containing superoxide dismutase (Scheme 11). The complex could react with  $\text{KO}_2$  to give  $\text{O}_2$  and the corresponding Ni(II) complex, which could then be re-converted into Ni(III) complex by oxidation with  $[\text{Cp}_2\text{Fe}]\text{PF}_6$ . Spin density plot of the complex calculated from DFT showed an important contribution from the ligand.



Scheme 11. Synthesis of Ni(III) pentadentate complex, from Lee W.Z. and coworkers.<sup>12</sup>

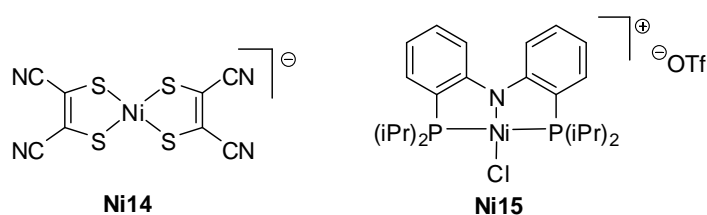
If obtaining of penta-coordinated Ni(III) complexes is already difficult, Ni(III) complexes of lower coordination number are even more difficult to achieve. For example, square-planar pyramidal nickel complex of bisamine dithiolate ligand and apical imidazole ligand has high valent Ni(III)<sup>13</sup> (Scheme 12). When the imidazole ligand is absent, the metal character of the redox-active molecular orbital drops drastically, and the square-planar complex could be considered as a Ni(II) radical complex.<sup>14</sup>



Scheme 12. Reversible apical coordination of imidazole on nickel complex, by Neese and coworkers.

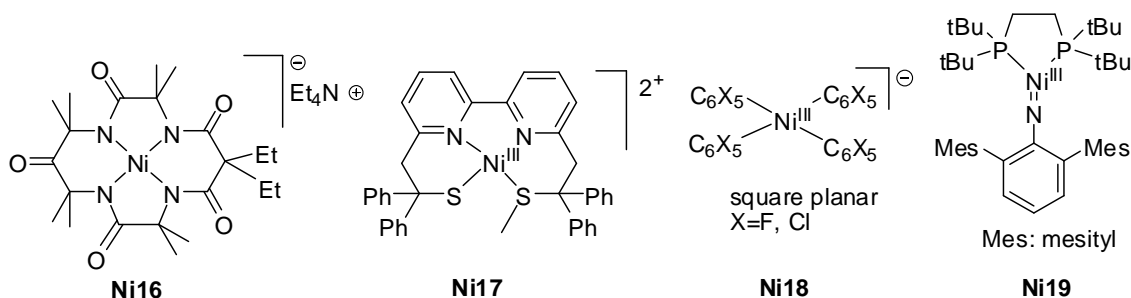
Some lower-coordinated complexes previously denoted as Ni(III) turned out to be Ni(II). For example, the complex **Ni14**  $[\text{NiL2}]^+$ , where L is the doubly deprotonated form of 1,2-

benzondithiol, has been the center of debate for several decades concerning the nature of Ni (Scheme 13). It was first supposed to be a Ni(III) complex in which the SOMO has a large contribution from the ligand.<sup>15</sup> It turned out, as been shown by Neese and Wieghart, that it is a Ni(II) complex, in which the SOMO is primarily ligand-based. This orbital is energetically close to the 3d<sub>xz</sub> of Ni, and is symmetrically allowed to mix with it, resulting in the 3d-Ni character part in the SOMO.<sup>16</sup> Another example of the ambiguity of formal Ni(III) and true Ni(III) compounds involves formally pincer Ni(III) complexes. They are used as catalysts for the Kharasch reaction and are often denoted as “Ni(III) complexes” but little has been studied about the true oxidation state of Ni.<sup>17</sup> In one of the study, it has been shown that the formally Ni(III) complex **Ni15** [Ni(PNP)Cl]OTf (Scheme 13) contains in fact Ni(II) centre bound to a radical cation.<sup>18</sup>



*Scheme 13. Ni(II) complexes often denoted as Ni(III)*

In 1991, Collins and coworkers reported the first isolation of a square-planar Ni(III) complex, which is based on N4 ligand system (**Ni16**, Scheme 14). In 2011 Neese and coworkers reported thiolate Ni(III) complex **Ni17** of a mixed thiolate-thioether ligand.<sup>14</sup> A three coordinated Ni(III) imide complex **Ni18** has been reported by the group of Hillhouse,<sup>19</sup> as part of their research in low-coordinated species that features multiple bond between nickel and light-elements like C, N, P. Tetra-coordinated homoleptic Ni(III) complexes **Ni19** were reported by Alonso and coworkers, using C6X5 ligands (Scheme 14).<sup>20</sup>



*Scheme 14. Examples of tetra- and tri- coordinated Ni(III) complexes*

In summary, due the interest in phenoxy radical and mix-valence complexes, oxidized species of nickel salen complexes have been the subjects pursued by many groups. We were thus interested in studying the oxidation of Ni(II) phosphasalens complexes to see the electronic differences conferred by the phosphasalens ligands compared to salens. Taking into account the rarity of Ni(III) complexes, and the inexistence of a tetracoordinated Ni(III) complex of a Salen-

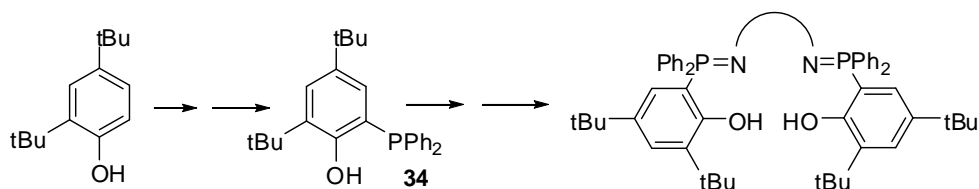
like ligand, and more generally, of a phenoxide-containing ligand, it would be interesting to see if the phosphasalen ligands could afford the high oxidation state Ni(III).

## II. Results.

### 1. Methods for Substituted Phosphasalen Ligand Synthesis

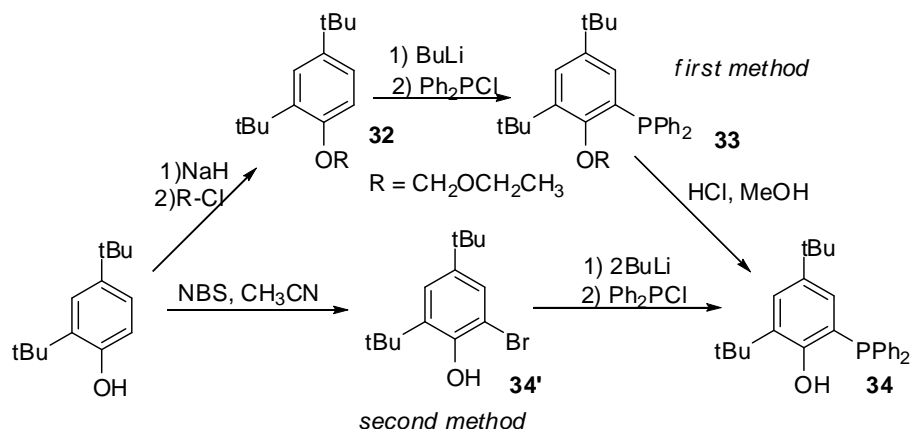
It is worth noting that all oxidised nickel salen complexes that are stable enough to be characterised do have substituents on *ortho*- and *para*- positions of the phenoxide rings. And they were not random choices. In fact, since 1989, Goldsby and co-workers have reported the oxidative polymerisation of Ni(II) salen complexes in moderately/weak donor solvents, giving polymer-modified electrodes.<sup>21</sup> The group also observed that polymer formation was inhibited by substituents at *para*- positions of the phenoxide rings, and proposed that the polymerisation took place by ligand-radical coupling mechanism with the formation of C-C linkages between phenyl rings, a process related to the oxidative polymerisation of phenol and substituted phenols.

Thus, before the study of any eventual oxidised phosphasalen nickel complex, it's important to develop substituted phosphasalen ligand. We chose to develop phosphasalen ligands with *tert*-butyl substituents on *ortho*- and *para*- positions of the phenoxide rings, starting from a cheap and readily available 2,4-di-*tert*-butylphenol. This starting compound is first converted to phosphinophenol **34** which would then be transformed into phosphasalen ligands by a sequence of Kirsanov reactions-deprotonation as has been seen for the synthesis of the non-substituted phosphasalen ligand. (Scheme 15)



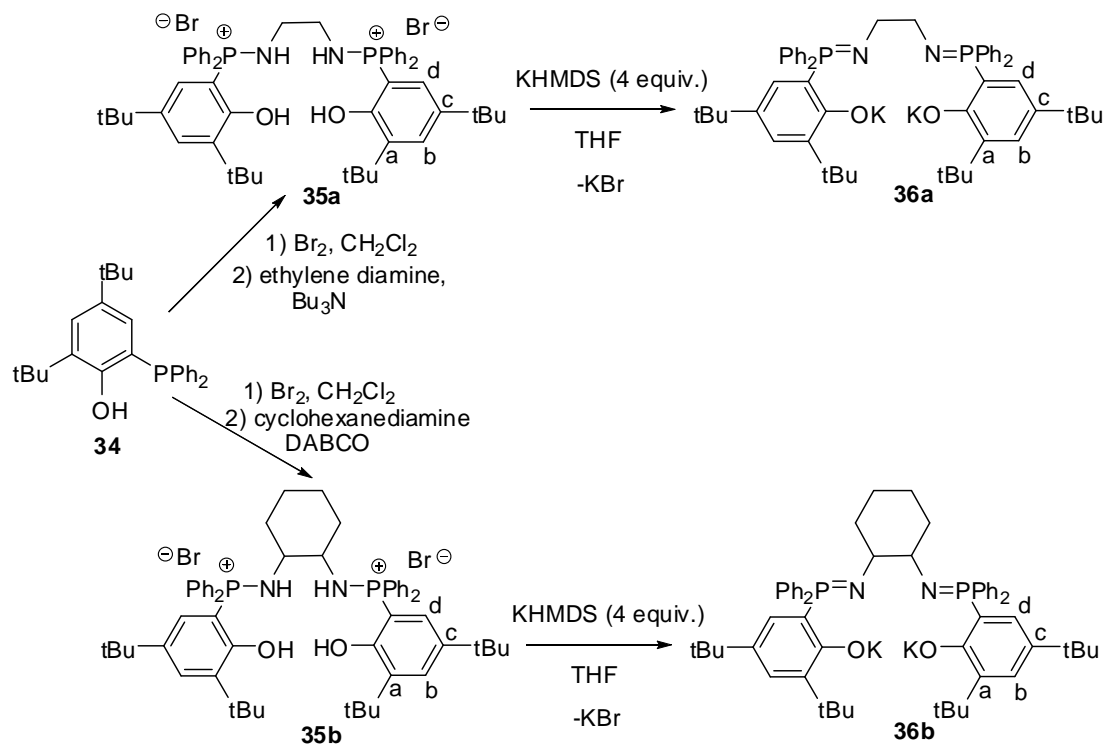
Scheme 15. Synthesis of substituted phosphasalen ligands.

The phosphinophenol **34** was first synthesised following the same procedure as reported for the unsubstituted phosphasalen ligands in chapter 3 (Scheme 16, first method). The phenol function was first protected, then was submitted to an ortholithiation reaction and treatment with diphenylphosphine chloride to introduce PPh<sub>2</sub> functional group at *ortho*-position of the protected phenol. Finally, the protection group of the phenol function was removed by an acidic treatment. This method gave compound **34** with high total yield, but employed an expensive and toxic compound (chloride methyl ethyl ether) to introduce the protecting group. Furthermore, the purification of the intermediate **33** by recrystallation in methanol often took long time. We thus searched for an alternative method.



Scheme 16. First and second synthesis of phosphinophenol

We later noticed that the phosphinophenol **34** could be obtained much faster and more easily by adopting the synthesis reported for dilithium bis(aryloxy)phosphines complexes by Fryzyk and coworkers<sup>22</sup> (Scheme 16, second method). The bromination of 2,4-di-*tert*-butylphenol with *N*-bromosuccinimide gave 2-bromo-4,6-di-*tert*-butylphenol **34'** in quantitative yield. Reaction of this product with *n*-BuLi, followed by nucleophilic substitution with chlorodiphenylphosphine and aqueous treatment gave the desired product **34** in high yield as a white crystalline solid. This method is not only faster and simpler than the synthesis of **34** by protection/deprotection, but also employs reagents that are much less expensive and less toxic than the reagents needed in the first method.



Scheme 17. Synthesis of phosphasalens ligands

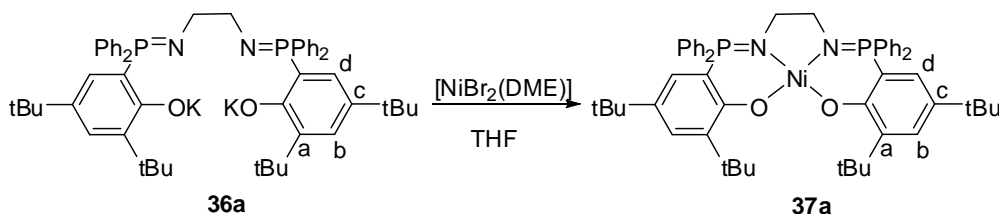
Kirsanov reaction of **34** with ethylenediamine and trans-1,2-cyclohexanediamine in the presence of the appropriate bases gave proligands **35a,b** in high yield (Scheme 17). Though these compounds have very limited solubility in common solvents, their characterisation by NMR multi-nuclear was still successfully carried out. In  $^{31}\text{P}\{^1\text{H}\}$  spectroscopy the equivalent phosphorus atoms of **35a** appear as a singlet at  $\delta(\text{CDCl}_3) = 40.3$  ppm, and those of **35b** at  $\delta(\text{CDCl}_3) = 38.5$  ppm, which are very close to the value reported for the unsubstituted phosphasalen proligand ( $\delta(\text{CDCl}_3) = 39.3$  ppm). In  $^1\text{H}$  NMR spectrum, the bridging ethylene protons of **35a** appear as a broad signal at  $\delta(\text{CDCl}_3) = 3.74$  ppm, those of **35b** at  $\delta(\text{CDCl}_3) = 3.82$  ppm, all slightly higher than the values reported for the unsubstituted phosphasalen proligand ( $\delta(\text{CDCl}_3) = 3.43$  ppm).

Upon reaction with 4 equiv. of KHMDS in THF, both these compounds are easily deprotonated to give the corresponding anionic phosphasalen ligands. Physically, a cloudy solution (containing KBr and the soluble anionic phosphasalen product) was formed instead of a white suspension (containing insoluble proligand and soluble KHMDS). The completion of reaction was monitored by the apparition of a unique singlet corresponding to the anionic phosphasalen ligands ( $\delta(\text{THF}) = 20.6$  ppm for **36a**, 15.8 ppm for **36b**). After removal of KBr by filtration, evaporation of THF and recrystallisation in petroleum ether to remove HMDS, phosphasalen ligand **36a** was obtained as a white solid in quantitative yield. In  $^1\text{H}$  NMR spectrum, the bridging ethylene protons of **36a** now as a virtual triplet at  $\delta(\text{THF-d}_8) = 3.20$  ppm, due to couplings with two phosphorus atoms ( $J_{\text{P,H}} = 5.0$  Hz). Although the formation of **36b** is also very clean, it could not be separated from HMDS. Thus, **36b** was not isolated and but was still characterised by NMR-multinuclear experiments for comparisons.

## 2. Neutral Complex Synthesis and Characterisation

### 2.1 Neutral Complexes Synthesis

The synthesis of nickel complex of ligand **36a** was carried out directly by reaction of  $[\text{NiBr}_2(\text{DME})]$  with a colorless solution of isolated **36a** in THF, giving immediately a deep purple solution (Scheme 18).



Scheme 18. Synthesis of **37a**.

In  $^{31}\text{P}\{^1\text{H}\}$  spectroscopy only one singlet was seen at  $\delta(\text{THF}) = 36$  ppm, indicating the completeness of the coordination reaction. THF was evaporated and the residue was taken in dichloromethane to completely precipitate insoluble potassium salt(s). After removal of

insoluble potassium salt by centrifugation and evaporation of dichloromethane, complex **37a** was obtained as a blue purple solid. In  $^1\text{H}$  spectroscopy, the ethylene bridge protons appear as a broad signal at  $\delta(\text{CD}_2\text{Cl}_2) = 2.05$  ppm, much higher field than in the ligand or proligand.

Definitive evidence concerning the structure of **37a** was provided by X-ray crystal analysis of the complex. Suitable crystals were obtained from slow diffusion of petroleum ether over a saturated dichloromethane solution of **37a** at room temperature. Ortep view of complex **37a** is presented in Figure 2. The complex crystallized with two molecules of dichloromethane. (The same structure of Nickel-complex was obtained by X-ray diffraction on crystals obtained from slow evaporation of a toluene solution at room temperature, and in this case the complex crystallize with two molecules of toluene).

As expected for a diamagnetic  $d^8$  complex **37a** adopts a square planar geometry around the metal and has a  $C_2$  axis going through the metal center. The four coordination sites are occupied by the iminophosphorane and phenoxide groups with slight deviation from planarity ( $\text{O1-N1-N1'-O1'}$  dihedral angle  $8.51^\circ$ ). The  $\text{O}_{\text{phenoxide}}\text{-C}_{\text{phenyl}}$ , Ni-O and Ni-N bond lengths are of almost the same values as those in the nickel complex of unsubstituted phosphasalen ligand. In the same manner, values of bond angles around the nickel center are very close to the ones reported for the unsubstituted complex.

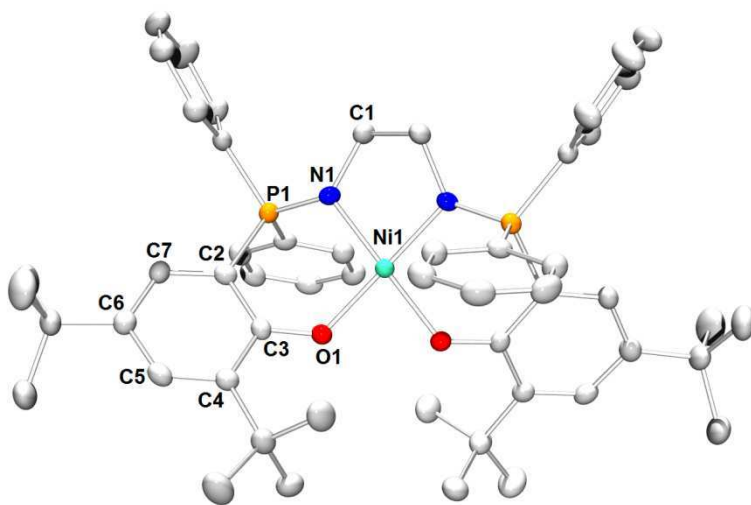
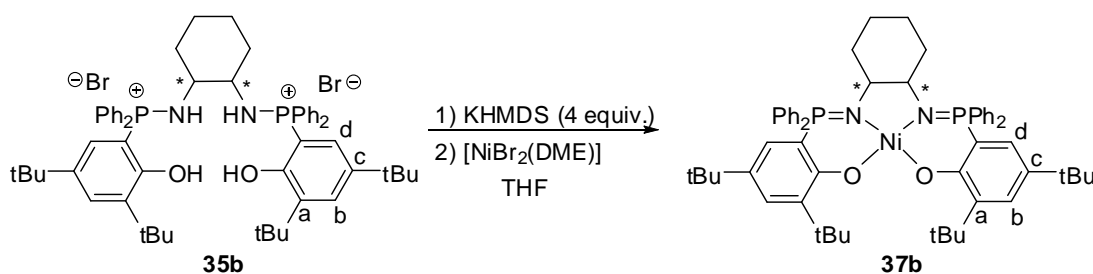


Figure 2. ORTEP view of complex **37a**. Solvent molecules and hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. The complex has a  $C_2$  symmetric axis passing through Ni. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ni-O1 1.881 (2), Ni-N1 1.887 (2), P1-N1 1.613 (2), O1-C3 1.317 (3), C2-C3 1.424 (4), C3-C4 1.426 (4), C4-C5 1.391(4), C5-C6 1.408 (4), C6-C7 1.375(4), C7-C2 1.398 (4), N1-Ni1-O1 95.7 (1), N1-Ni1-N1' 84.7 (1), O1-Ni1-O'1 84.7 (1).

The synthesis of **37b** is slightly different from the one for **37a**. As the anionic phosphasalen ligand **36b** was not isolated as a solid, the coordination was done by the reaction of  $[\text{NiBr}_2(\text{DME})]$  with an in situ-generated solution of **36b** in THF, as described above in Scheme

19. The addition of  $[\text{NiBr}_2(\text{DME})]$  induced immediately the change from a colourless to a deep blue-purple solution.  $^{31}\text{P}\{^1\text{H}\}$  spectrum showed the formation of a unique product at  $\delta$  (THF) = 30 ppm, which is in lower field compared to the anionic free ligand ( $\delta$  (THF) = 15.8 ppm). THF was evaporated and the residue was taken in dichloromethane to facilitate the precipitation of insoluble potassium salt(s). After removal of insoluble potassium salt by centrifugation, evaporation of dichloromethane and washing with petroleum ether to remove HMDS, complex **6b** was obtained as a blue solid. In  $^1\text{H}$  spectroscopy, the ethylene bridge protons appear as a virtual triplet at  $\delta(\text{CD}_2\text{Cl}_2) = 3.02$  ppm, due to couplings with vicinal protons and phosphorus atoms ( $^3J_{\text{H,H}} = ^3J_{\text{P,H}} = 9.0$  Hz).



Scheme 19. Synthesis of nickel complex **37b**.

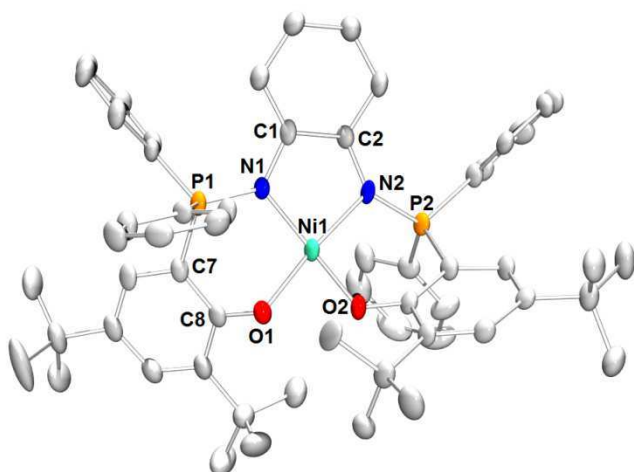


Figure 3. ORTEP view of complex **37b**. Solvent molecules and hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni-O1 1.877 (3), Ni-O2 1.882(3), Ni-N1 1.912 (4), Ni-N2 1.921(4), P1-N1 1.627 (4), P2-N2 1.618(4), O1-C8 1.303 (6), O2-C<sub>phenyl</sub> 1.306(6), N1-C1 1.478(6), N2-C2 1.477(6), N1-Ni1-O1 98.1 (2), O2-Ni1-N2 95.2(2), N1-Ni1-N2 85.7 (2), O1-Ni1-O2 83.3 (1), O1-N1-N2-O2 14.57.

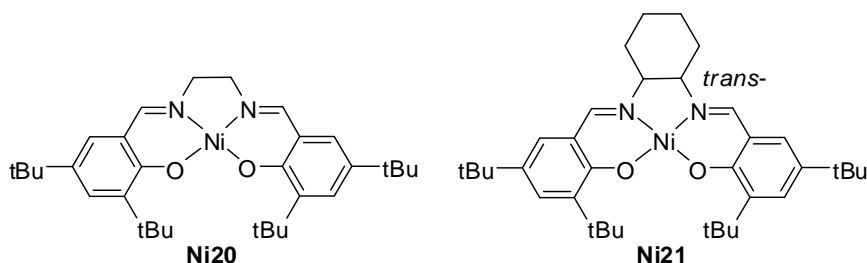
X-ray diffraction experiment was carried out on single crystals of **37b** obtained from slow diffusion of petroleum ether over a saturated dichloromethane solution and gave definite evidence of the structure of **37b** (Figure 3). The complex crystallised with two molecules of dichloromethane.

Whereas the ligand **36b** exists in racemic mixture of (R,R) and (S,S) configuration of the cyclohexane diamine bridge, **37b** crystallised as mixtures of enantiopure crystals (or conglomerates) (this phenomenon, known as chiral resolution by crystallization, concerns about 5-10% of all racemates). Thus the crystal on which X-ray diffraction was carried out is of (R,R) configuration for C1 and C2. Similarly to **37a**, **37b** adopts a slightly distorted square-planar geometry (O1-N1-N2-O2 dihedral angle  $14.57^\circ$ ). The  $O_{\text{phenoxide}}-C_{\text{phenyl}}$  bonds are slightly shorter than the ones in **37a** (1.303(6) and 1.306(6) vs 1.317(3)), whereas Ni-N bonds are longer (1.912(4) and 1.921(4) vs 1.887(2)). But those differences remain insignificant.

## 2.2. Electrochemistry of Nickel Complexes.

At the difference of nickel phosphasalen complex with unsubstituted ligand which only has irreversible oxidation wave in dichloromethane, in the same solvent **37a,b** present first oxidation waves which are reversible. This is expected because the change from unsubstituted ligand to ligands with substituents on *ortho*- and *para*- positions of the phenoxide rings would limited side-reactions that could happen to the oxidised nickel complexes, e.g oxidative polymerisation, as has been described before for the Salen complexes.

For reference, whereas simple nickel of unsubstituted salen ligand has irreversible oxidation process in dichloromethane, In this solvent and at room temperature, the complex [Ni(t-Bu-Salen)] (Scheme 20) exhibits a first reversible oxidation wave at  $E_{1/2}^1 = +0.58\text{V}$  (vs  $E_{1/2}(\text{Fc}^+/\text{Fc})$ ), and a second quasi-reversible one at  $E_{1/2}^2 = +1.04\text{V}$  (vs  $E_{1/2}(\text{Fc}^+/\text{Fc})$ ).<sup>9c, 23</sup> In the same solvent and at the same temperature, complex [Ni(t-Bu-Salcn)] (Scheme 20) exhibits two quasi-reversible oxidation waves at  $E_{1/2}^1 \sim 0.47\text{V}$  and  $E_{1/2}^2 \sim 0.79\text{V}$  (vs  $E_{1/2}(\text{Fc}^+/\text{Fc})$ ).<sup>7</sup> When the temperature was decreased to 230K, these two oxidation waves shift to  $E_{1/2}^1 \sim 0.37\text{V}$  and  $E_{1/2}^2 \sim 0.85\text{V}$  (vs  $E_{1/2}(\text{Fc}^+/\text{Fc})$ ).<sup>5b</sup> These oxidations have been established to be ligand-based to give mono- and bis-phenoxyradical species.<sup>9c</sup> The difference between the two half-wave potentials  $E_{1/2}^1$  and  $E_{1/2}^2$  is an indication of the communication through bond and space between the two phenoxide moieties: the bigger the difference, the stronger the communication.



Scheme 20. Nickel salen complexes analogs of **37a,b**.



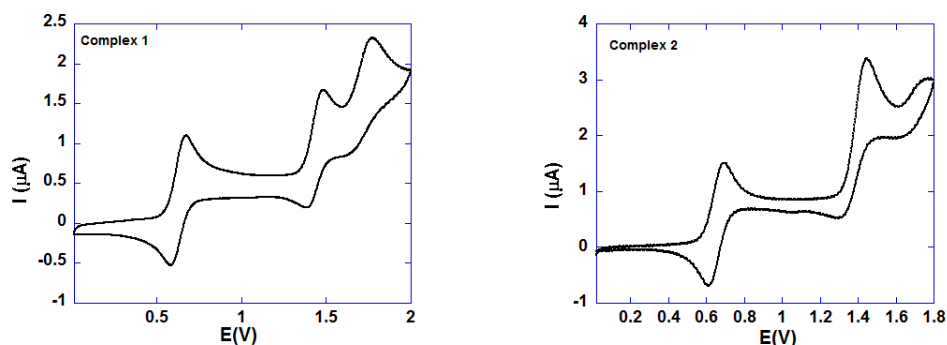


Figure 4. Cyclic voltammetry graphs of **37a** (left) and **37b** (right) in  $\text{CH}_2\text{Cl}_2$ . The potential values are relative to SCE Tetrabutylammonium tetrafluoroborate salt as electrolyte ( $c = 0.12 \text{ mol L}^{-1}$ ); scan rate =  $50 \text{ mV s}^{-1}$ ;  $c = 3.0 \text{ mmol L}^{-1}$ ;

To our surprise, for the two phosphasalens complexes, up to three reversible oxidation waves were observed (Figure 4). The first oxidation waves of these two complexes happen at +0.16V and +0.18V higher than  $E_{1/2}(\text{Fc}^+/\text{Fc})$ , thus much easier than the salen analogs (Table 1 and Table 2). This clearly demonstrates the better donating ability of phosphasalens ligands compared to salen ligands, which render more stable the oxidized species.

Table 1. Electrochemical data for nickel-phosphasalens complexes in  $\text{CH}_2\text{Cl}_2$ <sup>a</sup>

| Complex    | $E_a^1$ | $E_p^1$ | $E_a^2$ | $E_p^2$ | $E_a^3$ | $E_p^3$ | $E_{1/2}^1, \text{V}$ | $E_{1/2}^2, \text{V}$ | $E_{1/2}^3, \text{V}$ |
|------------|---------|---------|---------|---------|---------|---------|-----------------------|-----------------------|-----------------------|
| <b>37a</b> | 0.68    | 0.59    | 1.48    | 1.39    | 1.77    | 1.60    | 0.63                  | 1.43                  | 1.69                  |
| <b>37b</b> | 0.69    | 0.61    | 1.42    | 1.33    | 1.75    | 1.58    | 0.65                  | 1.37                  | 1.67                  |
| <b>Fc</b>  |         |         |         |         |         |         |                       |                       |                       |

<sup>a</sup> Measurements were done at room temperature. Potential values are relative to SCE. Tetrabutylammonium tetrafluoroborate salt as electrolyte ( $c = 0.12 \text{ mol L}^{-1}$ ); scan rate =  $50 \text{ mV s}^{-1}$ ;  $c = 3.0 \text{ mmol L}^{-1}$ ;

Table 2. Comparison of Electrochemical data for nickel complexes in  $\text{CH}_2\text{Cl}_2$ <sup>a</sup>

| Complex                       | $E_{1/2}^1, \text{V}$ | $E_{1/2}^2, \text{V}$ | $E_{1/2}^3, \text{V}$ |
|-------------------------------|-----------------------|-----------------------|-----------------------|
| <b>37a</b> <sup>a</sup>       | 0.16                  | 0.96                  | 1.22                  |
| <b>37b</b> <sup>a</sup>       | 0.18                  | 0.90                  | 1.20                  |
| [Ni(t-Bu Salen)] <sup>a</sup> | 0.58                  | 1.04                  |                       |
| [Ni(t-Bu Salcn)] <sup>a</sup> | 0.47                  | 0.79                  |                       |
| [Ni(t-Bu Salcn)] <sup>b</sup> | 0.37                  | 0.85                  |                       |

<sup>a</sup> Potential values are relative to  $E_{1/2}(\text{Fc}^+/\text{Fc})$ . Tetrabutylammonium tetrafluoroborate salt as electrolyte ( $c = 0.12 \text{ mol L}^{-1}$ ); scan rate =  $50 \text{ mV s}^{-1}$ ;  $c = 3.0 \text{ mmol L}^{-1}$ ; <sup>a</sup> measurements at room temperature; <sup>b</sup> measurements at 230K.

The second and third oxidation waves of complex **37a** are very close to each other, the difference between them being 0.26V. However, the difference between the first and second

oxidation waves is very large (0.8 V, Table 2). This value is much more important than the difference of second and first half wave potential for the analog salen complex **Ni20** (0.46 V).

In the same manner, the difference between the second and the third oxidation waves of complex **37b** is small (0.30 V) whereas the one between the first and the second half wave potentials is very large (0.72 V). Once again, this value of 0.72 V is much more important than the one reported for the analog nickel-salen complex **Ni21** featuring trans-cyclohexane diamine backbone.

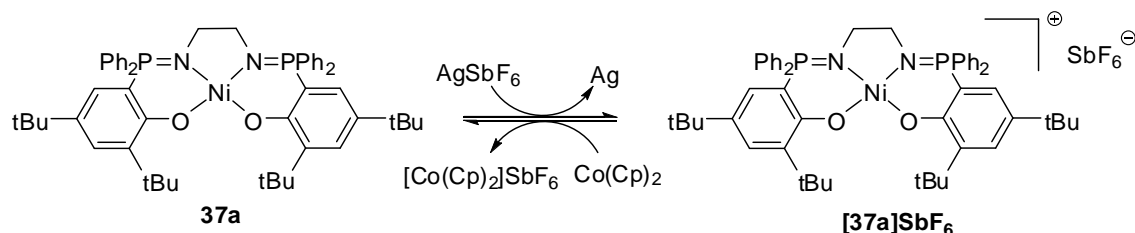
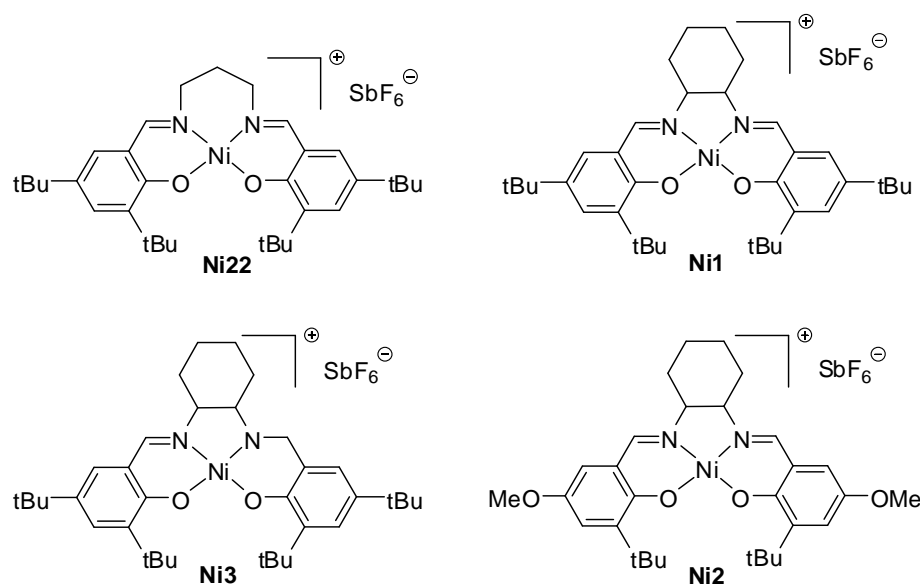
It is worth noting that studies have shown that oxidized species from the two cited nickel-salen complexes are of class III mixed-valence compounds, where there's almost no barrier to electronic communication between the two phenoxide moieties (which is done through the nickel center). Thus, for these complexes, the difference in half wave potentials of first and second oxidations to yield mono- and bisphenoxyl radicals are among the largest one, because the second oxidation is influenced by the first one. Weaker electrochemical communication or less flexibility resulting in weaker structural rearrangement to accommodate such communication would reduce the difference between first and second half-wave potentials.<sup>9c</sup> Thus for salen complexes, the difference of half wave potentials of processes giving mono- and bisphenoxyl radicals should be around, or less than those values reported for the cited salen complexes (0.46 V for **Ni20** and 0.32 V for **Ni21**).

Therefore the values of difference between first and second half-wave potentials for the two phosphasalens complexes **37a,b** (0.80 V and 0.72 V) suggest that these do not correspond to the formation of mono- and bisphenoxyl radicals. Along with the existence of three oxidation waves for those complexes, they suggest that the first oxidation happens in the metal, and the second and third ones are ligand-based giving phenoxyl or iminophosphoranyl radicals.

### 3. Oxidised Complexes Synthesis and Characterisation

The electrochemical studies suggests that it's possible to form stable one-electron oxidised species of nickel-phosphasalens complexes by silver salts in  $\text{CH}_2\text{Cl}_2$  (formal potential of  $\text{Ag}^+/\text{Ag}$  in  $\text{CH}_2\text{Cl}_2$  is of 0.65V vs  $\text{Fc}^+/\text{Fc}^{2+}$ ). Indeed, addition of a stoichiometric amount of  $\text{AgPF}_6$ ,  $\text{AgBF}_4$ ,  $\text{AgOTf}$  or  $\text{AgSbF}_6$  into a solution of complex **37a,b** in  $\text{CH}_2\text{Cl}_2$  induced immediately a change of colour from blue to deep red, with metal silver precipitated out from the solution, which sometimes gave a mirror layer on the wall-side of the test tube. In  $^{31}\text{P}\{^1\text{H}\}$  spectrum recorded after 2 hours of stirring, no signal was detected indicating the disappearance of the starting complex and the formation of a paramagnetic species.

Though for all reactions between **37a** or **37b** with any of those listed silver salts seemed to proceed well and gave the same physical aspects, only in the case of reaction of **37a** with  $\text{AgSbF}_6$  did the product crystallise. The further studies are thus centred on this species.

Scheme 21. Oxidation of phosphasalen complex **37a**.Scheme 22. Reported oxidized nickel-salen complexes as evidenced by X-ray diffraction.<sup>5a, 5c, d, 6</sup>

After removal of Ag by centrifugation, dichloromethane was evaporated almost completely and the residue was dissolved in toluene, giving a deep red-brown solution. Green crystals were obtained after one week of storage at  $-40^\circ\text{C}$  in almost quantitative yield (89%). The complex is stable for months in solid state or in solution in dichloromethane or toluene. It could be quantitatively reduced to the Ni(II) phosphasalen complex **37a** by one equiv. of  $\text{Co}(\text{Cp})_2$  (Scheme 21).

X-ray diffraction was carried out on crystals of the oxidised complex  $[\text{37a}][\text{SbF}_6]$  giving definite evidence for its structure (Figure 5). The obtainment of X-ray structure of  $[\text{37a}][\text{SbF}_6]$  is precious because X-ray structures of oxidised nickel-salen complexes and derivatives remain scarce in literature (Scheme 22).<sup>5a, 5c, d, 6</sup>

The complex  $[\text{37a}][\text{SbF}_6]$  crystallised with 4 molecules of toluene. The nickel is in a slightly distorted square planar geometry formed by the four donating atoms of the phosphasalen ligand, as seen by the dihedral angle  $\text{O1-N1-N2-O2} = 11.06^\circ$  (instead of  $8.51^\circ$  in the neutral complex). The anion  $\text{SbF}_6^-$  was found to be located quite far from the cation. No special stacking effect or hydrogen bonding was detected.

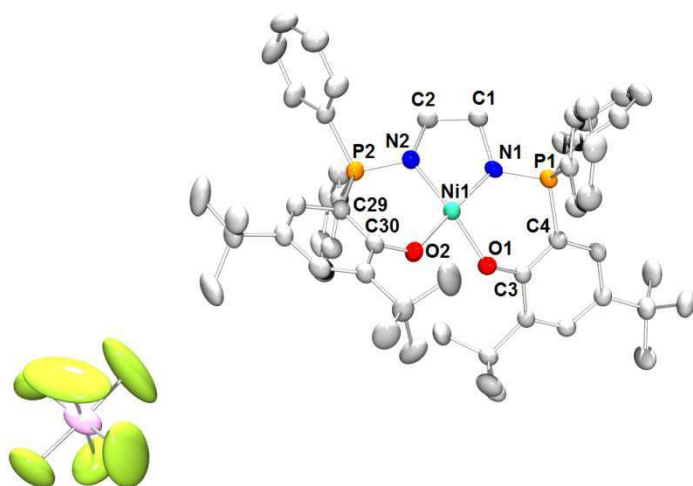
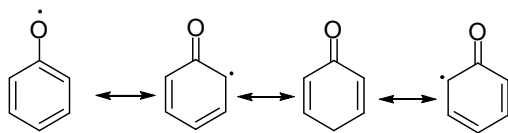


Figure 5. ORTEP view of complex  $[37a][SbF_6]$ . Solvent molecules and hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni-O1 1.828 (2), Ni-O2 1.844(2), Ni-N1 1.875 (3), Ni-N2 1.842(3), P1-N1 1.639 (3), P2-N2 1.650 (3), O1-C4 1.327 (4), O2-C30 1.326(5), N1-C1 1.486(5), N2-C2 1.486(5), N1-Ni1-O1 94.9 (1), O2-Ni1-N2 95.3 (1), N1-Ni1-N2 86.8 (1), O1-Ni1-O2 84.2 (1), O1-N1-N2-O2 11.06.

Selected bond lengths around the metal centre of  $[37a][SbF_6]$  and **37a** are presented in Table 3. Compared to the neutral complex, the two  $O_{\text{phenoxide}}-C_{\text{phenoxide}}$  bonds in  $[37a][SbF_6]$  are slightly longer (1.327(4) and 1.326(5) vs. 1.317(3)). This is in contrast with the case of phenoxyl radical salen complexes, where the  $O_{\text{phenoxide}}-C_{\text{phenoxide}}$  bonds are shorter than those in the corresponding neutral salen complexes, as a result of semi-quinone character of the phenoxyl radical (Scheme 23). All M-N and M-O bonds are contracted in the oxidised phosphasalene complex. Interestingly, contraction is more important along one axis O1-M-N2 than the other (O2-M-N1).



Scheme 23. Canonical forms of phenoxyl radical.

Table 3. Selected bondlengths in **37a** and  $[37a][SbF_6]$

| Complex               | Ni-N1     | Ni-N2     | Ni-O1     | Ni-O2    | O1- $C_{\text{phenoxide}}$ | O2- $C_{\text{phenoxide}}$ |
|-----------------------|-----------|-----------|-----------|----------|----------------------------|----------------------------|
| <b>37a</b> (exp)      | 1.887 (2) | 1.887 (2) | 1.881(2)  | 1.881(2) | 1.317(3)                   | 1.317(3)                   |
| <b>37a</b> (calc)     | 1.892     | 1.892     | 1.904     | 1.904    | 1.309                      | 1.309                      |
| $[37a][SbF_6]$ (exp)  | 1.875 (3) | 1.842(3)  | 1.828 (2) | 1.844(2) | 1.327 (4)                  | 1.326(5)                   |
| $[37a]^+$ (calc)      | 1.897     | 1.819     | 1.819     | 1.888    | 1.323                      | 1.327                      |
| $[37a][SbF_6]$ (calc) | 1.875     | 1.806     | 1.827     | 1.887    | 1.323                      | 1.320                      |

In most reported X-ray structures of oxidised nickel Salen complexes, which has been shown to be phenoxyl radical species, contraction of O-C<sub>phenoxide</sub> bonds have been observed, along with the contraction of M-N, M-O bonds.<sup>5a, 5c, d</sup> The only case where O-C<sub>phenoxide</sub> bonds are slightly elongated upon comparison with the neutral complex happened to complex with unsymmetrical ligand<sup>6</sup> (**Ni2**, Scheme 22), and in this case, the M-N and M-O are also elongated. The structural data thus suggest the formation of a nickel(III) complex. Further studies have been carried out in order to assess the nature of complex **[37a][SbF<sub>6</sub>]**.

### 3. EPR and Magnetic Studies of Complex **[37a][SbF<sub>6</sub>]**

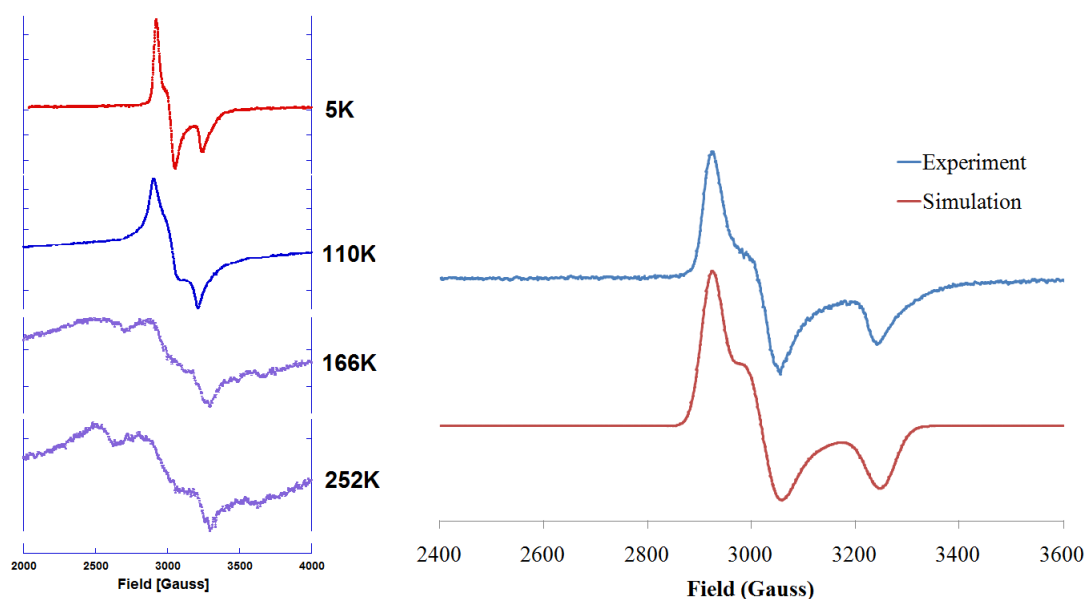


Figure 6. (left) EPR spectra of **[37a][SbF<sub>6</sub>]** at different temperature; (right) recorded EPR spectrum of **[37a][SbF<sub>6</sub>]** at 5K and the simulated spectrum. Conditions: **[37a][SbF<sub>6</sub>]** = 4 mM in toluene:benzene, frequency 9.3690 GHz, power = 0.1 mW at 5K, 60 mW at other temperatures.

EPR spectrum recorded for the complex **[37a][SbF<sub>6</sub>]** at 5K exhibited parameters with a large g-tensor anisotropy. Simulations gave three values of g as follow:  $g_1=2.290$ ,  $g_2=2.215$ ,  $g_3=2.061$ . These data indicate a rhombic symmetry typically known for low spin Ni(III).<sup>9, 6, 5d, 25, 23, 19</sup>

No transition from Ni(III)-radical was observed in increasing the temperature, instead the intensities of the signals in EPR spectra decreased dramatically (no signal was detected at room temperature). This is markedly different from the behaviour of reported oxidised Ni(Salen) complexes and derivatives. For these compounds, high valent Ni(III) exist at low temperature (less than 160K, sometimes even much lower) and phenoxyl radical complex exists at higher temperatures.<sup>5d, 7, 23</sup> At these temperatures and above, EPR spectra recorded for these complexes present a fine signal with  $g \sim 2.0$ , characteristic of an organic radical.

Thus these data clearly evidence the formation of a Ni(III)phosphasalen complex at low temperature and suggest that this oxidised complex is still a Ni(III) species at up to 252K.

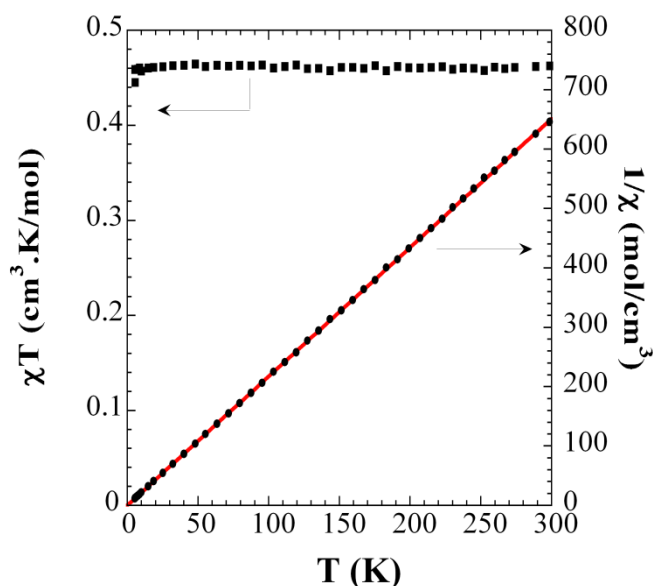


Figure 7. Plots of  $\chi T$  and  $1/\chi$  vs.  $T$  for  $[6a][SbF_6]$ .

The solid state SQUID measurements (SQUID = Superconducting Quantum Interference Device) in temperatures were performed at 1000G on dried crystals of  $[37a][SbF_6]$ . They showed that the magnetic susceptibility  $\chi$  follows a Curie law ( $\chi=C/T$ ) for a mononuclear complex. The plot of  $1/\chi$  vs.  $T$  is linear, and the product  $\chi T$  is constant from  $\sim 4K$  up to 300K. The constant  $C$  was then determined to be  $0.46 \text{ cm}^3.K/\text{mol}$ . From this value,  $g$  was deduced to be 2.22 ( $C = (Ng^2\mu_B^2S(S+1))/k_B$ ). Note that this value of  $g$  is in perfect consistence with the  $g_{\text{average}}$  calculated from EPR pectra (2.19).

The constant  $C$ , and thus  $g$  does not vary from  $\sim 4K$  up to 300K, strongly suggesting that in this range of temperatures, the complex  $[37a][SbF_6]$  remains a Ni(III) species. This hypothesis is consistent with what have been observed from EPR spectroscopy measurements.

Data from EPR and SQUID measurements thus strongly suggest that the complex  $[37a][SbF_6]$  is a high valent Ni(III) species and that this species is stable even at high temperature. DFT calculations have been carried out for better understanding of the nature of the complex.

#### 4. DFT Studies of $[37a][SbF_6]$

Density Functional Theory (DFT) calculations were performed on the two complexes **6a** and  $[37a][SbF_6]$  with the Gaussian 03 set of programs<sup>26</sup> in combination with the B3PW91 functional.<sup>27</sup> Nickel was represented by the relativistic effective core potential of Hay and Wadt<sup>28</sup> and the associated triple zeta quality basis set<sup>29</sup>, augmented by a  $f$  polarization function as proposed by Frenking<sup>30</sup> (lanl2tz(f)). Tert-butyl group on the phenoxide rings were described

with 3-21G Pople basis set to simplify the calculations. Phosphorus atoms were represented by 6-31G\* basis set reinforced with an f polarization function. All other atoms were described with the 6-31G\* Pople basis set.<sup>31</sup>

DFT calculations correctly represent the geometry of neutral nickel-phosphasalens complexes, the difference between calculated bond lengths and experimental ones are less than 0.02 Å. Details of the bonds around metal center could be seen in Table 3.

For the oxidized species, two structures were optimized: the cation with or without a counterion  $\text{SbF}_6^-$ . All bond distances on the ligand predicted for  $[\mathbf{6a}]^+$  are very close to the ones predicted for  $[\mathbf{37a}][\text{SbF}_6]$  and they all match experimental values. At the difference from oxidized nickel salen complex **Ni2** (Scheme 22) featuring methoxyl group at the *p*-position on the phenoxide rings, whose optimized DFT structure and X-ray structure both shown a non-negligible interaction of  $\text{SbF}_6^-$  and the cationic nickel complex, no such interaction was detected in the optimized DFT structure of  $[\mathbf{37a}][\text{SbF}_6]$ , which is coherent with what has been seen in X-ray structure of  $[\mathbf{37a}][\text{SbF}_6]$ .

Just like in the structure obtained from X-ray diffraction, in the optimized structures of  $[\mathbf{37a}]^+$  and  $[\mathbf{37a}][\text{SbF}_6]$  the two  $\text{C}_{\text{phenoxide}}-\text{O}$  bonds are not shortened but even slightly elongated and show no difference one to the other. The non-symmetric contraction of Ni-N and Ni-O bonds along one particular N-Ni-O axis (more precisely, N2-Ni-O1 axis in X-ray structure) is also correctly represented. Effectively, the calculations attributed an important spin density on the three atoms on this N2-Ni-O1 axis (Figure 8). Those densities are much higher than the ones on other atoms. Spin densities on the phenyl ring attached to O1 are also more important than the ones on the other side. The majority of spin density is on the Ni centre, which suggests that the oxidised complex contains high valent Ni(III) instead of a radical ligand.

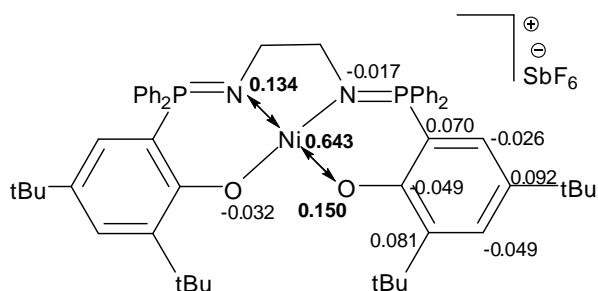
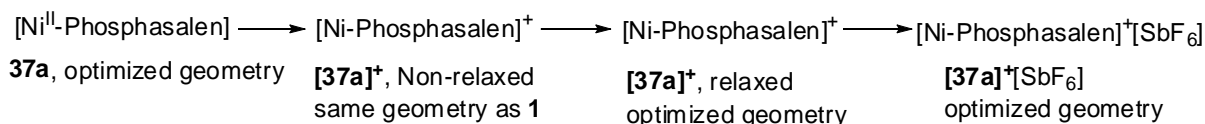


Figure 8. Spin densities on  $[\mathbf{37a}][\text{SbF}_6]$ , only the ones  $>0.02$  are printed.

In order to elucidate the electronic structure of the oxidised nickel-phosphasalens species and to understand the oxidation process, natural bond orbital (NBO) analysis was performed on all species involved in the following process:



In neutral complex **37a**, the d-block orbitals of Ni are all in important bonding or anti-bonding interaction with p-orbitals from nitrogen or oxygen. The resulting MOs are among the highest occupied MOs of the molecule and do not differ much in energy. This indicates close energy levels between d-block orbitals of Ni and  $p_z$  orbitals of N and O and  $\pi$ -orbitals of aromatic rings. The two highest occupied molecular orbitals are almost of the same energy and result from the anti-bonding combination of  $d_{xz}/d_{yz}$  orbital of Ni with  $p_\pi$  orbitals of the phenoxides on the ligand (Figure 9).

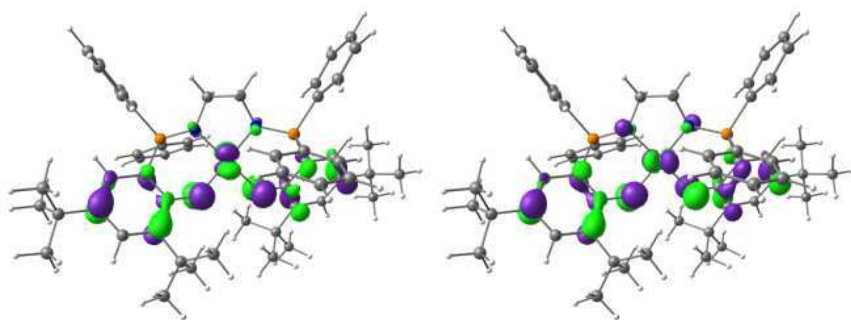


Figure 9. HOMO-1 and HOMO of neutral complex **37a**.

The oxidation was first done by removing one electron from one of these highest occupied orbitals. In the non-relaxed geometry, the resulted cation has two possible ground states with the same energy. According to the Jahn-Teller theorem, the compound will follow a geometric distortion in order to remove this degeneracy (Figure 10). Thus the two degenerate orbitals split in two energy levels: the singly occupied orbital at higher energy level than the doubly occupied one. This latter has been determined in the optimised  $[\mathbf{37a}]^+$  and is essentially the  $d_{xz}$  of nickel (Figure 10).

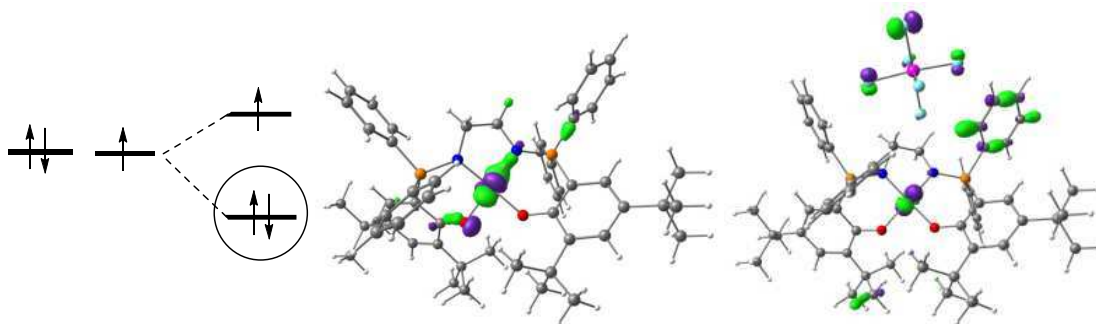


Figure 10. Jahn-Teller effect and the resulted doubly occupied orbital in  $[\mathbf{37a}]^+$  and  $[\mathbf{37a}]^+[\text{SbF}_6]$



The fact that there's almost no participation from the ligand in this molecular orbital is not surprising. In fact, it has been found that in  $[37a]^+$  and  $[37a][SbF_6]$  d-block orbitals of Nickel become relatively much more stabilised than other ligand-based ones and they pass from the highest block into the high-medium ones ( $d_{xz}$ ,  $d_{xy}$ ,  $d_{z^2}$ ). On the other hand, the  $p_\pi$ -orbitals of nitrogens and oxygens are still among the highest occupied orbitals. Thus, it is clear that the once existing bonding/antibonding interaction between these orbitals and ligand orbitals no longer exist. The relative stabilization of that d-block orbitals of Nickel is another indication of the high-valent Ni(III) complex.

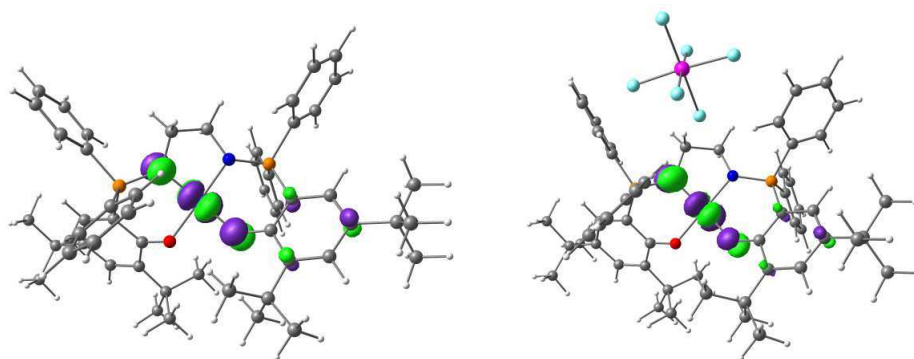


Figure 11. The “hole” in  $[37a]^+$  and  $[37a][SbF_6]$

The determination of the singly occupied orbital (SOMO) is difficult. In these big systems where energy levels of orbitals (alpha or beta) are very close to others, the SOMO seems to “blend” in combinations with other orbitals. Fortunately, the “hole” corresponding to the orbital from which the electron was removed has been determined (Figure 11). It consists of the  $d_{yz}$  of nickel in antibonding interactions with  $p_\pi$ -orbitals of N2 and O1. It is indeed the highest unoccupied molecular orbital (alpha and beta comprised) and is the one in which the electron would be added if the oxidized complex undergoes a reduction to give the neutral one.

The form of this orbital coincides perfectly with the spin density distribution in  $[37a]^+$  and  $[37a][SbF_6]$ . Furthermore, as this orbital consists of  $d_{yz}$  of nickel in antibonding interactions with  $p_\pi$ -orbitals of N2 and O1, removal of electron from it would shorten the bonds along the N2-Ni-O1 axis, a result which has been attested by X-ray diffraction and geometry optimization calculations.

In conclusion, from the DFT analysis, it could be seen that

- 1) the biggest spin density is on the Ni, with more than 60%;
- 2) the orbital from which the electron is removed is essentially  $d_{yz}$  of nickel in antibonding interactions with  $p_\pi$ -orbitals of N2 and O1, resulting in non-symmetrical shortening of bonds along one axis O1-M-N2;
- 3) in  $[37a]^+$  and  $[37a][SbF_6]$  d-block orbitals of Nickel become relatively much more stabilised than other ligand-based ones

All these three observations strongly indicate that the oxidized form of Nickel phosphasalen complex **37a** is a high-valent Ni(III) complex.

### III. Conclusion

The previous studies on nickel complex of the non-substituted phosphasalen ligand demonstrated the superior donating ability of this ligand compared to salen. This ability suggests that phosphasalens could be used for the obtainment of stabilised oxidised complexes. Taken into account the rarity of isolated Ni(III) complex with low-coordination number, as well as the study on oxidized metal-phenoxide complexes, we decided to study the oxidations of nickel phosphasalen complexes.

Two nickel complexes have been synthesised from modified phosphasalen ligands with *tert*-butyl substituents on the *o*- and *p*- positions of the phenoxide rings. They have been fully characterised and could be cleanly oxidised by one equivalent of silver salt in dichloromethane. X-ray structure was obtained one these two products (complex **[37a][SbF<sub>6</sub>]**). At the difference of all reported oxidised nickel-phenoxide complexes up to now, which have been shown to be Ni(II) complexes of phenoxyl radical, the oxidised species **[37a][SbF<sub>6</sub>]** is a Ni(III) complex. This has been shown by EPR spectroscopy and DFT calculations. This complex is the first example of four-coordinated high valent Ni(III) phenoxide species, and one of rare example of Ni(III) complexes with coordination number less than 5.

The easy formation and stability of these Ni(III) complexes would allow further studies of the reactivity of Ni(III) complexes and their roles in catalysis. Furthermore, these phosphasalen ligands, which could stabilise high valent Ni(III) state by their donating abilities, are expected to render possible the isolation of other high valent complexes, in particular the oxo complexes of Mn(III), the active intermediate supposed to be present in manganese-catalysed epoxidation of olefins, which has never been evidenced.

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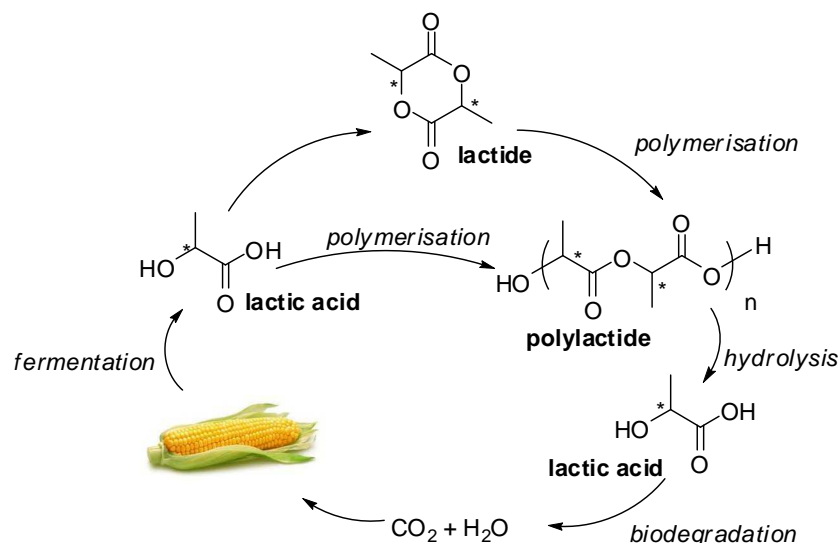
## **Chapter 5**

# **Phosphasalen Complexes in Ring-Opening Polymerisation of Lactide**

### **I. Introduction: PLA and ROP of Lactide**

#### **1. PLA: Utility and Synthesis**

Most of polymers for daily utility such as polypropylene, polystyrene, PVC, nylon, synthetic rubber, etc., are derived from petrochemical feedstock. The possible exhaustion of oil and gas feedstock in a near future, and the ecological problems linked to the disposal of those plastics have drawn towards the development of polymer from renewable sources and ideally, biodegradable. Poly(lactic acid) or polylactide (PLA) is a polymer derived from bioresources that fulfils both these criteria and thus its synthesis and development has been an active domain of research in industry and academics. It is up to date the most commercially viable biodegradable material. It is recently manufactured in large scale in US and in smaller scale in EU and Japon.<sup>1</sup> PLA has good mechanical and physical properties and its advantage is even enhanced by its biocompatibility and its ability to be adsorbed and degraded in vivo. PLA is an FDA approved substance for use in therapy.



*Scheme 1. Life-cycle of polylactide.*

PLA, like other polyester, could be produced by two main ways: condensation-polymerisation of lactic acid which bears both an acid and an alcohol function, or ring-opening polymerisation of lactide (Scheme 1). Lactic acid is obtained from fermentation of sugars, produced from high starch content plants. Direct condensation-polymerisation of lactic acid is often limited by the necessity of adding coupling agents and adjuvants in order to remove water to drive the equilibrium towards the formation of polyester. This method produces polylactide with poorly controlled chain length and often with low molar mass. Thus synthesis of polylactide is often directed to the second method which is ring-opening polymerisation of lactide. This product is formed by the thermal degradation of oligolactic acids, which in turn are produced by the condensation polymerisation of lactic acid.

Compared to condensation polymerisation, ring-opening polymerisation has a crucial advantage which is the possibility of having controlled polymerisation in terms of chain lengths/molar mass, and in terms of stereochemistry. Many researches have been actively carried out to attain polymerisation system which is both viable commercially and effective in producing PLA with special stereochemistry.

Before going any further, it is important to understand the meaning of control polymerisation and stereochemistry of such process. The next section is a brief introduction to all those notions, sometimes in direct relation with polylactide.

## 2. Controlled Polymerisation: Meaningful Indicators

### 2.1 PDI and Molar Mass Distribution

Polymer molecular weight is important because it greatly influences many physical properties of the polymer. These includes glass transition temperature (the temperature at which the

polymer changes from a hard and brittle state to a rubber-like one) or melt temperature (the temperature at which semi-crystallised domains of the polymer melt), viscoelasticity, strength, etc. The polymer molecular weight is thus reported for any polymerisation and its control is important.

Polymer masses are often given by physical methods, such as gel-exclusion chromatography, light-scattering, osmometry or viscosity measurements. Unlike small molecules, most synthetic polymers do not have unique molar mass but a range of masses of different polymer molecules. This weight distribution depends on the way the polymer is produced. Thus most physical methods deliver mass distributions. They are the molar mass  $M_i$  of a molecule of type  $i$ , the total mass  $m_i = n_i M_i$  of all molecules  $i$ , their mass fraction  $w_i = m_i / \sum_i m_i$ , or mass concentration  $c_i = m_i/V$ . Some physical methods deliver higher statistical weights. Common case is z-statistical weight  $z_i = m_i M_i = n_i M_i^2$ .

For practical purposes, the three most important molar masses are  $\bar{M}_n$  (the number average molecular weight),  $\bar{M}_w$  (the weight average molecular weight) and  $\bar{M}_z$  (the z-average molecular weight). Their definitions are described as follow:

$$\bar{M}_n = \sum_i x_i M_i = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

$$\bar{M}_w = \sum_i w_i M_i = \frac{\sum_i m_i M_i}{\sum_i m_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

$$\bar{M}_z = \sum_i Z_i M_i = \frac{\sum_i m_i M_i^2}{\sum_i m_i M_i} = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$$

Polymolecular index  $Q_{w,n} = \bar{M}_w/\bar{M}_n$ , or commonly called polydispersity index (PDI) is often used to determine the quality of control of the polymerisation. The broader the distribution of molar mass is, the higher PDI, thus the lower the degree of control of the polymerisation is.

## 2.2 Stereochemistry of Polymer and Tacticities

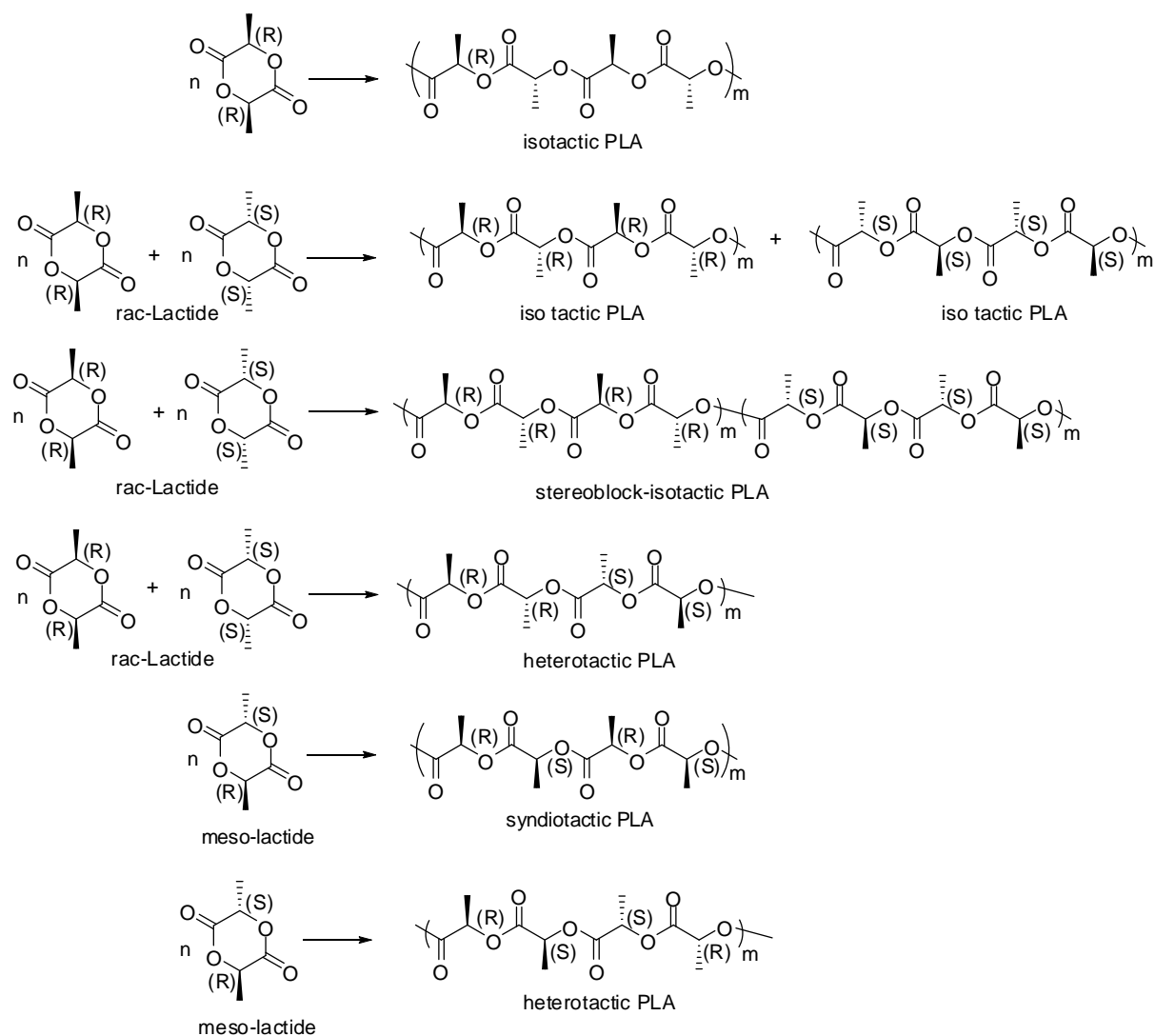
### 2.2.1 Introduction to Tacticity

Stereocontrol is an important issue in polymers containing asymmetric centres. Just like in simple small molecules where diastereoisomers do not have the same melting temperature or solubility, physical properties polymers depend on the enchainment those asymmetric centres. For example, isotactic PLA having only S-lactic acid monomer is crystalline thermoplastic with  $T_g \sim 60^\circ\text{C}$  and  $T_m \sim 170^\circ\text{C}$ , whereas atactic PLA having R-lactic acid monomers and S-lactic acid monomers in non-ordered enchainment is amorphous. The type of stereo-enchainment of monomers in the polymer molecule is called tacticity.

In general, the tacticity of polymer is determined by the probabilities of certain **stereo-sequences**, or stereorepeating units. A repeating unit or constitutional repeating unit is the



smallest constitutional unit whose repetition in a single sequential arrangement described a regular polymer molecule.<sup>2</sup> For PLA, the constitutional repeating unit is one half the lactide molecule, i.e.  $-\text{C}(=\text{O})-\text{CH}(\text{CH}_3)-\text{O}-$ . An **isotactic sequence** consists of a single constitutional repeating unit, in this case: a single enantiomer R or S. A **syndiotactic sequence** consists of two enantiomeric configurational repeating unit RS or SR. A **heterotactic repeating sequence** has four monomeric units RRSS or SSRR. The repetition of each of these stereosequences gives respectively **isotactic**, **syndiotactic** and **heterotactic** polymer. Different types of tacticity that could be derived from the polymerisation of lactides are shown in Scheme 2.

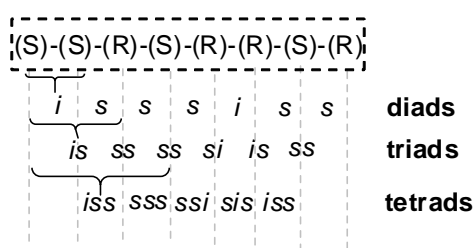


*Scheme 2. Tacticities of PLA*

Atactic polymer contains all types of configurational units (i.e R and S) with equal amounts in random distribution. Stereoblock polymers have different blocks, each of which contains the same type of stereosequences.

The tacticities of PLA depend on the lactide isomers and on the choice of the catalysts/initiator systems (Scheme 2). Polymerisation of R-LA or S-LA gives isotactic PLA. The one with *meso*-LA gives atactic, heterotactic or syndiotactic PLA. However, both *meso*-LA and enantiomerically pure lactide are expensive. The naturally lactide produced from fermentation is racemic lactide. It is thus much more interesting to have stereocontrolled polymerisation from *rac*-LA to obtain heterotactic polymer.

The smallest configurational units of a polymer with configurational tacticity are diads formed by two monomeric units. These diads are either isotactic (RR or SS, symbolized *i* or *m* in literature) or syndiotactic (RS, symbolized *s* or *r* in literature). Higher configurational units are triads, tetrads, pentads, etc. Scheme 3 shows the stereo-analysis on a sample polymer at the diad, triad, and tetrad levels.



Scheme 3. Diads, triads and tetrads in a configurational polymer.

The tacticity is often expressed in terms of  $P_i$  and  $P_s$  which is respectively the probability of isotactic or heterotactic enchainment. They are often measured by an analysis at the tetrad level of resonances observed in either homodecoupled  $^1\text{H}$  or  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra and by comparisons of the peak integrals with Bernoullian statistics.<sup>3</sup> The essential results could be found in many specialised books and have been described by Coudane and co-workers for lactide polymerisation.<sup>3a</sup> However, detailed reasoning was not provided. The following section resumes the determination of  $P_i$  and  $P_s$  and reasoning for those results.

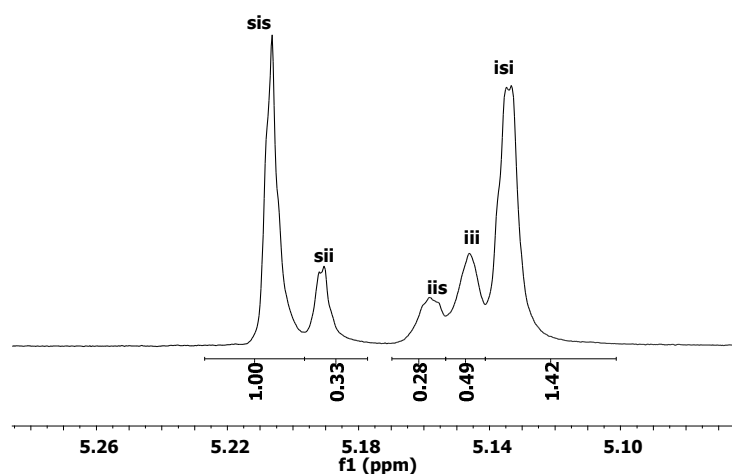


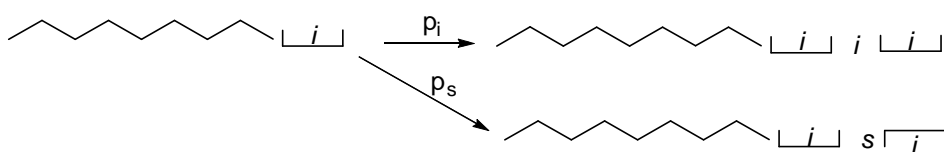
Figure 1. Example of tetrad level of resonances observed in homodecoupled  $^1\text{H}$  NMR spectrum.

### 2.2.2 Statistic of Polymerisation and Bernoulli Trials

In fact, in stereoselective polymerisation, there's always some influence of the present units which is expressed as a conditional probability of the connecting step, thus the statistics should follow a Markov trial. In Markov first order trials, only the last unit influences the addition of the new unit. For the polymerisation to yield PLA, four conditional probabilities must be considered, corresponding to the probability of adding R-LA or S-LA constitutional unit to a polymer with (r) or (s) propagating centre:  $p_{(r)/R}$ ,  $p_{(r)/S}$ ,  $p_{(s)/R}$ ,  $p_{(s)/S}$ . These probabilities obey this relation:

$$p_{(r)/R} + p_{(r)/S} = p_{(s)/R} + p_{(s)/S} = 1$$

As defined above,  $p_i$  and  $p_s$  is respectively the probability of isotactic or heterotactic enchainment, and in simplified cases, the probability of adding R-LA or S-LA constitutional unit to a polymer with (r) or (s) propagating centre only depends on the relative configuration between the arriving and the present units, we have thus  $p_{(r)/R} = p_{(s)/S} = p_i$  and  $p_{(r)/S} = p_{(s)/R} = p_s$ . As only two probabilities exist  $p_i + p_s = 1$ , the statistics is reduced to a zeroth-order Markovnikov chain or a Bernoulli statistics. That's why the polymerisation of lactide is said to follow Bernoulli statistics.

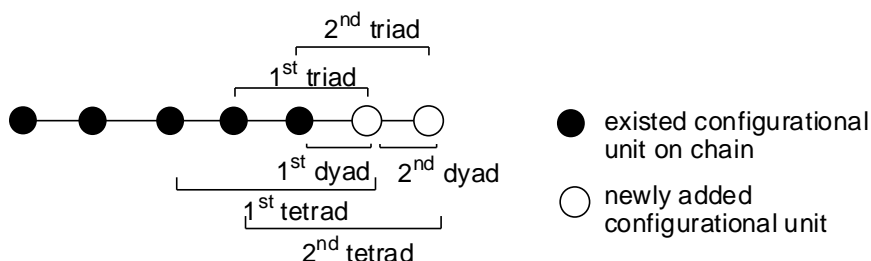


Scheme 4. Chain-growing polymerisation of dimers of lactide (after Coudane et al)<sup>3a</sup>

For the polymerization of lactide (which is in fact a dimer of constitutional unit), let  $x_a$  the proportion of sequences of type  $a$  in the polymer. For tetrads levels, we have:

$$x_{iii} + x_{iis} + x_{isi} + x_{iss} + x_{sss} + x_{sis} + x_{ssi} + x_{sii} = 1$$

For polymerisation from *rac*-LA,  $x_{sss} = x_{iss} = x_{ssi} = 0$  (because sequences with RSR or SRS are impossible to form), thus we have  $x_{iii} + x_{iis} + x_{isi} + x_{sis} + x_{sii} = 1$



Scheme 5. Diads, triads, tetrads formed from the addition of a dimer lactide.

When a new dimer lactide unit is added, two configurational unit are added to the polymer chain, thus two dyads, two triads, and two tetrads are formed (Scheme 5).

By applying some simple probability reasoning, one could find again the values for the probabilities of different dyads, triads, tetrads, pentads or hexads in function of  $p_i$  and  $p_s$ , as given by Coudane and coworkers<sup>3a</sup> (Table 1).

Table 1. Probability of  $n$ -ads ( $n=2-6$ ) in *rac*-lactide polymerisation with a Bernoullian statistics.

|         |                  |                |                  |                  |                |               |
|---------|------------------|----------------|------------------|------------------|----------------|---------------|
| Dyads   | $i$              | $s$            |                  |                  |                |               |
| Ratio   | $(1+p_i)/2$      | $(1-p_i)/2$    |                  |                  |                |               |
| Triads  | $ii$             | $is$           | $si$             |                  |                |               |
| Ratio   | $p_i$            | $(1-p_i)/2$    | $(1-p_i)/2$      |                  |                |               |
| Tetrads | $iii$            | $iis$          | $isi$            | $sii$            | $sis$          |               |
| Ratio   | $p_i(p_i+1)/2$   | $p_i(1-p_i)/2$ | $(1-p_i)/2$      | $p_i(1-p_i)/2$   | $(1-p_i)^2/2$  |               |
| Pentads | $iiii$           | $iisi$         | $iiis$           | $siii$           | $isii$         | $isis$        |
|         |                  |                |                  |                  |                | $sisi$        |
| Ratio   | $p_i^2$          | $p_i(1-p_i)/2$ | $p_i(1-p_i)/2$   | $p_i(1-p_i)/2$   | $p_i(1-p_i)/2$ | $(1-p_i)^2/2$ |
| Hexads  | $iiii$           | $isiii$        | $iiis$           | $iisis$          | $isii$         | $sisis$       |
|         |                  | $iiisi$        | $iisii$          | $siiis$          |                |               |
|         |                  |                | $siiii$          | $sisii$          |                |               |
| Ratio   | $p_i^2(p_i+1)/2$ | $p_i(1-p_i)/2$ | $p_i^2(1-p_i)/2$ | $p_i(1-p_i)^2/2$ | $(1-p_i)^2/2$  | $(1-p_i)^3/2$ |

Using these formulas, the heteroselectivity  $p_s$  for a polymer derived from *rac*-lactide could be calculated from the peak integrals in the homodecoupled  $^1\text{H}$  or  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra.

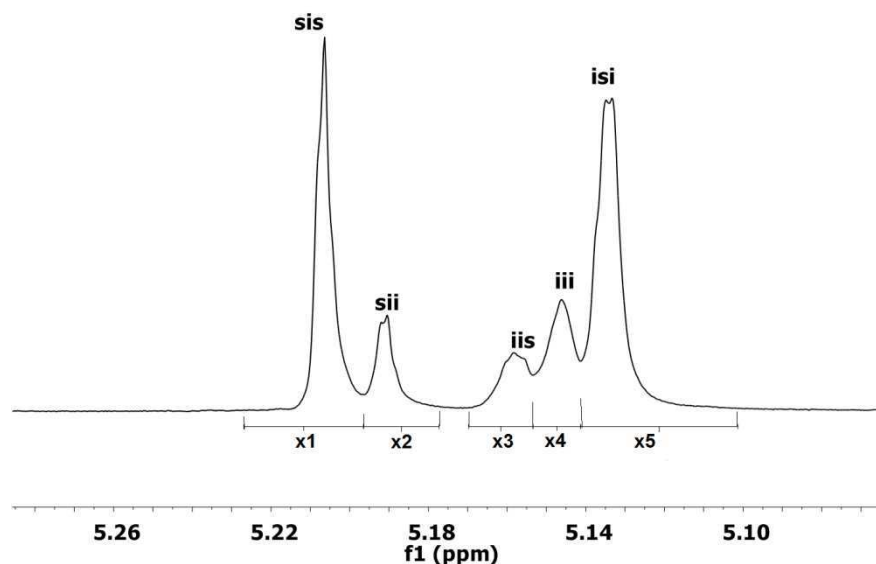


Figure 2. Example of tetrad level of resonances observed in homodecoupled  $^1\text{H}$  NMR spectrum.

The integrals of *sis*, *sii*, *iis*, *iii*, *isi* signals being  $x_1$ ,  $x_2$ ,  $x_3$ ,  $x_4$ ,  $x_5$ , respectively

From the *sis* signal:  $x_{sis} = x_1 / \sum_{i=1}^5 x_i$  and  $p_{i1} = 1 - \sqrt{2x_{sis}}$ ,  $p_{s1} = \sqrt{2x_{sis}}$

From the *sii* signal:  $x_{sii} = x_2 / \sum_{i=1}^5 x_i$  and

$$p_{i2} = (1 \pm \sqrt{1 - 8x_{sii}}) / 2, \quad p_{s2} = (1 \mp \sqrt{1 - 8x_{sii}}) / 2$$

(the value of  $p_{s2}$  is the one that is closer to  $p_{s1}$ )

From the *iss* signal:  $x_{iss} = x_3 / \sum_{i=1}^5 x_i$  and

$$p_{i3} = (1 \pm \sqrt{1 - 8x_{iss}}) / 2, \quad p_{s3} = (1 \mp \sqrt{1 - 8x_{iss}}) / 2$$

(the value of  $p_{s3}$  is the one that is closer to  $p_{s2}$ )

From the *iii* signal:  $x_{iss} = x_4 / \sum_{i=1}^5 x_i$  and

$$p_{i4} = (-1 + \sqrt{1 + 8x_{iii}}) / 2, \quad p_{s4} = (3 - \sqrt{1 + 8x_{iii}}) / 2$$

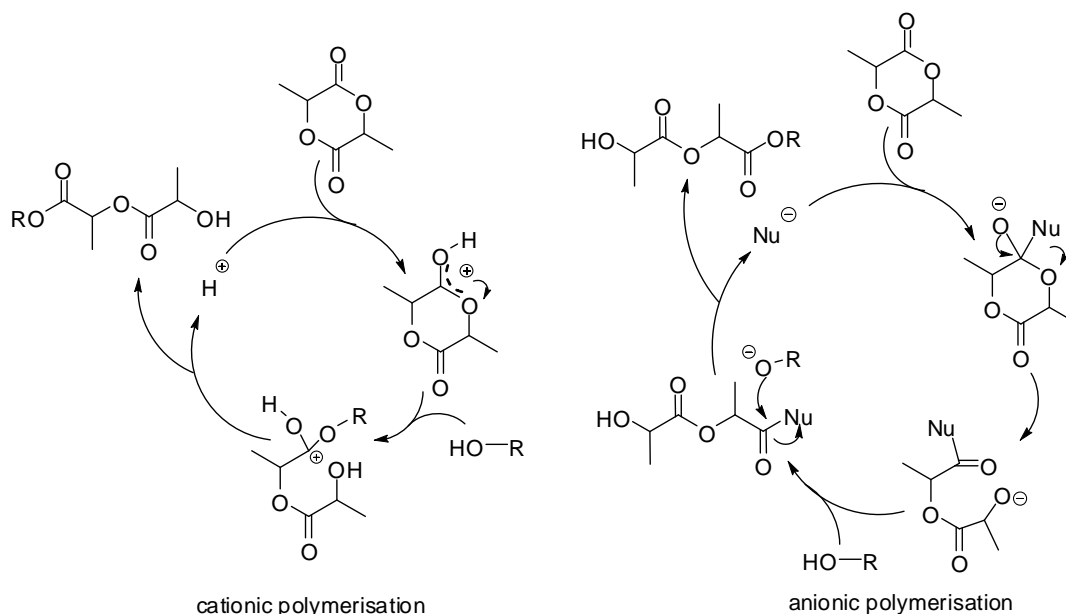
From the *isi* signal:  $x_{isi} = x_5 / \sum_{i=1}^5 x_i$  and  $p_{i5} = 1 - 2x_5$ ,  $p_{s5} = 2x_5$

The tacticity of the polymer  $p_i = \frac{1}{5} \sum_{j=1}^5 p_{ij}$  and  $p_s = \frac{1}{5} \sum_{j=1}^5 p_{sj}$

### 3. Mechanism of Ring-Opening Polymerisation of Lactide

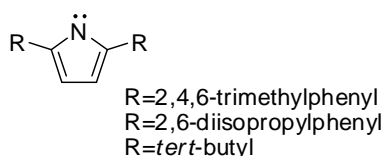
Depending on initiators, ring-opening polymerisation (ROP) of lactide could have different mechanisms. The three most often considered ones are coordination-insertion,<sup>4</sup> anionic,<sup>4,5</sup> and cationic<sup>4,6</sup> polymerisation (Scheme 6, Scheme 8).

The last two mechanisms are often proposed for the organo/cationic initiator and are called monomer-activated mechanism, because the monomer must be activated first by a nucleophile such as a carbene, or an electrophile (very often acid Bronsted) in order for the polymerisation to occur (Scheme 6).



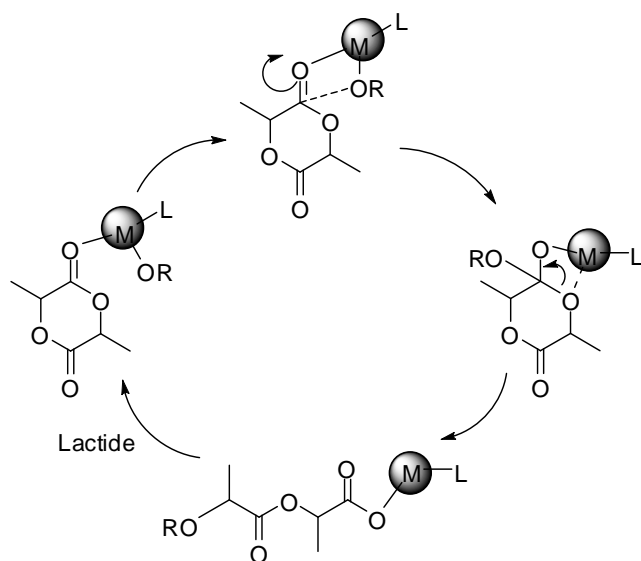
Scheme 6. Cationic and anionic lactide ring-opening polymerization.

In theory, by selecting the cation/nucleophile with appropriate steric properties, stereo-selective ROP can take place. However, to our knowledge, no such selectivity has been reported for ROP systems supposedly following cationic mechanisms. Examples of stereoselective ROP with anionic mechanism are rare. In 2004, Tolman and co-workers reported that ROP using free N-heterocyclic carbene and analogs give isotactic enriched PLA ( $P_s=0.75$ ) (Scheme 7).<sup>7</sup>



Scheme 7. Tolman's N-heterocyclic carbenes for ROP of lactide

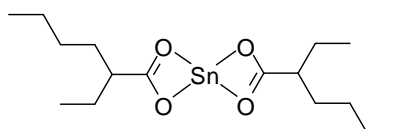
The coordination-insertion mechanism, represented in Scheme 8, involves the catalytic action of metal center and is supposed to be the most common mechanism in ROP of lactide involving organometallic compounds, a result supported by many experimental and theoretical studies. The great advantage of such polymerisation is the possible fine tuning of the steric and electronic properties of the metal centre which in turn would influence the control of the polymerisation process. Indeed, living polymerisation with very good control of  $M_n$  and excellent stereoselectivity (for example, heteroselectivity  $p_r$  up to 0.98) has been reported using various organometallic complexes. The next section gives more details about the performance of such systems.



Scheme 8. Coordination-insertion ROP of lactide.

#### 4. Initiators for ROP of Lactide

The most widely used complex for industrial preparation of PLA is tin (II) bis(2-ethylhexanoate), commonly referred as tin(II) octanoate  $\text{Sn}(\text{Oct})_2$ , whose structure is given in Scheme 9.<sup>8</sup> It is commercially available, easy to handle, and highly active, giving high activity in melt conditions and allows the preparation of PLA with very high molecular weight (up to  $10^5$ - $10^6$  Da). However, the polymers obtained show no stereoselectivity.



Scheme 9. tin(II) octanoate  $\text{Sn}(\text{Oct})_2$

Significantly efforts have been placed to the design and synthesis of efficient catalysts for the preparation of polylactide. And despite the existence of some functional catalytic systems, fundamental understanding about the process is still lacking. Thus research has often been draw towards well characterised, discrete systems as these would facilitate the understanding of the factors influencing the efficiency of the catalyst/initiators.

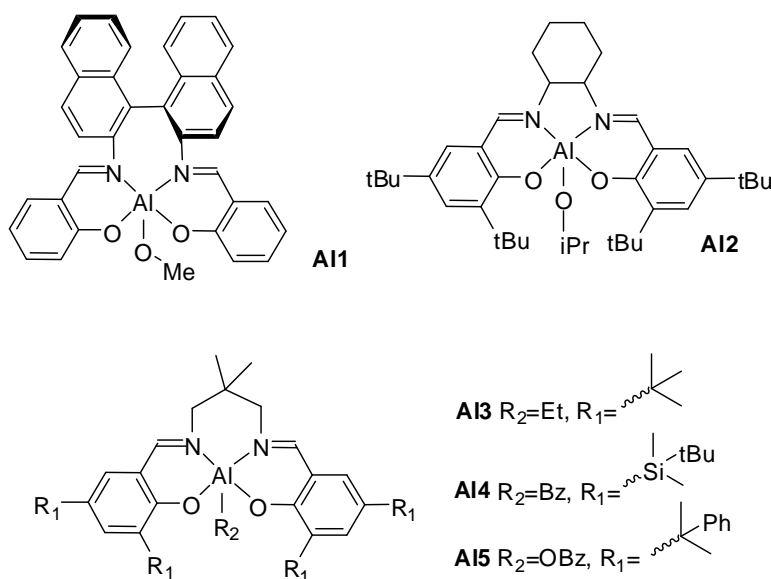
By far the most common organometallic initiators for ROP of LA are amide or alkoxide metal complexes. Almost all earth-alkaline metals, transition metals and rare-earth metals complexes have been tested. The scope of which has been the subjects of several reviews, like the one of Tolman group<sup>9</sup> in 2001, of Bourissou group<sup>10</sup> in 2004, of Williams group<sup>1b, 1d</sup> in 2008, or of Feijen group<sup>11</sup> in 2011. Of particular interest are metals of group 2 (Ca, Mg) and 12 (Zn) (oxidation state +2), 13 (Al, In) and rare-earth metals (Sc, Y, Nd, etc) (oxidation state +3), or

group 4 (Ti) (oxidation state +4), which are not only commercially viable and non-toxic, but also offer rather high activity and sometimes selectivity.

As salen ligands and derivatives were used in combination with different metals for the ROP of lactide, we were curious to evaluate the performance of phosphasalen complexes in this process. Given the dianionic properties of phosphasalen ligands and common requirement of having an alkoxide/amide group on the complex, we decided to investigate the activities of phosphasalen complexes of yttrium and aluminium. Both these metals are cheap, having non-reported toxicities and their complexes generally offer the best rates or control of polymerations.

#### 4.1. Aluminium Complexes

Although the rate for ROP of aluminium complexes are often lower than other metals, they have been extensively studied as they generally offer very good polymerisation control due to the lack of side reactions (e.g transesterification). More importantly, easily synthesised salen complexes of aluminium are among the most stereoselective initiators for ROP of lactide. In fact, the most important breakthrough in stereoselective polymerisation process was made by Spassky and co-workers. They found that aluminium complex of salen ligand derived from R-(+)-1,1'-binaphthyl-2,2'-diamine (Scheme 10, **Al1**) initiated the ROP of rac-lactide to predominantly isotactic PLA in reasonable time, the polymerisation rate of (R,R)-LA being 19 times higher than the one of (S,S)-LA.<sup>12</sup>



Scheme 10. Aluminium complexes for stereoselective ROP of lactide

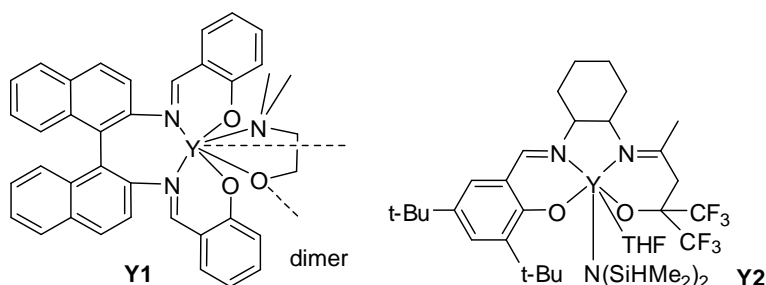
This finding started a rapid development in the studies of aluminium complexes of Salen and derivatives, and much has been obtained in terms of stereoselectivity. In a result reported by Feijen and co-workers in 2002, aluminium complex of *rac*-Jacobsen ligand (**Al2**, Scheme 10) could initiate and catalyse the formation of stereoblock PLA  $p_i$  with  $\alpha=0.93$  at 83% conversion of *rac*-lactide.<sup>13</sup> More interestingly, this excellent stereocontrol is maintained even in bulk



conditions. In 2003, Chen and co-workers reported on the complex **A13**/benzylalcohol (Scheme 10, **A13**) as the catalyst/initiator systems for ROP of rac-lactide which offers a high isoselectivity ( $p_i = 0.90$ ).<sup>14</sup> In 2007, Nomura and co-workers used the aluminium complex of a similar ligand with more bulky substituent  $t\text{BuMe}_2\text{Si}$  at the *o*- and *p*- positions of the phenoxide rings (Scheme 10, **A14**), and obtained an excellent isoselectivity of  $p_i = 0.98$  with rac-lactide.<sup>15</sup> The complex with Salen ligands featuring bulky cumyl groups (Scheme 10, **A15**) reported by Chen and co-workers in 2012 could initiate the ROP of rac-lactide to give highly isotactic PLA ( $p_i = 0.97$ ) in high conversion (94%) with very narrow PDI (1.07).<sup>16</sup>

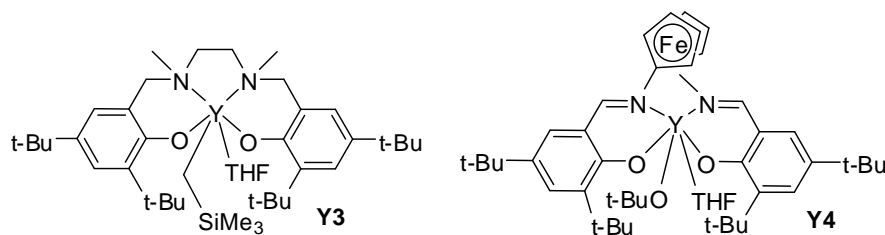
## 4.2. Yttrium Complexes

Yttrium complexes are particularly promising as they offer very fast rates for ROP of lactide and, through careful selection of the ancillary ligand, can enable stereocontrol. Most of the successful systems employ tetradentate ligands which ensure the stability and prevent redistribution reactions often seen for rare-earth complexes. From this point of view, the use of salen ligands are interesting. Yttrium salen complexes were first investigated nearly a decade ago by Ovitt and Coates, together with the aluminium complex of the same ligand (Scheme 12), for the ROP of meso-lactide. It showed moderate rates but lack polymerization or tacticity control ( $\text{LA/I} = 100/1$ , 14h, 97%).<sup>17</sup> Carpentier and colleagues have also studied alkoxide/phenolate ligands, related to salens, which were slow initiators and produced atactic PLA ( $\text{LA/I/iPA} = 100/1/1$ , 1d, 91%).<sup>18</sup>

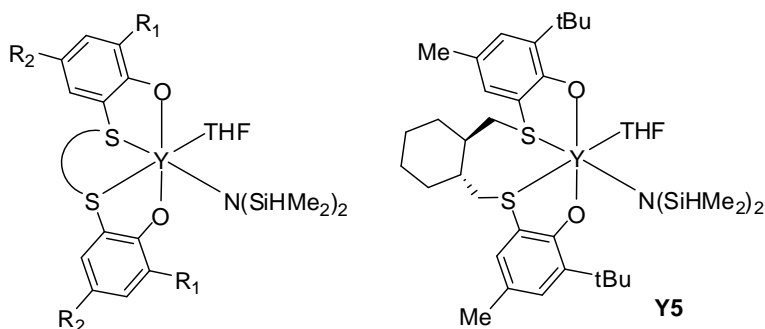


Scheme 11. Yttrium complexes of Salen ligands and derivatives

The activities of yttrium complexes with derivatives of salen ligands have been reported (Scheme 12). The salan complex featured in a report by Cui and co-workers in 2007 afforded PLA with moderate heterotacticity in much higher rate compared to the salen analogues ( $\text{LA/I} = 300/1$ , 1h, 100%,  $p_s = 0.65$ ).<sup>19</sup> Recently, Diaconescu and co-workers have reported a salen derivative with a ferrocenediyl unit in the imine backbone which showed even faster rates, but lacks stereocontrol ( $\text{LA/I} = 500/1$ , 40min, 92%, atactic).<sup>20</sup>



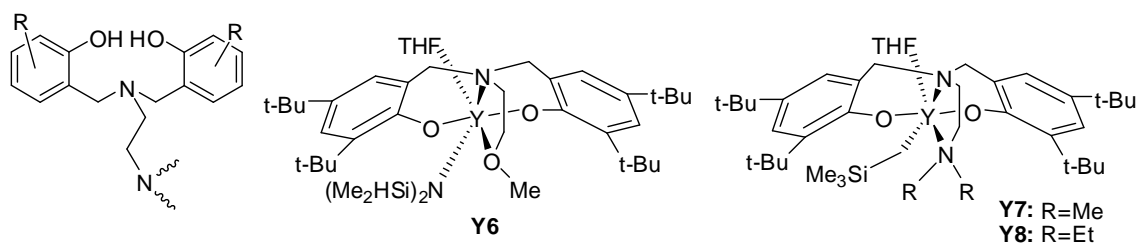
Scheme 12. Yttrium complexes of Salen ligands and derivatives



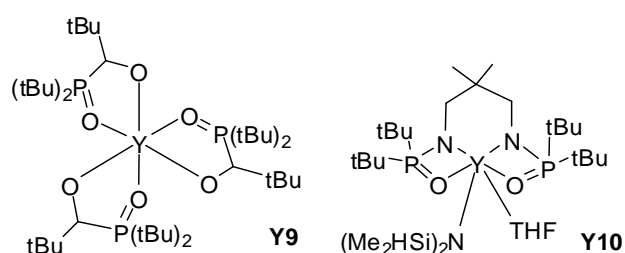
Scheme 13. Yttrium complexes of dithia-alkanediyl bridged diphenolate ligands

Okuda has pioneered the use of dithia-alkanediyl bridged diphenolate ligands with group 3 metals for the ROP of lactide (Scheme 13). Yttrium complexes of such ligands showed very fast rates and can be used at low initiator concentration (complex **Y5**: LA/I=300/1, 0.75h, 89%, or LA/I=3000/1, 6h, 92%). Some of them showed excellent heteroselectivity via a dynamic monomer recognition process controlled by the inter-conversion of initiator enantiomers ( $p_s=0.88$  for the same complex **Y5**).<sup>21</sup> The complexes also yield highly syndiotactic PLA from *meso*-LA.<sup>22</sup>

The most successful ligand systems up to date for the design of catalyst/initiator of the ROP of lactide up to date is tetradentate phenolate-amine ligands (Scheme 14). These compounds were synthesised in single-step Mannich condensation of primary amine, formaldehyde and substituted phenol. Their zirconium/hafnium complexes had given excellent results for olefin polymerisation,<sup>23</sup> as reported by Goldschmidt and coworkers, before Carpentier and co-workers realised the potential of such ligands in ROP of lactide. They reported rare-earth metal complexes of the modified ligands in 2003.<sup>24</sup> The yttrium complex (**Y6**, Scheme 14) appeared to be very active in ROP of lactide (LA/I=500/1, 1h, 100%) and afford PLA with high degree of heterotacticity ( $p_s=0.80$ ).<sup>25</sup> Eversince, this type of ligands have been studied intensively by the groups of Carpentier, Mountford, and others.<sup>26</sup> The complexes studied generally give highly stereocontrolled ROP and offer high rates all in the same time. For yttrium complexes, highly efficient systems with heterotacticity up to 0.99 and high rates have been achieved, for example in the systems reported by Cui and co-workers (LA/I=700/1, 3h, 86%,  $p_s=0.99$ ) (**Y7-8**, Scheme 14).<sup>19</sup>



Scheme 14. Tetradentate bis(phenoxy) amine ligands and some notable yttrium complexes.



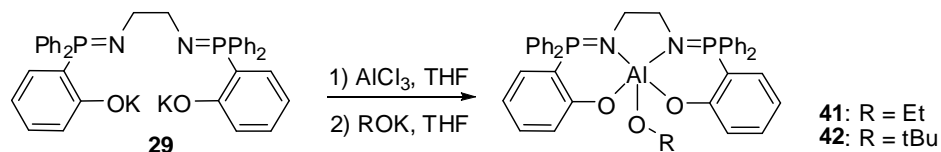
Scheme 15. Notable systems with ligands incorporating phosphinic functions.

Ligands incorporating phosphorus-containing function, such as phosphinic, thiophosphinic has given good results in ROP of lactide. Arnold and co-workers have recently reported an interesting initiating system comprising a racemic mixture of alkoxide-phosphine oxide yttrium complexes, which, in stark contrast of other yttrium systems which give heterotactic PLA, yielded isotactic PLA from *rac*-LA (LA/I=200/1, 10min, 98%,  $P_i=0.81$ ).<sup>27</sup> (**Y9**, Scheme 15). The Williams group prepared yttrium complexes of bis(phosphinic/thiophosphinic)diamido ligands which show very high rates of polymerization and, in some cases, good heteroselectivity ( $P_s = 0.85$ ) (**Y10**, Scheme 15).<sup>28</sup>

## II. Aluminium-Phosphasalen Complexes.

### 1. Synthesis

The aluminium phosphasalen complexes were synthesized easily by reaction of the anionic ligand **29** with  $\text{AlCl}_3$  in THF, followed by nucleophilic substitution with KOR ( $R=\text{Et}$ ,  $t\text{Bu}$ ) (Scheme 16).



Scheme 16. Synthesis of aluminium phosphasalen complexes

The addition of  $\text{AlCl}_3$  into a solution of the phosphasalen ligand in THF at room temperature quickly gives a white suspension after 10 minutes of stirring at room temperature. In  $^{31}\text{P}\{^1\text{H}\}\text{R}$  spectrum, the signal of free ligand at +18.6 ppm has disappeared. Although the precipitation of the product prevents its characterization, the total disappearance of the ligand suggested that the product is the phosphasalen aluminum chloride complex **40**.

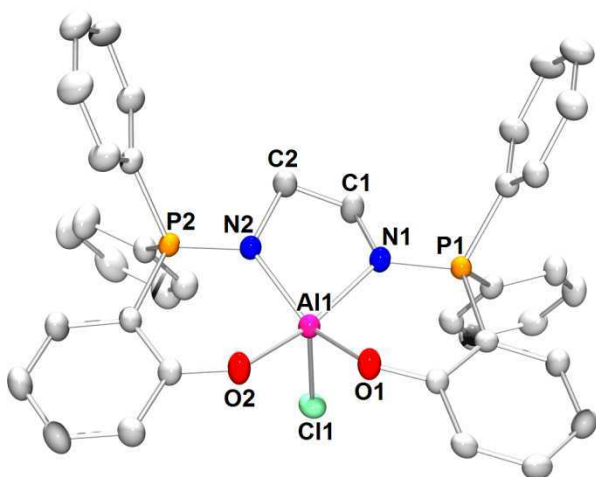


Figure 3. ORTEP view of complex **40**. Solvent molecules and hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Al1-Cl1 2.228(1), Al1-O1 1.804(2), Al1-O2 1.817(2), Al1-N1 1.982(2), Al1-N2 1.940(2), N1-P1 1.600(2), N2-P2 1.609(2), O1-Al1-O2 85.86(8), O1-Al1-N1 91.1(1), O2-Al1-N2 91.94(8), N1-Al1-N2 81.64(8), Cl1-Al1-O1 104.02(6), Cl1-Cl1-N2 107.70(7), Cl1-Al1-O2 98.80(7), Cl1-Al1-N1 98.60(7), O1-Cl1-N2-Al1 -1.68, O2-Cl1-N1-Al1 0.72.

Indeed, if stirring was turned off after 2 minutes, crystals of the product was obtained from the solution. X-ray diffraction experiment carried out on these crystals showed clearly the structure of phosphasalen aluminum chloride complex (Figure 3).

The complex crystallized with one molecule of THF, which lies far from the aluminum center and thus no THF coordination was observed. The metal center adopted a distorted square-based pyramidal geometry with the phosphasalen ligand being in *trans*-configuration.

Addition of one equiv. of ROK (R=Et or tBu) into the in situ generated suspension of complex **40** in THF induced slowly the dissolution of the precipitate and yielded a cloudy solution after overnight stirring.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the solution showed a unique singlet at +35.2 ppm for R=Et, or at +34.8 for R=tBu, indicating the clean formation of a phosphasalen complex. After removal of insoluble potassium salt, aluminum phosphasalen alkoxide complexes **41** and **42** were obtained as ivory solid. Crystals suitable for X-ray diffraction of these compounds were obtained from a saturated solution of **41** (or **42**) in toluene at -40°C.

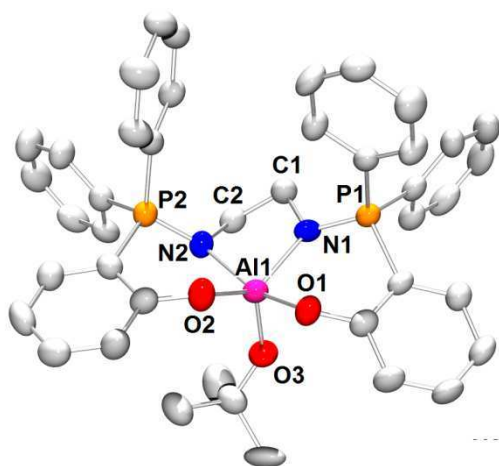


Figure 4. ORTEP view of complex **41**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Al1-O3 1.733(4), Al1-O1 1.861(4), Al1-O2 1.827(4), Al1-N1 1.973(4), Al1-N2 2.019(4), N1-P1 1.602(4), N2-P2 1.591(4), O1-Al1-O2 83.9(2), O1-Al1-N1 90.3(2), O2-Al1-N2 89.7(2), N1-Al1-N2 81.3(2), O3-Al1-O1 99.5(2), O3-Al1-O2 117.6(2), O3-Al1-N1 106.4(2), O1-O3-N2-Al1 -2.01, O2-O3-N1-Al1 0.67.

Both complexes adopted distorted square-based pyramidal geometry, with the metal center placed slightly out of the medial plane formed by O2N2 atoms of the phosphasalen ligand. The Al-O<sub>alkoxide</sub> bonds are slightly shorter than Al-O<sub>phenoxide</sub> bonds (1.733(4) vs. 1.861(4) and 1.827(4) in **41**, and 1.756(4) vs. 1.853(3) and 1.792(4) in **42**), which results from the better electron donating ability of alkoxides.

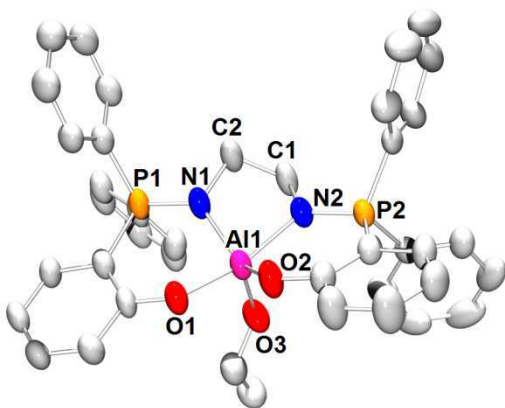


Figure 5. ORTEP view of complex **42**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Al1-O3 1.756(4), Al1-O1 1.853(3), Al1-O2 1.792(4), Al1-N1 1.948(4), Al1-N2 1.991(4), N1-P1 1.597(4), N2-P2 1.586(4), O1-Al1-O2 85.7(2), O1-Al1-N1 90.8(2), O2-Al1-N2 91.3(2), N1-Al1-N2 81.1(2), O3-Al1-O1 99.7(2), O3-Al1-N2 94.9(2), O3-Al1-O2 115.2(2), O3-Al1-N1 108.8(2), O1-O3-N2-Al1 2.33, O2-O3-N1-Al1 -2.30.

## 2. Catalytic Activities in ROP of Lactide

Both complexes **41** and **42** have been tested as initiators for the ROP of lactide. The choice of solvent is important, as both complexes decompose in dichloromethane and polymerization in THF were extremely slow. The best results have been obtained in toluene at high temperature.

Table 2. Activities of aluminum complexes

| Initiator (I)                   | [LA] <sub>0</sub> : [I] | T (°C) | Time / d | Conversion/% | P <sub>i</sub> |
|---------------------------------|-------------------------|--------|----------|--------------|----------------|
| <b>41</b>                       | 100:1                   | 80     | 1        | 73           | atactic        |
| <b>42</b>                       | 100:1                   | 80     | 1        | 70           | atactic        |
| <b>rac-Al2</b> <sup>13a</sup>   | 62:1                    | 70     | 12       | 85           | 0.93           |
| <b>(R,R)-Al2</b> <sup>13a</sup> | 62:1                    | 70     | 24       | 87.8         | -              |
| <b>Al3</b> <sup>14</sup>        | 122:1:1 <sup>a)</sup>   | 70     | 0.42     | 83.6         | 0.89           |
| <b>Al4</b> <sup>15</sup>        | 100/1/1 <sup>b)</sup>   | 70     | 0.79     | 62           | 0.97           |
| <b>Al5</b> <sup>16</sup>        | 100/1                   | 70     | 0.5      | 94           | 0.97           |

<sup>a</sup> presence of isopropanol LA/I/iPA=122/1/1, <sup>b</sup> presence of BzOH LA/I/BzOH=100/1/1,

Both complexes **41** and **42** are active in ROP of lactide. With the loading LA/I=100/1, in toluene at 80°C, initiator **41** gave 73% of conversion after 24h, and initiator **42** gave 70% of conversion after the same duration. These results are comparable with other aluminum initiators. Table 2 presents the performance of **41**, **42** and different initiators in the literature.

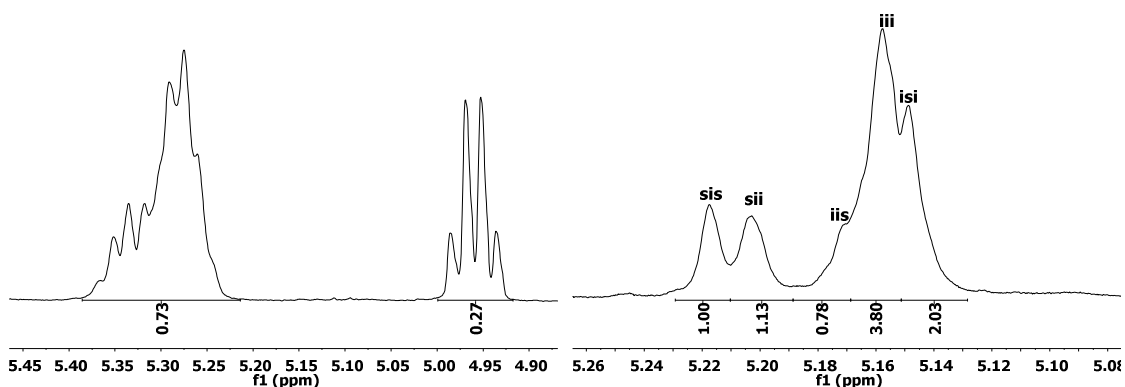
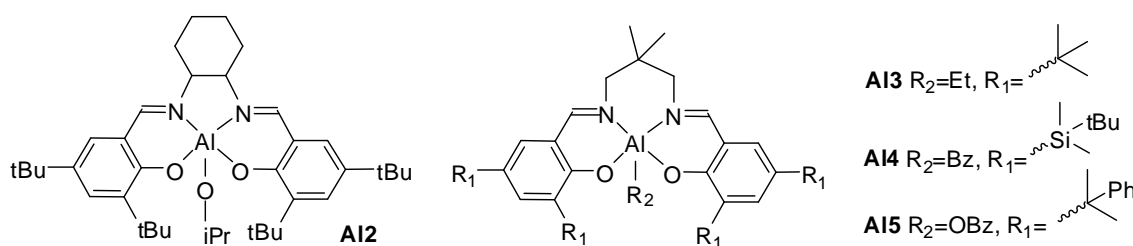


Figure 6.  $\{^1\text{H}\}$  and  $^1\text{H}\{^1\text{H}\}$  NMR spectrum of PLA in  $\text{CDCl}_3$ .  $[\text{LA}]_0 = 1\text{M}$ ,  $[\text{41}] = 0.01\text{M}$ , toluene, 80 °C, 73 % conversion of *rac*-LA, atactic

The polymers obtained from **41** and **42** are predominantly atactic, regardless of the conversion. For an example, the methine regions in  $\{^1\text{H}\}$  and  $^1\text{H}\{^1\text{H}\}$  NMR spectrum of PLA obtained from polymerization with **41** were presented in Figure 6. The poor control in stereochemistry might

probably due to a larger and more flexible phosphasalen ligand, which leaves an important space around the metal center and thus limits the stereocontrol by chain-end configuration.

As the performance in terms of catalytic activity of aluminum complexes are far behind the yttrium phosphasalen complexes (details of which would be presented in the next section), most of the work was focused in the study of yttrium complexes. Though these preliminary tests for ROP of lactide with aluminum complexes do not give good results in terms of stereoselectivity, further modifications brought to the phosphasalen ligands could improve the stereocontrol of ROP of lactide with these initiators. For example, all the examples of aluminum complexes presenting high stereoselectivity are based on very bulky systems (**A2-5**, Scheme 17), which reduce the space around the metal centre and improve the stereocontrol, and thus future work on aluminum phosphasalen complexes for ROP of lactide could be directed in this direction.



Scheme 17. Highly stereoselective aluminum complexes

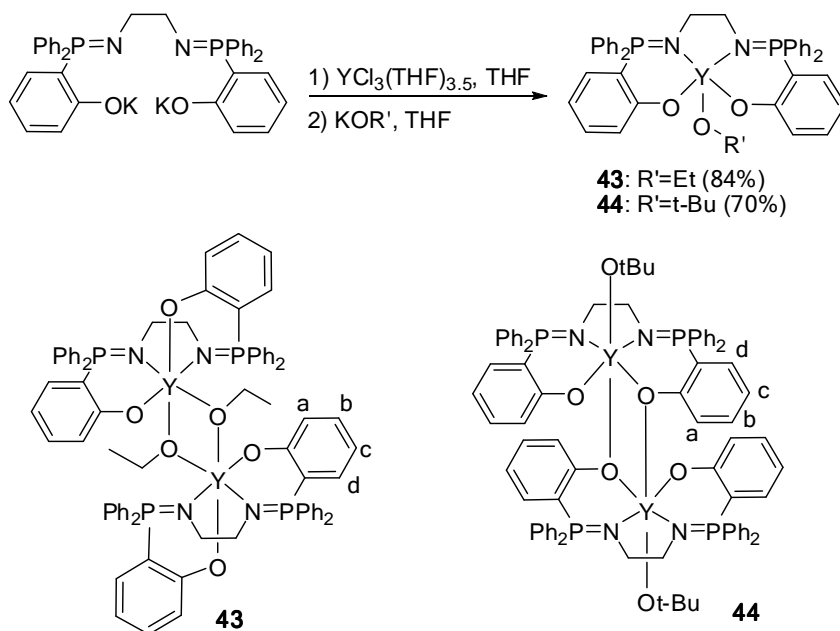
### III. Yttrium Phosphasalen Complexes: First Study

#### 1. Synthesis

The synthesis of the anionic phosphasalen ligand **29** has already been reported in chapter 3. Reaction of ligand **29** with  $[YCl_3(THF)_{3.5}]$  in tetrahydrofuran resulted in the immediate precipitation of a white product. The  $^{31}P\{^1H\}$ NMR spectrum showed the complete consumption of ligand, as evidenced by the disappearance of the signal at 18.6 ppm. The total insolubility of the product prevented any further analysis; the product is believed to be a cluster/polymer of the ligand-yttrium-chloride. A similar effect has been observed by Diaconescu and co-workers using related yttrium chloride Schiff base complexes.<sup>29, 20</sup> Furthermore, the apparition of an insoluble phosphasalen chloride complex has already happened in the case of aluminum, as has been shown in the previous section.

Despite the insolubility of the product, the addition of an equivalent of potassium *tert*-butoxide/ethoxide into the reaction mixture induced a slow dissolution. The  $^{31}P\{^1H\}$ NMR spectrum of the solution presented a single signal, at significantly lower field compared to the dianionic ligand, indicating the coordination of the phosphasalen ligand to the yttrium center. After removal of the potassium salt, the ethoxide and *tert*-butoxide phosphasalen-yttrium

complexes (complexes **43** and **44**, respectively) were isolated as white solids, which were characterized by multinuclear NMR spectroscopy, elemental analyses and using single crystal X-ray diffraction experiments.



Scheme 18. Synthesis of yttrium complexes with unsubstituted phosphasalen ligand.

Both complexes **43** and **44** adopt a dimeric structure in the solid state, with the yttrium centers exhibiting a distorted octahedral geometry formed by the tetradentate phosphasalen ligand, the alkoxide group and a phenoxide/alkoxide bridge. Both dimers are symmetric: there is no difference between the two yttrium centers in either complex, thus all the selected bond lengths and angles are represented for only one yttrium center.

In complex **43**, the ethoxide groups bridge between the two metal centers, forming a  $[Y_2O_2]$  four membered ring. The phosphasalen ligand is in *cis*- $\beta$  configuration: one phenoxide (O2) and one bridging ethoxide group (O3#2) occupy the axial positions. The yttrium center and the other four coordinated atoms (O1, N1, N2, O3) are almost in the same plan (dihedral angle (O1, N1, N2, O3)=1.52(22) Å, (Y, N1, O1, O3) =0.11(25)) Å. The yttrium- phenoxide (Y-O2) bond in axial position is slightly longer than the one in the equatorial position (Y-O1) (2.213(3) Å vs 2.182(3) Å), whereas the Y- ethoxide (Y-O3#2) bond in the axial position is slightly shorter than the one in the equatorial position (Y-O3) (2.243(3) Å vs 2.273(3) Å). The two yttrium-alkoxide bonds are all longer than the yttrium-phenoxide bonds (2.243(3) Å and 2.273(3) Å vs 2.182(3) Å and 2.213(3) Å), probably because they are in bridging positions.

There is almost no difference concerning the bond lengths of Y-N1 and Y-N2, or N1-P1 and N2-P2, respectively, but the distance Y-P1 is significantly longer than Y-P2 (3.561(1) Å vs 3.414(1) Å), and the Y-N1-P1 angle is larger than Y-N2-P2 (123.81(17) vs 114.05(17)). These differences clearly shows that the two phosphorus atoms are in slightly different environments,



which is also in accordance with the fact that they are linked to two phenoxide groups in different environment (axial or equatorial positions).

As a consequent,  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the complex **43** in THF, recorded in a Av500, exhibits two signals very close to each other, of equal intensity. These two signals were not separated and merged into a broad signal in an NMR-spectrum recorded by an Av300 instrument.

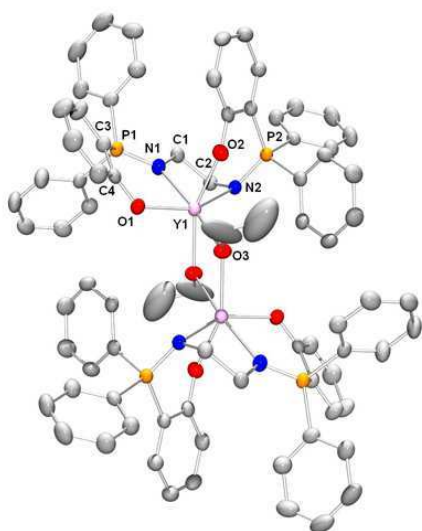


Figure 7. ORTEP view of complex **43** with thermal ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-Y1#2 = 3.6492(7), Y1-O1 2.182(3), Y1-O2 2.213(3), Y1-O3 2.273(3), Y1-O3#2 2.243(3), Y1-N1 2.415(3), Y1-N2 2.438(3), P1-N1 1.598(3), P2-N2 1.595(3), O1-Y1-N1 78.8(1), O2-Y1-N1 90.5(1), N1-Y1-N2 70.4(1), N2-Y1-O2 81.4(1), O1-Y1-O2 97.1(1), O2-Y1-O3 90.6(1), O2-Y1-O3#2 156.1(1), N1-Y1-N2-O2 86.40(11), O1-Y1-N2-N1 4.05(25).

Complex **44** is also a dimer in the solid state, however, changing the alkoxide co-ligand from ethoxide to *tert*-butoxide changes the structure of the complex (Figure 8). The two yttrium centers remain in distorted octahedral geometries, but the *tert*-butoxide ligands now occupy the axial positions, presumably due to steric hindrance preventing them adopting bridging coordination modes. The complex adopts a *trans*-coordination geometry with a single  $\mu$ -phenoxide coordination mode, per ligand. The Y-N and P-N bond lengths are comparable with those in complex **43**, but the Y-O( $\mu$ -phenoxide) bond is longer (2.338(2) Å vs 2.203(3) Å in **43**) and the Y-O(alkoxide) bond is significantly shorter (2.079(3) Å vs 2.243(3) Å in **43**).

Although the two phenoxide oxygen atoms adopt different coordination modes, the two phosphorus atoms are in almost identical environments, as shown by close similarity in the P-Y distances (3.490(1) Å vs 3.507(1) Å) and the P-N-Y bond angles (121.55(18)° vs 122.48(18)°). Indeed, in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of complex **44**, in THF, only a single doublet is observed, due to the coupling with the yttrium center. The value of the coupling constant ( $^2J_{\text{YP}}$  =

3.4 Hz) is comparable with other reported values for  $^2J_{\text{YP}}$  in similar complexes.<sup>28a-c, 28e</sup> This provides some indication that the solid state structure may be maintained in solution

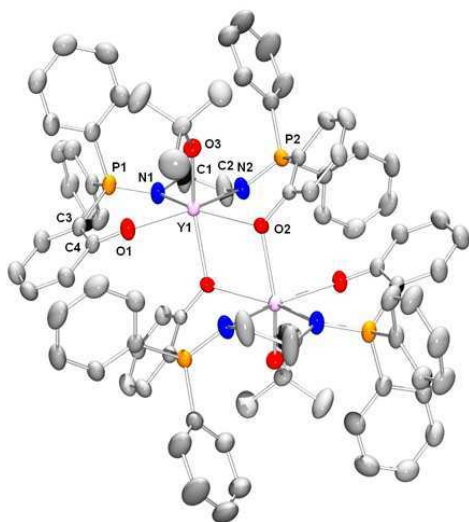


Figure 8. ORTEP view of the solid state structure of complex **44**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 2.203(3), Y1-O2 2.338(2), Y1-O3 2.079(3), Y1-O2#2 2.312(2), Y1-N1 2.398(3), Y2-N2 2.372(3), P1-N1 1.596(3), P2-N2 1.586(3), O1-Y1-N1 78.6(1), O2-Y1-N1 143.7(1), N1-Y1-N2 70.4(1), N2-Y1-O2 74.9(1), O1-Y1-O2 133.0(1), O2-Y1-O3 89.2(1), O2#2-Y1-O3 148.8(1), Y1-O2-N2-N1 9.39(24), Y1-O1-N1-N2 6.29(26); O1-N1-Y1-O3 88.49(11), O1-N1-Y1-O2#2 82.27(10).

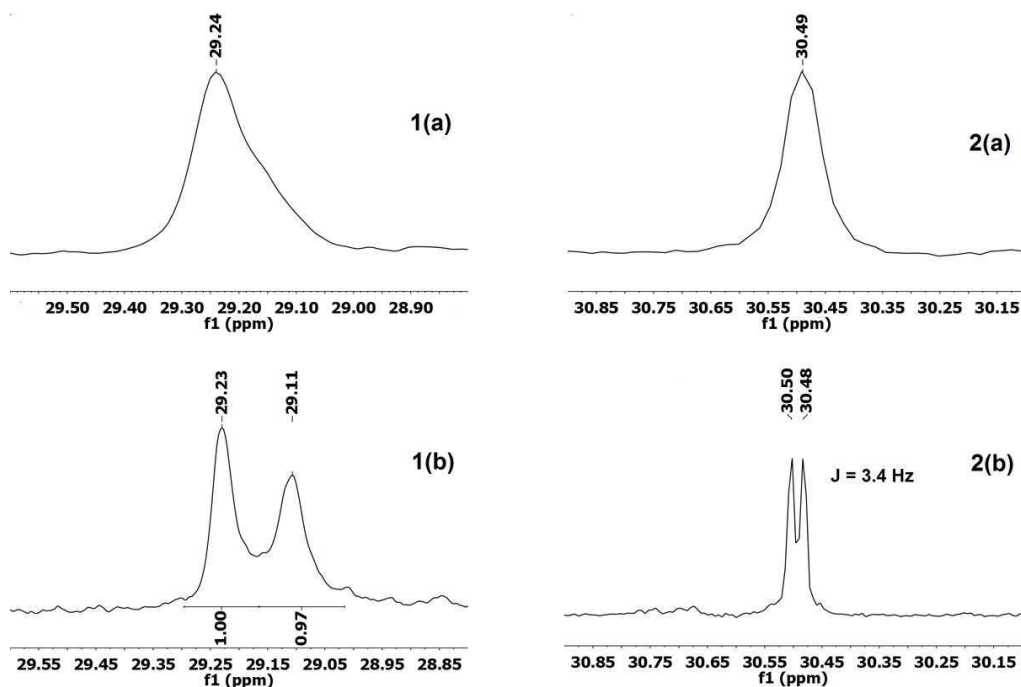
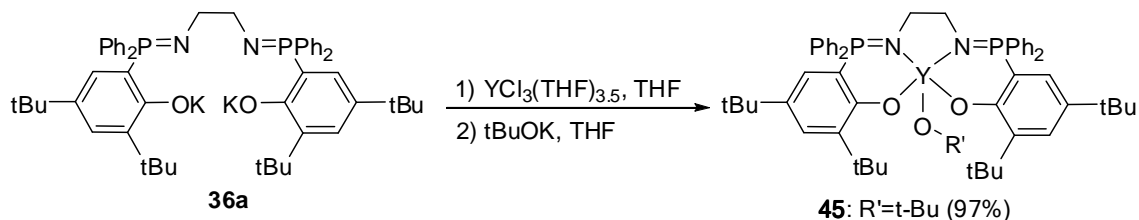


Figure 9.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of complexes **43** and **44**, recorded in THF on a (a) 300 MHz (b) 500 MHz instrument.

Complex **45** was prepared from the phosphasalen ligand **36a** with sterically hindered *tert*-butyl substituents on the phenoxide ring and with a *tert*-butyl alkoxide co-ligand (Scheme 19). This ligand was deliberately targeted so as to prevent dimerization and enable isolation of a mononuclear yttrium alkoxide complex. Its synthesis was reported in chapter 4.



Scheme 19. Synthesis of the yttrium complex **45**.

Addition of  $[\text{YCl}_3(\text{THF})_{3.5}]$  into a solution of ligand **36a** in tetrahydrofuran resulted in a cloudy solution.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed the complete disappearance of the free ligand signal at +20.6 ppm, and the apparition of a unique singlet at lower field (+31.0 ppm). This suggested the clean formation of a phosphasalen yttrium complex. One equiv. of potassium *tert*-butoxide was added into the solution and stirring was continued for 7h. After removal of insoluble potassium salt, THF was evaporated, giving the product as a viscous oil, which turned into an ivory solid after several days of storing at room temperature.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, in THF, showed a single doublet, at 31.6 ppm, with a coupling constant of 3.0 Hz, suggesting that complex **45** adopts a *trans*-configuration, in a manner analogous to complex **44**. On examination of the NMR spectra of complexes **44** and **45** some clear differences were observed. In particular, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra showed that the quaternary phenolate carbon atoms are equivalent in the spectrum of compound **45**, whereas they are different in the case of compound **44** (and compound **43**), giving rise to two doublets, likely due to the bridging and non-bridging coordination modes of the phenolate. This supported the notion that complex **45** has a mononuclear structure.

Definitive evidence concerning the structure of complex **45** was obtained by X-ray diffraction analysis of monocrystals grown from a saturated solution of **5** in cyclohexane (Figure 10). The complex adopts square based pyramidal geometry, with the four coordinating atoms of the phosphasalen ligands forming the basal plane, as shown by the dihedral angle O1-N1-N2-O2 (4.13(0.11)). The yttrium center is slightly out of the medial plane of these four atoms (0.7472 (0.0011) Å). The angle at O3 atom is close to 180°, which probably results from the steric hindrance of the phosphasalen ligand in the basal plane. All the yttrium-nitrogen and yttrium-oxygen bonds in complex **45** are slightly shorter compared to the corresponding values in complex **43** and **44**, probably as a result of the penta-coordination mode.

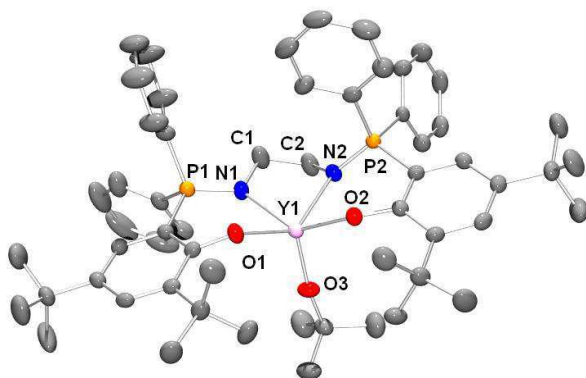


Figure 10. ORTEP view of the solid state structure of complex **45**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 2.1671(318), Y1-O2 2.1704(18), Y1-O3 2.025(2), Y1-N1 2.375(2), Y2-N2 2.324(2), P1-N1 1.595(2), P2-N2 1.584(2), O1-Y1-N1 80.51(7), O2-Y1-N1 139.87(8), N1-Y1-N2 71.78(8), N2-Y1-O2 79.68(7), O1-Y1-O2 102.03(7), O2-Y1-O3 109.16(8), O1-Y1-O3 115.03(8), C55-O3-Y1 171.40 (19), O1-N1-N2-O2 4.13(0.11), O1-N1-N2-Y1 25.13(0.10)

## 2. Catalytic Activities and Kinetics Studies

### 2.1 Overall

All three complexes were highly active initiators for the ring opening polymerization (ROP) of lactide. The selection of the polymerization solvent was critical, with initiator decomposition occurring in methylene chloride and the partial solubility of lactide in toluene (at ambient temperature) leading to heterogeneous polymerization, albeit extremely rapidly. The optimum solvent for use at ambient temperature (25 °C) was THF; all experiments were conducted using an initial concentration of lactide of 1 M, so as to enable accurate comparison between the different initiators and additives.

Table 3. Data for the ROP of lactide using yttrium initiators **43-45**  $[LA]_0 = 1$  M.

| Initiator | $[LA]_0:[I]$ | Time / s         | Conversion <sup>a)</sup> / % | $M_n(\text{calc})^b$<br>/ kg mol <sup>-1</sup> | $M_n(\text{exp})^c$<br>/ kg mol <sup>-1</sup> | PDI <sup>c)</sup>  | $P_s^d$            | $k_{obs}^e$          |
|-----------|--------------|------------------|------------------------------|--|---|--------------------|--------------------|----------------------|
| (I)       |              |                  |                              |  |   |                    |                    |                      |
| <b>43</b> | 200:1        | 3360<br>(56 min) | 90                           | 25.9   | 27.1  | 1.36               | 0.78               | 0.0031 <sup>f)</sup> |
| <b>44</b> | 200:1        | 40               | 91                           | 26.2   | 57.6  | 1.42               | 0.78               | 0.2522 <sup>f)</sup> |
| <b>44</b> | 200:1        | 5                | 98                           | 28.8   | 64.6 <sup>l)</sup>                            | 1.20 <sup>l)</sup> | 0.86 <sup>m)</sup> |                      |
| <b>45</b> | 1000:1       | 45               | 97                           | 140  | 223   | 1.34               | 0.86               | 0.0799 <sup>g)</sup> |

|                        |          |                      |    |     |     |      |      |   |
|------------------------|----------|----------------------|----|-----|-----|------|------|---|
| <b>45<sup>h)</sup></b> | 1000:1:1 | 70                   | 80 | 115 | 105 | 1.08 | 0.90 | - |
| <b>45<sup>i)</sup></b> | 1000:1   | 120 <sup>l)</sup>    | 99 | 144 | 332 | 1.31 | 0.87 | - |
| <b>45<sup>j)</sup></b> | 2000:1   | 10 min <sup>l)</sup> | 99 | 288 | 330 | 1.35 | 0.87 | - |
| <b>45<sup>k)</sup></b> | 5000:1   | 30 min <sup>l)</sup> | 98 | 720 | 700 | 1.23 | 0.88 | - |

<sup>a</sup> Conversions were determined from the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of the crude products, by integration of the methine resonance assigned to LA ( $\delta$ =4.92 ppm) and to PLA ( $\delta$ =5.00-5.30 ppm).

<sup>b</sup>  $M_n(\text{calc}) = 144 \times [\text{LA}]_0 / [\text{I}] \times \% \text{ conversion LA}$ .

<sup>c</sup>  $M_n(\text{exp})$  was determined using GPC, in THF, using multi-angle laser light scattering (GPC-MALLS) according to the method described earlier.<sup>28a, b</sup> The polydispersity index was also determined from GPC,  $\text{PDI} = M_w / M_n$ .

<sup>d</sup>  $P_s$  is the probability of racemic linkages between monomer units and is determined by comparison of the integrals of tetrads in the homonuclear decoupled <sup>1</sup>H NMR spectrum with those calculated using Bernoullian statistics, according to the method described by Coudane *et al.*<sup>3a</sup>

<sup>e</sup> Determined from the gradients of the  $\ln\{[\text{LA}]_0 / [\text{LA}]_t\}$  (for first-order reaction) or  $1/[\text{LA}]_t$  (for second-order reaction) versus time plots

<sup>f</sup> expressed in  $\text{M}^{-1} \text{s}^{-1}$ . The reaction is second-order in lactide.

<sup>g</sup> expressed in  $\text{s}^{-1}$ . The reaction is first order in lactide,  $[\text{I}] = 1 \text{ mM}$ .

<sup>h</sup> isopropanol was added,  $[\text{LA}]/[\text{I}]/[\text{iPA}] = 1000/1/1$

<sup>i</sup> A reaction using unpurified lactide.

<sup>j</sup> Slurry of 2 mmol lactide in 1 mL THF at 25 °C.

<sup>k</sup> Slurry of 5 mmol lactide in 1 mL THF at 25 °C.

<sup>l</sup> Reaction time unoptimized.

<sup>m</sup> This experiment showed a rapid increase of PDI and decrease of  $P_s$ , over time.

The catalytic activities of the dimeric complexes differ markedly from the ones of the monomeric complex. Studies of their catalytic behaviors are presented separately below.

## 2.2 Catalytic Activities and Kinetics Studies: Dimeric Complexes

### 2.2.1 Complex 43

The polymerizations using **43** were analyzed by taking aliquots throughout the polymerizations. They were well controlled, as shown by the linear evolution in the molecular weight with conversion and the narrow PDI for the PLA (Figure 11). In general, there was a good agreement between  $M_n(\text{calc})$  and  $M_n(\text{exp})$ , suggesting that both alkoxide groups in the dimer initiate the polymerisation.

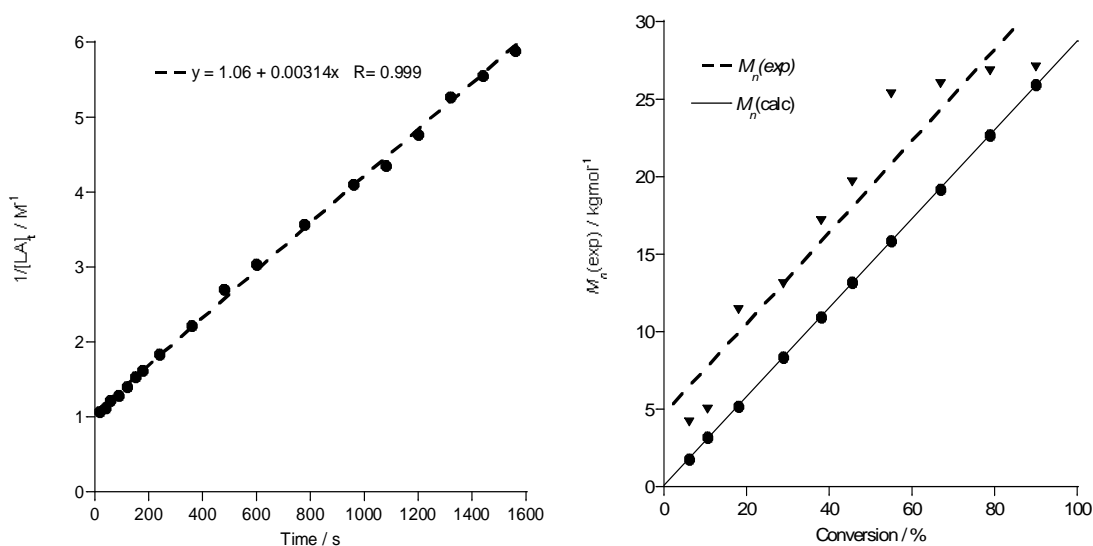


Figure 11. (Left) Plot illustrating  $1/[LA]_t$  ( $M^{-1}$ ) versus time (s) for LA ROP using **43**. (Right) Plot showing the evolution of experimental  $M_n$  ( $kgmol^{-1}$ ) vs. conversion (%) for LA ROP using initiator **43**. Polymerization conditions:  $[LA]_0 = 1$  M,  $[43] = 5$  mM, THF, 25 °C.

For a polymerization initiated and catalysed by an initiator, the rate law can be expressed according to the equation below:

$$\frac{-d[LA]_t}{dt} = k_p [LA]_t^m [I]_t^n \quad (\text{Equation 1})$$

Where  $[LA]$ : concentration of the lactide ( $mol.L^{-1}$ ),  $[I]$ : concentration of the initiator ( $mol.L^{-1}$ ),  $m$ : order of the reaction on Lactide,  $n$ : order of the reaction in initiator,  $k_p$ : rate constant of the reaction ( $s^{-1}.mol^{-(n+m-1)}.L^{(n+m-1)}$ ).

Lactide polymerization often follows a first-order in substrate. Curiously the polymerisations with **43** as initiator showed a second order dependence on the concentration of lactide. The plots of  $\ln\{[LA]_0/[LA]_t\}$  versus time did not show a linear fit to the data, indicating the reaction was not first order in lactide concentration. In contrast, a plot of  $1/[LA]_t$  versus time showed a good linear fit (Figure 11), the y-axis intercept ( $t = 0$  s) corresponds well with the starting concentration of lactide (1 M). This indicates a second order dependence on lactide concentration, an unusual finding in this type of polymerisation catalysis. There are only a few other examples of such second order dependence, including a dinuclear Salen-magnesium complex<sup>30</sup> and trinuclear zinc- $\beta$ -diketiminato complex.<sup>31</sup> Delbridge also observed a second order dependence using lanthanide amide initiators of the type  $[L_2LnN(SiMe_3)_2]$ , they attributed this to initiation from both the amide and the ancillary ligand, L.<sup>32</sup>

The end group of the polymers were analysed by mass spectroscopy using MALDI (Matrix-Assisted Laser Desorption/Ionisation) technique, a soft ionisation one that is often used for the analysis of macromolecules that are often fragile and tend to fragment with other conventional

ionization techniques (Figure 12). A solution containing the matrix (which is a specific crystallisable molecule) and the analyte is spotted on the sample plate. Solvent was evaporated and laser beam is fired at the recrystallised matrix/analyte. The clusters ejected from the surface consists of analyte molecules surrounded by matrix and salt ions. The matrix molecules evaporate away from the clusters to leave the free analyte in the gas-phase. The photo-excited matrix molecules are stabilised through proton/cation transfer to the analyte. It is in this way that the characteristic  $[M+X]^+$  ( $X = H, Na, K$  etc.) analyte ions are formed, which would then be detected using a mass spectrometer (normally time-of-flight mass spectrometer, hence the notation MALDI-ToF).

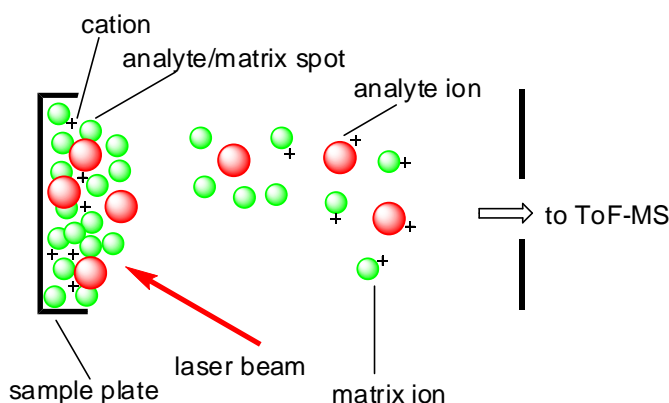


Figure 12. MALDI technique.

The MALDI-ToF spectrum on a sample of polymers obtained from the polymerization with complex **43**, using a dithranol matrix with potassium trifluoroacetate as the cationising agent, showed that all polymers have OEt endgroups (Figure 13). This suggests that the polymerization follows a traditional coordination-insertion mechanism (Scheme 8).

The detailed mechanism of the ROP initiated with **43** is however still non-elucidated, especially the second-order in lactide. This probably have some relation with the dimeric structure of the initiator. A mechanism could be proposed to explain the observations on  $M_n$ , kinetic data and end-group analysis. But much data would be needed to put more life into such mechanism. Due to the relatively low activity of complex **3** compared to **44** and **45**, no further investigation was pursued.

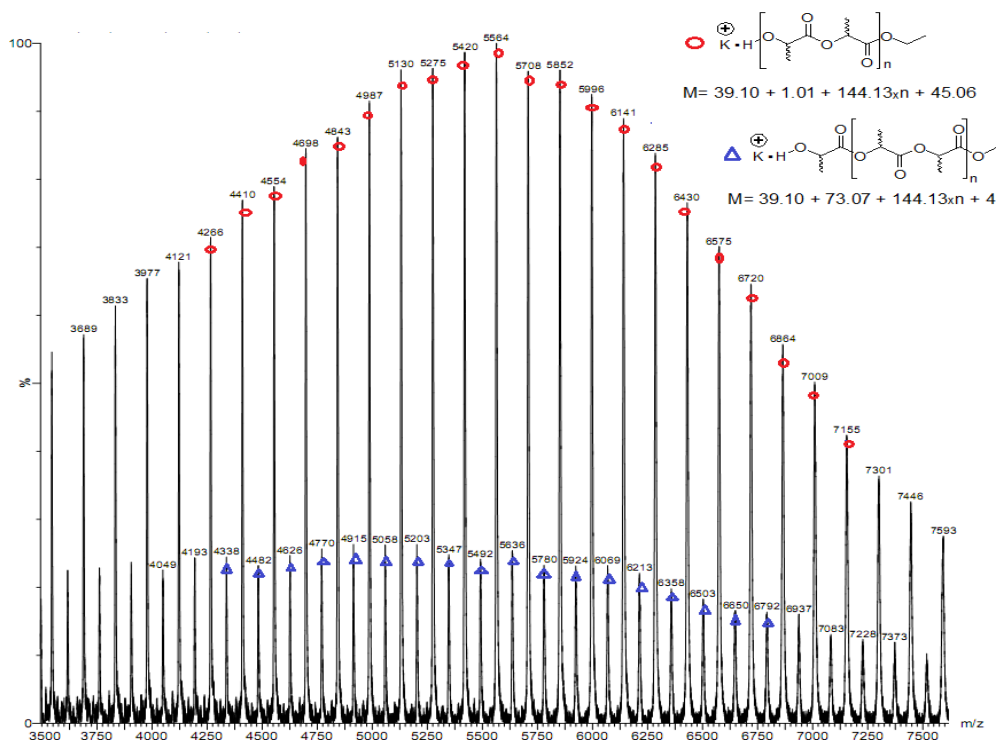


Figure 13. Selected area of the MALDI-ToF mass spectrum of PLA, synthesised by ROP using **43** in THF. Polymerisation conditions:  $[LA]_0 = 1\text{ M}$ ,  $[43]_0 = 5\text{ mM}$ , reaction stopped at  $t=50\text{ s}$  to obtained PLA with  $M_n \sim 6\text{ kg mol}^{-1}$  (calculated first from kinetic plots). The MALDI-ToF conditions were using a dithranol matrix, in dichloromethane at a loading of 1:5, with potassium trifluoroacetate as the cationising agent.

## 2.2.2 Complex 44

The relative high rate of reactions with complex **44** allows studying kinetics of the reactions with different catalytic loading. Thus a full analysis of the kinetics for polymerizations was undertaken for polymerization with this initiator: first  $k_{\text{obs}}$  was determined from each polymerization run with a known concentration of initiator  $[I]_0$ , then plot of  $k_{\text{obs}}$  vs.  $[I]_0$  was analysed in order to determined the order in initiator and  $k_p$ . (equation 1 and 2).

$$\frac{-d[LA]_t}{dt} = k_p [LA]_t^m [I]_t^n \quad (\text{Equation 1})$$

$$k_{\text{obs}} = k_p [I]_t^n \quad (\text{Equation 2})$$

This species showed a complex kinetic behavior, with a second order dependence in lactide concentration (Figure 14), just like the case with complex **43**, and a third order dependence on yttrium concentration (Figure 15). Such data are indicative of substantial aggregation occurring under the conditions of the catalysis and underscore the importance of the phosphasalen ancillary ligand structure.



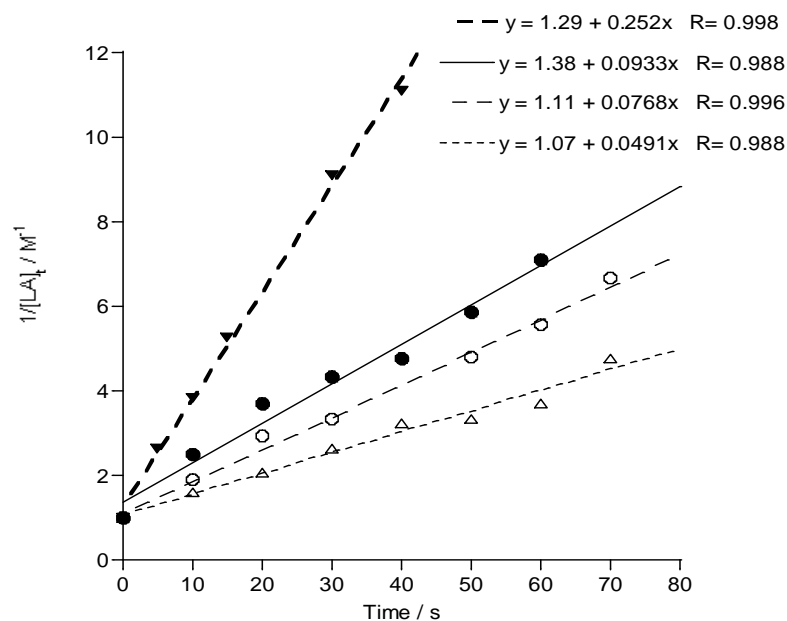


Figure 14. Plot showing  $1/[LA]_t$  ( $M^{-1}$ ) versus time (s) for LA ROP using **44** over the concentration range 2.5-5 mM. Polymerization conditions:  $[LA]_0 = 1$  M, THF, 25 °C,  $[4] = 5$  mM (filled triangles,  $k_{obs} = 0.252$   $M^{-1}s^{-1}$ );  $[44] = 3.3$  mM (filled circles,  $k_{obs} = 0.0933$   $M^{-1}s^{-1}$ );  $[44] = 2.9$  mM (open circles,  $k_{obs} = 0.0768$   $M^{-1}s^{-1}$ );  $[44] = 2.5$  mM (open triangles,  $k_{obs} = 0.0491$   $M^{-1}s^{-1}$ ).

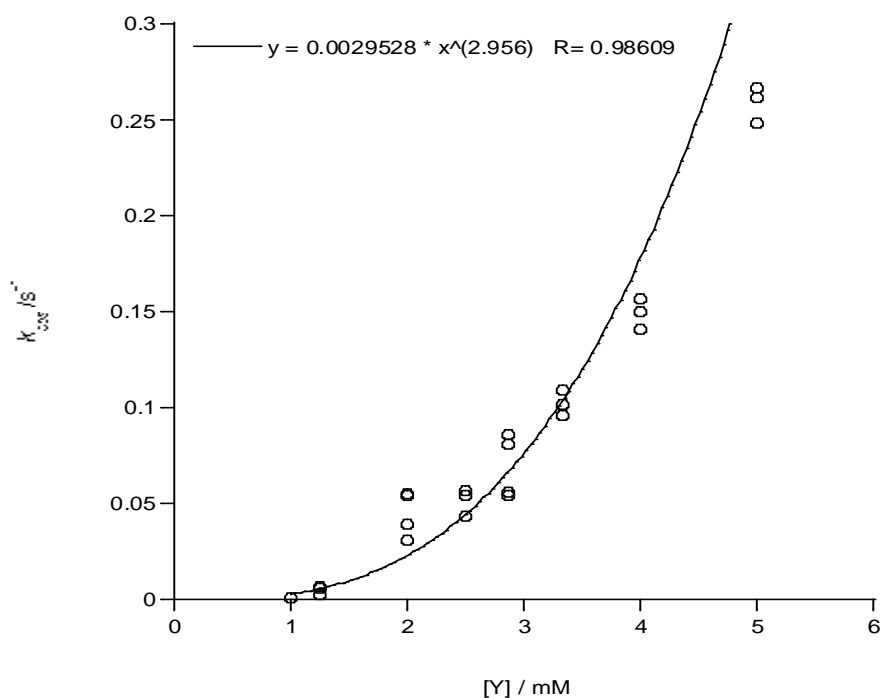


Figure 15. Plot of  $k_{obs}$  versus  $[Y]$ , polymerization conditions;  $[LA]_0 = 1$  M, THF, 25 °C,  $[44] = 1$ -5 mM.

MALDI-ToF spectrum done on polymers sample obtained from polymerisation with **44** showed that these molecules all have tBuO- endgroup, which is indicative of a coordination-insertion mechanism (Figure 16). At the difference from polymerization with **43**, where  $M_n(\text{exp})$  fit with  $M_n(\text{calc})$ , suggesting that both the ethoxides in the dimer initiate the ROP, for complex **44**, the  $M_n(\text{exp})$  values were approximately double the  $M_n(\text{calc.})$  (Figure 17). This indicates that only half the alkoxide groups initiate, consistent with only a single site in the dinuclear complex being active.

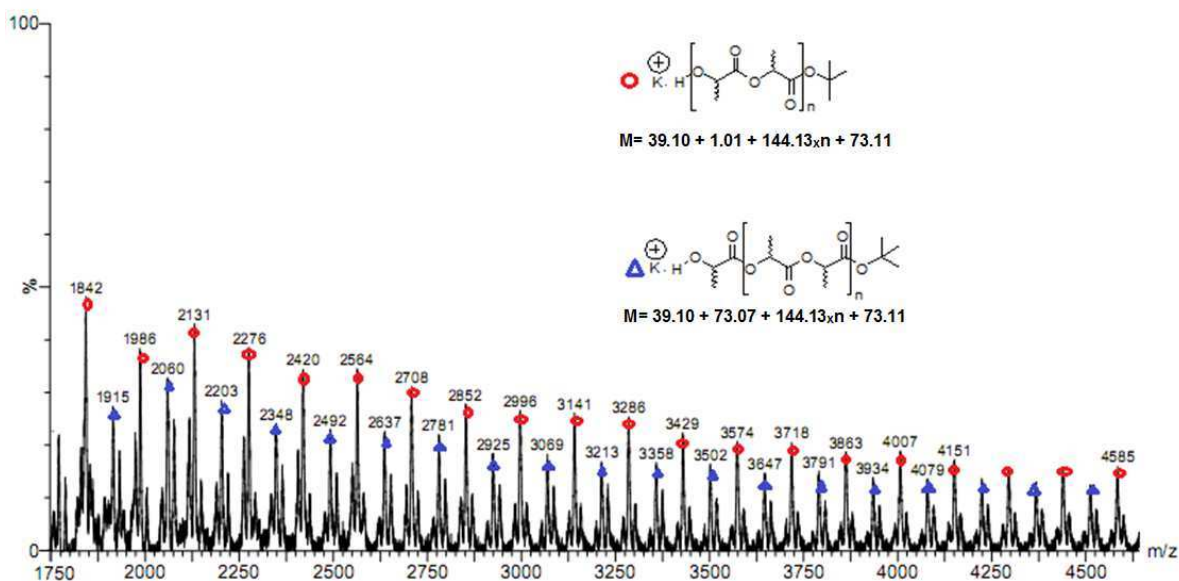


Figure 16. Selected area of the MALDI-ToF mass spectrum of PLA, synthesised by ROP using **44** in THF. Polymerisation conditions:  $[LA]_0 = 1\text{ M}$ ,  $[44]_0 = 2\text{ mM}$ , reaction stopped at  $t = 2\text{ s}$  to obtained PLA with  $M_n < 10\text{ kg mol}^{-1}$  (calculated first from kinetic plots). The MALDI-ToF conditions were using a dithranol matrix, in dichloromethane at a loading of 1:5, with potassium trifluoroacetate as the cationising agent.

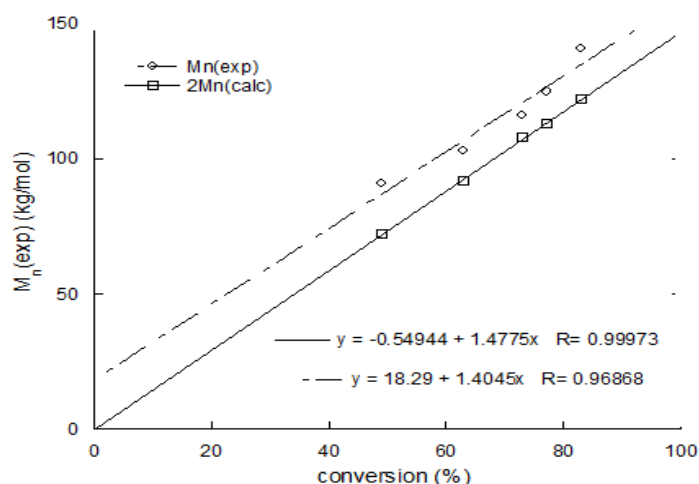


Figure 17. Plot showing evolution of  $M_n$  ( $\text{kg mol}^{-1}$ ) vs. conversion (%) for LA ROP using initiator **44**. Polymerisation conditions:  $[LA]_0 = 1\text{ M}$ ,  $[44] = 2\text{ mM}$ , THF,  $25\text{ }^\circ\text{C}$ .

In situ  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy was used to monitor a mixture of complex **4** and 25 equivalents of LA. The spectrum was quite different to complex **44** alone; it showed four non-equivalent phosphorus nuclei (Figure 18), data which could support aggregation under the conditions of the catalysis. Currently, we are unable to unambiguously assign the solution structure of complex **44**, under the polymerization conditions.

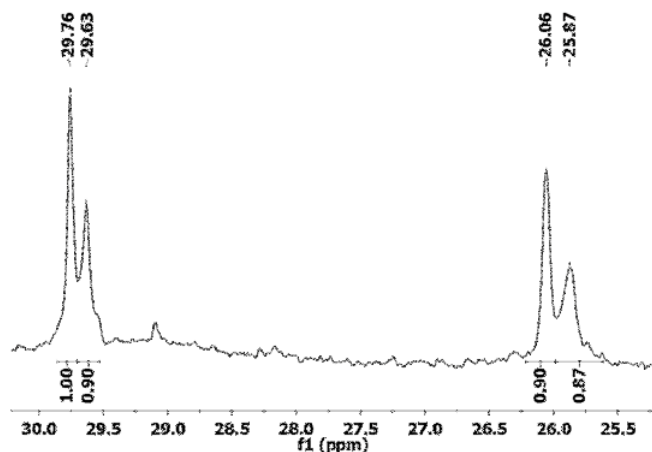


Figure 18.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a mixture of **44** and 25 equiv. of *rac*-lactide in THF recorded with an Av500 instrument.

## 2.3 Catalytic Activities and Kinetics Studies: Monomeric Complex

### 2.3.1 General

Complex **45** is extremely active, it is even able to polymerize unpurified lactide; near quantitative conversion is reached within 2 minutes at low initiator loadings ( $[\mathbf{45}] = 1 \text{ mM}$ ). Kinetic study for the polymerizations analysed by taking aliquots showed that the reaction follows a first-order rate in lactide (Figure 19). This rate law is thus the same as common ROP of lactide reactions and contrasts with the cases of complex **43** and **44**. The pseudo first order rate constant,  $k_{\text{obs}}$ , was  $0.08 \text{ s}^{-1}$ , at  $[\mathbf{45}]$  of  $1 \text{ mM}$ . The rate of polymerization is thus amongst the highest values reported for this reaction, easily comparing with related yttrium systems and outstripping many other metal centres.

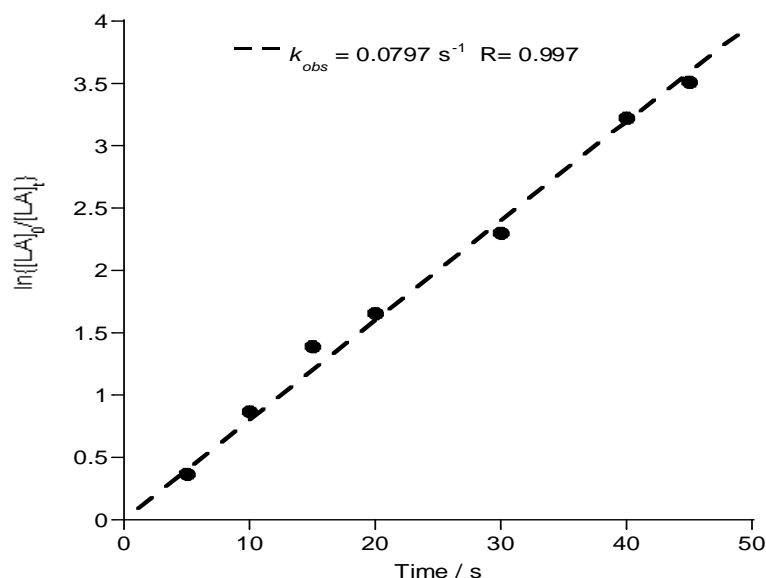


Figure 19.  $\ln([LA]_0/[LA]_t)$  versus time for LA ROP using initiator **45**. Polymerization conditions:  $[LA]_0 = 1\text{ M}$ ,  $[3] = 1\text{ mM}$ , THF, 25 °C.

In comparison with yttrium complexes of salens and derivatives, it is clear that initiator **6** shows remarkably enhanced rates, even under significantly lower loadings, although caution should be applied in comparing values as the experiments were not run under identical conditions (Table 4). For example, complex **Y1**<sup>17</sup> took 14 h to reach complete conversion at 100:1 loading of lactide:initiator, complex **Y3**<sup>19</sup> took an hour to reach complete conversion at a loading of 300:1 and, the ferrocenyl salen complex **Y4**<sup>20</sup> took 40 min to reach high conversions at a loading of 500:1. In contrast, complex **45** was able to completely polymerize as many as 5000 equivalents of lactide in 30 mins and 1000 equivalents in less than a minute. It is also notable that initiator **45** can be used at rather low loadings, down to  $[LA]:[45] = 5000$ , which is useful for production of high molecular weight PLA (up to 700 kg/mol). Finally, it is apparent that the other yttrium salen complexes do not allow significant stereocontrol in *rac*-lactide ROP, in contrast complex **45** enables a high degree of heteroselectivity in *rac*-LA ROP.

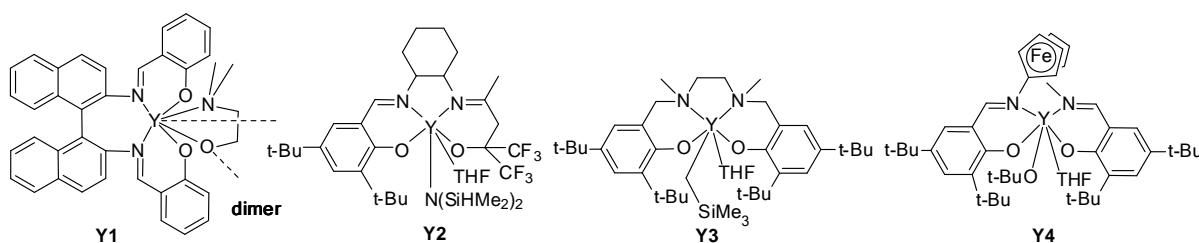


Table 4. Data for the ROP of lactide using yttrium initiators.

| Initiator<br>(I)       | [LA] <sub>0</sub> : [I] | Time / s | Conversion/% | $M_n(\text{calc})^{\text{b}}$<br>/ kg mol <sup>-1</sup> | $M_n(\text{exp})$<br>/ kg mol <sup>-1</sup> | PDI  | P <sub>s</sub> |
|------------------------|-------------------------|----------|--------------|---|---|------|----------------|
| <b>45</b>              | 1000:1                  | 45       | 97           | 140   | 223   | 1.34 | 0.86           |
| <b>45<sup>a)</sup></b> | 2000:1                  | 10 min   | 99           | 288   | 330   | 1.35 | 0.87           |
| <b>45<sup>b)</sup></b> | 5000:1                  | 30 min   | 98           | 720   | 700   | 1.23 | 0.88           |
| <b>Y1<sup>17</sup></b> | 100:1                   | 14 hours | >98          | -   | -   | -    | -              |
| <b>Y2<sup>18</sup></b> | 100:1                   | 3 days   | 80           | 12  | 10  | 1.18 | 0.72           |
| <b>Y3<sup>19</sup></b> | 300:1                   | 60 min   | >98          | 43  | 37  | 1.64 | 0.65           |
| <b>Y4<sup>20</sup></b> | 500:1                   | 40 min   | 90           | 72  | 93  | 1.13 | -              |

<sup>a</sup> Slurry of 2 mmol lactide in 1 mL THF at 25 °C. <sup>b</sup> Slurry of 5 mmol lactide in 1 mL THF at 25 °C.

The LA ROP using initiator **45** is quite well controlled, with the number averaged molecular weight ( $M_n$ ) of the PLA increasing linearly with the percentage conversion and the polydispersity indices remaining narrow throughout the polymerization (<1.4).

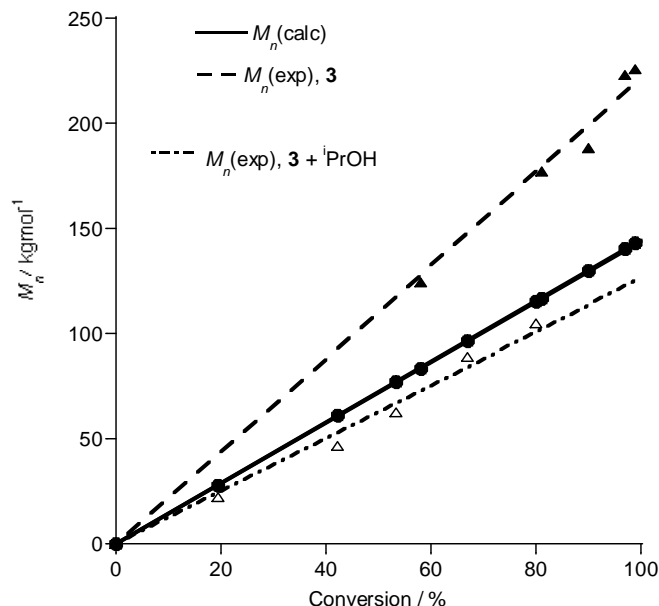


Figure 20. Evolution of  $M_n$  (kg/mol) versus conversion (%) for LA ROP using **45** (filled triangles), and with an extra equivalent of *i*PrOH (hollow triangles). Also plotted is the  $M_n(\text{calc})$  (filled circles). Polymerization conditions:  $[LA]_0 = 1 \text{ M}$ ,  $[45] = [i\text{PrOH}] = 1 \text{ mM}$ , THF, 25 °C.

The experimentally determined values for the number averaged molecular weight exceed those calculated (on the basis of initiator concentration and conversion). This could either be due to incomplete initiation from the *tert*-butyl alkoxide groups or to partial deactivation of the initiator.

In order to test the above hypothesis, and to bring the experimental  $M_n$  close to its calculated values, an experiment was carried out where an equivalent of *iso*-propyl alcohol was added. An yttrium *iso*-propyl alkoxide complex is expected to be a better initiator due to its reduced steric hindrance and is also a good model for the secondary alkoxide propagating species. The addition of an equivalent of *iso*-propyl alcohol led to an improved control, as evidenced by the excellent agreement between the experimentally determined and calculated values for  $M_n$  and the PDI being below 1.10, in almost all samples. These results indicate that *iso*-propyl alcohol is a viable chain transfer agent and a more effective initiator.

NMR experiments at variable temperature (VT-NMR) were carried out to investigate the formation of an yttrium isopropoxide complex upon addition of isopropanol (1 equivalent), and its exchange with the alcohol in solution. Details are presented in the following section. The study showed the formation of an LYOiPr complex and its rapid exchange with free *t*BuOH was demonstrated. As isopropoxide is a better initiating group than *tert*-butoxide, the equilibrium between LYOiPr and LYOtBu is driven towards the formation of the isopropoxide complex during the reaction. Moreover, HO*t*Bu is a poor chain transfer agent. Taking into account all data, the polymerizations are expected to be dominated by the yttrium isopropoxide initiator, hence the good fit between  $M_n(\text{exp})$  and  $M_n(\text{calc})$  in this case.

### 2.3.2 NMR Studies of the Addition of *iso*-Propanol on Complex 45.

Upon the addition of 1 equivalent of iPA into a solution of complex **45** in THF-*d*<sub>8</sub>, minor changes were observed in the <sup>31</sup>P-NMR and <sup>1</sup>H-NMR spectra. The protons of the *tert*-butoxide group experienced the largest shift from a broad singlet at 0.68 ppm (in the complex) to a fine one at 0.98 ppm, the methyl protons of isopropoxide appear as a doublet at 0.90 ppm. (Figure 21). When 3 or 5 equivalents of *isopropanol* were added, the changes in the signals for the phosphasalen ligand in both <sup>31</sup>P-NMR and <sup>1</sup>H-NMR are minor compared to those observed upon the addition of only one equivalent of *isopropanol*. This suggests that the ligand is still coordinated to the yttrium center, and that the complex(es) remain(s) essentially unchanged.

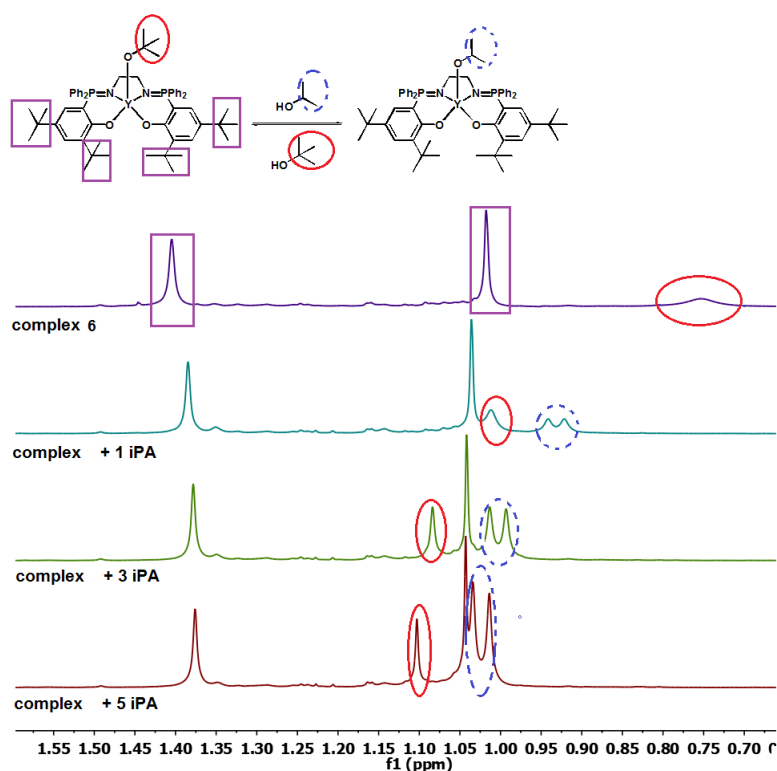


Figure 21. Addition of 1 to 5 equivalents of iPA on **45** (spectra between 0.6 and 1.6 ppm)

From the addition of 3 and 5 equivalents of isopropanol, it was observed that the proton signals of the isopropyl group in both the complex and free isopropanol are almost identical. This may point towards a rapid exchange in the solution between coordinated isopropoxide and isopropanol. In the same manner, rapid exchanges between coordinated *t*BuO and free HO*t*Pr (and the reverse) are conceivable. Therefore variable temperature NMR experiments were performed.

Comparisons between NMR spectra at variable temperatures obtained from a mixture (**6** + iPA) and those from (**45** + 3 iPA) show important differences (Figure 22). In presence of 3 equivalents of isopropanol, at all temperature, the Y-*Ot*Bu complex disappeared (no doublet at 6.33 ppm corresponding to  $C_dH$ ), and only signals corresponding to the L- Y-*Oi*Pr are observable (doublet at 6.45 ppm for  $C_dH$ ).

Spectra recorded for **45** in the presence of one equivalent of isopropanol is typical for an exchange process. Signals corresponding to  $C_dH$  of the L- Y-*Ot*Bu complex can clearly be seen at 178K (see Figure 22, spectrum of **45** alone and **45**+ iPA at 178K). Upon heating, signals corresponding to L- Y-*Ot*Bu complex (doublet at 6.32 ppm at 178K) and the one corresponding to the L- Y-*Oi*Pr complex (doublet at 6.55 ppm at 198K) merge ( $T = 238K$ ). Afterwards, a clear doublet corresponding to both complexes in rapid exchange appears at 6.47 ppm.

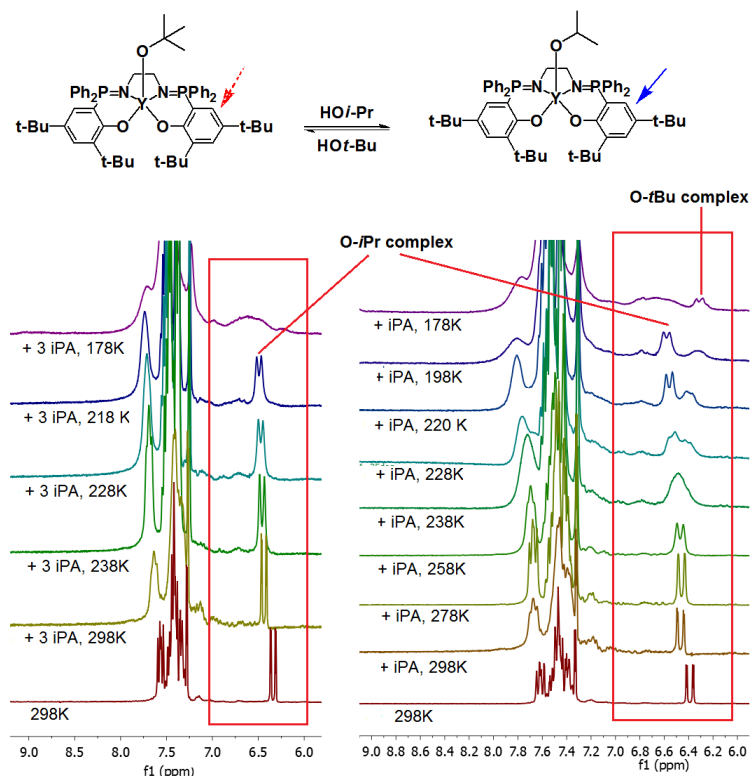
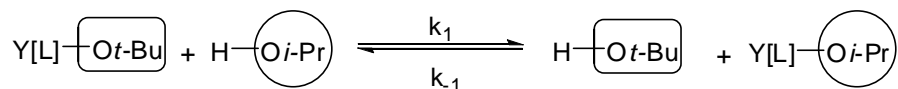


Figure 22. Addition of 1 and 3 equivalents of iPA on **45** at variable temperatures (spectrum between 9.0 and 6.0 ppm).

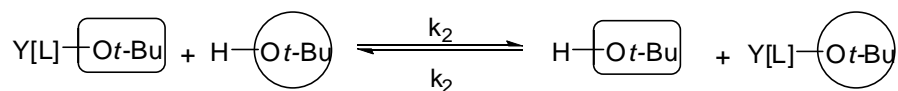
Considering the following reaction which takes place when 1 equiv. of isopropanol is added into a solution of L- Y-O*t*Bu complex



The activation parameters were determined:  $\Delta G^\ddagger = 11.4 \text{ kcal.mol}^{-1}$

$$k_{-1} = 1770 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}, k_1 = 7110 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$$

Variable Temperature-NMR also allowed to study the exchange between coordinated O*t*Bu and free HO*t*Bu in the solution.



In fact, at  $T \leq 238\text{K}$ , in presence of 1 equivalent of HO*i*Pr, signals corresponding to coordinated *t*BuO (singlet at 0.69 ppm at 298K) and free HO*t*Bu (singlet at 1.13 ppm) are differentiated (Figure 23). The rate constant was determined  $k_2 = 7110 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$ , as well as the activation barrier for such exchange  $G^\ddagger = 12.0 \text{ kcal.mol}^{-1}$  at 238K.



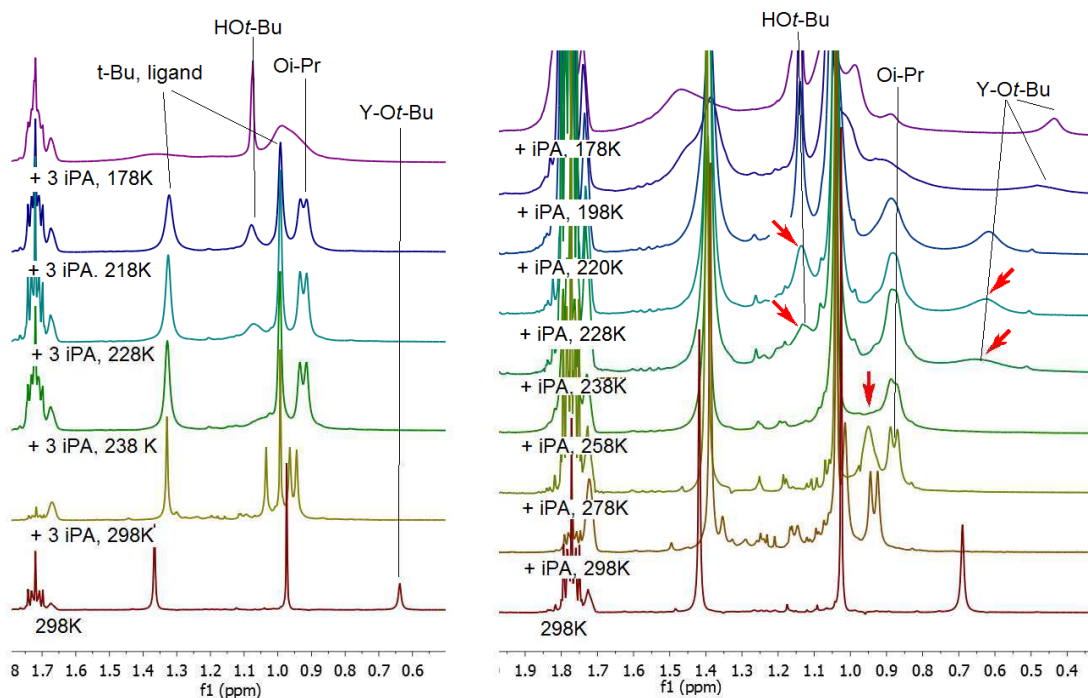


Figure 23. Addition of 1 and 3 equivalents of iPA on **45** at variable temperatures (spectrum between 2.0 and 0.4 ppm).

## 2.4 Stereoselectivity of the Polymerisations

The polylactide produced from *rac*-lactide using the three initiators shows a heterotactic bias ( $P_s$ ). The determination of  $P_s$  was carried out using the probabilities calculated by Coudane *et al.*,<sup>3a</sup> every tetrad signal was analysed and the average value for  $P_s$  reported (Figure 24 and Figure 25). PLA produced using initiators **43** and **44** had  $P_s$  values in the range 0.78-0.81, regardless of the *rac*-LA conversion or initiator concentration.

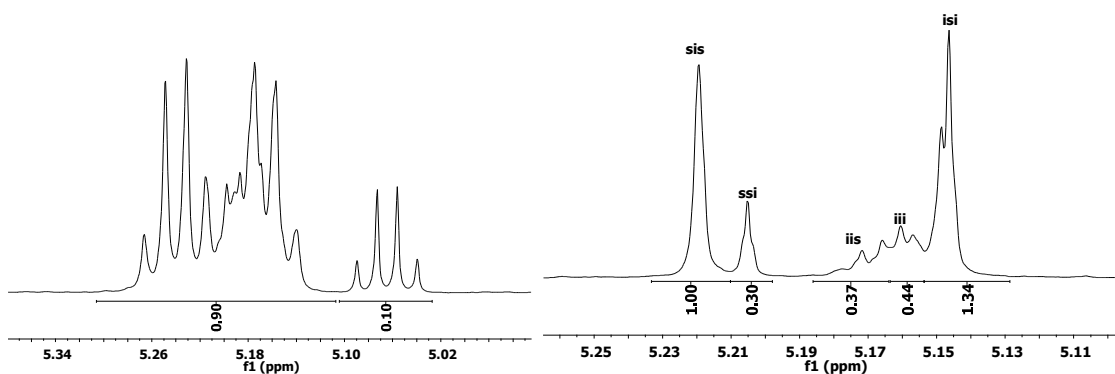


Figure 24.  $\{^1\text{H}\}$  and  $^1\text{H}\{^1\text{H}\}$  NMR spectra of PLA produced using initiator **43**.  $[\text{LA}]_0 = 1 \text{ M}$ ,  $[\text{I}] = 5 \text{ mM}$ , 90 % conversion of LA, THF, 25 °C,  $P_s = 0.78$ .

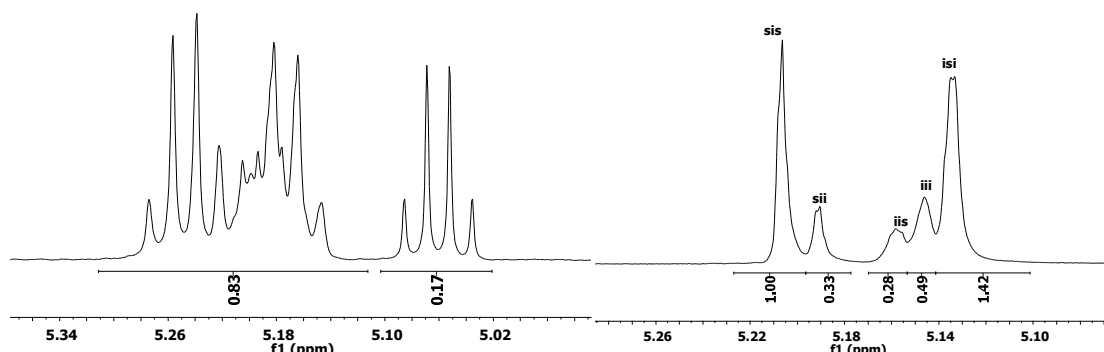


Figure 25.  $\{^1\text{H}\}$  and  $^1\text{H}\{^1\text{H}\}$  NMR spectra of PLA produced using initiator **44**.  $[\text{LA}]_0 = 1 \text{ M}$ ,  $[\text{2}] = 2 \text{ mM}$ , 83% conversion of LA, THF,  $25^\circ\text{C}$ ,  $P_s = 0.79$ .<sup>1</sup>

Complex **45** shows considerably enhanced heteroselectivity, with  $P_s$  0.86-0.90. Once again, the probability of heterotactic enchainment was independent of the conversion of *rac*-LA, the addition of *iso*-propyl alcohol or the concentration of the initiator. It is quite interesting to observe that highly heterotactic PLA was produced from either purified or crude LA. As an illustration of the high degrees of heteroselectivity conferred by this initiator, the methyne region of the  $^1\text{H}$  NMR spectrum of PLA (Figure 26) is illustrated; it is dominated by two quartets, assigned to heterotactic PLA.

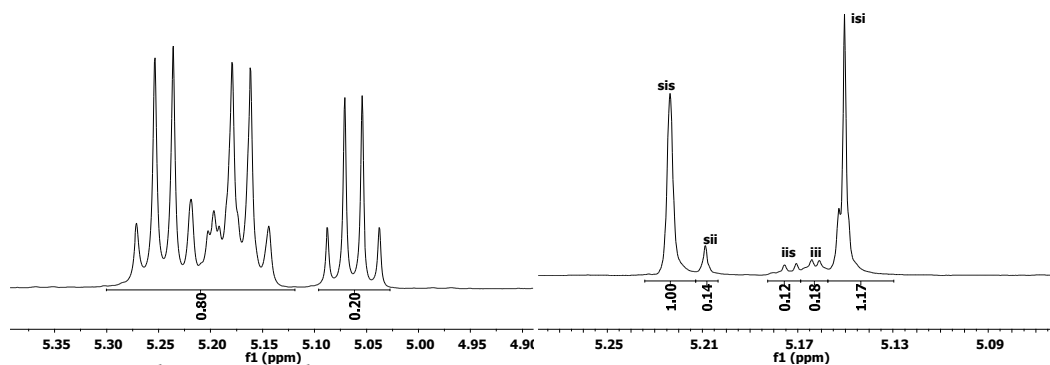


Figure 26.  $\{^1\text{H}\}$  and  $^1\text{H}\{^1\text{H}\}$  NMR spectra of PLA produced using initiator **45**. Polymerisation conditions:  $[\text{LA}]_0 = 1 \text{ M}$ ,  $[\text{3}] = [\text{iPrOH}] = 1 \text{ mM}$ , 80% conversion of LA, THF,  $25^\circ\text{C}$ ,  $P_s = 0.90$ .

### 3. Discussion

#### 3.1 Generalities

Complexes **43** and **44** are proposed to initiate and propagate ROP via a coordination insertion mechanism. The MALDI-TOF spectra of the PLA produced using these initiators show chain end-capped with ethyl ester and *tert*-butyl ester groups respectively (as well as the expected

hydroxyl group at the opposite chain end), consistent with this mechanism. Both complexes exhibit dimeric structures in the solid state, with complex **43** having bridging ethoxide groups whilst complex **44** bridges through a phenoxide group from each phosphasalen ligand. It is likely that the solid state structures are maintained in THF solutions, as the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra differ despite having the yttrium centre coordinated by the same phosphasalen ligand. Thus, complex **43** displays two signals, assigned to two phosphorus atoms in different chemical environments, in accordance with the solid state structure, whilst complex **44** displays a single doublet, indicating all the phosphorus atoms are in equivalent environments, again in accordance with the solids state structures.

The polymerization data also indicate differences between the two initiators with **43** being significantly slower than **44**. Indeed at 5 mM initiator concentration, complete conversion was observed after approximately 1 h using complex **43** and after only 40 s using complex **44**. Both initiators show a second order dependence of the rate of polymerization on the concentration of lactide, implicating two molecules of lactide in the rate determining step. Even more curiously, the molecular weights agree well with calculated values on the basis of two active sites per molecule of **43** but only for a single active site for complex **44**.

It is proposed that the dimeric structures are maintained under the conditions of the polymerization, with initiation and propagation occurring from both bridging alkoxide groups in the case of **43** and from a single tert-butoxide group in the case of **44**. The order in LA concentration and the molecular weight observations for complex **43** imply that two chains are propagated per dimer molecule. However, in the case of complex **44** it is not clear why a second order dependence in lactide concentration is observed but only a single chain propagates per dimer molecule. But again, this phenomenon has already been observed for some other second-order reactions in LA, where the experimental  $M_n$ s imply that only half of the possible initiating groups are active, although they are all in the same environment in the starting complex.<sup>31, 30</sup> In our case, NMR experiments and full kinetic study showing a third order in initiator suggested an aggregation of the complexes in the conditions of polymerizations. This underlines the importance of having bulky substituents on the phosphasalen ligand to prevent such phenomenon.

Complex **45** was targeted to have a mononuclear structure in solution, via the use of a sterically hindered phophasalen ancillary ligand and a hindered initiating group, tert-butyl alkoxide. Based on NMR data and solid state structure, it is proposed that this species retains a mononuclear structure in solution. Polymerizations using this initiator show extremely rapid rates, indeed the pseudo first order rate constant (at  $[\mathbf{45}] = 1 \text{ mM}$ ) is very high ( $k_{\text{obs}} = 0.008 \text{ s}^{-1}$ ) and the rate depends to the first order in the concentration of LA.

A mixture of complex **45** and 25 eq. of LA was analyzed by  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy which showed that the P=N groups remain coordinated to the yttrium centres, indicating that the ligand is not dissociated during the polymerization. Furthermore, complex **45** shows excellent heteroselectivity for *rac*-LA ROP. This interesting finding further confirms earlier experiments

using bis(phosphinic amido) yttrium complexes developed by the Williams' group, where high degrees of heteroselectivity were only observed from a mononuclear complex.<sup>28b</sup>

The stereocontrol is proposed to arise via a chain end control mechanism, that is where the stereochemistry of the last inserted lactide unit controls the stereochemistry of the coordination/insertion into the next lactide unit. This enhancement in stereocontrol for yttrium initiators in THF has been reported by many group are is presumably due, in part, to its ability to coordinate to the yttrium centre and control the active site stereochemistry.<sup>26g, 25, 33a, b, 10, 19, 33c,</sup>

<sup>1d</sup> An NMR scale experiment involving addition of increasing quantities of THF to a solution of **45** in toluene did not lead to a significant shift in the THF resonances, either due to rapid exchange or a lack of coordination. It is, however, clear that the THF solvent is important for the high stereocontrol as an experiment conducted in toluene ([LA]= 1 M, [**45**] = 1 mM in THF, 80 °C, 91% conversion) yielded a PLA with much lower heteroselectivity ( $P_s = 0.73$  vs. 0.89 in pure THF).

### 3.2 Comparisons with Other Yttrium Complexes

The groups of Coates,<sup>17a</sup> and Carpentier's<sup>18</sup> have both studied yttrium complexes of (substituted) tetradentate salen ligands. The yttrium complexes, either as monomers (**Y2**) or dimers (**Y1**, bridging through the alkoxide group), were not particularly active in lactide ROP and no stereocontrol was reported (Table 4). These phosphasalen yttrium complexes showed markedly different behaviour giving very high activities for lactide polymerisation and heteroselectivity to rac-LA ROP. In fact, the electronic properties of the iminophosphorane functional group, in the phosphasalen ligand, differ notably from the imine moiety in the salen analogue. Figure 27 recalls the divergent electronic properties of the ligands, as a result from NBO (Natural Bond Orbital) analyses on the structures of model compounds optimized using the Density Functional Theory, with the B3PW91 as the functional and the 6-31G\* basis set.

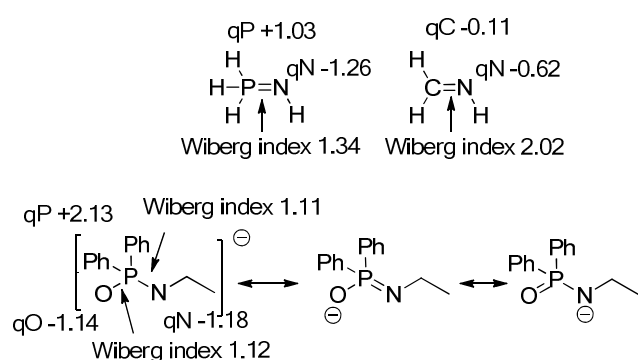
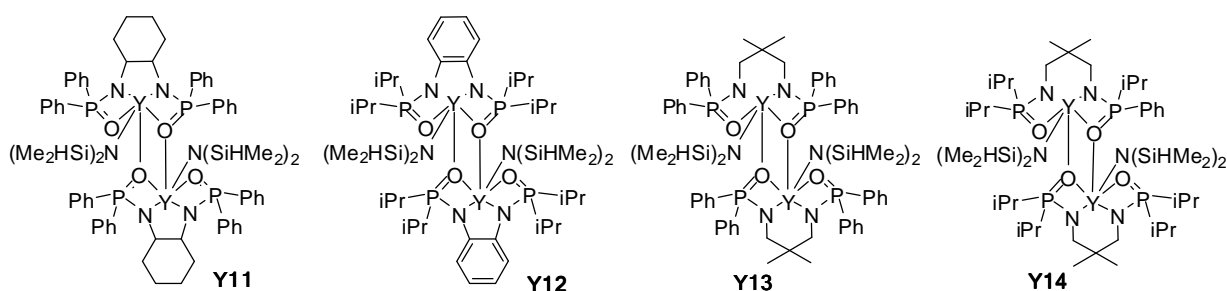


Figure 27. Comparisons of the Wiberg indices and NBO charge for various model compounds, calculated using Gaussian09, using B3PW91 functional and 6-31G\* basis set.

With this in mind, it is interesting to re-examine a series of bis(phosphinic)diamido yttrium complexes, developed by the Williams' group and show excellent activities in lactide polymerization.<sup>28a, b, 28d</sup> All the complexes have tetradentate bis(phosphinic amido) ancillary

ligands, coordinated to the yttrium centres via the N and O atoms. They were highly active; furthermore a monomeric complex gave highly enriched heterotactic PLA ( $P_s=0.85$ ) (whereas the dimeric complexes give moderately heterotactic PLA). An NBO analysis performed on a model of diphenylphosphinic amido derivative shows some similarities with iminophosphorane derivatives (Figure 27). Indeed the NBO charges at P, N, and O were calculated at +2.13, -1.18, and -1.14, respectively. Moreover, both the P-N, and P-O bond indices are close to 1. This is in agreement with the existence of two resonance forms for this functionality, one of which corresponds to an iminophosphorane ( $N=P-O^-$ ). The X-ray crystal structures of these complexes show that the P-N bond lengths and the geometries at the P and N centers fit with the ligands having some degree of iminophosphorane functionality (Scheme 20, Table 5).



Scheme 20. Dimeric bis(phosphinic amido) yttrium complexes, by Williams and coworkers

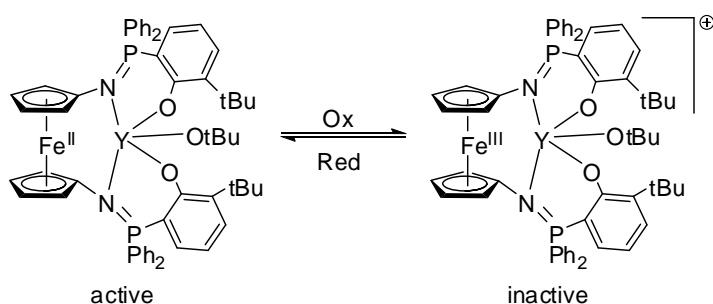
Table 5. Structural data for dimeric bis(phosphinic amido) and phosphasalen yttrium complexes (Y-N and Y-O distances relative to ancillary ligand)

| Complex                   | P-N (Å)                | Y-N (Å)                 | Y-O (Å)                 |
|---------------------------|------------------------|-------------------------|-------------------------|
| <b>Y11</b> <sup>28b</sup> | 1.576(2), 1.568(2)     | 2.336(2), 2.395(2)      | 2.3336(17), 2.4444(16)  |
| <b>Y12</b> <sup>28b</sup> | 1.5907(18), 1.5989(18) | 2.3560(17), 2.3348(17)  | 2.3409(15), 2.4720(13)  |
| <b>Y13</b> <sup>28b</sup> | 1.5922(13), 1.5821(12) | 2.3681(12), 2.3542(12), | 2.3548(10), 2.4621(10)  |
| <b>Y14</b> <sup>34</sup>  | 1.596(6), 1.582(6)     | 2.216(6), 2.345(6)      | 2.315(5), 2.524(5)      |
| <b>43</b>                 | 1.598(3), 1.595(3)     | 2.415(3), 2.438(3)      | 2.182(3), 2.213(3),     |
| <b>44</b>                 | 1.596(3), 1.586(3)     | 2.398(3), 2.372(3)      | 2.203(3), 2.338(2),     |
| <b>45</b>                 | 1.595(2), 1.584(2)     | 2.375(2), 2.324(2)      | 2.1671(318), 2.1704(18) |

Experimentally, it appears that this iminophosphorane ligand motif accelerates ROP at the yttrium centres, leading to much enhanced activities and even enabling stereochemical control. The iminophosphorane functionality is significantly more electron donating than the imine analogue in the salen ligand. In lactide ROP, there is a balance between requiring a Lewis acidic

yttrium centre to facilitate lactide coordination whilst also requiring a labile yttrium alkoxide bond to accelerate insertion of the lactide unit. Thus, it seems that a better donor ligand is desirable, this may be due to weakening or labilizing of the yttrium-alkoxide bond and acceleration of the insertion step.

Diaconescu and coworkers recently reported a switchable activity in lactide ROP using an yttrium alkoxide complex, with a tetradentate ligand featuring in the backbone an iminophosphorane linked to a ferrocene.<sup>35</sup> Whereas the complex bearing the neutral ligand (featuring a ferrocene), with an electron rich nitrogen donor group is active for the ROP of lactide, the oxidized complex (featuring a ferrocenium) is completely inactive (Scheme 21). Thus, the polymerization activity is switched ‘off’ when the electron density at the nitrogen decreases. It was hypothesized that although the insertion of the monomer to the oxidized complex is possible, the propagation from such a species is unfavourable, since the alkoxide would be connected to a more electron deficient metal.



Scheme 21. Redox control polymerization, by Diaconescu and coworkers.

This observation strongly supports the benefit of a good donor ligand for the ROP of lactide. The flexibility of the ligand could also play an important role, as the coordination geometry at yttrium is expected to change during the coordination-insertion steps in ROP, and a more flexible ligand could be beneficial.

#### 4. DFT calculations

Following the experimental study on the catalytic activity of complex **45** on ROP of lactide, theoretical studies have been carried out in order to investigate the mechanism of the reaction and to find out, if possible, factors that are important for the ROP of lactide using such systems.

Density Functional Theory (DFT) calculations were performed on these two complexes with the Gaussian 03 set of programs<sup>36</sup> in combination with the B3PW91 functional<sup>37</sup>. The choice of basis sets and functions was made based on the computational costs and validated by comparisons between the optimised and experimental structures of complex **45** (details of which would not be presented here). The optimised structures were characterised by vibration frequencies calculations. Yttrium was represented by the nonrelativistic Stuttgart effective core

potential ECP28MHF and the associated basis set. In fact, on this system, it had been tested that the use of relativistic Stuttgart effective core potential ECP28MDF and the associated basis set ECP28MDF-VTZ gave almost the same values of activation energies for several steps of the mechanism, so nonrelativistic effective core potential was chosen in order to reduce the calculation cost. Phosphorus atoms were described by the SDDALL basis set<sup>38</sup> with Stuttgart potentials, reinforced with polarisation functions P ( $\zeta(d) = 0.340$ ).<sup>39</sup> All other atoms were described with the 6-31G\* Pople basis set.<sup>40</sup> Tert-butyl groups were not represented with lower basis sets because steric interactions have been shown to be important in these systems, and calculations using 3-21G basis set for tert-butyl groups gave significantly different activation energies than those using 6-31G\* basis sets.

#### 4.1. Initiation step

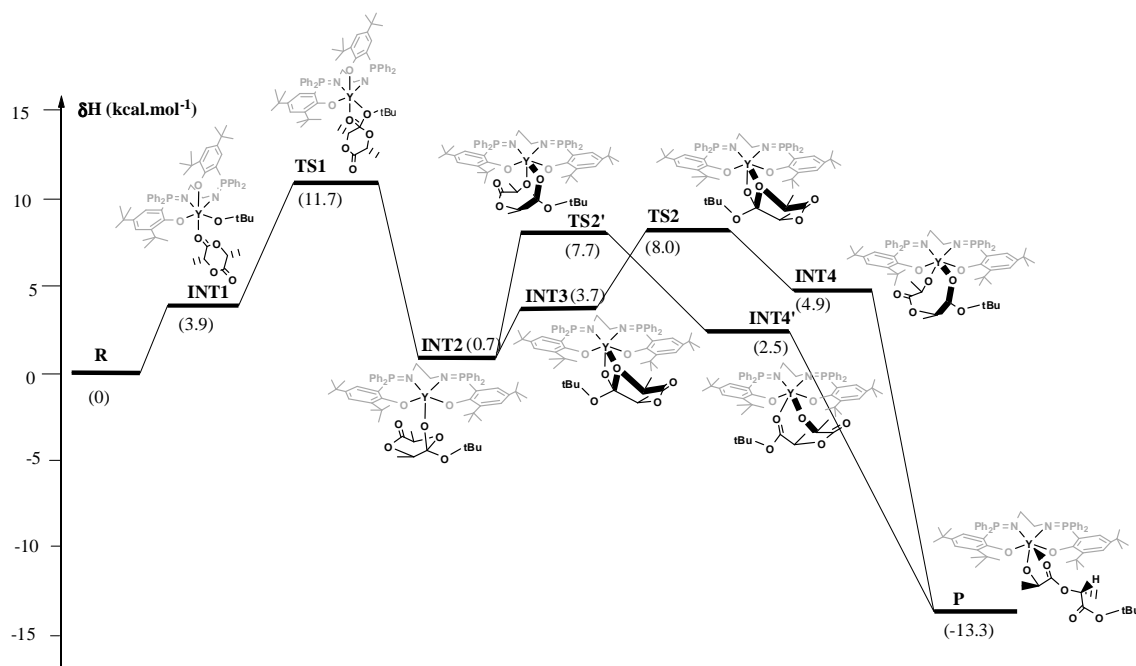
Experimental data on the ROP of lactide initiated by complex **45** were strongly in favor of a coordination-insertion mechanism (Scheme 8). Thus the calculations were directed into this mechanism and were divided into several steps: coordination of the lactide unit to the yttrium center, interaction of this lactide with *tert*-butoxide group in close proximity, leading to the nucleophilic addition of the alkoxide to the coordinated carbonyl function of the lactide, followed by the ring opening of the lactide unit which occurs at this carbon.

DFT calculations have been done to determine the structure of **45** in THF, and more precisely, to see whether THF could coordinate to the yttrium center. In fact, one optimized structure of **6**.THF was found. The complex adopts a distorted octahedral geometry, the phosphasalen ligand takes the four positions of the equatorial plane, THF and the *tert*-butoxide group occupy the axial positions. It has been found that  $\Delta H$  of the reaction **45**+THF  $\rightleftharpoons$  **45**.THF (\*) is equal to -0.9 kcal/mol, taken into account that THF is solvent, the coordination of THF is likely in solution. Therefore, the mechanism has been calculated starting from **45**.THF. It is however worth noting that because the value of  $\Delta H$  for (\*) is very small, even when supposing that the active species be **45**, almost the same values of  $\Delta H$  for the steps in the mechanism would be obtained.

Coordination of two molecules of THF to yttrium center in **45** is not possible, as has been shown by DFT calculations: optimization of the supposed molecule **45**.2THF led to the structure of **45**.THF and one separated THF molecule. This is indicative that for complex **45**, hepta-coordination is not possible or strongly disfavored. This would still be seen in the following steps.

Arbitrarily, the first inserted lactide unit was chosen to be (R,R)-lactide. The lactide coordinates to the yttrium center and takes an equatorial position, “pushing” one phenoxide arm to the axial position, and the phosphasalen changes from *trans*-configuration to *cis*-configuration. From this intermediate **INT1**, intramolecular nucleophilic reaction takes place between the *tert*-butoxide group and the activated carbonyl function of the coordinated lactide. The transition state **TS1** is characterised by a four-member ring formed between the yttrium, the two atoms O<sub>carbonyl</sub> and O<sub>alkoxide</sub>, and the C<sub>carbonyl</sub> atom which had become tetrahedral. The C<sub>carbonyl</sub>-O<sub>carbonyl</sub> bond is

lengthened (1.25 Å vs 1.21 Å in **INT1**), as well as the Y-O<sub>alkoxide</sub> bond (2.34 Å vs 2.09 Å in **INT1**), whereas the Y-O<sub>carbonyl</sub> bond is shortened (2.32 Å vs 2.53 Å in **INT1**). The C<sub>carbonyl</sub>-O<sub>alkoxide</sub> distance is of 1.91 Å.



Scheme 22. Initiation step for ROP of lactide catalysed by **45**.

The nucleophilic attack results in the formation of intermediate **INT2**. In this intermediate, the Y-O<sub>alkoxide</sub> bond is completely broken and the complex recover its distorted square-based pyramidal geometry as in **45**, the phosphasalen ligand changes configuration from *cis*- to *trans*-.

Two possible pathways are possible for the ring-opening step. In the first pathway, **INT2** directly undergoes the ring-opening reaction, as the O<sub>lactide ring</sub> approaches the yttrium centre. This results in the intermediate **INT4'**, in which both the O<sub>carbonyl</sub> and the O<sub>lactide ring</sub> atoms still coordinate to the metal centre, but the C<sub>carbonyl</sub>-O<sub>lactide ring</sub> bond has been completely broken. The corresponding transition state is characterised by a four membered-ring composed of Y, O<sub>lactide ring</sub>, C<sub>carbonyl</sub>, and O<sub>carbonyl</sub> atoms.

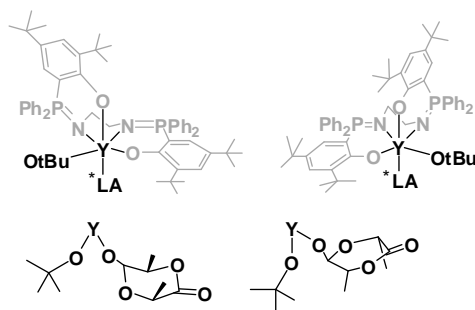
In the second pathway, rotation of the lactide unit around the Y-O<sub>carbonyl</sub> bond leads to the formation of the intermediate **INT3**, in which a four-membered ring is formed between Y, C<sub>carbonyl</sub>, O<sub>carbonyl</sub>, and O<sub>lactide ring</sub> atoms. This intermediate is higher in energy than **INT2**, and the Y-O<sub>lactideRing</sub> bond is quite weak, as evidenced by the long bondlength (2.73 Å). In the corresponding transition state **TS2** this four-membered ring is still maintained, but with significant changes in bond lengths: elongation of the C<sub>carbonyl</sub>-O<sub>lactide ring</sub> bond and shortening of the C<sub>carbonyl</sub>-O<sub>carbonyl</sub>. The resulted intermediate **INT4** resembles **INT4'** described above, but with different relative orientation of Y-O<sub>lactideRing</sub> and Y-O<sub>carbonyl</sub> bonds (Scheme 22).



Both intermediates **INT4** and **INT4'** evolve towards the final product **P**, characterised by a five-membered ring formed from the coordination of the other  $O_{\text{carbonyl}}$  atom of the former lactide unit to the yttrium center, the phosphasalen ligand being in trans-configuration. This product is the most stable one. Another possible product, **P'**, deprived of this coordination, adopts distorted square-based pyramidal geometry and is higher in energy than **P** of about 3 kcal/mol. In total, the formation of these final products are exothermic, which recompense the possible loss of entropy.

Several observations have been drawn out concerning the mechanism:

1) In order for the insertion to occur, the intermediates resulting from the coordination of lactide to **45** must have the phosphasalen ligand in *cis*-configuration, so that the alkoxide and the lactide are in *cis*-position, close to each other.



Scheme 23. Illustration for the relative configurations

In total, eight configurations could be envisaged, arising from the possibilities of 1) the *tert*-butoxide group to be either on axial or equatorial positions; 2) the (R,R)-lactide to place either with the methyl groups in the same or opposite direction of the alkoxide group; 3) because the lactide is chiral, with the same position of LA and OtBu groups, two *cis*-conformations of the phosphasalen ligand lead to two different conformations of the product, of different energies (Scheme 23).

In all cases, the enthalpies of these coordination reactions are higher than the total enthalpies of the starting compounds by 3.8-5.4 kcal/mol. These positive and close values suggest that one has to look into the activation barrier of the insertion in order to know which configuration gives better chance for the following steps to occur.

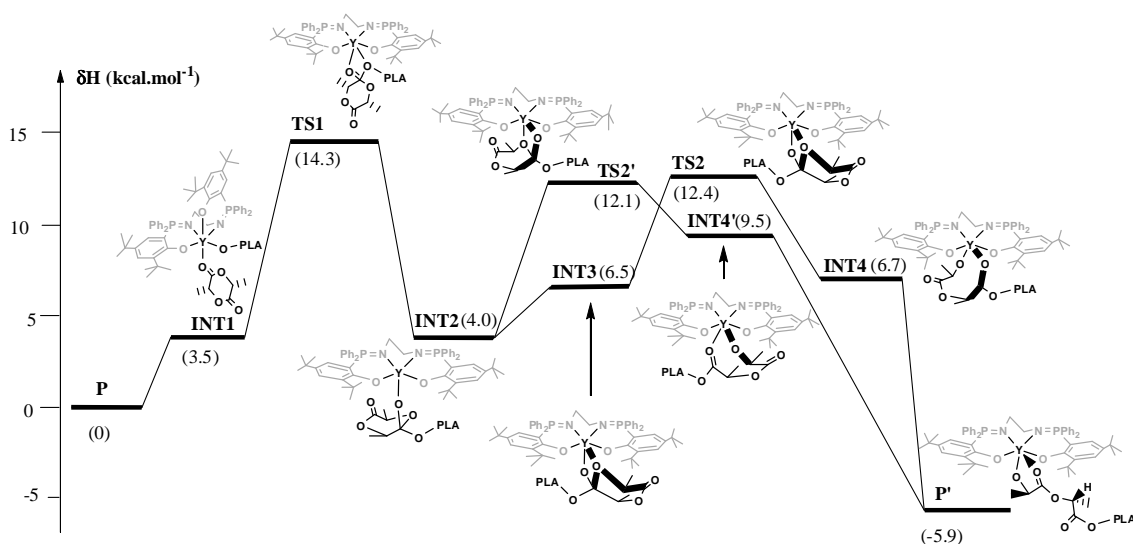
Transition states for the insertion step resulting from such configurations have been determined. **TS1** is the transition state with the lowest activation barrier. All the transition states corresponding to other conformations of **INT1** are higher in energy of 2-5kcal/mol. Steric interactions between the phosphasalen ligand (mainly from the *tert*-butyl and phenyl groups), the *tert*-butoxide group, and the methyl groups on the lactide are important. This explains the necessity of representing the whole molecule in DFT calculations, as well as the difficulty of modeling them.

2) The energy barrier for the ring-opening step is lower than the one for the insertion step. The latter is thus the rate-determining step for the initiation. Not that for the ring-opening step, both transition states **TS2** and **TS2'** have approximately the same energy. Thus it seems that steric influences in this step are not very important.

3) The configuration of the PLA chain is very important and it has been observed that slightly different configurations of this chain may lead to energy difference of several kcal/mol. The configuration with the lowest energy was found to be the one with stabilizing hydrogen bonds between the  $O_{\text{carbonyl}}$  atoms and the appropriate hydrogen(s) in close proximity, and minimized steric repulsion between methyl and *tert*-butyl groups.

## 2. Propagation step

The starting species for the first propagation step was supposed to be the most stable product resulted from the initiation step (**P**). The second lactide unit was chosen to be of the same configuration as the first one, i.e. (R,R)-lactide, so that comparisons could be made easily between the initiation and propagation step.



Scheme 24. First propagation step for the ROP of lactide initiated by **45**.

The profile of the propagation step in the ROP of lactide by **45** resembles a lot to the one of the initiation step. All transition states and intermediates have similar conformations as the corresponding species in the initiation step, with the exception of **TS1**. The phosphasalen ligand in this transition state adopts a *trans*- configuration, while the first transition state for the initiation step has the ligand in *cis*- configuration. All the energies for the intermediates and transition states in the propagation step are slightly higher than the ones in the initiation step.

In summary, from the calculations for the initiation and the first propagation step of the ROP of *rac*-lactide initiated by **45**, it could be seen that

1) the activation energies are small, thus explaining the excellent rate of this polymerization

- 2) the polymerization is exothermic. The negative value of enthalpy is the driving force of the polymerisation.
- 3) the rate-determining step seems to be the insertion step. In this step, steric interactions are very important and probably determinant for the stereoselectivities of the ROP of lactide.
- 4) the ring-opening step is not much influenced by steric interactions
- 5) the most stable configuration of the propagating chain is characterised by a five-membered ring formed from the coordination of the other O<sub>carbonyl</sub> atom of the former lactide unit to the yttrium center.

When the second lactide unit was chosen to be (S,S)-lactide in order to modeling the heteroselectivity of the ROP initiated with **45**, it has been found that: 1) the structures and energies of the intermediates are very close to the ones obtained from the above calculations, supposing that the second lactide unit is (R,R)-lactide; 2) the energies of the transition states are slightly higher than the ones obtained from the above calculations, of less than 1 kcal/mol, in gas-phase and in solution (model PCM). These very close values did not allow to draw any conclusion about the heteroselectivity of the ROP of *rac*-lactide initiated by **45**.

As it seems that steric factors are important for the performance of **45** in the ROP of *rac*-lactide, we decided to prepare other yttrium complexes with different steric properties and determine their activities of the ROP of lactide.

## IV. Monomeric yttrium complexes: factors influencing the activity

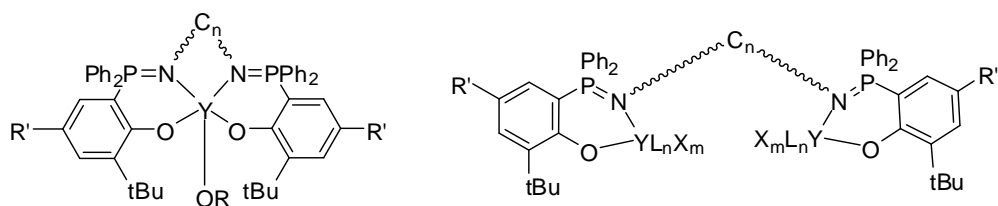
### 1. New yttrium phosphasalen complexes

#### *1.1 New complexes with modified steric properties*

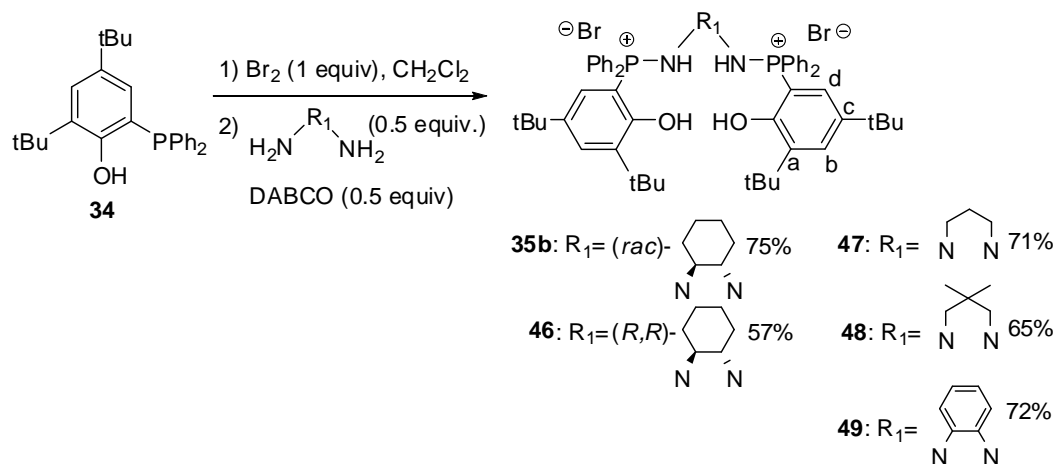
Encouraged by the excellent performance of the monomeric yttrium complex **45**, we decided to synthesise more complexes based on similar systems in order to investigate, experimentally, the factors underlying the rate and stereoselectivity of ROP of lactide by yttrium-phosphasalen systems. Monomeric complexes were targeted as ROP of lactide initiated by dimeric phosphasalen complexes were shown to be complex and less efficient.

In order to achieve well defined monomeric complexes, the presence of bulky substituents on the *ortho*-position of the phenoxide rings is essential. For this purpose, *tert*-butyl groups are maintained at this position. Furthermore, for the formation of well defined monomeric complexes, the diamine bridge must not be too large, otherwise one phosphasalen ligand could coordinate two yttrium centers by the two sides of the ligand, each containing one phenoxide

and one iminophosphorane group (Scheme 25). The diamine bridge are thus chosen to be the ones with 2 or 3 carbons.

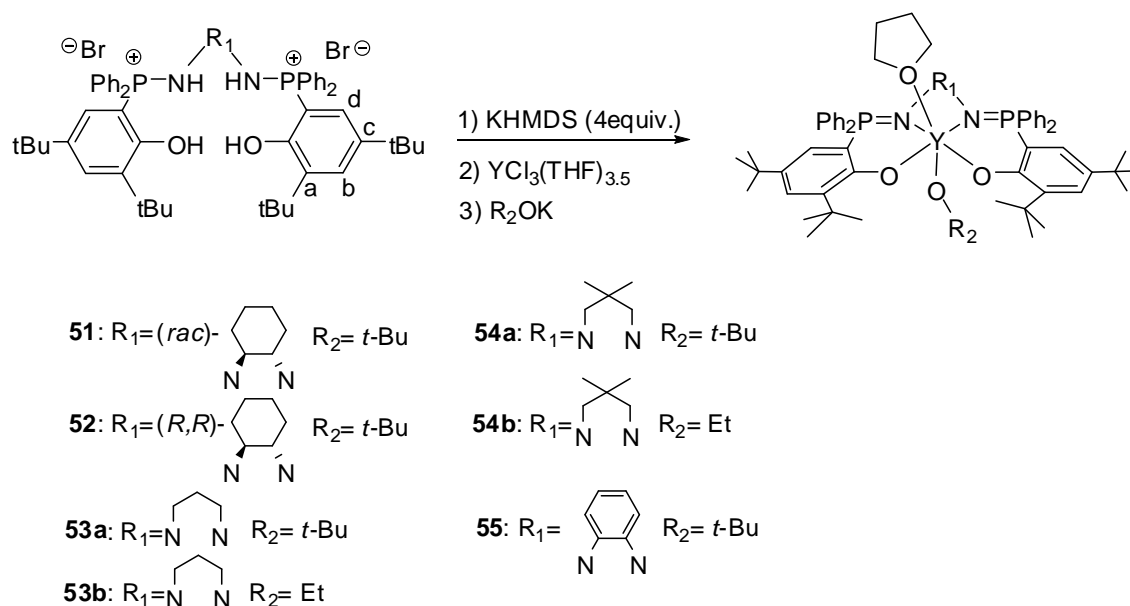


Scheme 25. (left) Monomeric yttrium phosphasalen complexes, small diamine bridge. (right) One phosphasalen ligand coordinated to two yttrium centers, large diamine bridge.



Scheme 26. New Phosphasalen proligands having C2 and C3 diamine bridges

The synthesis of **35b** has been described in chapter 4. The proligands **46-49** were synthesized from 2,4-di-tert-butyl-6-phosphinophenol by the Kisanov reaction with dibromine and the appropriate diamines in dichloromethane, using DABCO as base. After evaporation of dichloromethane, the mixture was taken in THF in order to remove insoluble DABCO salts. THF was evaporated and the solid was washed with Et<sub>2</sub>O and the product was isolated as a white solid. This method gave the phosphasalen proligands **46-49** in high yield. They were all fully characterized by NMR multinuclear experiments and elemental analysis.



Scheme 27. Synthesis of yttrium phosphasalen complexes

Addition of 4 equiv. of KHMDS into a slurry of the phosphasalen proligands in THF gave cloudy colorless solutions, indicating the formation of anionic phosphasalen ligands. Completeness of the reaction was verified by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra which showed singlets in much higher field compared to the signals of aminophosphonium salt in the proligands (+18 ppm instead of +38.5 ppm to for **35b** and **46**, +23.8 ppm instead of +40.4 ppm for **47**, +22.3 ppm instead of +41.7 ppm for **48**, +13.2 ppm instead of +38.9 ppm for **49**).

After removal of insoluble potassium salts by centrifugation, addition of  $[\text{YCl}_3(\text{THF})_{3.5}]$  into this solution gave a unique product which showed one singlet at lower field in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, compared to the phosphasalen ligands. This indicated the formation of yttrium phosphasalen complexes. Finally, addition of potassium ethoxide or tert-butoxide into the mixture caused the nucleophilic substitution which yielded the desired phosphasalen alkoxide complexes, with in general an upfield shift in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. Evaporation of THF and recrystallisation in cyclohexane gave the products as colorless crystals or white solids.

All the complexes have been fully characterized by NMR experiments and elemental analysis. In some cases, crystals suitable for X-ray diffraction has been obtained, allowing to determine the structures of the complexes without ambiguity.

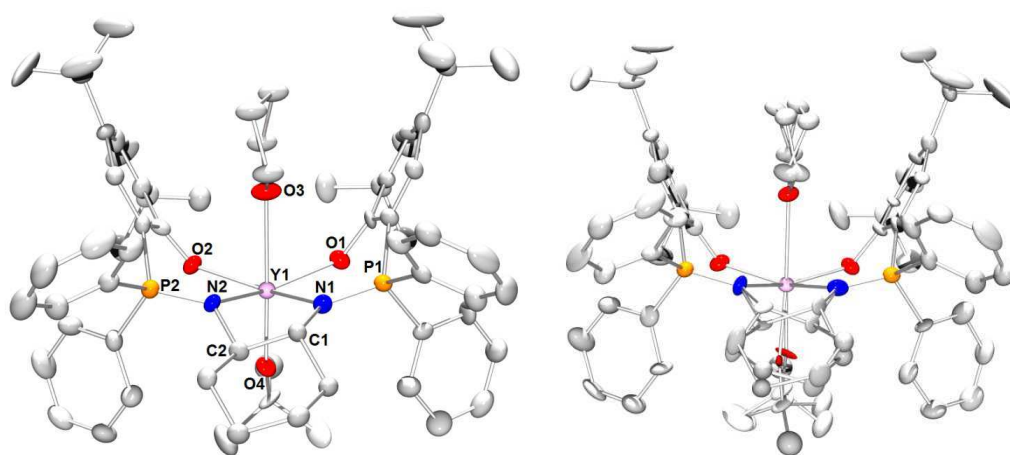


Figure 28. (left) ORTEP view of the solid state structure of complex **52**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 2.23(6), Y1-O2 2.25(6), Y1-O3 2.53(6), Y1-O4 2.04(2), Y1-N1 2.38(7), Y1-N2 2.40(7), P1-N1 1.59(7), P2-N2 1.59(7), O1-Y1-N1 82(2), N1-Y1-N2 70(1), N2-Y1-O2 83(2), O1-Y1-O2 120(1), O2-Y1-O3 84(3), O2-Y1-O4 95(2), O3-Y1-O4 179(3), O2-Y1-N1 151(2), O1-Y1-N2 148(2). (right) ORTEP view of the solid state structure of complex **51**, showing the existence of two isomers (R,R) and (S,S) with equal percentage. Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity.

Structure of complex **51**, prepared from the phosphasalen ligand with *rac*-1,2-diaminocyclohexane backbone has been resolved. As expected, the two isomers having (R,R) and (S,S)-1,2-diaminocyclohexane backbone cocrystallised in 50/50 proportion (Figure 28), each of them could be seen as a mirror image of each other. Complex **52** featuring the enantiometrically pure (R,R)-1,2-diaminocyclohexane backbone present the same structural data as the one resolved for complex **51**. It has yttrium center in octahedral geometry: the two nitrogen and two oxygen atoms of the phosphasalen ligand occupy the equatorial plane, the tert-butoxide group and one molecule of THF occupy the axial positions. This is very different from complex **45** which also features a C2-backbone diamine and has a penta-coordinated yttrium center.

The bond lengths Y-O<sub>phosphasalen</sub> and Y-N in **52** are almost comparable to those in **45** (2.23 (6) Å and 2.25(6) Å vs 2.1671(318) Å and 2.1704(318) Å for Y-O bonds, 2.38(7) Å and 2.40(7) Å vs 2.375(2) Å and 2.324(2) Å for Y-N bonds), and the P-N, N-C1/2 and C1-C2 bondlengths in **52** are sensibly the same as those in **45**. Thus, the reason why an extra THF molecule could be accommodated in **52**, rather in **45** does not lay on the hypothesis that bondlengths in the phosphasalen ligand of **52** are longer than those in **45**. It is thought that for **52**, steric interaction between the phenyl groups on P atoms with carbons and hydrogen atoms on the cyclohexylene backbone prevents the contraction of phosphasalen ligand as with **45**, and thus resulted in an “exposed” space around the yttrium center where THF molecule is coordinated.

Probably for the same reason, complex **55** featuring *ortho*-phenylene diamine also present a coordinated THF (Figure 29). It adopts a distorted octahedral geometry, the phosphasalen ligand

occupying the 4 equatorial positions, the two axial positions being occupied by the tert-butoxide group and THF molecule. In general, Y-O<sub>phosphasalén</sub> and Y-N bond length values in **55** are very close to the ones in **52** and **45**.

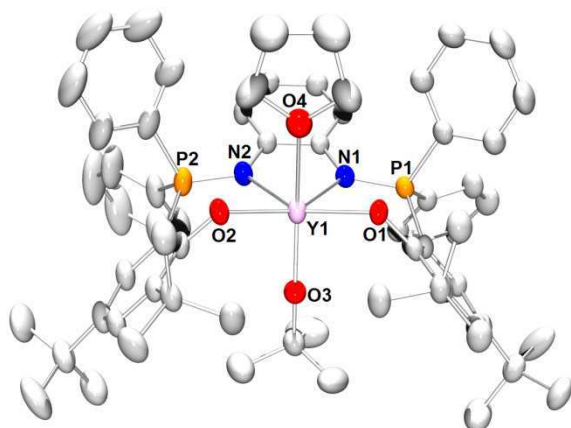


Figure 29. ORTEP view of the solid state structure of complex **55**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 2.243(3), Y1-O2 2.220(3), Y1-O3 2.040(3), Y1-O4 2.467(3), Y1-N1 2.389(4), Y1-N2 2.406(3), P1-N1 1.606(4), P2-N2 1.604(4), O1-Y1-N1 80.8(1), N1-Y1-N2 68.3(1), N2-Y1-O2 80.9(1), O1-Y1-O2 126.1(1), O2-Y1-O3 95.5(1), O2-Y1-O4 75.4(1), O3-Y1-O4 160.6(1), O2-Y1-N1 147.6(1), O1-Y1-N2 146.9(1)

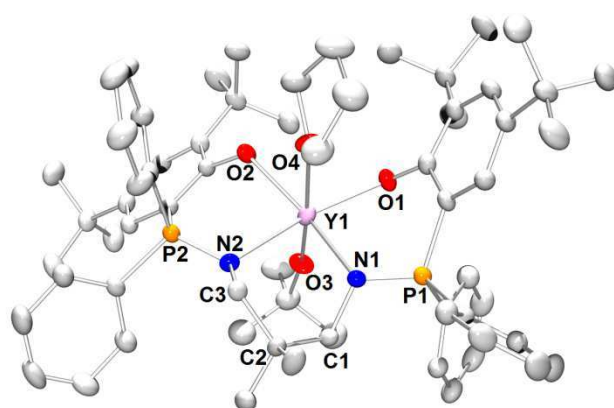
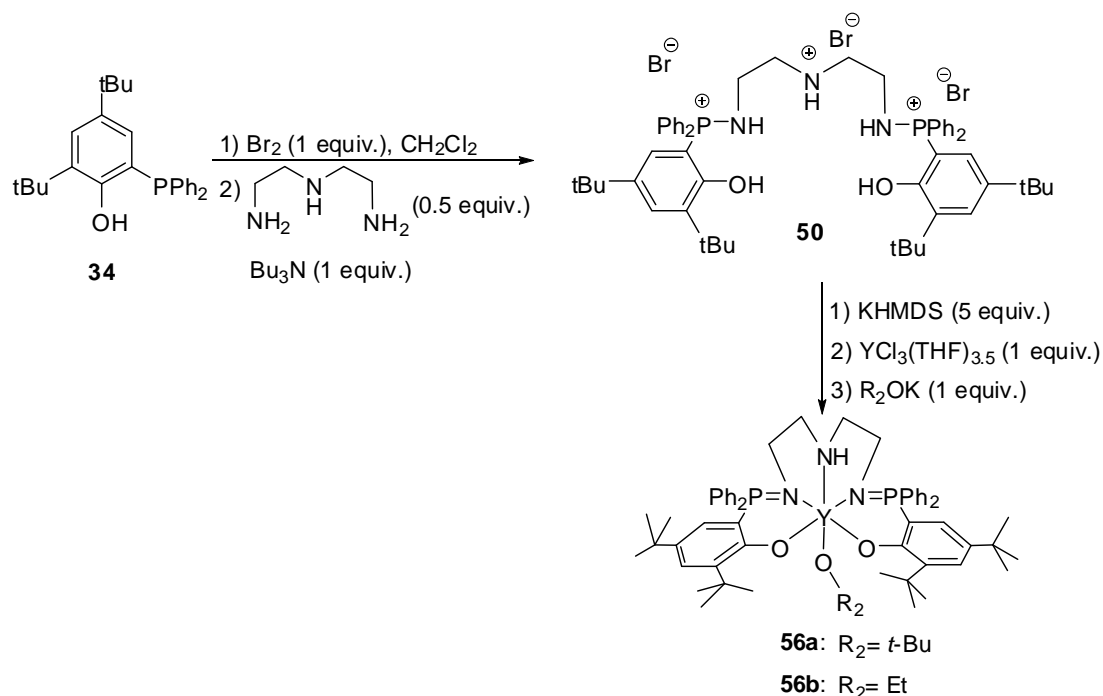


Figure 30. ORTEP view of the solid state structure of complex **54a**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 2.232(3), Y1-O2 2.191(3), Y1-O3 2.072(3), Y1-O4 2.462(3), Y1-N1 2.432(4), Y1-N2 2.402(4), P1-N1 1.597(4), P2-N2 1.599(4), O1-Y1-N1 84.0(1), N1-Y1-N2 80.8(1), N2-Y1-O2 83.2(1), O1-Y1-O2 109.3(1), O2-Y1-O3 95.6(1), O2-Y1-O4 78.3(1), O3-Y1-O4 173.5(1), O2-Y1-N1 155.8(1), O1-Y1-N2 163.7(1)

A phosphasalén ligand with C3 diamine backbone, which is longer than the ethylene diamine backbone, logically give a larger “exposed” space around the yttrium center compared to complex **45**. Thus, complex **54a** featuring a 2,2-dimethyl-1,3-diaminopropane backbone also has a coordinated THF molecule (Figure 30). No particularity has been found for the structural data of this complex.

Though X-ray structures has not obtained for other phosphasalen complexes of this series, based on these observations, it is supposed that these compounds would also carry a coordinated THF, which has been attested by elemental analysis and NMR analysis.

A modified phosphasalen ligand presenting a supplementary coordination site on the diamine backbone has also been prepared (Scheme 28). Kisanov reaction on 2,4-di-*tert*-butyl-6-phosphinophenol with dibromine and diethylene triamine in dichloromethane, using Bu<sub>3</sub>N (only in 1 equiv. quantity) as base yielded a cloudy solution. After evaporation of dichloromethane, the mixture was taken in THF and the product precipitated, giving a white solid, which was isolated by centrifugation and washed several times with THF in order to remove tributylammonium salt. After drying under vacuum, the phosphasalen proligand **50** was isolated in high yield (78%) and was fully characterized by NMR multinuclear experiments and elemental analysis.



Scheme 28. Synthesis of yttrium complex of a modified penta-dentate phosphasalen ligand.

Addition of 5 equiv. of KHMDS into a slurry of the phosphasalen proligands **50** in THF gave cloudy colorless solutions after 4h, indicating the formation of anionic phosphasalen ligand. In <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, a unique singlet was observed at 24.2 ppm, thus in much higher field compared to the signal of aminophosphonium salt in the proligand (41.8 ppm). Insoluble potassium salts were removed by centrifugation. Addition of [YCl<sub>3</sub>(THF)<sub>3.5</sub>] into the resulting solution gave a unique product which showed one singlet at lower field in <sup>31</sup>P{<sup>1</sup>H} NMR spectra (35.0 ppm). This indicated the clean formation of yttrium phosphasalen complexes. Finally, addition of potassium ethoxide or *tert*-butoxide into the mixture led to the nucleophilic substitution which yielded the desired phosphasalen alkoxide complexes **56a,b**, which presented



a unique singlet in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (+33.6 ppm for **56a**, 34.2 ppm for **56b**). Evaporation of THF and recrystallisation in cyclohexane gave the products as white solids. All the complexes have been fully characterized by NMR experiments and elemental analysis.

No crystals of suitable size for X-ray diffraction has been obtained for complexes **56a,b**. The few crystals obtained from the crystallization tests were those of partly hydrolysed compounds. One resolved structure is presented in Figure 31. Though this structure is not the one of the desired or isolated product, based on this structure, several observations could be made: 1) the amine group on the backbone is coordinated strongly to the yttrium center; 2) even though the phosphasalen ligand takes up to five coordination positions, there's still space around the yttrium center to coordinate two more groups (this is important, because the ROP of lactide could thus proceed).

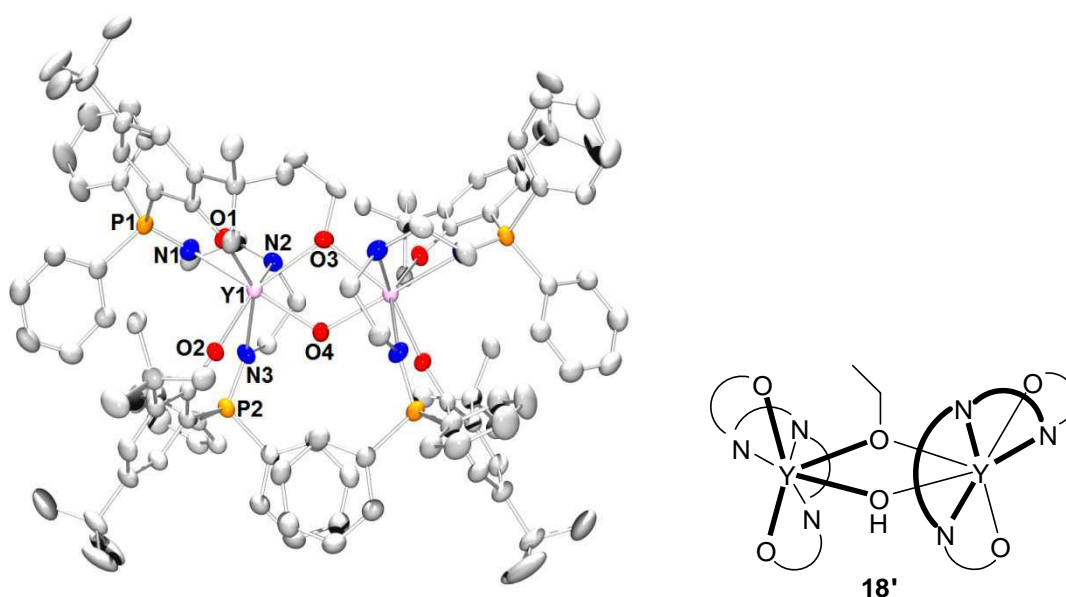
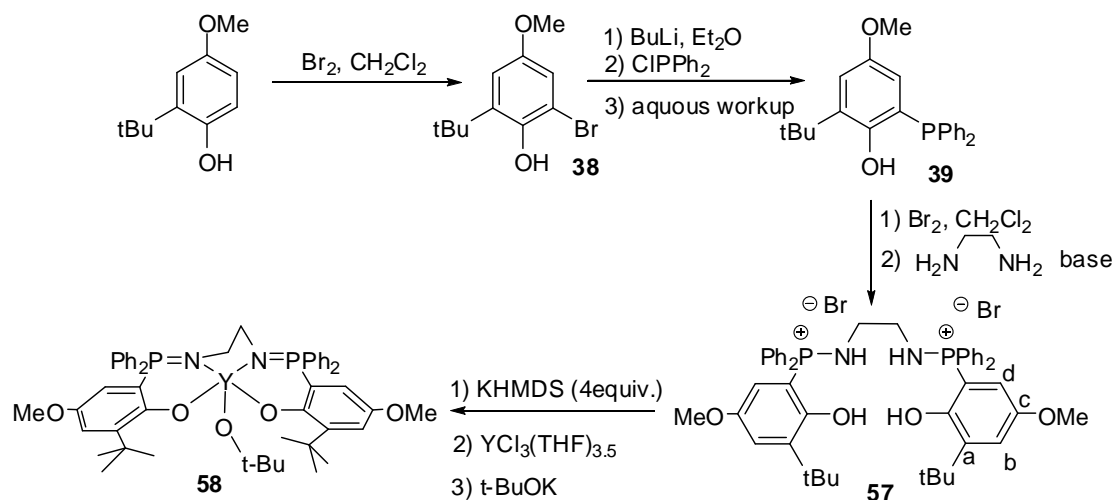


Figure 31. ORTEP view of the solid state structure of complex one yttrium complex with pentadentate phosphasalen ligand **56'**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 2.271(2), Y1-O2 2.230(2), Y1-O3 2.411(2), Y1-O4 2.248(2), Y1-N1 2.433(3), Y1-N2 2.511(3), Y1-N3 2.517(3), P1-N1 1.583(3), P2-N3 1.596(3), O1-Y1-N1 75.7(1), N1-Y1-N2 68.1(1), N2-Y1-N3 65.9(1), N3-Y1-O2 74.5(1), O3-Y1-O4 64.8(1).

## 1.2 New complexes with modified electronic properties

For all the phosphasalen yttrium alkoxide complexes described above, only modifications on the diamine backbone have been made with the main objective of modifying the steric properties of the yttrium complexes. In fact, based on the structures of yttrium phosphasalen complexes obtained by X-ray diffraction experiments, it could be seen that substituents on the phenoxide rings, except the ones at the *ortho*-position of the phenoxide, would not exert much influence on the steric properties of the complexes. However, these substituents may have great influence in terms of electronic properties on the phenoxide, thus on the yttrium complexes. We thus

targeted the modifications on the phenoxide rings with the objective of modifying the electronic properties. From the earlier observations on the activities of complex **45**, it has been speculated that the better donating ability of the phosphasalen ligand, compared to salen, might contribute largely to the better performance of this complex. We were then interested in the synthesis of the phosphasalen proligand **57** having OMe groups at the *para*-position of the phenoxide rings (Scheme 29).



Scheme 29. Synthesis of the phosphasalen proligand having OMe groups on phenoxide rings, and the corresponding yttrium complex

The bromination of 4-methoxy-2-*tert*-butylphenol with  $\text{Br}_2$  in dichloromethane at  $0^\circ\text{C}$  gave 2-bromo-4-methoxy-6-*tert*-butylphenol **38** which was isolated by chromatography (71%). Reaction of this product with *n*-BuLi, followed by nucleophilic substitution with chlorodiphenylphosphine and aqueous treatment gave the desired product **39** in 84% yield as a yellow viscous oil.

Kirsanov reaction of **39** with bromine and ethylenediamine in the presence of tributylamine as base gave proligand **57** in 69% yield (Scheme 29). This compound, isolated as a white solid, has been fully characterized by multinuclear NMR spectroscopy and elemental analysis. In  $^{31}\text{P}\{^1\text{H}\}$  spectroscopy the equivalent phosphorus atoms of **57** appear as a singlet at  $\delta(\text{CDCl}_3) = 40.1$  ppm, which is very close to the value reported for the phosphasalen proligand having ethylene diamine bridge and *tert*-butyl groups at *ortho*- and *para*- positions of the phenoxide rings (compound **35a**,  $\delta(\text{CDCl}_3) = 40.3$  ppm). In  $^1\text{H}$  NMR spectrum, the bridging ethylene protons of **57** appear as a doublet of doublet, due to couplings with two phosphorus atoms ( $^3J_{\text{P,H}} = 6.5$  Hz,  $^4J_{\text{P,H}} = 2.0$  Hz), at 3.66 ppm. These values are also very close to the chemical shift of the ethylene protons in the same reference ( $\delta(\text{CDCl}_3) = 3.74$  ppm).

Addition of 4 equiv. of  $\text{KHMDs}$  into a slurry of the phosphasalen proligand **57** in THF gave a cloudy colorless solution after 4h, which is indicative of the formation of soluble anionic phosphasalen ligand. Completion of the deprotonation was monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, which showed a unique singlet at 20.3 ppm, thus in much higher field compared to

the signal of aminophosphonium salt in the proligand (40.1 ppm). Insoluble potassium salts were removed by centrifugation. Addition of  $[\text{YCl}_3(\text{THF})_{3.5}]$  into the resulting solution gave a unique product which showed one singlet at lower field in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (31.5 ppm), indicating the clean formation of the yttrium phosphasalen complex. Finally, addition of potassium *tert*-butoxide into the mixture entrained the nucleophilic substitution which yielded the desired phosphasalen alkoxide complex **58**.

Evaporation of THF and recrystallisation in cyclohexane gave the products as white solids. The complex has been fully characterized by NMR experiments and elemental analysis. The complex presented a unique singlet in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra at 31.6 ppm, which is quite close to the chemical shift of the in situ generated phosphasalen yttrium chloride complex, but its  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra evidenced the incorporation of *tert*-butoxide group and its structure as described in Scheme 29.

Though single crystals were easily obtained, they did not diffract well and thus X-ray structure for this compound was not obtained. However, based on NMR data and elemental analysis, it is strongly believed that the structure in solid state and in solution of **58** resembles the one of complex **45**. This compound has the same chemical structure as **58**, but with *tert*-butyl groups at the *para*-positions of the phenoxide rings, instead of methoxy groups.

## 2. Activities

The experiences determining the activities of different synthesized complexes in the ROP of *rac*-lactide were done in collaboration with the Williams group at Imperial College, London. Preliminary results are given in Table 6. The solvent of choice for use at ambient temperature (25 °C) was THF; all experiments were conducted using an initial concentration of lactide of 1 M, so as to enable accurate comparison between the different initiators and additives.

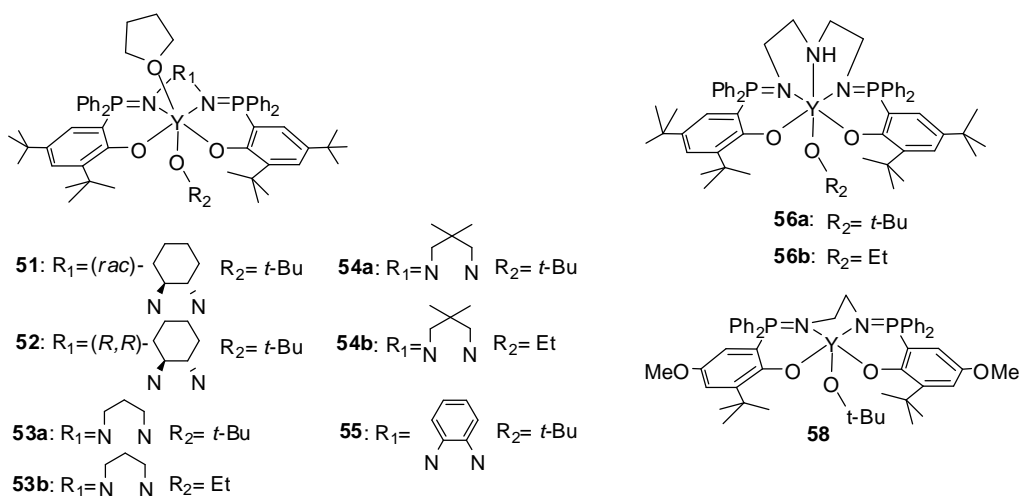


Table 6. Activities of different yttrium phosphasalén complexes in ROP of *rac*-lactide.

| Initiator<br>(I) | [LA] <sub>0</sub> : [I] | Time / s | Conversion <sup>a</sup> /% | $M_n(\text{calc})^b$<br>/ kg mol <sup>-1</sup> | $M_n(\text{exp})^c$<br>/ kg mol <sup>-1</sup> | $k_{\text{obs}}(\text{s}^{-1})^d$ | $P_s$          |
|------------------|-------------------------|----------|----------------------------|--|---|-----------------------------------|----------------|
| <b>45</b>        | 1000:1                  | 45       | 97                         | 140  | 223 (1.34)                                    |                                   | 0.86           |
| <b>51</b>        | 500:1                   | 240      | 89                         | 64.08  | 84.0 (1.05)                                   | 0.0085                            | 0.75           |
| <b>52</b>        | 500:1                   | 240      | 95                         | 68.4   | 120.5 (1.07)                                  | 0.0123                            | 0.76           |
| <b>53a</b>       | 500:1                   | 480      | 84                         | 60.5   | 66.8 (1.07)                                   | 0.0038                            | 0.68           |
| <b>53b</b>       | 500:1                   | 600      | 82                         | -  | -   | 0.0027                            | -              |
| <b>54a</b>       | 500:1                   | 1200     | 91                         | 65.5   | 76.5 (1.02)                                   | 0.0020                            | 0.71           |
| <b>54b</b>       | 500:1                   | 1560     | 89                         | 64.1   | 70.9 (1.01)                                   | 0.0015                            | 0.65           |
| <b>55</b>        | 500:1                   | 360      | 90                         | 64.8   | 196.2 (1.05)                                  | 0.0067                            | 0.83           |
| <b>56a</b>       | 500:1                   | 2160     | 87                         | -  | -   | 0.0011                            | 0.74 ( $P_i$ ) |
| <b>56b</b>       | 500:1                   | 2520     | 84                         | 60.5   | 61.6 (1.04)                                   | 0.0007                            | 0.66 ( $P_i$ ) |
| <b>58</b>        | 1000:1                  | 90       | 83                         |  |   |                                   | 0.85           |

<sup>a</sup> Conversions were determined from the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of the crude products, by integration of the methine resonance assigned to LA ( $\delta$ =4.92 ppm) and to PLA ( $\delta$ =5.00-5.30 ppm).

<sup>b</sup>  $M_n(\text{calc}) = 144 \times [\text{LA}]_0/[\text{I}] \times \% \text{ conversion LA}$ .

<sup>c</sup>  $M_n(\text{exp})$  was determined using GPC, in THF, using multi-angle laser light scattering (GPC-MALLS) according to the method described earlier.<sup>28a, b</sup> The polydispersity index was also determined from GPC,  $\text{PDI} = M_w/M_n$ .

<sup>d</sup> Determined from the gradients of the  $\ln\{[\text{LA}]_0/[\text{LA}]_t\}$  versus time plots, expressed in s<sup>-1</sup>. The reactions are first order in lactide,  $[\text{I}] = 1 \text{ mM}$

As expected from monomeric complexes, all ROP reactions initiated by these yttrium phosphasalén complexes are first-order in lactide. Activities in ROP of lactide vary drastically with the change of the steric properties, induced by modifying the diamine bridge.

Several clear observations can be made:

1) All complexes **51-56a,b** are far less active than complex **45**. Even complexes with C2 linkers like **51**, **52**, **55** have activities that are incomparable with the activity of complex **45**, which could polymerise the lactide in very low catalytic loading (1000/1) in less than one minutes. The reason of such drastic change in catalytic activities lie in fact in the structure of complex. It has been seen, from the complexes characterizations above, that **51**, **52**, **54a**, **55** adopt monomeric

structures, but with the coordination of one molecule of THF, and that it is strongly believe that other complexes (**53a,b**, **54b**) have the same structure, i.e. containing one coordinated THF molecule. As to complex **45**, its solid structure shows no coordination of THF. So probably, because of the coordination of THF, the space for the coordination of lactide is reduced, and the ROP of lactide is rendered more difficult.

Poly lactides obtained from ROP of lactide initiated with complexes **51-56a,b** are less hetero-enriched than those obtained from the action of complex **45**. Once again, the presence of one more ligand (THF in case of **51-55**, NH in case of **56a,b**) seems to render the systems more “rigid” and lowers the stereoselectivity of the ROP.

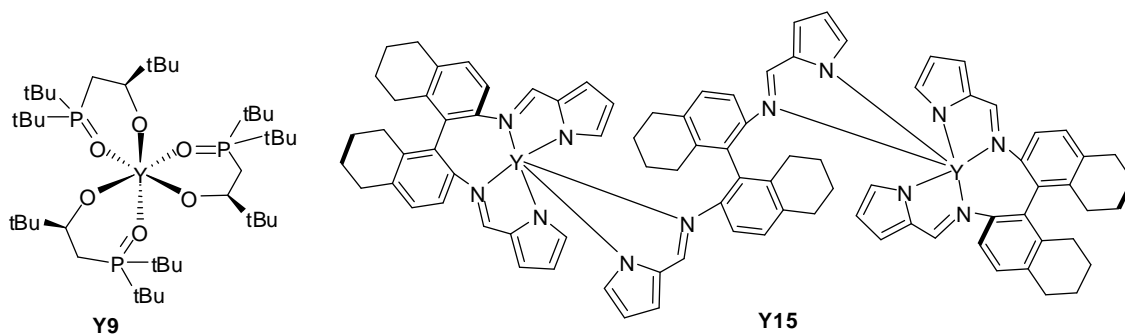
The ideal yttrium complex for the ROP of lactide should thus be the one where the yttrium center is only penta-coordinated. Complex **58**, with the ethylenediamine linker like complex **45**, is expected to adopt the same structure as **45** and to offer a better activity in ROP of lactide compared to complexes **51-56a,b**. Indeed, complex **58** is highly active in ROP of lactide. The polymerization of *rac*-lactide initiated by **58**, using only a very low catalyst loading (LA/I=1000/1), is fast (83% after 90s) and offers highly heterotactic polymers ( $P_s=0.85$ ). The activity and heteroselectivity of complex **58** are thus comparable with the ones of complex **45**.

2) In general, complexes with C2 linkers are much more active than complexes with C3 linkers. For example, for a ratio LA/I=500/1, ROP of *rac*-lactide initiated by the complexes **51**, **52**, **55** require between 240-360s to achieve high conversion (more than 90%), whereas those initiated by **53a,b**, **54a,b** attained conversions about 80% in longer time (480-1600s). This could also be seen by comparing  $k_{obs}$  for ROP of lactide initiated by these complexes.

3) When comparing the performances of complexes with C3 linker, with or without substituents on the diamine linker, it is observed that the introduction of these substituents is not beneficial. Hence, the ROP of lactide initiated by **53a,b** require only 480-600 s to attain approximately the same conversions as those initiated by complexes **54a,b** after more than 900s. The  $k_{obs}$  for ROP initiated by **53a,b** are two or three times higher than  $k_{obs}$  for ROP initiated by **54a,b**. The reason of these differences in performance is probably because the presence of additional bulkiness renders difficult the coordination of lactide to the yttrium center.

4) Interestingly, complexes **56a,b** with additional coordination site of the diamine linker initiated the polymerization of *rac*-lactide to give isotactic polymers. The isotacticity is reasonable at room temperature ( $P_i=0.74$  for **56a** and 0.66 for **56b**) and could be greatly improved by lowering the temperature ( $P_i=0.81$  for **56a** at  $-15^\circ\text{C}$ , and 0.76 for **56b** at  $-18^\circ\text{C}$ ). These complexes are among the very rare examples of yttrium complexes catalyse the formation of isotactic PLA from *rac*-lactide. Other examples are the systems of Arnold and coworkers (**Y9**, Scheme 30),<sup>41</sup> and of Zi and coworkers (**Y15**, Scheme 30).<sup>42</sup> ROP of *rac*-lactide initiated by **Y9** (LA/I=200/1) in dichloromethane, at  $-18^\circ\text{C}$ , achieved 98% of conversion after 10 min and gave polymers with  $P_i=0.81$ . At  $40^\circ\text{C}$  and in THF, complex **Y15** initiated the ROP of *rac*-lactide (LA/I=1000/1), giving 45% of conversion after 3h and polymers with  $P_i=0.67$ .

Compared to these systems, complexes **56a,b** offer better activity and iso-selectivity. More studies about the performances of these two complexes are being carried out.



Scheme 30. Examples of yttrium complexes having isoselectivity in ROP of *rac*-lactide

### 3. Conclusion

New yttrium phosphasalen complexes **51-55a,b**, **58** have been synthesized their activities in ROP of lactide have been studied in order to evaluate the influences of steric and electronic factors in their performance. They are targeted to be monomeric and indeed, X-ray structures obtained for several of them are in accord with this hypothesis. Compared to complex **45**, complexes **51-55** present different C2 and C3 diamine linkers. From this minor change in chemical structure, whereas complex **45** is penta-coordinated and adopts distorted square-based pyramidal geometry, these complexes have hexa-coordinated yttrium centers with the coordination of one THF molecule, completing the coordination sphere constituted by the phosphasalen ligand occupying the four positions of the equatorial plane and the alkoxide group. Because of this difference, these complexes (**51-55**) are much less active than complex **45** in ROP of lactide, likely because the space available for the coordination of lactide is expected to be reduced which renders the ROP difficult. Their heteroselectivities also decrease.

Complex **58** is formed from a ligand with ethylenediamine linker as in **45**, but presenting methoxy groups, which are strong electron donating, instead of *tert*-butyl group at the *para*-positions of the phenoxide rings. This complex is strongly believe to adopt the same distorted square-planar geometry as complex **45**, with a penta-coordinated yttrium center. It presents comparable activity in ROP of lactide as complex **45**.

Complex **56a,b** feature a phosphasalen ligand with an additional amine group which could act as additional coordination site upon complexation. These two complexes are among the rare examples of yttrium complexes presenting isoselectivity in ROP of *rac*-lactide.

These results thus evidence the strong and subtle influence of steric factors in the performance of these yttrium complexes in ROP of *rac*-lactide. In particular, the shift from excellent heteroselectivities achieved with **45** and **58**, to very good isoselectivities with **56a,b** suggests a great potential in tuning the activities and stereoselectivities in yttrium-phosphasalen complexes by careful design of the phosphasalen ligands.

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## Conclusion

The presented work describes the development of new multidentate ligands combining iminophosphorane and anionic donors such as thiolate or phenolate. These ligands can be easily synthesised from inexpensive, readily available starting materials and in large scale.

Chapter 1 is centered on the development of bidentate ligands [S, P=N], taking into account the importance of sulfur-containing ligands in nature and in coordination chemistry. The synthesis of such ligands relied on ortho-lithiation reaction. Working on such syntheses, we discovered the conditions for a clean nucleophilic substitution on iminophosphorane. This reaction opened a way to various mixed bidentate ligands combining iminophosphorane and different heteroatoms-containing groups (phosphine, phosphole, silane, borane, etc) with a special ligand skeleton [N=P-CH<sub>2</sub>-X]. The thiolate-containing ligand having such skeleton showed a great coordination ability and was coordinated to different transition metal precursors of groups 8, 9, 10. In particular, the discrete [NiN<sub>2</sub>S<sub>2</sub>] complex resulted from the reaction of the ligand with 2 equiv. of [NiBr<sub>2</sub>(DME)] could act as bidentate ligand through electron pairs on sulfur atoms, leading to bimetallic complexes.

Chapter 2 describes the development of nickel complexes of new bidentate [O, P=N] ligands, containing phenoxide and iminophosphorane groups for the oligomerisation of ethylene. The presence of the anionic phenoxide group on the ligands allowed the coordination of a second metal centre, such as lithium or aluminum, leading to bimetallic complexes. Mono-nuclear complexes were obtained by using additional auxiliary ligands. The activities and selectivities of the synthesized nickel iminophosphorane-phenoxide complexes are in general significantly higher than complexes of (N,O) and (P,O) ligands existing in the literature. Their performances in terms of TOF and selectivities (in C<sub>4</sub> and in 1-C<sub>4</sub>) vary greatly in function of the auxiliary ligand or substituents at the nitrogen atoms. The comparisons of performances between the synthesized complexes could be used for the fine design of new nickel complexes efficient for the dimerisation of ethylene. Furthermore, the formation of bimetallic nickel-lithium and nickel-aluminum complexes is interesting and opens the possibility to develop of self-activated bimetallic nickel-aluminum complexes for the oligomerisation of ethylene, based on iminophosphorane ligands.

Chapters 3, 4, 5 focused on the development of tetradentate phosphasalen ligands, associating two iminophosphoranes and two phenoxides. They are the phosphorus analogues of a well-known and important class of ligands in coordination and catalysis: the salens. Chapter 3 described the conception and the synthesis of phosphasalen ligands in general, and the unsubstituted phosphasalen in particular. Experimental and theoretical studies have been carried

out on nickel and palladium complexes, in order to better understand their differences from the salen analogs. It has been found that as expected, the phosphasalen ligand is better donating and slightly more flexible than the analogue salen.

These properties prompted us to test the utility of phosphasalens in the stabilization of oxidized metal complexes. Due the interest in phenoxyl radical and mix-valence complexes, oxidized species of nickel salen complexes have been the subjects pursued by many groups. We were thus interested in studying the oxidation of Ni(II) phosphasalen complexes to see the electronic differences conferred by the phosphasalen ligands compared to salens. This is the subject of chapter 4. Two new nickel phosphasalen complexes were synthesised and were cleanly oxidised by one equivalent of silver salt in dichloromethane. X-ray structure was obtained for one of these two products (complex **[6a][SbF<sub>6</sub>]**). At the difference of all reported oxidised nickel-phenoxide complexes up to now, which have been shown to be Ni(II) complexes of phenoxyl radical, the oxidised species **[6a][SbF<sub>6</sub>]** is a Ni(III) complex. This has been shown by EPR spectroscopy and DFT calculations. This complex is one of rare example of Ni(III) complexes with coordination number less than 5, and is the first example of four-coordinated high valent Ni(III) phenoxide species.

The obtainment of this Ni(III) complex could be seen as the first, encouraging example for the use of phosphasalen ligands in stabilising high-valent metal centres. One can imagine, for example, the development of phosphasalen oxo complexes of metals such as chromium or manganese in order to shed more light into the mechanism of catalysed asymmetric epoxidation, as this process is often carried out using chromium or manganese salen complexes and is suspected to involve an oxo intermediate. Up to date, no oxo salen complex of manganese has been isolated, likely because of their instability. Due to their better donating ability, phosphasalen ligands could help stabilise such oxidised complexes.

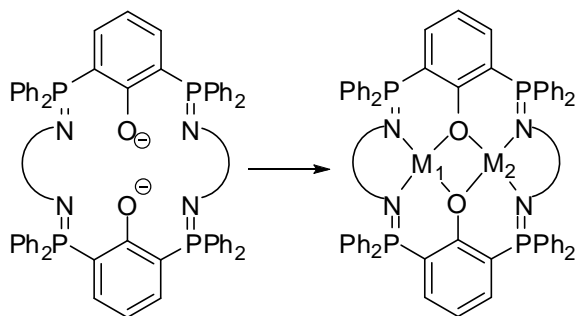
Chapter 5 presents the use of aluminium and yttrium phosphasalen complexes in the ring opening polymerisation of lactide. In particular, interesting results have been obtained for the yttrium complexes, both in terms of coordination chemistry and catalysis.

In the coordination point of view, it has been observed that due to the flexibilities of the phosphasalen ligands, their complexes adopt completely different geometries, depending on the diamine linker, the substituents on the phosphasalen ligands, the auxiliary alkoxide ligand. Dimeric and monomeric complexes were obtained, and showed completely different activities in ROP of rac-lactide. Whereas ROP initiated by the dimeric complexes follow a second-order in lactide, the ones initiated by monomeric complexes are first order in lactide. Inside the monomeric complexes, activities change drastically with different structures. The most actives and heteroselective complexes are the monomeric ones with ethylene diamine linker. Interestingly, yttrium complexes of a penta-dentate phosphasalen ligand even offer good isoselectivities, which is really rare for yttrium chemistry. The comparisons of activities between different complexes help clarify the design of the ideal initiator for the ROP of lactide.

In particular, whereas the yttrium salen complexes only have limited performance in ring-opening polymerisation of lactide, yttrium complexes of phosphasalen ligands are among the

best initiators in terms of both activity and stereo-selectivity. These results demonstrate the various perspectives of phosphasalen ligands in catalysis.

The method for the synthesis of phosphasalen ligands, and the very encouraging results obtained with their complexes in coordination and catalysis could also inspired new phosphasalen-like ligands, such as the hexa-dentate ones (whose general structure is presented below) for the development of bimetallic species.



## Experimental Section

### I. Chapter 1.

#### General Considerations

All experiments, unless otherwise stated, were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, diethylether, petroleum ether), from P<sub>2</sub>O<sub>5</sub> (dichloromethane). **1a,c**,<sup>1</sup> [NiBr<sub>2</sub>(DME)],<sup>2</sup> [Ir(COD)Cl]<sub>2</sub>, [Rh(COD)Cl]<sub>2</sub>,<sup>3</sup> [RuCl<sub>2</sub>(*p*-cymene)]<sup>4</sup> were prepared according to the literature. All other reagents and chemicals were obtained commercially and used without further purification.

Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C and 121.5 MHz for <sup>31</sup>P. Solvent peaks were used as internal references for <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm). <sup>31</sup>P{<sup>1</sup>H} are relative to a 85% H<sub>3</sub>PO<sub>4</sub> external reference. Coupling constant are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual. The labeling schemes of the ligands and ligand precursors are given in schemes 7 and 9. Elemental analyses (for several compounds) were performed by the Elemental analysis service of the London Metropolitan University (United Kingdom).

#### Synthesis of aminophosphonium compounds by Kirsanov reaction

**1b**: Br<sub>2</sub> (0.98 mL, 19.07 mmol) was added dropwise to a solution of PPh<sub>3</sub> (5g, 19.07 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) at -78°C under nitrogen. The cold bath was removed and stirring was continued for 45 minutes at room temperature. The obtained suspension was then cooled again to -78°C and Et<sub>3</sub>N (2.65 mL, 19.07 mmol) was added, followed by the addition of adamantylamine RNH<sub>2</sub> (2.88 g, 19.07 mmol). Stirring was continued for several hours at room temperature to give a transparent solution. After washing twice with H<sub>2</sub>O, the organic layer was dried over MgSO<sub>4</sub>, the solvent was reduced in volume and THF was added. The white precipitated product was separated by filtration, dried in vacuum. (6.0 g, 64%)

**1b**: <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 32.0 (s, *P*<sup>V</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.94 (ddd, <sup>4</sup>J<sub>H,H</sub>=1.0 Hz, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, <sup>3</sup>J<sub>P,H</sub>=13.0 Hz, 6H, *o*-CH(PPh<sub>3</sub>)), 7.69 (vtd, <sup>4</sup>J<sub>H,H</sub>=1.0 Hz, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, 3H, *p*-

*CH*(PPh<sub>2</sub>)), 7.59 (vtd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.5$  Hz,  $^4J_{\text{P,H}}=3.5$  Hz, 6H, *m-CH*(PPh<sub>2</sub>)), 7.18 (d,  $^2J_{\text{P,H}}=6.0$  Hz, 1H, *NH*), 1.89 (s, 9H, *NH-CH<sub>2</sub>-CH-* and *-CH(CH<sub>2</sub>-)<sub>3</sub>*), 1.44 (m, 6H, *-CH-CH<sub>2</sub>-CH-*);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta$  134.8 (d,  $^4J_{\text{P,C}}=2.8$  Hz, *p-CH*(PPh<sub>3</sub>)), 134.0 (d,  $^2J_{\text{P,C}}=11.5$  Hz, *o-CH*(PPh<sub>3</sub>)), 129.6 (d,  $^3J_{\text{P,C}}=13.0$  Hz, *o-CH*(PPh<sub>3</sub>)), 123.4 (d,  $^1J_{\text{P,C}}=102.1$  Hz, *C<sup>IV</sup>*(PPh<sub>3</sub>)), 57.7 (d,  $^2J_{\text{P,C}}=4.7$  Hz, *NH-C*(CH<sub>2</sub>)<sub>3</sub>), 44.7 (d,  $^3J_{\text{P,C}}=4.4$  Hz, *NH-C*(CH<sub>2</sub>)<sub>3</sub>), 36.6 (s, *-CH-CH<sub>2</sub>-CH-*), 30.0 (s, *-CH(CH<sub>2</sub>-)<sub>3</sub>*);

### Synthesis of 2a,b

MeLi (1.6M in Et<sub>2</sub>O, 1.25 mL, 2 mmol) was added dropwise to a suspension of the starting aminophosphonium salt (1 mmol) in THF (10 mL) at -78°C. The cold bath was removed and stirring is continued at room temperature for 3h to give an orange-red (or red wine) solution. S<sub>8</sub> (32 mg, 1/8 mmol) was then added in the dry box to give a yellow-to-orange solution. Stirring was continued for 30 minutes. HBF<sub>4</sub>·Et<sub>2</sub>O (322 mg, 2mmol) was added to protonate the thiolate-iminophosphorane. THF was removed in vacuum and CH<sub>2</sub>Cl<sub>2</sub> (25mL) was added. The reaction mixture was washed twice with an aqueous solution of HBF<sub>4</sub> 0.1M (15 mL), once with a saturated solution of NaBF<sub>4</sub> (15 mL) in water and dried over MgSO<sub>4</sub>. CH<sub>2</sub>Cl<sub>2</sub> was evaporated and the recrystallisation was taken in THF, giving the desired product as a white solid.

**2a:** (370 mg, 81%).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta$  36.1 (s, *P<sup>V</sup>*);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  7.85 (ddd,  $^4J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{H,H}}=7.5$  Hz,  $^3J_{\text{P,H}}=13.2$  Hz, 4H, *o-CH*(PPh<sub>2</sub>)), 7.85 (m, 1H, *C<sub>d</sub>H*), 7.75 (vtd,  $^4J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{H,H}}=7.5$  Hz, 2H, *p-CH*(PPh<sub>2</sub>)), 7.65 (vtd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.5$  Hz,  $^4J_{\text{P,H}}=3.5$  Hz, 4H, *m-CH*(PPh<sub>2</sub>)), 7.60 (m, 2H, *C<sub>b</sub>H* and *C<sub>a/c</sub>H*), 7.47 (vtdd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.5$  Hz,  $^4J_{\text{H,H}}=1.0$  Hz,  $^4J_{\text{P,H}}=3.0$  Hz, 1H, *C<sub>a/c</sub>H*), 4.82 (d,  $^2J_{\text{P,H}}=8.0$  Hz, 1H, *NH*), 4.02 (s, 1H, *SH*), 1.29 (s, 9H, *C<sup>IV</sup>*(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta$  138.8 (d,  $^2J_{\text{P,C}}=8.4$  Hz, *SC<sup>IV</sup>*), 136.6 (d,  $^2J_{\text{P,C}}=11.50$  Hz, *C<sub>d</sub>H*), 135.5 (d,  $^3J_{\text{P,C}}=10.0$  Hz, *C<sub>a/c</sub>H*), 135.5 (s, *C<sub>b</sub>H*), 135.3 (d,  $^4J_{\text{P,C}}=3.0$  Hz, *p-CH*(PPh<sub>2</sub>)), 133.9 (d,  $^2J_{\text{P,C}}=11.3$  Hz, *o-CH*(PPh<sub>2</sub>)), 130.4 (d,  $^3J_{\text{P,C}}=13.5$  Hz, *m-CH*(PPh<sub>2</sub>)), 127.4 (d,  $^3J_{\text{P,C}}=12.7$  Hz, *C<sub>a/c</sub>H*), 122.2 (d,  $^1J_{\text{P,C}}=103.8$  Hz, *C<sup>IV</sup>*(PPh<sub>2</sub>)), 121.8 (d,  $^1J_{\text{P,C}}=105.1$  Hz, *C<sup>IV</sup>*-PPh<sub>2</sub>), 57.2 (d,  $^2J_{\text{P,C}}=4.5$  Hz, *C<sup>IV</sup>*(CH<sub>3</sub>)<sub>3</sub>), 32.0 (d,  $^3J_{\text{P,C}}=4.0$  Hz, *C<sup>IV</sup>*(CH<sub>3</sub>)<sub>3</sub>)

**2b:** (345 mg, 65%).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta$  34 (s, *P<sup>V</sup>*);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  7.88 (ddd,  $^4J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{H,H}}=7.0$  Hz,  $^3J_{\text{P,H}}=13.5$  Hz, 4H, *o-CH*(PPh<sub>2</sub>)), 7.78 (m, 1H, *C<sub>d</sub>H*), 7.74 (vtd,  $^4J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{H,H}}=7.0$  Hz, 2H, *p-CH*(PPh<sub>2</sub>)), 7.65 (vtd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.0$  Hz,  $^4J_{\text{P,H}}=3.5$  Hz, 4H, *m-CH*(PPh<sub>2</sub>)), 7.59 (m, 2H, *C<sub>b</sub>H* and *C<sub>a</sub>H*), 7.48 (vtdd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.5$  Hz,  $^4J_{\text{H,H}}=1.0$  Hz,  $^4J_{\text{P,H}}=3.0$  Hz, 1H, *C<sub>c</sub>H*), 4.78 (d,  $^2J_{\text{P,H}}=7.5$  Hz, 1H, *NH*), 1.97 (m, 3H, *CH*(CH<sub>2</sub>)<sub>3</sub>), 1.86 (s, 6H, *NH-CH<sub>2</sub>-CH-*), 1.50 (m, 6H, *-CH-CH<sub>2</sub>-CH-*);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta$  140.3 (d,  $^2J_{\text{P,C}}=6.0$  Hz, *SC<sup>IV</sup>*), 136.4 (d,  $^2J_{\text{P,C}}=12.50$  Hz, *C<sub>d</sub>H*), 135.5 (d,  $^3J_{\text{P,C}}=9.5$  Hz, *C<sub>a/c</sub>H*), 135.2 (d,  $^4J_{\text{P,C}}=2.5$  Hz, *C<sub>b</sub>H*), 135.0 (d,  $^4J_{\text{P,C}}=2.7$  Hz, *p-CH*(PPh<sub>2</sub>)), 134.2 (d,  $^2J_{\text{P,C}}=11.3$  Hz, *o-CH*(PPh<sub>2</sub>)), 130.0 (d,  $^3J_{\text{P,C}}=13.3$  Hz, *m-CH*(PPh<sub>2</sub>)), 126.8 (d,  $^3J_{\text{P,C}}=13.1$  Hz, *C<sub>a/c</sub>H*), 123.2 (d,  $^1J_{\text{P,C}}=102.9$  Hz, *C<sup>IV</sup>*(PPh<sub>2</sub>)), 122.1 (d,  $^1J_{\text{P,C}}=105.5$  Hz, *C<sup>IV</sup>*-PPh<sub>2</sub>), 58.4 (d,  $^2J_{\text{P,C}}=5.1$  Hz, *NH-C*(CH<sub>2</sub>)<sub>3</sub>), 44.7 (d,  $^3J_{\text{P,C}}=4.0$  Hz, *NH-C*(CH<sub>2</sub>)<sub>3</sub>), 35.9 (s, *-CH-CH<sub>2</sub>-CH-*), 30.3 (s, *-CH(CH<sub>2</sub>-)<sub>3</sub>*)



**Synthesis of 2a' from 2a**

MeLi (1.6M in Et<sub>2</sub>O, 250  $\mu$ L, 0.4 mmol) was added dropwise to a suspension of the starting thiol aminophosphonium salt **2a** (181 mg, 0.4 mmol) in THF (4 mL) at -20°C. The cold bath was removed and stirring is continued at room temperature for 15 min to give an bright orange solution. <sup>31</sup>P{<sup>1</sup>H} NMR exhibited a singlet at +36 ppm. Addition of dibromoethane (17  $\mu$ L, 0.2 mmol) into the solution yielded a white slurry after overnight stirring at room temperature. The precipitate was isolated, washed with THF and dried in vacuum. (104 mg, 55%)

**2a'**: <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  32 (s,  $P^V$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.99 (dd, <sup>3</sup>J<sub>H,H</sub>= 7.5 Hz, <sup>3</sup>J<sub>H,H</sub>= 14.0 Hz, 2H, C<sub>d</sub>H), 7.92 (vtd, <sup>3</sup>J<sub>H,H</sub>=<sup>3</sup>J<sub>H,H</sub>=7.5 Hz, <sup>4</sup>J<sub>P,H</sub>=4.0 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.85 (dd, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, <sup>3</sup>J<sub>P,H</sub>=13.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.61 (m, 16H, CH(PPh<sub>2</sub>) + C<sub>a/c,b</sub>H), 7.48 (vtd, <sup>3</sup>J<sub>H,H</sub>=<sup>3</sup>J<sub>H,H</sub>=7.5 Hz, <sup>4</sup>J<sub>P,H</sub>=3.0 Hz, 2H, C<sub>a/c</sub>H), 2.32 (s, 2H, CH<sub>2</sub>-CH<sub>2</sub>), 1.42 (s, 2H, CH<sub>2</sub>-CH<sub>2</sub>), 1.41 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  142.2 (d, <sup>2</sup>J<sub>P,C</sub>=6.0 Hz, SC<sup>IV</sup>), 136.3 (d, <sup>2</sup>J<sub>P,C</sub>=12.0 Hz, C<sub>d</sub>H), 135.8 (d, <sup>4</sup>J<sub>P,C</sub>=1.0 Hz, C<sub>b</sub>H), 134.6 (d, <sup>4</sup>J<sub>P,C</sub>=2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 133.7 (d, <sup>2/3</sup>J<sub>P,C</sub>=11.3 Hz, *o*- or *m*-CH(PPh<sub>2</sub>)), 133.3 (d, <sup>3</sup>J<sub>P,C</sub>=9.5 Hz, C<sub>a/c</sub>H), 129.9 (d, <sup>2/3</sup>J<sub>P,C</sub>=9.5 Hz, *o*- or *m*-CH(PPh<sub>2</sub>)), 127.7 (d, <sup>3</sup>J<sub>P,C</sub>=12.5 Hz, C<sub>a/c</sub>H), 124.0 (d, <sup>1</sup>J<sub>P,C</sub>=101.5 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 123.5 (d, <sup>1</sup>J<sub>P,C</sub>=104.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 57.0 (d, <sup>2</sup>J<sub>P,C</sub>=4.5 Hz, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 34.3 (s, CH<sub>2</sub>-CH<sub>2</sub>), 30.8 (d, <sup>3</sup>J<sub>P,C</sub>=4.0 Hz, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>)

**Synthesis of 3a**

Addition of 2 equiv. of MeLi (1.6M, 250  $\mu$ L, 0.4 mmol) into a slurry of the thiol-aminophosphonium salt **2a** (90.6 mg, 0.2 mmol) in THF gave rapidly a cloudy colorless solution. After 30 min, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (140.4 mg, 0.2 mmol) was added, inducing a rapid change of color from deep red wine to bright orange-red. Completeness of the reaction after one day was monitored in <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum by the disappearance of the signal of free ligand at +12.9 ppm, and the apparition of two doublets at +31.8 ppm (<sup>3</sup>J<sub>P,P</sub>=3.5 Hz) and + 15.4 ppm (<sup>3</sup>J<sub>P,P</sub>=3.5 Hz). THF was evaporated and dichloromethane was introduced to precipitate insoluble lithium salt, which were then removed by centrifugation. The product was isolated by evaporation of dichloromethane as a red solid. (120 mg, 78%)

**3a**: <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  31.3 (d, <sup>3</sup>J<sub>P,P</sub>=3.5 Hz,  $P^V$ ), 15.5 (d, <sup>3</sup>J<sub>P,P</sub>=3.5 Hz, PPh<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.18 (m, 2H, *o*-CH(PPh<sub>2</sub>)), 7.68 (m, 4H, C<sub>d</sub>H + *o*-CH(PPh<sub>2</sub>) + *p*-CH(PPh<sub>2</sub>)), 7.29 (m, 13H, *o*-CH(PPh<sub>3</sub>) + *p*-CH(PPh<sub>3</sub>) + *m*-CH(PPh<sub>2</sub>)), 7.17 (m, 7H, *m*-CH(PPh<sub>3</sub>) + C<sub>b</sub>H), 7.07 (m, 2H, C<sub>a</sub>H + *p*-CH(PPh<sub>2</sub>)), 6.87 (m, 1H, C<sub>c</sub>H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  152.0 (dd, <sup>2</sup>J<sub>P,C</sub>=7.0 Hz, <sup>3</sup>J<sub>P,C</sub>=4.0 Hz, SC<sup>IV</sup>), 134.9 (d, <sup>2</sup>J<sub>P,C</sub>=10.5 Hz, *o*-CH(PPh<sub>2</sub>)), 134.4 (d, <sup>2</sup>J<sub>P,C</sub>=10.5 Hz, *o*-CH(PPh<sub>2</sub>) and C<sub>d</sub>H), 134.3 (d, <sup>2</sup>J<sub>P,C</sub>=10.5 Hz, *o*-CH(PPh<sub>3</sub>)), 133.9 (d, <sup>3</sup>J<sub>P,C</sub>=11.0 Hz, C<sub>a</sub>H), 131.6 (d, <sup>4</sup>J<sub>P,C</sub>=3.0 Hz, *p*-CH(PPh<sub>2</sub>)), 131.3 (s, C<sub>c</sub>H), 130.1 (d, <sup>4</sup>J<sub>P,C</sub>=2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 129.6 (d, <sup>1</sup>J<sub>P,C</sub>=52.0 Hz, C<sup>IV</sup>(PPh<sub>3</sub>)), 129.4 (d, <sup>4</sup>J<sub>P,C</sub>=2.5 Hz, *p*-CH(PPh<sub>3</sub>)), 128.7 (d, <sup>1</sup>J<sub>P,C</sub>=56.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 127.7 (d, <sup>3</sup>J<sub>P,C</sub>=12.0 Hz, *m*-CH(PPh<sub>2</sub>)), 121.0 (d, <sup>1</sup>J<sub>P,C</sub>=93.5 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 119.8 (d, <sup>3</sup>J<sub>P,C</sub>=11.0 Hz, C<sub>c</sub>H), 57.3 (dd, <sup>2</sup>J<sub>P,C</sub>=4.5 Hz, <sup>3</sup>J<sub>P,C</sub>=2.0 Hz, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 25.0 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>)

### Synthesis of **5**

MeLi (1.6 M in Et<sub>2</sub>O, 4 mL, 6.4 mmol) was added dropwise to a suspension of **1c** (1.390 g, 3.2 mmol) in THF (32 mL) at -78°C. The cold bath was removed and stirring is continued at room temperature for four hours to give an orange-red solution. S<sub>8</sub> (102 mg, 0.4 mmol) was then added in the dry box to give a yellow-to-orange solution. A precipitate appeared after one hour. After three hours, the precipitate was isolated, washed with THF and dried in vacuum. This white solid, which is **5** could be used for further complexation tests. (710 mg, 55%)

**5**: <sup>31</sup>P {<sup>1</sup>H} NMR (Pyr-d<sub>5</sub>) δ 21.3 (s) ; <sup>1</sup>H NMR (Pyr-d<sub>5</sub>) δ 8.22 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 9.5 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.64 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2H, *p*-CH (PPh<sub>2</sub>)), 7.54 (td, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>P,H</sub> = 1.0 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.40 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H, *o*-CH(NPh)), 7.28 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H, *m*-CH(NPh)), 6.89 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 1H, *p*-CH(NPh)), 4.18 (d, <sup>2</sup>J<sub>P,H</sub> = 7.0 Hz, 2H, PCH<sub>2</sub>), 3.84 (m, 4H, OCH<sub>2</sub>(THF)), 1.80 (m, 4H, CH<sub>2</sub>(THF)); <sup>13</sup>C NMR (Pyr-d<sub>5</sub>): δ 155.8 (d, <sup>2</sup>J<sub>P,C</sub> = 5.5 Hz, C<sup>IV</sup>(NPh)), 135.4 (d, <sup>2</sup>J<sub>P,C</sub> = 8.0 Hz, *o*-CH(PPh<sub>2</sub>)), 134.1 (d, <sup>4</sup>J<sub>P,C</sub> = 2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 133.6 (d, <sup>1</sup>J<sub>P,C</sub> = 78.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 131.6 (d, <sup>3</sup>J<sub>P,C</sub> = 1.0 Hz, *m*-CH(NPh)), 131.1 (d, <sup>3</sup>J<sub>P,C</sub> = 10.5 Hz *m*-CH(PPh<sub>2</sub>)), 125.4 (d, <sup>3</sup>J<sub>P,C</sub> = 17.6 Hz, *o*-CH(NPh)), 119.8 (s, *p*-CH(NPh)), 70.2 (s, OCH<sub>2</sub>(THF)), 31.5 (d, <sup>1</sup>J<sub>P,C</sub> = 88.0 Hz, PCH<sub>2</sub>), 28.2 (s, CH<sub>2</sub>(THF)).

### Synthesis of **6**

HBF<sub>4</sub>(Et<sub>2</sub>O)<sub>2</sub> (0.46 mmol, 63 μl) was added to a solution of **5** (92 mg, 0.23 mmol) in THF giving a colorless solution. The solvent was removed and the residue was taken in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) . After removal of insoluble lithium salts by filtration under N<sub>2</sub>, the solvent was evaporated to afford aminophosphonium salt **6** (67 mg, 70%).

**6**: <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 35.9 (s) ; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.86 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 9.5 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.69 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2H, *p*-CH (PPh<sub>2</sub>)), 7.56 (td, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>P,H</sub> = 3.5 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.34 (d, <sup>2</sup>J<sub>P,H</sub> = 9.5 Hz, 1H, NH), 7.00 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2H, *m*-CH(NPh)), 6.87 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 1H, *p*-CH(NPh)), 6.80 (d, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2H, *o*-CH(NPh)), 3.85 (d, <sup>2</sup>J<sub>P,H</sub> = 7.5 Hz, 2H, PCH<sub>2</sub>), 2.00 (td, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, <sup>3</sup>J<sub>P,H</sub> = 2.0 Hz, 1H, SH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 18.7 (d, <sup>1</sup>J<sub>P,C</sub> = 69.0 Hz, PCH<sub>2</sub>), 116.8 (d, <sup>1</sup>J<sub>P,C</sub> = 99.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 119.0 (d, <sup>3</sup>J<sub>P,C</sub> = 17.6 Hz, *o*-CH(NPh)), 123.1 (s, *p*-CH(NPh)), 128.6 (s, *m*-CH(NPh)), 129.2 (d, <sup>3</sup>J<sub>P,C</sub> = 13.5 Hz, *m*-CH(PPh<sub>2</sub>)), 132.5 (d, <sup>2</sup>J<sub>P,C</sub> = 10.5 Hz, *o*-CH(PPh<sub>2</sub>)), 134.7 (d, <sup>4</sup>J<sub>P,C</sub> = 3.0 Hz, *p*-CH(PPh<sub>2</sub>)), 136.3 (d, <sup>2</sup>J<sub>P,C</sub> = 3.0 Hz, C<sup>IV</sup>-(NPh)). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>BF<sub>4</sub>NPS: C, 55.50; H, 4.66; N, 3.41. Found: C, 55.21; H, 4.94; N, 3.09.

### Synthesis of **9**

MeLi (1.6 M in Et<sub>2</sub>O, 725 μL, 1.16 mmol) was added dropwise to a suspension of **1c** (0.58 mmol, 250 mg) in THF (6 mL) at -78°C. The cold bath was removed and stirring is continued at room temperature for four hours to give an orange-red solution. Dicyclohexylphosphine chloride (0.58 mmol, 128 μl) was added giving a clear yellow solution. After 30 minutes of stirring at room temperature, solvent was evaporated, the residue was taken in dichloromethane (7 mL). The reaction mixture was washed with aqueous HCl 2M solution (2x7 mL), the organic

phase was then dried on Na<sub>2</sub>SO<sub>4</sub> and filtered under N<sub>2</sub>. The solvent was evaporated and the product was precipitated in petroleum ether was a white solid (228 mg, 75%).

**9:** <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -22.2 (d, <sup>2</sup>J<sub>P,P</sub> = 87.5 Hz, PCy<sub>2</sub>), 34.8 (d, <sup>2</sup>J<sub>P,P</sub> = 87.5 Hz, PPh<sub>2</sub>); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.01 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, <sup>3</sup>J<sub>P,H</sub> = 13.0 Hz, 4H, *o*-CH(Ph<sub>2</sub>P)), 7.57 (m, 6H, *m*- and *p*-CH(Ph<sub>2</sub>P)), 6.99 (d, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2H, *m*-CH(NPh)), 6.90 (d, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2H, *o*-CH(NPh)), 6.82 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 1H, *p*-CH(NPh)), 3.22 (d, <sup>2</sup>J<sub>P,H</sub> = 16.5 Hz, 2H, PCH<sub>2</sub>), 0.80-1.52 (22H, m, Cy); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 138.5 (d, <sup>2</sup>J<sub>P,C</sub> = 3.0 Hz, C<sup>IV</sup>(NPh)), 133.8 (d, <sup>4</sup>J<sub>P,C</sub> = 3.0 Hz, *p*-CH(PPh<sub>2</sub>)), 133.0 (dd, <sup>3</sup>J<sub>P,C</sub> = 10.1 and <sup>3</sup>J<sub>P,C</sub> = 4.5 Hz, *o*-CH(PPh<sub>2</sub>)), 128.2 (s, *m*-CH(NPh)), 128.7 (d, <sup>2</sup>J<sub>P,C</sub> = 13.0 Hz, *m*-CH(PPh<sub>2</sub>)), 122.0 (s, *p*-CH(NPh)), 119.7 (d, <sup>1</sup>J<sub>P,C</sub> = 97.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 119.3 (d, <sup>3</sup>J<sub>P,C</sub> = 7.5 Hz, *o*-CH(NPh)), 33.1 (dd, <sup>3</sup>J<sub>P,C</sub> = 8.0 Hz and <sup>1</sup>J<sub>P,C</sub> = 15.0 Hz, CH(Cy)), 28.2 (t, <sup>3</sup>J<sub>P,C</sub> = 13.0 Hz, CH<sub>2</sub>(Cy)), 26.2 (d, <sup>1</sup>J<sub>P,C</sub> = 12.0 Hz, CH<sub>2</sub>(Cy)), 25.2 (s, CH<sub>2</sub>(Cy)), 18.7 (dd, <sup>1</sup>J<sub>P,C</sub> = 39.0 Hz and <sup>1</sup>J<sub>P,C</sub> = 68.0 Hz, PCH<sub>2</sub>). Anal. Calcd for C<sub>31</sub>H<sub>40</sub>ClNP<sub>2</sub>: C, 71.05; H, 7.69; N, 2.67. Found: C, 71.28; H, 7.47; N, 2.36.

### Synthesis of 10

**10** (0.139 g, 60 %) was obtained with a procedure similar to that used for **9** using trimethylsilylchloride (0.58 mmol, 75 μl) as the electrophile.

**10:** <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 37.2 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.91 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>2</sup>J<sub>P,H</sub> = 13.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.78 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>P,H</sub> = 6.0 Hz, 2H, *p*-CH (PPh<sub>2</sub>)), 7.57 (td, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 3.5 Hz, 4H, *m*-CH (PPh<sub>2</sub>)), 7.03 (m, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 4H, *o*- and *m*-CH(NPh)), 6.86 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 1H, *p*-CH(NPh)), 2.71 (d, <sup>2</sup>J<sub>P,H</sub> = 18.0 Hz, 2H, PCH<sub>2</sub>), 0.0 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 139.0 (d, <sup>2</sup>J<sub>P,C</sub> = 2.5 Hz, C<sup>IV</sup>(NPh)), 134.4 (d, <sup>4</sup>J<sub>P,C</sub> = 3.0 Hz, *p*-CH(PPh<sub>2</sub>)), 132.6 (d, <sup>3</sup>J<sub>P,C</sub> = 11.0 Hz, *m*-CH(PPh<sub>2</sub>)), 129.7 (d, <sup>2</sup>J<sub>P,C</sub> = 13.0 Hz, *o*-CH(PPh<sub>2</sub>)), 129.0 (s, *m*-CH(NPh)), 122.9 (s, *p*-CH(NPh)), 122.5 (d, <sup>1</sup>J<sub>P,C</sub> = 96.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 120.0 (d, <sup>3</sup>J<sub>P,C</sub> = 6.0 Hz, *o*-CH(NPh)), 14.5 (d, <sup>1</sup>J<sub>P,C</sub> = 58.5 Hz, PCH<sub>2</sub>), 0.0 (s, CH<sub>3</sub>). Anal. Calcd for C<sub>22</sub>H<sub>27</sub>BrNP<sub>2</sub>Si: C, 59.46; H, 6.12; N, 3.50. Found: C, 58.81; H, 5.93; N, 3.40.

### Synthesis of 11

MeLi (1.6 M in Et<sub>2</sub>O, 725 μL, 1.16 mmol) was added dropwise to a suspension of **1c** (0.58 mmol, 250 mg) in THF (6 mL) at -78°C. The cold bath was removed and stirring is continued at room temperature for four hours to give an orange-red solution. A solution of trimethyltinchloride (0.58 mmol, 0.116 g) in THF (2 mL) was added, giving a pale yellow solution. After 20 minutes of stirring at room temperature, solvent was removed and toluene was added to filter off the lithium salts. After evaporation of toluene, iminophosphorane **11** was obtained as a white solid (341 mg, 75 %).

**11:** <sup>31</sup>P {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ -6.88 (s+sat, <sup>2</sup>J<sub>P,Sn</sub> = 60.0 Hz); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.66 (m, 4H, *o*-CH(PPh<sub>2</sub>)), 7.18 (m, 2H, *p*-CH(NPh)), 6.99 (m, 6H, *p*- and *m*-CH(PPh<sub>2</sub>)), 6.76 (m, 3H, *p*- and *m*-CH(NPh)), 1.55 (d+sat, <sup>2</sup>J<sub>P,H</sub> = 11.0 Hz, <sup>2</sup>J<sub>Sn,H</sub> = 52.0 Hz, 2H, CH<sub>2</sub>P), 0.10 (s +sat, <sup>2</sup>J<sub>Sn,H</sub> = 50.0 Hz, 9H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 152.8 (<sup>2</sup>J<sub>P,C</sub> = 3.0 Hz, C<sup>IV</sup>(NPh)), 134.9 (d, <sup>1</sup>J<sub>P,C</sub> = 87.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 133.8 (d, <sup>3</sup>J<sub>P,C</sub> = 3.0 Hz, *p*-CH(PPh<sub>2</sub>)), 131.6 (d, <sup>2</sup>J<sub>P,C</sub> = 9.0 Hz, *o*-CH(PPh<sub>2</sub>)),

129.7 (d,  $^3J_{P,C} = 12.0$  Hz, *m*-CH(PPh<sub>2</sub>)), 128.6 (d,  $^3J_{P,C} = 11.0$  Hz, *o*-CH(NPh)), 123.2 (d,  $^3J_{P,C} = 20.0$  Hz, *m*-CH(NPh)), 117.1 (s, *p*-CH(NPh)), 12.0 (d+sat,  $^1J_{P,C} = 75.0$  Hz,  $^1J_{Sn,C} = 296.0$  Hz, CH<sub>2</sub>P), -7.4 (d+sat,  $^3J_{P,C} = 1.5$  Hz,  $^1J_{Sn,C} = 362.0$  Hz, Sn(CH<sub>3</sub>)<sub>3</sub>).

### Synthesis of 12

**12** (260 mg, 85 %) was obtained with a procedure similar to that employed for **11** using a solution of 1-cyano-2,5-diphenylphosphole (0.58 mmol, 0.15 g) in THF.

**12:**  $^{31}\text{P}$  { $^1\text{H}$ } NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -23.7 (d,  $^2J_{P,P} = 48.5$  Hz,  $P^{\text{III}}$ ), 0.8 (d,  $^2J_{P,P} = 48.5$  Hz, PPh<sub>2</sub>) ;  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.61 (m, 2H, *o*-CH(NPh)), 7.52 (dd,  $^3J_{H,H} = 7.0$  Hz,  $^4J_{P,H} = 1.0$  Hz, 4H, *o*-CH(Ph<sub>phosphole</sub>)), 7.45 (dd,  $^3J_{P,H} = 11.5$  Hz,  $^3J_{H,H} = 7.0$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.07 (d,  $^3J_{P,H} = 8.0$  Hz, 2H, CH <sub>$\beta$</sub>  phosphole), 6.91 (m, 6H, *m* and *p*-CH(Ph<sub>phosphole</sub>)), 7.02 (m, 6H, *m*- and *p*-CH(NPh)), 6.82 (td,  $J_{H,H} = 7.5$  Hz,  $J_{P,H} = 3.0$  Hz, 6H, *m*- and *p*-CH(PPh<sub>2</sub>)), 2.75 (dd,  $^2J_{P,H} = 10.0$  Hz,  $^2J_{P,H} = 4.0$  Hz, 2H, PCH<sub>2</sub>P);  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  152.4 (d,  $^1J_{P,C} = 68.0$  Hz, C <sub>$\alpha$</sub>  phosphole), 136.5 (d,  $^2J_{P,C} = 17.0$  Hz, C<sup>IV</sup>(NPh)), 135.6 (dd,  $^1J_{P,C} = 97.0$  Hz,  $^3J_{P,C} = 8.0$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 132.5 (d,  $^2J_{P,C} = 9.0$  Hz, C <sub>$\beta$</sub>  phosphole), 132.3 (d,  $^2J_{P,C} = 9.0$  Hz, *o*-CH(PPh<sub>2</sub>)), 131.8 (d,  $J_{P,C} = 3.0$  Hz, CH(Ph)), 131.5 (s, CH(Ph)), 131.3 (s, CH(Ph)), 128.8 (d,  $J_{P,C} = 9.0$  Hz, CH(Ph)), 127.8 (d,  $^3J_{P,C} = 8.0$  Hz, *o*-CH(NPh)), 126.7 (d,  $^3J_{P,C} = 5.0$  Hz, *o*-CH(Ph<sub>phosphole</sub>)), 123.9 (s, CH(Ph)), 123.6 (s, C<sup>IV</sup>(Ph<sub>phosphole</sub>)), 117.6 (s, CH(Ph)), 24.8 (dd,  $^1J_{P,C} = 44.0$  Hz,  $^1J_{P,C} = 37.5$  Hz, PCH<sub>2</sub>).

### Synthesis of 13

THF (1 mL) was added to a mixture of dichloro(*p*-cymene)ruthenium(II) dimer (23.2 mg, 0.38 mmol) and **5** (30 mg, 0.075 mmol) at room temperature giving immediately a red solution. After 2h of stirring, THF was removed and the residue was dissolved in dichloromethane (3 mL). After removal of the insoluble lithium salts by filtration and evaporation of dichloromethane, the obtained solid was washed with hexanes (3 mL) to give **13** as a red solid (25 mg, 76%).

**13:**  $^{31}\text{P}$  { $^1\text{H}$ } NMR (*d*<sup>8</sup>-THF):  $\delta$  36.9 (s);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  7.82 (td,  $^3J_{H,H} = 7.0$  Hz,  $^3J_{P,H} = 10.1$  Hz, 2H, *m*-CH (PPh<sub>2</sub>)), 7.57 (d,  $^3J_{H,H} = 7.0$  Hz, 1H, *p*-CH (PPh<sub>2</sub>)), 7.52 (dd,  $^3J_{H,H} = 7.0$  Hz,  $^3J_{P,H} = 11.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.38 (d,  $^3J_{H,H} = 7.5$  Hz, 2H, *m*-CH(NPh)), 7.25 (t,  $^3J_{H,H} = 7.0$  Hz, 1H, *p*-CH(PPh<sub>2</sub>)), 7.18 (m, 2H, *m*-CH(PPh<sub>2</sub>)), 6.85 (t,  $^3J_{H,H} = 7.5$  Hz, 2H, *o*-CH(PPh<sub>2</sub>)), 6.64 (vtd,  $^3J_{H,H} = 7.5$  Hz,  $^4J_{H,H} = 0.5$  Hz, 1H, *p*-CH(NPh)), 4.90 (d,  $^3J_{H,H} = 5.5$  Hz, 1H, CH(*p*-cymene)), 4.76 (d,  $^3J_{H,H} = 5.5$  Hz, 2H, CH(*p*-cymene)), 4.64 (d,  $^3J_{H,H} = 5.5$  Hz, 1H, CH(*p*-cymene)), 4.12 (vt,  $^3J_{H,H} = ^2J_{P,H} = 13.0$  Hz, 1H, PCH<sub>2</sub>), 2.80 (sept.,  $^3J_{H,H} = 7.0$  Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.67 (d,  $^3J_{H,H} = 13.0$  Hz, 1H, PCH<sub>2</sub>), 1.99 (3H, s, CH<sub>3</sub>), 1.15 (d,  $^3J_{H,H} = 7.0$  Hz, 6H, C(CH<sub>3</sub>)<sub>2</sub>);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  151.2 (s, C<sup>IV</sup>(NPh)), 130.1 (d,  $J_{P,C} = 9.0$  Hz, CH(PPh<sub>2</sub>)), 129.8 (d,  $J_{P,C} = 9.0$  Hz, CH(PPh<sub>2</sub>)), 128.4 (s, CH(PPh<sub>2</sub>)), 127.9 (s, CH(PPh<sub>2</sub>)), 126.1 (d,  $^1J_{P,C} = 89.0$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 125.3 (d,  $J_{P,C} = 7.0$  Hz, CH(NPh)), 124.6 (d,  $J_{P,C} = 11.5$  Hz, CH(PPh<sub>2</sub>)), 124.4 (d,  $J_{P,C} = 9.0$  Hz, CH(PPh<sub>2</sub>)), 124.0 (d,  $J_{P,C} = 1.0$  Hz, CH(NPh)), 118.3 (d,  $J_{P,C} = 2.0$  Hz, *p*-CH(NPh)), 99.0 (s, C<sup>IV</sup>-(*p*-cymene)), 90.9 (s, C<sup>IV</sup>-(*p*-cymene)), 80.8 (s, CH(*p*-cymene)), 79.3 (s, CH(*p*-cymene)), 79.2 (s, CH(*p*-cymene)), 73.2 (s, CH(*p*-cymene)), 28.8 (d,  $^1J_{P,C} = 84.0$  Hz, PCH<sub>2</sub>), 27.1 (s,

CH(CH<sub>3</sub>)<sub>2</sub>), 18.5 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.3 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 14.0 (s, CH<sub>3</sub>). Anal. Calcd for C<sub>29</sub>H<sub>31</sub>ClNPRuS: C, 58.72; H, 5.27; N, 2.36. Found: C, 58.61; H, 5.20; N, 2.21.

### Synthesis of **14**

THF (1 mL) was added to a mixture of CoCl<sub>2</sub> (9.8 mg, 0.075 mmol) and **5** (30 mg, 0.075 mmol) at room temperature giving immediately a blue solution, then a blue suspension after 10 minutes. After 2h of stirring, THF was removed and the residue was dissolved in dichloromethane (3 mL). After removal of the insoluble lithium salts by filtration and evaporation of dichloromethane, the obtained solid was washed with hexanes (3 mL) to give **14** as a blue/green solid (24 mg, 76%). Single crystals suitable for X-ray diffraction was obtained by slow diffusion of petroleum ether over a solution in dichloromethane.

### Synthesis of **15**

Toluene (1 mL) was added to a mixture of chloro(1,5-cyclooctadiene)rhodium(I) dimer (19 mg, 0.038 mmol) and **5** (30 mg, 0.075 mmol) at room temperature giving immediately a yellow solution. After 2h of stirring, THF was removed and the residue was dissolved in dichloromethane (3 mL). After removal of insoluble lithium salts by filtration and evaporation of dichloromethane, the obtained solid was washed with hexanes (3 mL) to give **15** as a yellow solid (20 mg, 68%).

**15:** <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 47.7 (d, <sup>2</sup>J<sub>Rh,P</sub> = 5.0 Hz, P=N); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.81 (ddd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 10.0 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.56 (vtd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.47 (vtd, <sup>3</sup>J<sub>H,H</sub> = <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>P,H</sub> = 2.5 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 6.93 (vt, <sup>3</sup>J<sub>H,H</sub> = <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H, *m*-CH(NPh)), 6.83 (d, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H, *o*-CH(NPh)), 6.75 (d, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 1H, *p*-CH(NPh)), 3.87 (m, 4H, CH(COD)), 3.23 (d, <sup>2</sup>J<sub>P,H</sub> = 5.5 Hz, 2H, PCH<sub>2</sub>), 2.37 (m, 4H, CH<sub>2</sub>(COD)), 1.80 (m, 4H, CH<sub>2</sub>(COD)); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 147.9 (s, C<sup>IV</sup>(NPh)), 133.7 (d, <sup>2</sup>J<sub>P,C</sub> = 9.0 Hz, *o*-CH(PPh<sub>2</sub>)), 132.6 (d, <sup>4</sup>J<sub>P,C</sub> = 2.0 Hz, *p*-CH(PPh<sub>2</sub>)), 129.3 (s, CH(COD)), 129.0 (d, <sup>3</sup>J<sub>P,C</sub> = 7.5 Hz, *o*-CH(NPh)), 128.6 (d, <sup>3</sup>J<sub>P,C</sub> = 11.5 Hz, *m*-CH(PPh<sub>2</sub>)), 128.5 (s, CH(COD)), 128.3 (d, <sup>4</sup>J<sub>P,C</sub> = 1.5 Hz, *m*-CH(NPh)), 127.7 (d, <sup>1</sup>J<sub>P,C</sub> = 83.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 125.6 (s, CH(COD)), 123.0 (d, <sup>5</sup>J<sub>P,C</sub> = 2.0 Hz, *p*-CH(NPh)), 31.1 (s, b, CH<sub>2</sub>(COD)), 25.9 (d, <sup>1</sup>J<sub>P,C</sub> = 90.0 Hz, PCH<sub>2</sub>),

### Synthesis of **16**

THF (1 mL) was added to a mixture of chloro(1,5-cyclooctadiene)Iridium(I) dimer (25.5 mg, 0.038 mmol) and **5** (150 mg, 0.38 mmol) at room temperature giving immediately an orange-red solution. After 2h of stirring, THF was removed and the residue was dissolved in dichloromethane (3 mL). After removal of insoluble lithium salts by filtration and evaporation of dichloromethane, the obtained solid was washed with hexanes (3 mL) to give **16** as a red solid (25 mg, 71%).

**16:** <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 63.0 (s); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.77 (ddd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 11.0 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.56 (vtd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, 2H, *p*-

*CH*(PPh<sub>2</sub>)), 7.45 (vtd,  $^3J_{\text{H,H}} = ^3J'_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{P,H}} = 3.0$  Hz, 4H, *m-CH*(PPh<sub>2</sub>)), 6.94 (vt,  $^3J_{\text{H,H}} = ^3J'_{\text{H,H}} = 7.5$  Hz, 2H, *m-CH*(NPh)), 6.79 (dd,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 2H, *o-CH*(NPh)), 6.77 (td,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 1H, *p-CH*(NPh)), 3.41 (m, 2H, *CH*(COD)), 3.35 (d,  $^2J_{\text{P,H}} = 5.5$  Hz, 2H, PCH<sub>2</sub>), 3.05 (m, 2H, *CH*(COD)), 2.15 (m, 4H, CH<sub>2</sub>(COD)), 1.57 (m, 2H, CH<sub>2</sub>(COD)), 1.45 (m, 2H, CH<sub>2</sub>(COD));  $^{13}\text{C}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  146.2 (s, C<sup>IV</sup>(NPh)), 134.0 (d,  $^2J_{\text{P,C}} = 9.0$  Hz, *o-CH*(PPh<sub>2</sub>)), 132.9 (d,  $^4J_{\text{P,C}} = 2.0$  Hz, *p-CH*(PPh<sub>2</sub>)), 129.4 (d,  $^3J_{\text{P,C}} = 7.0$  Hz, *o-CH*(NPh)), 128.6 (d,  $^3J_{\text{P,C}} = 11.5$  Hz, *m-CH*(PPh<sub>2</sub>)), 128.1 (d,  $^4J_{\text{P,C}} = 1.0$  Hz, *m-CH*(NPh)), 126.6 (d,  $^1J_{\text{P,C}} = 86.0$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 123.8 (d,  $^5J_{\text{P,C}} = 2.0$  Hz, *p-CH*(NPh)), 65.0 (s, *CH*(COD)), 56.5 (s, *CH*(COD)), 31.9 (s, CH<sub>2</sub>(COD)), 31.3 (s, CH<sub>2</sub>(COD)), 25.3 (d,  $^1J_{\text{P,C}} = 89.0$  Hz, PCH<sub>2</sub>),

### Synthesis of 17

THF (1 mL) was added to a mixture of trans-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (53 mg, 0.075 mmol) and **5** (30 mg, 0.075 mmol). After 4h stirring the yellow slurry has turned to an orange solution. THF was removed by evaporation and the residue was taken in dichloromethane (4 mL). Insoluble lithium salts were removed by filtration. After evaporation of dichloromethane, the obtained solid residue was washed with hexanes (3 mL) to give **17** as an orange solid (31.7 mg, 87%).

**17**:  $^{31}\text{P}$  { $^1\text{H}$ } NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  33.5 (d,  $^3J_{\text{P,P}} = 6.5$  Hz, P<sup>III</sup>), 46.2 (d,  $^3J_{\text{P,P}} = 6.5$  Hz, P<sup>V</sup>);  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.83 (ddd,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^3J_{\text{P,H}} = 11.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 4H, *o-CH*(PPh<sub>2</sub>)), 7.65 (ddd,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^3J_{\text{P,H}} = 11.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 6H, *o-CH*(PPh<sub>3</sub>)), 7.64 (tt,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 2H, *p-CH*(PPh<sub>2</sub>)), 7.63 (vtd,  $^3J_{\text{H,H}} = ^3J'_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{P,H}} = 3.0$  Hz, 4H, *m-CH*(PPh<sub>2</sub>)), 7.46 (tt,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 2H, *p-CH*(PPh<sub>3</sub>)), 7.37 (vtd,  $^3J_{\text{H,H}} = ^3J'_{\text{H,H}} = 7.5$  Hz,  $^4J_{\text{P,H}} = 2.5$  Hz, 6H, *m-CH*(PPh<sub>3</sub>)), 7.37 (vt,  $^3J_{\text{H,H}} = ^3J'_{\text{H,H}} = 6.0$  Hz, 2H, *m-CH*(NPh)), 6.94 (dd,  $^3J_{\text{H,H}} = 6.0$  Hz,  $^4J_{\text{H,H}} = 2.5$  Hz, 2H, *o-CH*(NPh)), 6.67 (td,  $^3J_{\text{H,H}} = 6.0$  Hz,  $^4J_{\text{H,H}} = 2.5$  Hz, 1H, *p-CH*(NPh)), 3.14 (d,  $^2J_{\text{P,H}} = 6.0$  Hz, 2H, PCH<sub>2</sub>);  $^{13}\text{C}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  149.6 (dd,  $^2J_{\text{P,C}} = 3.0$  Hz,  $^3J_{\text{P,C}} = 1.5$  Hz, C<sup>IV</sup>(NPh)), 136.5 (d,  $^2J_{\text{P,C}} = 11.0$  Hz, *o-CH*(PPh<sub>3</sub>)), 134.9 (d,  $^2J_{\text{P,C}} = 9.0$  Hz, *o-CH*(PPh<sub>2</sub>)), 134.4 (d,  $^4J_{\text{P,C}} = 2.5$  Hz, *p-CH*(PPh<sub>2</sub>)), 132.2 (d,  $^2J_{\text{P,C}} = 2.5$  Hz, *p-CH*(PPh<sub>3</sub>)), 131.9 (d,  $^1J_{\text{P,C}} = 53.5$  Hz, C<sup>IV</sup>(PPh<sub>3</sub>)), 130.3 (d,  $^3J_{\text{P,C}} = 11.5$  Hz, *m-CH*(PPh<sub>2</sub>)), 130.1 (dd,  $^3J_{\text{P,C}} = 10.5$  Hz,  $^4J_{\text{P,C}} = 1.0$  Hz, *o-CH*(NPh)), 129.4 (d,  $^3J_{\text{P,C}} = 11.0$  Hz, *m-CH*(PPh<sub>3</sub>)), 129.0 (s, *m-CH*(NPh)), 128.5 (d,  $^1J_{\text{P,C}} = 86.0$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 123.3 (s, *p-CH*(NPh)), 29.5 (dd,  $^1J_{\text{P,C}} = 85.0$  Hz,  $^3J_{\text{P,C}} = 4.5$  Hz, PCH<sub>2</sub>); Anal. Calcd for C<sub>37</sub>H<sub>32</sub>ClNPdP<sub>2</sub>S: C, 61.17; H, 4.44; N, 1.93. Found: C, 61.03; H, 4.364; N, 2.02.

### Synthesis of 18

THF (1 mL) was added to a mixture of [NiBr<sub>2</sub>(DME)] (11.6 mg, 0.038 mmol) and **5** (30 mg, 0.075 mmol) at room temperature giving immediately deep green solution, then a green suspension after 10 minutes. After 2h of stirring, THF was removed and the residue was dissolved in dichloromethane (3 mL). After removal of insoluble lithium salts by filtration and evaporation of dichloromethane, the obtained solid was washed with hexanes (3 mL) to give **18** as a green solid (22 mg, 82%). Single crystals suitable for X-ray diffraction was obtained from slow diffusion of petroleum ether over a solution in dichloromethane.

# Experimental Section

## II. Chapter 2

### General considerations

All experiments, unless otherwise stated, were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were taken directly from a M-Braun MB-SPS 800 Solvent Purification Machine. *O*-diphenylphosphinophenol,<sup>5</sup> [NiBr<sub>2</sub>(DME)]<sup>2</sup> were prepared according to the literature. Methylaluminoxane (10% wt in toluene) and diethylaluminum chloride was purchased from Acros. Ethylene (N25 grade) was purchased from Air Liquide. All other reagents and chemicals were obtained commercially and used without further purification.

Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C and 121.5 MHz for <sup>31</sup>P. Solvent peaks were used as internal references for <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm). <sup>31</sup>P{<sup>1</sup>H} are relative to a 85% H<sub>3</sub>PO<sub>4</sub> external reference. Coupling constant are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual. The labeling of the ligands and ligand precursors are given in scheme 15. Elemental analyses were performed by the Elemental analysis service of the London Metropolitan University (United Kingdom).

### General procedure for ethylene oligomerisation

All catalytic reactions were carried out in glass container in a magnetically stirred stainless steel autoclave (40 mL), equipped with a pressure gauge and needle valves for injections. The interior of the autoclave was protected from corrosion by a Teflon protective coating. A typical reaction was performed by introducing in the reactor under nitrogen atmosphere a suspension of the complex (8 μmol) in toluene (20 mL). After injection of the cocatalyst solution (in toluene), the reactor was immediately brought to the desired working pressure, and continuously fed with ethylene using a reserve bottle. The reaction was stopped by closing the ethylene supply and cooling down the system to -70°C. After release of residual pressure, the reaction was quenched by adding methanol (5 mL). *n*-heptane used as internal standard was also introduced and the

mixture was analyzed by quantitative GC (PERICHRON 2100 gas chromatograph equipped with a HP PONA column (50 m × 0.2 mm × 0.5 μm)), first calibrated with authentic samples.

### Kirsanov reaction

**21a-c:** 1equiv. of Br<sub>2</sub> (200 μL, 3.883 mmol) was added dropwise to a solution of the protected phosphinophenol **X2** (1304 mg, 3.883 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (38 mL) at -78°C under nitrogen. The cold bath was removed and stirring was continued for 45 minutes at room temperature. The obtained suspension was then cooled again to -78°C and DABCO (218 mg, 1.942 mmol) was added, followed by the addition of 1 equiv. of RNH<sub>2</sub>. Stirring was continued overnight at room temperature to give a white suspension. Dichloromethane was evaporated and the residue was taken in THF (50 mL). After removal of DABCO salts by centrifugation, the solvent was evaporated in vacuum, giving white solid. The products were verified in <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and are used directly without further purification for the deprotection step.

**21d:** 1equiv. of Br<sub>2</sub> (200 μL, 3.883 mmol) was added dropwise to a solution of the protected phosphinophenol **X2** (1304 mg, 3.883 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL/mmol) at -78°C under nitrogen. The cold bath was removed and stirring was continued for 45 minutes at room temperature. The obtained suspension was then cooled again to -78°C and o-phenylenediamine (420 mg, 3.883 mmol) was added. Stirring was continued overnight at room temperature to give a pale yellow slurry. Dichloromethane was evaporated and the residue was washed with THF (2 × 10 mL), giving a white solid. verified in <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and are used directly without further purification for the deprotection step.

### Deprotection reaction

The aminophosphonium salt resulted from the Kirsanov reaction was put into distilled dichloromethane (15 mL) and the solution was saturated with HCl gaseous. After 15 minutes of stirring, a cloudy pale yellow solution was formed.

**22a:** Dichloromethane and HCl was evaporated, the residue was taken in MeOH (10 mL) giving a pale pink solution. Water (3 mL) was added dropwise, leading to the formation of colorless crystallised solid. The white solid was separated by centrifugation, washed with THF (3 × 5 mL) and dried in vacuum.

**22b-d:** Dichloromethane and HCl were evaporated, the residue was taken in THF (20 mL) giving a yellow slurry. The white solid was separated by centrifugation, washed again with THF (5 mL) and dried in vacuum.

**22a:** (0.87 g, 2.2 mmol, 57%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 35.2 (s, P<sup>V</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.96 (ddd, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, <sup>4</sup>J<sub>H,H</sub>=1.8 Hz, <sup>4</sup>J<sub>P,H</sub>=5.5 Hz, 1H, C<sub>a</sub>H), 7.75 (dd, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, <sup>3</sup>J<sub>P,H</sub>=13.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.70 (vt, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.58 (vtd, <sup>3</sup>J<sub>H,H</sub>=<sup>3</sup>J'<sub>H,H</sub>=7.5 Hz, <sup>4</sup>J<sub>P,H</sub>=2.4 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.41 (vtd, <sup>3</sup>J<sub>H,H</sub>=<sup>3</sup>J'<sub>H,H</sub>=7.5 Hz, <sup>4</sup>J<sub>H,H</sub>=3.0 Hz, 1H, C<sub>b</sub>H), 6.80 (m, 2H, C<sub>c</sub>H+C<sub>d</sub>H), 4.94 (s, 1H, NH), 1.15 (s, 9H, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 161.6 (d, <sup>2</sup>J<sub>P,C</sub>=1.8 Hz, OC<sup>IV</sup>), 136.7 (d, <sup>4</sup>J<sub>P,C</sub>=1.7 Hz, C<sub>b</sub>H), 134.8 (d, <sup>4</sup>J<sub>P,C</sub>=3.0 Hz, *p*-CH(PPh<sub>2</sub>)), 134.0



(d,  $^2J_{P,C}=11.4$  Hz, *o*-CH(PPh<sub>2</sub>)), 132.1 (d,  $^2J_{P,C}=10.5$  Hz, *C<sub>d</sub>H*), 129.8 (d,  $^3J_{P,C}=13.3$  Hz, *m*-CH(PPh<sub>2</sub>)), 128.8 (d,  $^3J_{P,C}=12.4$  Hz, *C<sub>a/c</sub>H*), 122.7 (d,  $^1J_{P,C}=101.8$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 120.2 (d,  $^3J_{P,C}=13.9$  Hz, *C<sub>a/c</sub>H*), 107.1 (d,  $^1J_{P,C}=107.3$  Hz,  $C^{IV}$ -PPh<sub>2</sub>), 55.8 (d,  $^2J_{P,C}=4.8$  Hz,  $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 32.1 (d,  $^3J_{P,C}=4.4$  Hz,  $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>)

**22b:** (1.24 g, 2.8 mmol, 72%).  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta$  36.4 (s,  $P^V$ );  $^1H$  NMR (CDCl<sub>3</sub>):  $\delta$  8.15 (s, b, OH), 8.02 (dd,  $^3J_{H,H}=7.5$  Hz,  $^4J_{P,H}=6.5$  Hz, 1H, *C<sub>a</sub>H*), 7.80 (ddd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^3J_{P,H}=13.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.75 (vtt,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=7.5$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.62 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz,  $^4J_{P,H}=3.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.46 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz,  $^4J_{H,H}=2.0$  Hz, 1H, *C<sub>b</sub>H*), 6.88 (m, 2H, *C<sub>c</sub>H*+*C<sub>d</sub>H*), 4.96 (d,  $^2J_{P,H}=2.0$  Hz, 1H, NH), 1.46 (s, 2H, CH<sub>2</sub>- $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 1.19 (s, 9H,  $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>);  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta$  161.4 (d,  $^2J_{P,C}=1.8$  Hz, OC $^{IV}$ ), 136.7 (d,  $^4J_{P,C}=2.0$  Hz, *C<sub>b</sub>H*), 134.8 (d,  $^4J_{P,C}=2.8$  Hz, *p*-CH(PPh<sub>2</sub>)), 133.9 (d,  $^2J_{P,C}=11.7$  Hz, *o*-CH(PPh<sub>2</sub>)), 132.4 (d,  $^{2/3}J_{P,C}=11.0$  Hz, *C<sub>d/c</sub>H*), 129.8 (d,  $^3J_{P,C}=12.0$  Hz, *m*-CH(PPh<sub>2</sub>)), 122.7 (d,  $^1J_{P,C}=102.0$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 120.3 (d,  $^{2/3}J_{P,C}=13.5$  Hz, *C<sub>d/c</sub>H*), 119.4 (d,  $^2J_{P,C}=7.4$  Hz, *C<sub>a</sub>H*), 107.2 (d,  $^1J_{P,C}=106.3$  Hz,  $C^{IV}$ -PPh<sub>2</sub>), 55.8 (d,  $^2J_{P,C}=5.0$  Hz, CH<sub>2</sub>- $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 53.5 (s,  $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 32.1 (d,  $^3J_{P,C}=4.3$  Hz,  $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>)

**22c:** (1.35 g, 3.01 mmol, 78%).  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta$  39.9 (s,  $P^V$ );  $^1H$  NMR (CDCl<sub>3</sub>):  $\delta$  7.97 (ddd,  $^3J_{H,H}=6.5$  Hz,  $^4J_{H,H}=1.0$  Hz,  $^4J_{P,H}=8.5$  Hz, 1H, *C<sub>a</sub>H*), 7.68 (vtt,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=7.5$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.66 (ddd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^3J_{P,H}=14.0$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.54 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz,  $^4J_{P,H}=3.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.54 (m, 1H, *C<sub>b</sub>H*), 7.10 (vt,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz, 2H, *m*-CH(NPh)), 7.02 (vtd,  $^3J_{H,H}=^3J'_{H,H}=6.5$  Hz,  $^4J_{H,H}=1.0$  Hz, 1H, *C<sub>c</sub>H*), 7.00 (t,  $^3J_{H,H}=7.5$  Hz, 1H, *p*-CH(PPh<sub>2</sub>)), 6.93 (ddd,  $^3J_{H,H}=6.5$  Hz,  $^4J_{H,H}=1.0$  Hz,  $^3J_{P,H}=3.5$  Hz, 1H, *C<sub>d</sub>H*), 6.85 (d,  $^3J_{H,H}=7.5$  Hz, 2H, *o*-CH(PPh<sub>2</sub>));  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta$  161.8 (d,  $^2J_{P,C}=2.5$  Hz, OC $^{IV}$ ), 137.8 (d,  $^2J_{P,C}=3.0$  Hz,  $C^{IV}$ (NPh)), 137.6 (d,  $^4J_{P,C}=2.0$  Hz, *C<sub>b</sub>H*), 135.2 (d,  $^4J_{P,C}=3.0$  Hz, *p*-CH(PPh<sub>2</sub>)), 133.8 (d,  $^2J_{P,C}=11.5$  Hz, *o*-CH(PPh<sub>2</sub>)), 133.1 (d,  $^3J_{P,C}=10.5$  Hz, *C<sub>c</sub>H*), 130.0 (d,  $^3J_{P,C}=13.6$  Hz, *m*-CH(PPh<sub>2</sub>)), 129.6 (s, *m*-CH(NPh)), 124.5 (s, *p*-CH(NPh)), 121.6 (d,  $^3J_{P,C}=6.0$  Hz, *o*-CH(NPh)), 120.6 (d,  $^3J_{P,C}=13.8$  Hz, *C<sub>a</sub>H*), 120.3 (d,  $^1J_{P,C}=104.0$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 119.5 (d,  $^2J_{P,C}=7.5$  Hz, *C<sub>d</sub>H*), 105.9 (d,  $^1J_{P,C}=105.2$  Hz,  $C^{IV}$ -PPh<sub>2</sub>)

**22d:** (1.95 g, 3.56 mmol, 92%).  $^{31}P\{^1H\}$  NMR (MeOD-*d*<sub>4</sub>):  $\delta$  39.0 (s);  $^1H$  NMR (MeOD-*d*<sub>4</sub>):  $\delta$  7.93 (ddd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^3J_{P,H}=14.0$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.85 (tdt,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=8.0$  Hz,  $^5J_{P,H}=2.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.79 (dddd,  $^3J_{H,H}=8.5$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^4J_{H,H}=1.0$  Hz,  $^5J_{P,H}=1.5$  Hz, 1H, *C<sub>b</sub>H*), 7.71 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz,  $^4J_{P,H}=4.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.53 (ddd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=8.0$  Hz,  $^3J_{P,H}=15.0$  Hz, 1H, *C<sub>d</sub>H*), 7.46 (dvt,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=8.0$  Hz,  $^4J_{P,H}=1.0$  Hz, 1H, *C<sub>c</sub>H*), 7.26 (vtd,  $^3J_{H,H}=^3J'_{H,H}=8.0$  Hz,  $^4J_{H,H}=1.0$  Hz, 1H, *C<sub>f</sub>H*), 7.20 (vtdd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=^3J'_{H,H}=8.0$  Hz,  $^4J_{P,H}=3.0$  Hz, 1H, *C<sub>e</sub>H*), 7.15 (ddd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=8.0$  Hz,  $^4J_{P,H}=6.0$  Hz, 1H, *C<sub>a</sub>H*), 7.15 (vtd,  $^3J_{H,H}=^3J'_{H,H}=8.0$  Hz,  $^4J_{H,H}=1.0$  Hz, 1H, *C<sub>g</sub>H*), 6.93 (dd,  $^3J_{H,H}=8.0$  Hz,  $^4J_{H,H}=1.0$  Hz, 1H, *C<sub>h</sub>H*);  $^{13}C\{^1H\}$  NMR (MeOD-*d*<sub>4</sub>):  $\delta$  162.8 (d,  $^2J_{P,C}=3.5$  Hz,  $C^{IV}$ -O), 140.0 (d,  $^4J_{P,C}=2.0$  Hz, *C<sub>b</sub>H*), 136.8 (d,  $^4J_{P,C}=3.0$  Hz, *p*-CH(PPh<sub>2</sub>)), 136.3 (d,  $^2J_{P,C}=9.5$  Hz, *C<sub>d</sub>H*), 135.4 (d,  $^2J_{P,C}=11.5$  Hz, *o*-CH(PPh<sub>2</sub>)), 133.3 (d,  $^2J_{P,C}=1.0$  Hz,  $C^{IV}$ -N-P), 132.7 (d,  $^3J_{P,C}=14.0$  Hz, *m*-CH(PPh<sub>2</sub>)), 130.9 (s, *C<sub>f</sub>H*), 128.4 (s, *C<sub>g</sub>H*), 127.7 (d,  $^3J_{P,C}=8.0$  Hz,

$C^{IV}$ -N-C), 127.1(d,  $^3J_{P,C}$  = 4.0 Hz,  $C_eH$ ), 126.4 (s,  $C_hH$ ), 122.7 (d,  $^3J_{P,C}$ =13.5 Hz,  $C_eH$ ), 121.6 (d,  $^1J_{P,C}$ =106.0 Hz,  $C^{IV}(PPh_2)$ ), 118.8 (d,  $^3J_{P,C}$  = 7.5 Hz,  $C_aH$ ), 107.8 (d,  $^1J_{P,C}$  = 104.5 Hz,  $C^{IV}$ -PPh<sub>2</sub>).

### Synthesis of complexes **23a-d**

KHMDS (200 mg, 1 mmol and 300 mg, 1.5 mmol in the case of **23d**) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min of stirring at RT, insoluble potassium salts (KCl) was removed by centrifugation. [NiBr<sub>2</sub>(DME)] (154 mg, 0.5 mmol) was added resulting immediately in a change of color. Stirring was continued for 2h. Insoluble potassium salt was removed by centrifugation. THF was evaporated to give the product as a pale solid which is washed with petroleum ether to remove traces of HMDS. **23a** (220 mg, 0.21 mmol, 82%), pale purple solid. Anal. Calcd for **23a** (C<sub>44</sub>H<sub>46</sub>Br<sub>3</sub>KN<sub>2</sub>Ni<sub>2</sub>O<sub>2</sub>P<sub>2</sub>): C, 48.35; H, 4.24; N, 2.56. Found: C, 48.82; H, 5.38; N, 2.73. **23b**. (195 mg, 0.18 mmol, 74%), pale blue solid. Anal. Calcd for **23b** (C<sub>46</sub>H<sub>50</sub>Br<sub>3</sub>KN<sub>2</sub>Ni<sub>2</sub>O<sub>2</sub>P<sub>2</sub>): C, 49.28; H, 4.50; N, 2.50. Found: C, 49.09; H, 4.82; N, 4.08. **23c**. (230 mg, 0.21 mmol, 84%). pale green solid. Anal. Calcd for **23c** (C<sub>48</sub>H<sub>38</sub>Br<sub>3</sub>KN<sub>2</sub>Ni<sub>2</sub>O<sub>2</sub>P<sub>2</sub>): C, 50.89; H, 3.38; N, 2.47. Found: C, 49.22; H, 4.82; N, 2.97. **23d** (200 mg, 0.39 mmol, 78%) deep red solid. Anal. Calcd for **23d** (C<sub>24</sub>H<sub>20</sub>BrN<sub>2</sub>NiOP): C, 55.22; H, 3.86; N, 5.37. Found: C, 55.15; H, 3.75; N, 5.28.

### Synthesis of complexes **24a-c**

KHMDS (200 mg, 1 mmol) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min of stirring at RT, insoluble potassium salts (KCl) was removed by centrifugation. [NiBr<sub>2</sub>(DME)] (154 mg, 0.5 mmol) was added resulting immediately in a change of color. Stirring was continued for 2h. Insoluble potassium salt was removed by centrifugation. LiBr (44 mg, 0.5 mmol) was added. The solution changed immediately to a deep blue/purple one. THF was reduced in volume (0.2 mL). The crystallised solid was washed with petroleum ether to remove traces of HMDS. **24a**. (329 mg, 0.46 mmol, 92 %). blue purple solid. Anal. Calcd for **24a** (C<sub>30</sub>H<sub>37</sub>Br<sub>2</sub>LiNNiO<sub>3</sub>P): C, 50.32; H, 5.21; N, 1.96. Found: C, 49.91; H, 5.61; N, 1.80. **24b**. (300 mg, 0.42 mmol, 84%). blue solid. Anal. Calcd for **24b** (C<sub>31</sub>H<sub>39</sub>Br<sub>2</sub>LiNNiO<sub>3</sub>P): C, 51.00; H, 5.38; N, 1.92. Found: C, 50.76; H, 5.63; N, 1.83. **24c**. (300 mg, 0.41 mmol, 82%). green solid. Anal. Calcd for **24c** (C<sub>32</sub>H<sub>33</sub>Br<sub>2</sub>LiNNiO<sub>3</sub>P): C, 52.22; H, 4.52; N, 1.90. Found: C, 51.87; H, 4.68; N, 1.79.

### Synthesis of complexes **25a-c**

KHMDS (200 mg, 1 mmol) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min of stirring at RT, insoluble potassium salts (KCl) was removed by centrifugation. [NiBr<sub>2</sub>(DME)] (154 mg, 0.5 mmol) was added resulting immediately in a change of color. Stirring was continued for 2h. Insoluble potassium salt was removed by centrifugation. AlBr<sub>3</sub> (134 mg, 0.5 mmol) was added. The solution changed immediately to a deep blue/purple one. After one night stirring, blue solid precipitated out. THF was reduced in volume (2 mL) to favor the precipitation. The solid was separated by centrifugation, washed with petroleum ether to remove traces of HMDS, dried in vacuum. **25a**.

(240 mg, 0.32 mmol, 64%). brown solid. Anal. Calcd for **25a** ( $C_{22}H_{23}AlBr_4NNiOP$ ): C, 35.06; H, 3.08; N, 1.86. Found: C, 35.15; H, 3.12; N, 1.76. **25b**. (230 mg, 0.31 mmol, 62%). brown solid. Anal. Calcd for **25b** ( $C_{23}H_{25}AlBr_4NNiOP$ ): C, 35.98; H, 3.28; N, 1.82. Found: C, 36.08; H, 3.40; N, 1.92. **5c**. (240 mg, 0.31 mmol, 62%). brown solid. Anal. Calcd for **25c** ( $C_{24}H_{19}AlBr_4NNiOP$ ): C, 37.26; H, 2.48; N, 1.81. Found: C, 37.33; H, 2.55; N, 1.75.

### Synthesis of complexes **26a-c**

KHMDS (200 mg, 1 mmol) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min of stirring at RT, insoluble potassium salts (KCl) was removed by centrifugation.  $[NiBr_2(DME)]$  (154 mg, 0.5 mmol) was added resulting immediately in a change of color. Stirring was continued for 2h. Insoluble potassium salt was removed by centrifugation.  $PPh_3$  (122 mg, 0.5 mmol) was added. The solution changed immediately to a deep green one. After stirring overnight, THF was reduced in volume (1 mL) and a green solid precipitated out. The solid was separated by centrifugation and washed with petroleum ether to remove traces of HMDS, dried in vacuum. **26a**. (260 mg, 0.35 mmol, 70%). green solid. Anal. Calcd for **26a** ( $C_{40}H_{38}BrNNiOP_2$ ): C, 64.12; H, 5.11; N, 1.87. Found: C, 63.98; H, 5.22; N, 1.76. **26b**. (280 mg, 0.37 mmol, 73 %). Green solid. Anal. Calcd for **26b** ( $C_{41}H_{40}BrNNiOP_2$ ): C, 64.51; H, 5.28; N, 1.84. Found: C, 65.08; H, 4.40; N, 1.92. **26c**. (315 mg, 0.41 mmol, 83%). green solid. Anal. Calcd for **26c** ( $C_{42}H_{34}BrNNiOP_2$ ): C, 65.58; H, 4.45; N, 1.82. Found: C, 65.44; H, 4.52; N, 1.90.

## Experimental Section

### III. Chapter 3

#### General considerations

All experiments, unless otherwise stated, were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, diethylether, petroleum ether), from P<sub>2</sub>O<sub>5</sub> (dichloromethane). (Protected) *o*-phosphinophenol compounds **X1** and **X2**,<sup>5</sup> [NiBr<sub>2</sub>(DME)]<sup>2</sup> and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>]<sup>6</sup> were prepared according to the literature. All other reagents and chemicals were obtained commercially and used without further purification.

Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C and 121.5 MHz for <sup>31</sup>P. Solvent peaks were used as internal references for <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm). <sup>31</sup>P{<sup>1</sup>H} are relative to a 85% H<sub>3</sub>PO<sub>4</sub> external reference. Coupling constant are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual. The labeling schemes of the phosphasalen derivatives are given in schemes 1 and 2. IR spectra were recorded on a Perkin Elmer spectrometer and are reported in terms of frequency of absorption (cm<sup>-1</sup>) using for the intensity the following abbreviations: w (weak), m (medium), s (strong). Electronic ionization mass spectra (EI-MS) were recorded with a JEOL GCmate instrument. Elemental analyses were performed by the Elemental analysis service of the London Metropolitan University (United Kingdom).

#### Electrochemical study

The electrochemical experiments were performed using a Vestastat potentiostat/galvanostat with a three-electrode cell using a Au disk as the working electrode, a Pt gauze as the counter electrode, and a Saturated Calomel Electrode as the reference electrode. Measurements were made in a CH<sub>2</sub>Cl<sub>2</sub>/DMF solvent mixture (60/40) with a concentration, of 3.8 mmol L<sup>-1</sup> and 2.0 mmol L<sup>-1</sup> for the nickel and palladium complexes respectively. Tetrabutylammonium tetrafluoroborate salt served as electrolyte (concentration 0.12 mol L<sup>-1</sup>). Potentials were recorded at 50 mV s<sup>-1</sup>.

## Synthesis of 27

150  $\mu\text{L}$  of  $\text{Br}_2$  (2.92 mmol) is added to the solution of the protected phosphine (981.1 mg, 2.92 mmol) in dichloromethane (15 mL) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . The cold bath was then removed. After one hours of stirring at room temperature, the resulting lemonade solution is cooled down to  $-78^\circ\text{C}$ . Triethylamine (407  $\mu\text{L}$ , 2.92 mmol) and then ethylenediamine (97.6  $\mu\text{L}$ , 1.96 mmol) is added to this solution. Stirring is continued for 2 days at room temperature to yield a yellow solution and a white precipitate (probably the oxidation byproducts). The mixture is extracted three times with water (3x15 mL); the organic layer is dried over  $\text{MgSO}_4$  and dichloromethane is evaporated in vacuum. The residue is dissolved in THF (5 mL) and the product precipitates from this solution as a white solid. (900 mg, 70%). It is easily oxidized in solution, especially in MeOH solution to give the phosphorane oxide.

**27:**  $^{31}\text{P}$  { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ ):  $\delta$  38.9 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.62 (m, 24H,  $\text{CH}(\text{PPh}_2) + \text{C}_b\text{H} + \text{C}_d\text{H}$ ), 7.17 (m, 4H,  $\text{C}_a\text{H} + \text{C}_c\text{H}$ ), 5.02 (s, 4H,  $\text{O}-\text{CH}_2-\text{O}$ ), 3.30 (b, 4H,  $\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}$ ), 3.01 (q,  $^3\text{J}_{\text{H,H}}=7.0$  Hz, 4H,  $\text{O}-\text{CH}_2-\text{CH}_3$ ), 0.86 (t,  $^3\text{J}_{\text{H,H}}=7.0$  Hz, 6H,  $\text{O}-\text{CH}_2-\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  159.1 (d,  $^2\text{J}_{\text{P,C}}=3.0$  Hz,  $\text{OC}^{\text{IV}}$ ), 136.7 (d,  $^4\text{J}_{\text{P,C}}=1.0$  Hz,  $\text{C}_b\text{H}$ ), 134.9 (d,  $^2\text{J}_{\text{P,C}}=8.5$  Hz,  $\text{C}_d\text{H}$ ), 133.8 (d,  $^4\text{J}_{\text{P,C}}=3.0$  Hz,  $p\text{-CH}(\text{PPh}_2)$ ), 132.7 (d,  $^2\text{J}_{\text{P,C}}=11.5$  Hz,  $o\text{-CH}(\text{PPh}_2)$ ), 129.2 (d,  $^3\text{J}_{\text{P,C}}=13.5$  Hz,  $m\text{-CH}(\text{PPh}_2)$ ), 122.2 (d,  $^3\text{J}_{\text{P,C}}=14.0$  Hz,  $\text{C}_{a/c}\text{H}$ ), 120.8 (d,  $^1\text{J}_{\text{P,C}}=106.5$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 114.3 (d,  $^3\text{J}_{\text{P,C}}=7.0$  Hz,  $\text{C}_{c/a}\text{H}$ ), 109.2 (d,  $^2\text{J}_{\text{P,C}}=104.5$  Hz,  $\text{C}^{\text{IV}}\text{-PPh}_2$ ), 92.7 (s,  $\text{O}-\text{CH}_2-\text{O}$ ), 64.2 (s,  $\text{CH}_3-\text{CH}_2-\text{O}$ ), 42.9 (d,  $^2\text{J}_{\text{P,C}}=7.5$  Hz,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 14.3 (s,  $\text{CH}_3-\text{CH}_2-\text{O}$ )

## Synthesis of 28

From **27**: The protected daminophosphonium salt (2 g, 2.92 mmol) was added into a solution of  $\text{CH}_2\text{Cl}_2$  (20 mL) saturated with  $\text{HCl}(\text{g})$ . The solution  $\text{HCl}/\text{CH}_2\text{Cl}_2$  was prepared under  $\text{N}_2$  whereas the addition was not under  $\text{N}_2$ . The resulting clear yellow solution became slightly cloudy and after ten minutes, the quantity of solid became significant. The schlenk was exposed to air during one minute and then reclosed. After another ten minutes, the solution had turned into heavy white slurry.  $\text{HCl}$  and  $\text{CH}_2\text{Cl}_2$  was evaporated, then  $\text{CH}_2\text{Cl}_2$  (20 mL) was reintroduced and the solid was separated by centrifugation, washed with  $\text{CH}_2\text{Cl}_2$  (2.1 g, 2.35 mmol, 81%).

From **X2**:  $\text{Br}_2$  (213  $\mu\text{L}$ , 4.14 mmol) is added to a solution of *o*-diphenylphosphinophenol **X2** (1.153 g, 4.14 mmol) in dichloromethane (30 mL) at  $-78^\circ\text{C}$ . The cold bath was then removed. After one hour stirring at room temperature, the resulting pale yellow solution is cooled down to  $-78^\circ\text{C}$ . Tributylamine (987  $\mu\text{L}$ , 4.14 mmol) and then ethylenediamine (138.5  $\mu\text{L}$ , 2.07 mmol) is added to this solution. Stirring is continued for 2 days at room temperature to yield a yellow solution and a white precipitate. Dichloromethane was evaporated in vacuum. THF (30 mL) was introduced resulting in the formation of a heavy white slurry. The white solid was separated by filtration under  $\text{N}_2$ , washed with THF (4x10mL), dried in vacuum (1.060 g, 63%).

$^{31}\text{P}$  { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ ):  $\delta$  39.3 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.67-7.59 (12H, m,  $p\text{-CH}(\text{PPh}_2)$ ,  $o\text{-CH}(\text{PPh}_2)$ ), 7.52-7.46 (12H, m,  $m\text{-CH}(\text{PPh}_2)$ ,  $\text{CH}_a$ ,  $\text{CH}_b$ ), 6.86-6.75 (4H, m,  $\text{CH}_c$ ,  $\text{NH}$ ), 6.57

(2H, dd,  $^3J_{\text{H,H}} = 8.0$  Hz,  $^3J_{\text{P,H}} = 14.5$  Hz,  $\text{CH}_d$ ), 3.43 (4H, d,  $^3J_{\text{P,H}} = 10.5$  Hz,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  159.7 (d,  $^2J_{\text{P,C}} = 0.5$  Hz,  $\text{OC}^{\text{IV}}$ ), 136.1 (d,  $^4J_{\text{P,C}} = 1.0$  Hz,  $\text{C}_b\text{H}$ ), 133.3 (d,  $^2J_{\text{P,C}} = 11.5$  Hz,  $\text{C}_d\text{H}$ ), 133.1 (d,  $^4J_{\text{P,C}} = 3.0$  Hz,  $p\text{-CH}(\text{PPh}_2)$ ), 131.9 (d,  $^2J_{\text{P,C}} = 11.5$  Hz,  $o\text{-CH}(\text{PPh}_2)$ ), 128.5 (d,  $^3J_{\text{P,C}} = 13.5$  Hz,  $m\text{-CH}(\text{PPh}_2)$ ), 121.4 (d,  $^1J_{\text{P,C}} = 106.5$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 119.6 (d,  $^3J_{\text{P,C}} = 13.5$  Hz,  $\text{C}_c\text{H}$ ), 117.7 (d,  $^3J_{\text{P,C}} = 7.0$  Hz,  $\text{C}_a\text{H}$ ), 106.8 (d,  $^2J_{\text{P,C}} = 104.0$  Hz,  $\text{PPh}_2\text{C}^{\text{IV}}$ ), 43.3 (d,  $^2J_{\text{P,C}} = 1.5$  Hz,  $\text{CH}_2$ ). HR-EI-MS: 307.1132 ( $[\text{M}-2\text{Br}]^{2+}$ ;  $\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_2\text{P}_2^{2+}$ ; calcd 307.1126).

## Synthesis of 29

KHMDS (7.0 g, 35.1 mmol) was added to a suspension of the aminophosphonium salt (8.8 mmol) in THF (320 mL) at ambient temperature. After 16 h, a cloudy solution was formed. The white potassium bromide by-product was removed by centrifugation. The solvent was removed in vacuum and the residue was dissolved in petroleum ether (60 mL). After 5 minutes of sonification, a white slurry was formed. The white solid was separated by centrifugation, washed with petroleum ether (20 mL) and dried in vacuum.

**29:** (6.0 g, 8.7 mmol, 99%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  18.6 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  7.73-7.67 (m, 8H,  $o\text{-CH}(\text{PPh}_2)$ ), 7.62-7.57 (m,  $^5J_{\text{P,H}} = 1.5$  Hz, 4H,  $p\text{-CH}(\text{PPh}_2)$ ), 7.55-7.49 (d,  $^4J_{\text{P,H}} = 2.0$  Hz, 8H,  $m\text{-CH}(\text{PPh}_2)$ ), 7.09 (m, 2H,  $^3J_{\text{H,H}} = 8.5$  Hz,  $^3J_{\text{H,H}} = 7.0$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 2H,  $\text{C}_b\text{H}$ ), 6.6-6.61 (m, 2H,  $^3J_{\text{H,H}} = 8.5$  Hz, 2H,  $\text{C}_a\text{H}$ ), 6.47 (ddd,  $^4J_{\text{H,H}} = 1.5$  Hz,  $^3J_{\text{H,H}} = 7.0$  Hz,  $^3J_{\text{P,H}} = 16.0$  Hz, 2H,  $\text{C}_d\text{H}$ ), 6.05 (ddd,  $^3J_{\text{H,H}} = ^3J'_{\text{H,H}} = 7.0$  Hz,  $^4J_{\text{P,H}} = 3.0$  Hz, 2H,  $\text{C}_c\text{H}$ ), 3.42 (dd,  $^3J_{\text{P,H}} = 6.0$  Hz,  $^3J'_{\text{P,H}} = 6.5$  Hz, 4H,  $\text{N-CH}_2\text{-CH}_2\text{-N}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  174.3 (d,  $^2J_{\text{P,C}} = 3.6$  Hz,  $\text{O-C}^{\text{IV}}$ ), 132.9 (d,  $^2J_{\text{P,C}} = 12.9$  Hz,  $\text{C}_d\text{H}$ ), 132.8 (d,  $^1J_{\text{P,C}} = 77.2$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 132.1 (d,  $^4J_{\text{P,C}} = 1.3$  Hz,  $\text{C}_b\text{H}$ ), 131.7 ( $^2J_{\text{P,C}} = 8.2$  Hz,  $o\text{-CH}(\text{PPh}_2)$ ), 129.0 (d,  $^4J_{\text{P,C}} = 2.1$  Hz,  $p\text{-CH}(\text{PPh}_2)$ ), 127.0 (d,  $^3J_{\text{P,C}} = 10.3$  Hz,  $m\text{-CH}(\text{PPh}_2)$ ), 121.8 (d,  $^3J_{\text{P,C}} = 9.0$  Hz,  $\text{C}_a\text{H}$ ), 112.5 (d,  $^1J_{\text{P,C}} = 128.7$  Hz,  $\text{C}^{\text{IV}}\text{-PPh}_2$ ), 107.0 (d,  $^3J_{\text{P,C}} = 15.2$  Hz,  $\text{C}_c\text{H}$ ), 50.4 (dd,  $^2J_{\text{P,C}} = 26.9$  Hz,  $^3J_{\text{P,C}} = 8.0$  Hz,  $\text{N-CH}_2\text{-CH}_2\text{-N}$ ). Anal. Calcd for  $\text{C}_{38}\text{H}_{32}\text{K}_2\text{N}_2\text{O}_2\text{P}_2$ : C, 66.26; H, 4.68; N, 4.07. Found: C, 66.19; H, 4.73; N, 3.99.

## Synthesis of 30

THF (5 mL) was added to a mixture of KHMDS (94.3 mg, 0.47 mmol) and **28** (91.4 mg, 0.12 mmol). After 2h, potassium salt was removed by centrifugation and  $[\text{PdCl}_2(\text{PhCN})_2]$  (45.3 mg, 0.12 mmol) was added to the obtained colorless solution, which became immediately yellow. After 16h, the precipitated brown solid was separated by centrifugation, dissolved in dichloromethane to remove the insoluble potassium salt. Then the solvent was evaporated and the obtained residue was washed with petroleum ether (5 mL) to give **30** as a yellow solid (63 mg, 73%)

**30:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  33.7 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.55-7.46 (12H, m,  $o\text{-CH}(\text{PPh}_2)$ ,  $p\text{-CH}(\text{PPh}_2)$ ), 7.44-7.38 (8H, m,  $m\text{-CH}(\text{PPh}_2)$ ), 7.07 (2H, vtdd,  $^3J_{\text{H,H}} = 7.0$  Hz,  $^3J_{\text{H,H}} = 8.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz,  $^5J_{\text{P,H}} = 0.5$  Hz,  $\text{C}_b\text{H}$ ), 6.78 (2H, ddd,  $^3J_{\text{H,H}} = 8.5$  Hz,  $^4J_{\text{H,H}} = 1.0$  Hz,  $^4J_{\text{P,H}} = 6.5$  Hz,  $\text{C}_a\text{H}$ ), 6.32 (2H, ddd,  $^3J_{\text{H,H}} = 8.0$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz,  $^3J_{\text{P,H}} = 16.0$  Hz,  $\text{C}_d\text{H}$ ), 6.18 (2H, dddd,  $^3J_{\text{H,H}} = 8.0$  Hz,  $^3J_{\text{H,H}} = 7.0$  Hz,  $^4J_{\text{H,H}} = 1.0$  Hz,  $^4J_{\text{P,H}} = 3.0$  Hz,  $\text{C}_c\text{H}$ ), 2.54 (4H, vt,  $J_{\text{P,H}} = 4.5$  Hz,  $\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  172.5 (s,  $\text{OC}^{\text{IV}}$ ), 134.9 (br, s,  $\text{C}_b\text{H}$ ); 134.2 (d,  $^2J_{\text{P,C}} = 10.0$  Hz,  $o\text{-CH}(\text{PPh}_2)$ ).

CH(PPh<sub>2</sub>)), 133.3 (br. s, <sup>4</sup>J<sub>P,C</sub> = 1.0 Hz, *p*-CH(PPh<sub>2</sub>)), 133.1 (<sup>2</sup>J<sub>P,C</sub> = 13.0 Hz, C<sub>d</sub>H), 129.7 (d, <sup>3</sup>J<sub>P,C</sub> = 12.0 Hz, *m*-CH(PPh<sub>2</sub>)), 127.2 (d, <sup>1</sup>J<sub>P,C</sub> = 89.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 122.8 (d, <sup>3</sup>J<sub>P,C</sub> = 8.0 Hz, C<sub>a</sub>H), 114.0 (d, <sup>3</sup>J<sub>P,C</sub> = 15.0 Hz, C<sub>e</sub>H), 110.4 (d, <sup>1</sup>J<sub>P,C</sub> = 122.0 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 53.8 (dd, <sup>2</sup>J<sub>P,C</sub> = 17.5 Hz, <sup>3</sup>J<sub>P,C</sub> = 5.0 Hz, CH<sub>2</sub>); IR (cm<sup>-1</sup>): 1586 (m), 1534 (w), 1459 (m, ν<sub>CC</sub> aromatic), 1442 (s), 1327 (m), 1257 (m), 1124 (w), 1110(s), 1084(w), 1069(w), 1020 (w), 1000 (w), 867 (m, b), 800 (m), 769 (w), 747 (s), 722 (w), 710 (w), 693 (s). Anal. Calcd for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pd: C, 63.65; H, 4.50; N, 3.91. Found: C, 63.74; H, 4.30; N, 3.94.

### Synthesis of **31**

THF (5 mL) was added to a mixture of KHMDS (94.3 mg, 0.47 mmol) and **28** (91.4 mg, 0.12 mmol). After 2h, potassium salt was removed by centrifugation and [NiBr<sub>2</sub>(DME)] (36.4 mg, 0.12 mmol) was added to the obtained colorless solution which became immediately deep purple. After 30 min, a purple solid precipitated out from the mixture and the color of the solution faded. The solid was separated by centrifugation, and then dissolved in dichloromethane to remove the insoluble potassium salt. After evaporation of the solvent residue was washed with petroleum ether (5mL) giving **31** as a purple solid (65 mg, 82%).

**31**: <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 32.8 (s, P<sup>V</sup>); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.76-7.66 (12H, m, *o*-CH(PPh<sub>2</sub>), *p*-CH(PPh<sub>2</sub>)), 7.62-7.56 (8H, m, *m*-CH(PPh<sub>2</sub>)), 7.10 (2H, vtd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, C<sub>b</sub>H), 6.69 (2H, dd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 6.5 Hz, C<sub>a</sub>H), 6.49 (2H, ddd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 15.0 Hz, C<sub>d</sub>H), 6.26 (2H, vtd, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>P,H</sub> = 3.0 Hz, C<sub>e</sub>H), 2.16-2.13 (4H, m, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 170.1 (s, OC<sup>IV</sup>), 133.3 (d, <sup>4</sup>J<sub>P,C</sub> = 1.0 Hz, C<sub>b</sub>H), 133.1 (d, <sup>2</sup>J<sub>P,C</sub> = 10.0 Hz, *o*-CH(PPh<sub>2</sub>)), 132.3 (d, <sup>4</sup>J<sub>P,C</sub> = 2.0 Hz, *p*-CH(PPh<sub>2</sub>)), 131.2 (<sup>2</sup>J<sub>P,C</sub> = 12.0 Hz, C<sub>d</sub>H), 128.9 (d, <sup>3</sup>J<sub>P,C</sub> = 12.0 Hz, *m*-CH(PPh<sub>2</sub>)), 127.4 (d, <sup>1</sup>J<sub>P,C</sub> = 90.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 122.7 (d, <sup>3</sup>J<sub>P,C</sub> = 8.0 Hz, C<sub>a</sub>H), 113.1 (d, <sup>3</sup>J<sub>P,C</sub> = 14.5 Hz, C<sub>e</sub>H), 108.0 (d, <sup>1</sup>J<sub>P,C</sub> = 119.6 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 50.0 (dd, <sup>2</sup>J<sub>P,C</sub> = 16.0 Hz, <sup>3</sup>J<sub>P,C</sub> = 2.0 Hz, CH<sub>2</sub>); IR (cm<sup>-1</sup>): 1586 (m), 1534 (w), 1459 (m), 1440 (s), (1300 m), 1275 (m), 1137 (w), 1116(s), 1098(m), 1081(m), 1027 (m), 1000 (w), 889 (w), 867 (w), 861(w), 811 (m), 778 (w), 752 (s), 727 (w), 710 (w), 697 (s). Anal. Calcd for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>NiO<sub>2</sub>P<sub>2</sub>: C, 68.19; H, 4.82; N, 4.19. Found: C, 68.00; H, 4.74; N, 4.05.

## Experimental Section

### IV. Chapter 4

#### General considerations

All experiments, unless otherwise stated, were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were directly taken from a MBraun MB-SPS 800 Solvent Purification Machine.  $[\text{NiBr}_2(\text{DME})]_2$  was prepared according to the literature. All other reagents and chemicals were obtained commercially and used without further purification.

Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for  $^1\text{H}$ , 75.5 MHz for  $^{13}\text{C}$  and 121.5 MHz for  $^{31}\text{P}$ . Solvent peaks were used as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts (ppm).  $^{31}\text{P}\{^1\text{H}\}$  are relative to a 85%  $\text{H}_3\text{PO}_4$  external reference. Coupling constant are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual. The labeling schemes of the phosphasalen derivatives are given in schemes 1 and 2. Elemental analyses were performed by the Elemental analysis service of the London Metropolitan University (United Kingdom).

#### Electrochemical study

The electrochemical experiments were performed using a Vestastat potentiostat/galvanostat with a three-electrode cell using a Au disk as working electrode, a Pt gauze as the counter electrode, and a Saturated Calomel Electrode as reference electrode. Measurements were made in  $\text{CH}_2\text{Cl}_2$  with a concentration, of  $3.0 \text{ mmol L}^{-1}$  for the nickel complexes. Tetrabutylammonium tetrafluoroborate salt served as electrolyte (concentration  $0.12 \text{ mol L}^{-1}$ ). Potentials were recorded at  $50 \text{ mV s}^{-1}$ .

#### Synthesis of 32

At  $0^\circ\text{C}$ , 2,4-ditert-butyl phenol (23.127 g, 112.1 mmol) was added to a slurry of NaH (60% in mineral oil, 5.605 g, 140.1 mmol) in DMF (60 mL), resulted in a yellow slurry. Stirring was continued for 90 minutes at  $0^\circ\text{C}$ , then chloromethyl ethyl ether (13 mL, 140.1 mmol) was added dropwise and the cold bath was removed. After 90 minutes of stirring at room temperature, 90 mL of distilled water was added. The mixture was extracted with petroleum ether (4x100 mL).



The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. Petroleum ether was evaporated at low temperature (the product was rather volatile), resulting in a yellow oil. The crude oil contains traces of solvent and will be used for the next step without further purification (30g, 112 mmol, 100%).

**32:** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.34 (d, <sup>4</sup>J<sub>H,H</sub> = 2.5 Hz, 1H, tBu-C<sup>IV</sup>-CH-C<sup>IV</sup>-tBu), 7.17 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 2.5 Hz, 1H, tBu-C<sup>IV</sup>-CH-CH), 7.08 (d, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, 1H, tBu-C<sup>IV</sup>-CH-CH), 5.27 (s, 2H, O-CH<sub>2</sub>-O), 3.75 (q, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>), 1.41 (s, 9H, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.32 (s, 9H, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.26 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>)

### Synthesis of 33

At -78°C, a solution containing n-BuLi (1.6M/hexanes, 76 mL, 121 mmol) and TMEDA (tetramethylethylenediamine, 18 mL, 121 mol) in petroleum ether (20 mL) was added into a solution of **32** (30g, 112 mmol) in petroleum ether (100 mL). The cold bath was removed and stirring was continued at room temperature. After 2h, ClPPh<sub>2</sub> (20.3 mL, 115 mmol) was added into the resulted yellow suspension at -78°C. After removal of the cold bath, a red-purple solution was obtained, which transformed into an orange slurry after 16h. The solvents were evaporated and the residue was taken in Et<sub>2</sub>O (170 mL) and extracted with H<sub>2</sub>O (100 mL). The aqueous phase is extracted three times with Et<sub>2</sub>O (3x100 mL) and the total organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of Et<sub>2</sub>O, the viscous residue was recrystallised in dried MeOH, giving the product as colorless crystals (42g, 93mmol, 83%)

**33:** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -12.6 (s, P<sup>V</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.29 (d, <sup>4</sup>J<sub>H,H</sub> = 2.5 Hz, 1H, C<sub>b</sub>H), 7.24-7.21 (m, 6H, CH(PPh<sub>2</sub>)), 7.17-7.12 (m, 4H, CH(PPh<sub>2</sub>)), 6.57 (dd, <sup>4</sup>J<sub>H,H</sub> = 2.5 Hz, <sup>3</sup>J<sub>P,H</sub> = 4.6 Hz, 1H, C<sub>d</sub>H), 5.15 (d, <sup>3</sup>J<sub>H,H</sub> = 1.7 Hz, 2H, O-CH<sub>2</sub>-O), 3.67 (q, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>), 1.33 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.03 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>), 0.98 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 156.7 (d, <sup>2</sup>J<sub>P,C</sub> = 19.7 Hz, OC<sup>IV</sup>), 146.0 (s, C<sub>c</sub><sup>IV</sup>), 142.4 (d, <sup>4</sup>J<sub>P,C</sub> = 3.0 Hz, C<sub>a</sub><sup>IV</sup>), 137.8 (d, <sup>1</sup>J<sub>P,C</sub> = 11.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 133.9 (d, <sup>2/3</sup>J<sub>P,C</sub> = 19.9 Hz, *o*-or *m*-CH(PPh<sub>2</sub>)), 130.6 (d, <sup>1</sup>J<sub>P,C</sub> = 11.5 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 130.5 (d, <sup>2</sup>J<sub>P,C</sub> = 2.6 Hz, C<sub>d</sub>H), 130.2 (s, *p*-CH(PPh<sub>2</sub>)), 130.0 (d, <sup>2/3</sup>J<sub>P,C</sub> = 7.0 Hz, *o*-or *m*-CH(PPh<sub>2</sub>)), 125.9 (d, <sup>4</sup>J<sub>P,C</sub> = 1.5 Hz, C<sub>b</sub>H), 98.8 (d, <sup>4</sup>J<sub>P,C</sub> = 17.5 Hz, O-CH<sub>2</sub>-O), 65.7 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 35.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 15.5 (s, O-CH<sub>2</sub>-CH<sub>3</sub>)

### Synthesis of 34'

At 0°C, NBS (N-bromosuccinimide, 18.2g, 102,3 mmol) was added into a solution of 2,4-di-tert-butylphenol (20.1 g, 97.4 mmol) in acetonitrile (300 mL). Stirring was continued at room temperature overnight, giving an orange solution. 10 mL of saturated aqueous solution of sodium bisulfide was added and induced the precipitation of a white solid. After filtration of this precipitate, the mixture was extracted four times with petroleum ether (4x70 mL). The total organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, giving the product as a slightly yellow solid (24.9g, 90%).

**34'**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.33 (d,  $^4J_{\text{H,H}} = 2.5$  Hz, 1H,  $\text{tBu-C}^{\text{IV}}\text{-CH-C}^{\text{IV}}\text{-tBu}$ ), 7.25 (d,  $^4J_{\text{H,H}} = 2.5$  Hz, 1H,  $\text{tBu-C}^{\text{IV}}\text{-CH-CBr}$ ), 5.65 (s, 1H, OH), 1.41 (s, 9H,  $\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 1.29 (s, 9H,  $\text{C}^{\text{IV}}(\text{CH}_3)_3$ ).

### Synthesis of 34

From **33**: The protected phosphine (2g, 4.46 mmol) was added into a solution of dry MeOH (20 mL) saturated with HCl (g) at room temperature and under  $\text{N}_2$ . After 45 minutes, HCl and MeOH was evaporated. 15 mL of dry MeOH was added to dissolve the residue, resulting in a colorless solution with several small drops of oil. 1mL of petroleum ether was added to extract the oil. 5 mL of  $\text{H}_2\text{O}$  was added. Scrubbing the flask with a glass pipette led to formation of colorless crystals. More water (7 mL) was added and methanol was evaporated under vacuum for 5 minutes, resulting in more crystal formation and a clear solution. The white solid was separated and dried in vacuum. (1.64 g, 94%)

From **34'**: n-BuLi (1.6M in hexanes, 107.8 mL, 173 mmol) was added into a solution of **3'** (23g, 80.6 mmol) in  $\text{Et}_2\text{O}$  (170 mL) at  $-78^\circ\text{C}$ , giving immediately a white suspension. The cold bath was removed and stirring was continued at room temperature for 30 min, giving a pale yellow solution.  $\text{ClPPh}_2$  (14.5 mL, 80.6 mmol) was added into this solution at  $-78^\circ\text{C}$ . After overnight stirring, a white suspension was formed. The mixture was extracted quickly twice with aqueous solutions of  $\text{NaH}_2\text{PO}_4$  (0.1M, 2x100 mL). the organic layer was filtered to removed inorganic salts. MeOH (30 mL) was added and the solution was evaporated under vacuum until the volume of the remaining solvent was about 30 mL. A white solid precipitated out from the green solution. This solid was separated by filtration, washed with MeOH (2x5mL) and dried in vacuum. (28 g, 90%)

**34**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -30.8 (s, P);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.26-7.25 (m, 11H,  $\text{CH}(\text{PPh}_2) + \text{C}_b\text{H}$ ), 6.81 (dd,  $^4J_{\text{H,H}} = 1.5$  Hz,  $^3J_{\text{P,H}} = 5.5$  Hz, 1H,  $\text{C}_d\text{H}$ ), 6.60 (d,  $^4J_{\text{P,H}} = 10.0$  Hz, 1H, OH), 1.34 (s, 9H,  $\text{C}_a\text{-C}(\text{CH}_3)_3$ ), 1.08 (s, 9H,  $\text{C}_c\text{-C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  156.3 (d,  $^2J_{\text{P,C}} = 19.2$  Hz,  $\text{OC}^{\text{IV}}$ ), 142.5 (d,  $^3J_{\text{P,C}} = 3.0$  Hz,  $\text{C}_c^{\text{IV}}$ ), 135.6 (d,  $^1J_{\text{P,C}} = 3.0$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 135.5 (d,  $^3J_{\text{P,C}} = 1.0$  Hz,  $\text{C}_a^{\text{IV}}$ ), 133.6 (d,  $^{2/3}J_{\text{P,C}} = 18.5$  Hz, *o*-or *m*- $\text{CH}(\text{PPh}_2)$ ), 129.5 (d,  $^2J_{\text{P,C}} = 3.5$  Hz,  $\text{C}_d\text{H}$ ), 129.1 (s, *p*- $\text{CH}(\text{PPh}_2)$ ), 128.8 (d,  $^{2/3}J_{\text{P,C}} = 7.5$  Hz, *o*-or *m*- $\text{CH}(\text{PPh}_2)$ ), 126.6 (s,  $\text{C}_b\text{H}$ ), 120.1 (s,  $\text{C}^{\text{IV}}\text{-PPh}_2$ ), 35.4 (d,  $^4J_{\text{P,C}} = 2.0$  Hz,  $\text{C}_c\text{-C}(\text{CH}_3)_3$ ), 34.7 (s,  $\text{C}_a\text{-C}(\text{CH}_3)_3$ ), 31.7 (s,  $\text{C}_c\text{-C}(\text{CH}_3)_3$ ), 29.2 (s,  $\text{C}_a\text{-C}(\text{CH}_3)_3$ ),

### Synthesis of 35a

At  $-78^\circ\text{C}$ , bromine (200  $\mu\text{L}$ , 3.88 mmol) was added dropwise to a solution of the phenolphosphine (1.516 g, 3.88 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL). The cold bath was removed and stirring was continued for 45 minutes at room temperature. Then the solution was cooled down to  $-78^\circ\text{C}$ .  $\text{Bu}_3\text{N}$  (926  $\mu\text{L}$ , 3.88 mmol) was added, followed by ethylene diamine (129.8  $\mu\text{L}$ , 1.94 mmol). The cold bath was removed. After 16h, a cloudy yellow solution was formed.  $\text{CH}_2\text{Cl}_2$  was evaporated, 15 mL of THF was added. With sonification, a heavy white slurry was formed. The white solid was separated by filtration, washed with THF (5x7 mL), dried in vacuum (1.47 g, 71%)

**35a.THF:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  40.3 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.15(b, 2H,  $\text{CH}(\text{PPh}_2)$ ), 7.75-7.56 (m, 18H,  $\text{CH}(\text{PPh}_2)$ ), 6.93 (b, 2H,  $\text{C}_b\text{H}$ ), 6.44 (dd,  $^4\text{J}_{\text{H,H}}=2.1$  Hz,  $^3\text{J}_{\text{P,H}}=15.2$  Hz, 2H,  $\text{C}_d\text{H}$ ), 3.78 (m, 4H,  $\text{O}-\text{CH}_2$  (THF)), 3.74 (b, 4H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 1.85 (m, 4H,  $\text{O}-\text{CH}_2-\text{CH}_2$  (THF)), 1.59 (b, 2H,  $\text{OH}$ ), 1.52 (s, 18H,  $\text{C}_a-\text{C}(\text{CH}_3)_3$ ), 1.08 (s, 18H,  $\text{C}_c-\text{C}(\text{CH}_3)_3$ ).

The insolubility of the product in all regular deuterated solvents prevents  $^{13}\text{C}\{^1\text{H}\}$  NMR characterization.

### Synthesis of 35b

At  $-78^\circ\text{C}$ , bromine (500  $\mu\text{L}$ , 9.71 mmol) was added dropwise to a solution of the phenolphosphine (3.781 g, 9.71 mmol) in  $\text{CH}_2\text{Cl}_2$  (120 mL). The cold bath was removed and stirring was continued for 3 hours at RT. Then the solution was cooled down to  $-78^\circ\text{C}$ . DABCO (1,4-diazabicyclo[2.2.2]octane, 545 mg, 4.86 mmol) was added, followed by *rac*-1,2-diaminocyclohexane (582.9  $\mu\text{L}$ , 4.86 mmol). The cold bath was removed. After 16h, a cloudy yellow solution was formed.  $\text{CH}_2\text{Cl}_2$  was evaporated, 200 mL of THF was added. The insoluble DABCO salt was removed by centrifugation. THF was evaporated and the white solid was washed with  $\text{Et}_2\text{O}$  (2x5 mL), dried in vacuum (3.8 g, 75%)

**35b:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  38.5 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.59 (s, 2H,  $\text{NH}$ ), 7.77 (dd,  $^3\text{J}_{\text{H,H}}=7.5$  Hz,  $^3\text{J}_{\text{P,H}}=12.8$  Hz, 4H, *o*- $\text{CH}(\text{PPh}_2)$ ), 7.69 (dd,  $^3\text{J}_{\text{H,H}}=7.5$  Hz,  $^3\text{J}_{\text{P,H}}=14.2$  Hz, 4H, *o*- $\text{CH}(\text{PPh}_2)$ ), 7.70 (s, 1H,  $\text{OH}$ ), 7.69 (s, 1H,  $\text{OH}$ ), 7.50 (vtd,  $^3\text{J}_{\text{H,H}}=^3\text{J}'_{\text{H,H}}=7.5$  Hz,  $^4\text{J}_{\text{P,H}}=3.0$  Hz, 2H, *m*- $\text{CH}(\text{PPh}_2)$ ), 7.63 (vt,  $^3\text{J}_{\text{H,H}}=^3\text{J}'_{\text{H,H}}=7.5$  Hz, 2H, *m*- $\text{CH}(\text{PPh}_2)$ ), 7.40 (vt,  $^3\text{J}_{\text{H,H}}=^3\text{J}'_{\text{H,H}}=7.5$  Hz, 4H, *m*- $\text{CH}(\text{PPh}_2)$ ), 7.13 (vtd,  $^3\text{J}_{\text{H,H}}=^3\text{J}'_{\text{H,H}}=7.5$  Hz,  $^4\text{J}_{\text{P,H}}=3.3$  Hz, 4H, *p*- $\text{CH}(\text{PPh}_2)$ ), 6.56 (dd,  $^4\text{J}_{\text{H,H}}=2.2$  Hz,  $^5\text{J}_{\text{P,H}}=8.0$  Hz, 1H,  $\text{C}_b\text{H}$ ), 6.53 (dd,  $^4\text{J}_{\text{H,H}}=2.2$  Hz,  $^5\text{J}_{\text{P,H}}=8.0$  Hz, 1H,  $\text{C}_b\text{H}$ ), 6.37 (dd,  $^4\text{J}_{\text{H,H}}=2.2$  Hz,  $^3\text{J}_{\text{P,H}}=15.6$  Hz, 2H,  $\text{C}_b\text{H}$ ), 3.82 (m, 2H,  $\text{N}-\text{CH}-\text{CH}-\text{N}$ ), 2.05 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 1.59 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 1.53 (s, 18H,  $\text{C}_a-\text{C}(\text{CH}_3)_3$ ), 1.30 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 1.03 (s, 18H,  $\text{C}_c-\text{C}(\text{CH}_3)_3$ ), 0.93 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  155.9 (d,  $^3\text{J}_{\text{P,C}}=0.9$  Hz,  $\text{C}^{\text{IV}}-\text{O}$ ), 145.7 (d,  $^3\text{J}_{\text{P,C}}=8.2$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ); 144.5 (d,  $^3\text{J}_{\text{P,C}}=7.0$  Hz,  $\text{C}_{a,c}^{\text{IV}}$ ), 135.0-133.0 (m,  $\text{CH}(\text{PPh}_2)$ ), 131.8 (d,  $^4\text{J}_{\text{P,C}}=0.9$  Hz, *p*- $\text{CH}(\text{PPh}_2)$ ), 131.5 (d,  $^4\text{J}_{\text{P,C}}=0.9$  Hz, *p*- $\text{CH}(\text{PPh}_2)$ ), 129.7-128.9 (m,  $\text{CH}(\text{PPh}_2)$  +  $\text{C}_b\text{H}$ ), 128.6 (d,  $^2\text{J}_{\text{P,C}}=12.2$  Hz,  $\text{C}_d\text{H}$ ), 123.0 (d,  $^1\text{J}_{\text{P,C}}=109.7$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 121.7 (d,  $^1\text{J}_{\text{P,C}}=97.5$  Hz,  $\text{C}^{\text{IV}}-\text{PPh}_2$ ), 116.0 (d,  $^1\text{J}_{\text{P,C}}=106.2$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 59.0 (m,  $\text{N}-\text{CH}-\text{CH}-\text{N}$ ), 35.6 (s,  $\text{C}_a^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 34.7 (s,  $\text{C}_c^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 30.2 (s,  $\text{CH}_2(\text{cyclohexane})$ ), 30.0 (s,  $\text{CH}_2(\text{cyclohexane})$ ), 29.8 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 29.7 (s,  $\text{C}_{a,c}^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 29.5 (s,  $\text{C}_{a,c}^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 29.4 (s,  $\text{CH}_2(\text{cyclohexane})$ ), 28.8 (s,  $\text{CH}_2(\text{cyclohexane})$ ). Anal. Calcd for  $\text{C}_{58}\text{H}_{74}\text{Br}_2\text{N}_2\text{O}_2\text{P}_2$ : C, 66.16; H, 7.08; N, 2.66. Found: C, 66.29; H, 7.15; N, 2.67.

### Synthesis of 36a

KHMDS (7.0 g, 35.1 mmol) was added to a suspension of the aminophosphonium salt (8.8 mmol) in THF (320 mL) at ambient temperature. After 16 h, a cloudy solution was formed. The white potassium bromide by-product was removed by centrifugation. The solvent was removed *in vacuo* and the residue was dissolved in petroleum ether (60 mL). After 5 minutes of

sonification, a white slurry was formed. The white solid was separated by centrifugation, washed with petroleum ether (20 mL) and dried *in vacuo* (7.2 g, 78%)

**36a.2THF.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ ):  $\delta$  20.6 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR (Toluene- $d_8$ ):  $\delta$  7.52-7.50 (m, 10H,  $\text{CH}(\text{PPh}_2) + \text{C}_b\text{H}$ ), 7.05-7.01 (m, 12H,  $\text{CH}(\text{PPh}_2)$ ), 6.30 (dd,  $^4J_{\text{H,H}}=2.4$  Hz,  $^3J_{\text{P,H}}=17.1$  Hz, 2H,  $\text{C}_d\text{H}$ ), 3.41-3.38 (m, 8H,  $\text{O}-\text{CH}_2(\text{THF})$ ), 3.20 (vt,  $J_{\text{P,H}}=J'_{\text{P,H}}=5.0$  Hz, 4H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 1.70 (s, 18H,  $\text{C}_a-\text{C}(\text{CH}_3)_3$ ), 1.36 (m, 8H,  $\text{O}-\text{CH}_2-\text{CH}_2(\text{THF})$ ), 1.08 (s, 18H,  $\text{C}_c-\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ ):  $\delta$  173.4 (d,  $^2J_{\text{P,C}}=4.0$  Hz,  $\text{C}^{\text{IV}}-\text{O}$ ), 140.1 (d,  $^3J_{\text{P,C}}=9.5$  Hz,  $\text{C}_c^{\text{IV}}$ ), 134.2 (d,  $^1J_{\text{P,C}}=81.4$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 133.7 (d,  $^{2/3}J_{\text{P,C}}=7.5$  Hz, *o*- or *m*- $\text{CH}(\text{PPh}_2)$ ), 130.5 (d,  $^4J_{\text{P,C}}=1.9$  Hz, *p*- $\text{CH}(\text{PPh}_2)$ ), 128.8 (d,  $^2J_{\text{P,C}}=15.6$  Hz,  $\text{C}_d\text{H}$ ), 128.6 (d,  $^3J_{\text{P,C}}=17$  Hz,  $\text{C}_a^{\text{IV}}$ ), 128.4 (d,  $^{2/3}J_{\text{P,C}}=10.3$  Hz, *o*- or *m*- $\text{CH}(\text{PPh}_2)$ ), 127.4 (d,  $^4J_{\text{P,C}}=0.8$  Hz,  $\text{C}_b\text{H}$ ), 112.8 (d,  $^1J_{\text{P,C}}=134.2$  Hz,  $\text{C}^{\text{IV}}-\text{PPh}_2$ ), 52.1 (dd,  $J_{\text{P,C}}=9.3$  Hz,  $J'_{\text{P,C}}=29.7$  Hz,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 36.0 (d,  $^4J_{\text{P,C}}=2.1$  Hz,  $\text{C}_a^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 34.0 (d,  $^4J_{\text{P,C}}=0.6$  Hz,  $\text{C}_c^{\text{IV}}-\text{C}(\text{CH}_3)_3$ ), 31.9 (s,  $\text{C}(\text{CH}_3)_3$ ), 29.9 (s,  $\text{C}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{62}\text{H}_{80}\text{K}_2\text{N}_2\text{O}_4\text{P}_2$ : C, 70.42; H, 7.63; N, 2.65. Found: C, 70.57; H, 7.80; N, 2.49.

### Synthesis of 36b

**36b** was synthesised following the same procedure as **36a**.

**36b.HMDS.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (benzen- $d_6$ ):  $\delta$  15.8 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR (benzen- $d_6$ ):  $\delta$  7.72 (m, 4H,  $\text{CH}(\text{PPh}_2)$ ), 7.65 (m, 4H,  $\text{CH}(\text{PPh}_2)$ ), 7.65 (d,  $^4J_{\text{H,H}}=2.6$  Hz, 2H,  $\text{C}_b\text{H}$ ), 7.14 (m, 6H,  $\text{CH}(\text{PPh}_2)$ ), 7.02 (m, 6H,  $\text{CH}(\text{PPh}_2)$ ), 6.29 (dd,  $^4J_{\text{H,H}}=2.6$  Hz,  $^3J_{\text{P,H}}=16.8$  Hz, 2H,  $\text{C}_d\text{H}$ ), 3.09 (m, 2H,  $\text{N}-\text{CH}-\text{CH}-\text{N}$ ), 2.26 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 1.82 (s, 18H,  $\text{C}_a^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 1.49 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 1.22 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 1.17 (s, 18H,  $\text{C}_c^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 0.87 (m, 2H,  $\text{CH}_2(\text{cyclohexane})$ ), 0.02 (18H,  $\text{CH}_3\text{-HMDS}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzen- $d_6$ ):  $\delta$  173.3 (d,  $^3J_{\text{P,C}}=3.4$  Hz,  $\text{C}^{\text{IV}}-\text{O}$ ), 140.3 (d,  $^1J_{\text{P,C}}=73.2$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 140.3 (d,  $^3J_{\text{P,C}}=9.2$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ), 133.8 (d,  $^{2/3}J_{\text{P,C}}=13.8$  Hz, *m*-or *o*- $\text{CH}(\text{PPh}_2)$ ), 133.5 (d,  $^{2/3}J_{\text{P,C}}=12.5$  Hz, *m*-or *o*- $\text{CH}(\text{PPh}_2)$ ), 133.2 (d,  $^{2/3}J_{\text{P,C}}=8.4$  Hz, *m*-or *o*- $\text{CH}(\text{PPh}_2)$ ), 133.0 (d,  $^{2/3}J_{\text{P,C}}=9.8$  Hz, *m*-or *o*- $\text{CH}(\text{PPh}_2)$ ), 130.2 (d,  $^2J_{\text{P,C}}=17.2$  Hz,  $\text{C}_d\text{H}$ ), 130.3 (d,  $^4J_{\text{P,C}}=1.0$  Hz, *p*- $\text{CH}(\text{PPh}_2)$ ), 129.8 (d,  $^3J_{\text{P,C}}=15.7$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ), 128.4 (d,  $^{2/3}J_{\text{P,C}}=10.6$  Hz, *m*-or *o*- $\text{CH}(\text{PPh}_2)$ ), 128.0 (d,  $^4J_{\text{P,C}}=1.0$  Hz, *p*- $\text{CH}(\text{PPh}_2)$ ), 127.8 (s,  $\text{C}_b\text{H}$ ), 127.7 (d,  $^{2/3}J_{\text{P,C}}=11.0$  Hz, *m*-or *o*- $\text{CH}(\text{PPh}_2)$ ), 112.1 (d,  $^1J_{\text{P,C}}=133.9$  Hz,  $\text{C}^{\text{IV}}-\text{PPh}_2$ ), 65.7 (dd,  $J_{\text{P,C}}=9.2$  Hz,  $J'_{\text{P,C}}=26.1$  Hz,  $\text{N}-\text{CH}-\text{CH}-\text{N}$ ), 40.7 (s, b,  $\text{CH}_2(\text{cyclohexane})$ ), 36.2 (d,  $^4J_{\text{P,C}}=1.7$  Hz,  $\text{C}_a^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 34.1 (s,  $\text{C}_c^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 32.3-31.7 (m,  $\text{C}_c^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3 + \text{CH}_2(\text{cyclohexane})$ ), 30.2 (s,  $\text{C}_a^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 30.1 (s,  $\text{C}_a^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 2.0 (s,  $\text{CH}_3\text{-HMDS}$ ).

### Synthesis of 37a

To a solution of the phosphasalen dianion **36a** (372 mg, 0.35 mmol) in THF (10 mL) was added  $[\text{NiBr}_2(\text{DME})]$  (108 mg, 0.35 mmol) resulting immediately in a purple solution. After overnight stirring, precipitated KBr salt was removed by filtration under nitrogen. The product was obtained after evaporation of THF as a purple solid (285 mg, 0.32 mmol, 92%).

**37a:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  36.8 (s,  $\text{P}^{\text{V}}$ );  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.94 (m, 8H,  $\text{CH}(\text{PPh}_2)$ ), 7.60 (m, 12H,  $\text{CH}(\text{PPh}_2)$ ), 7.21 (s, 2H,  $\text{C}_b\text{H}$ ), 6.12 (d, b,  $^3J_{\text{P,H}}=14.2$  Hz, 2H,  $\text{C}_d\text{H}$ ), 2.05 (b, 4H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 1.36 (s, 18H,  $\text{C}_a-\text{C}(\text{CH}_3)_3$ ), 1.02 (s, 18H,  $\text{C}_c-\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR

(CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  168.2 (s, C<sup>IV</sup>-O), 142.2 (d,  $^3J_{P,C} = 7.8$  Hz, C<sup>IV</sup>), 134.7 (d,  $^3J_{P,C} = 15.2$  Hz, C<sup>IV</sup>), 133.9 (d,  $^{2/3}J_{P,C} = 9.2$  Hz, *o*- or *m*-CH(PPh<sub>2</sub>)), 132.4 (s, *p*-CH(PPh<sub>2</sub>)), 129.0 (d,  $^{2/3}J_{P,C} = 11.4$  Hz, *o*- or *m*-CH(PPh<sub>2</sub>)), 128.2 (s, C<sub>b</sub>H), 127.8 (d,  $^1J_{P,C} = 87.8$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 124.6 (d,  $^2J_{P,C} = 13.2$  Hz, C<sub>d</sub>H), 112.2 (d,  $^1J_{P,C} = 120.8$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 50.5 (dd,  $J_{P,C} = 3.8$  Hz,  $J_{P,C} = 18.8$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 35.8 (s, C<sub>a</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 34.0 (s, C<sub>c</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 31.4 (s, C<sub>c</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (s, C<sub>a</sub>-C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>54</sub>H<sub>64</sub>N<sub>2</sub>NiO<sub>2</sub>P<sub>2</sub>: C, 72.57; H, 7.22; N, 3.13. Found: C, 72.42; H, 7.13; N, 3.05.

### Synthesis of 37b

KHMDS (299 mg, 1.5 mmol) was added into a suspension of **35b** (398 mg, 0.374 mmol) in THF (10 mL), inducing the rapid dissolution of the solid and the formation of a couly colorless solution. After 2h, the insoluble potassium salt was removed by centrifugation. [NiBr<sub>2</sub>(DME)] (115 mg, 0.37 mmol) was added into the solution, leading immediately to a color change to deep purple/blue. After 3h, the insoluble potassium salt was removed by centrifugation, THF was evaporated. The blue/purple solid was washed with petroleum ether (8 mL), dried under vacuum. (300mg, 85%)

**37b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  30.0 (s, P<sup>V</sup>);  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.67 (ddd,  $^4J_{H,H} = 1.5$  Hz,  $^3J_{H,H} = 7.5$  Hz,  $^3J_{P,H} = 12.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.65 (vtd,  $^4J_{H,H} = 1.5$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.57 (vtd,  $^4J_{P,H} = 2.5$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.56 (vtd,  $^4J_{H,H} = 1.5$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.48 (ddd,  $^4J_{H,H} = 1.5$  Hz,  $^3J_{H,H} = 7.5$  Hz,  $^3J_{P,H} = 12.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.41 (vtd,  $^4J_{P,H} = 2.5$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.17 (d,  $^4J_{H,H} = 2.5$  Hz, 2H, C<sub>b</sub>H), 6.34 (dd,  $^4J_{H,H} = 2.5$  Hz,  $^3J_{P,H} = 15.5$  Hz, 2H, C<sub>d</sub>H), 3.02 (vtd,  $^3J_{H,H} = ^3J_{P,H} = 9.0$  Hz,  $^4J_{P,H} = 3.0$  Hz, 2H, N-CH-CH-N), 1.13 (s, b, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.10 (s, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.01 (m, 2H, CH<sub>2</sub>(cyclohexane)), 0.86 (m, 2H, CH<sub>2</sub>(cyclohexane)), 0.63 (m, 2H, CH<sub>2</sub>(cyclohexane)), 0.47 (m, 2H, CH<sub>2</sub>(cyclohexane));  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  168.4 (d,  $^3J_{P,C} = 2.5$  Hz, C<sup>IV</sup>-O), 141.9 (d,  $^3J_{P,C} = 8.2$  Hz, C<sub>c,a</sub><sup>IV</sup>), 134.7 (d,  $^{2/3}J_{P,C} = 9.7$  Hz, *m*- or *o*-CH(PPh<sub>2</sub>)), 133.8 (d,  $^1J_{P,C} = 82.1$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 133.7 (d,  $^3J_{P,C} = 15.2$  Hz, C<sub>c,a</sub><sup>IV</sup>), 133.7 (d,  $^{2/3}J_{P,C} = 9.8$  Hz, *m*- or *o*-CH(PPh<sub>2</sub>)), 132.7 (d,  $^4J_{P,C} = 2.9$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.8 (d,  $^4J_{P,C} = 2.9$  Hz, *p*-CH(PPh<sub>2</sub>)), 130.4 (d,  $^1J_{P,C} = 88.5$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 129.0 (d,  $^{2/3}J_{P,C} = 11.8$  Hz, *m*- or *o*-CH(PPh<sub>2</sub>)), 128.5 (d,  $^{2/3}J_{P,C} = 11.5$  Hz, *m*- or *o*-CH(PPh<sub>2</sub>)), 128.1 (d,  $^4J_{P,C} = 1.8$  Hz, C<sub>b</sub>H), 126.2 (d,  $^2J_{P,C} = 13.2$  Hz, C<sub>d</sub>H), 112.1 (d,  $^1J_{P,C} = 124.2$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 67.3 (dd,  $J_{P,C} = 5.8$  Hz,  $J'_{P,C} = 15.8$  Hz, N-CH-CH-N), 35.6 (d,  $^4J_{P,C} = 1.7$  Hz, C<sub>a,c</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.4 (s, CH<sub>2</sub>(cyclohexanediamine)), 34.1 (d,  $^4J_{P,C} = 1.0$  Hz, C<sub>c</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.6 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 29.8 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 25.5 (s, CH<sub>2</sub>(cyclohexanediamine)). Anal. Calcd for C<sub>58</sub>H<sub>70</sub>N<sub>2</sub>NiO<sub>2</sub>P<sub>2</sub>: C, 73.50; H, 7.44; N, 2.96. Found: C, 73.66; H, 7.35; N, 3.01.

### Synthesis of [37a][SbF<sub>6</sub>]

Addition of AgSbF<sub>6</sub> (34.4 mg, 0.1 mmol) into a solution of complex **37a** (89.4 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) induced a rapid colour change from blue to deep red and precipitation of silver. After removal of Ag by centrifugation, dichloromethane was evaporated and the residue was dissolved in toluene (1.5 mL), giving a deep red-brown solution. Green crystals were obtained

after one week of storage at  $-40^{\circ}\text{C}$ , which was then isolated by centrifugation and dried under vacuum. (104 mg, 95 %). Anal. Calcd for **[37a][SbF<sub>6</sub>]** C<sub>54</sub>H<sub>64</sub>F<sub>6</sub>N<sub>2</sub>NiO<sub>2</sub>P<sub>2</sub>Sb: C, 57.42; H, 5.71; N, 2.48. Found: C, 57.50; H, 5.80; N, 2.37.

## Experimental Section

### V. Chapter 5.

#### General considerations

All reactions were conducted under an atmosphere of dry nitrogen, or argon, using standard Schlenk and glovebox techniques. Solvents and reagents were obtained from commercial sources. Tetrahydrofuran, toluene, pentane, hexane and petroleum ether were distilled from sodium/benzophenone, under dry nitrogen. Dichloromethane was distilled from  $\text{CaH}_2$ , under dry nitrogen. *Rac*-lactide was recrystallised from anhydrous toluene and sublimed three times prior to use.  $[\text{YCl}_3(\text{THF})_{3.5}]^7$  was prepared following literature procedure.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Av300 spectrometer operating at 300 MHz for  $^1\text{H}$ , 75.5 MHz for  $^{13}\text{C}\{^1\text{H}\}$ , and 121.5 MHz for  $^{31}\text{P}\{^1\text{H}\}$ . Solvent peaks were used as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts (ppm).  $^{31}\text{P}$  peaks were referenced to external 85%  $\text{H}_3\text{PO}_4$ . When needed, higher resolution  $^{31}\text{P}\{^1\text{H}\}$  NMR and  $^1\text{H}\{^1\text{H}\}$  NMR (homo-decoupled spectroscopy) experiments were performed on a Bruker Av500 spectrometer, equipped with a z-gradient bbo/5 mm tuneable probe and a BSMS GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G/cmA.  $^1\text{H}$  NMR spectra for all lactide polymerizations were performed on a Bruker Av400 instrument. Coupling constant are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual.

Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University, Science Centre. Mass spectra were performed on a Micromass MALDI micro MX, using potassium salts for ionisation. PLA number averaged molecular weight,  $M_n$ , and polydispersity index ( $M_w/M_n$ ; PDI) were determined using gel permeation chromatography, equipped with multi-angle laser light scattering (GPC-MALLS). Two Polymer laboratories Mixed D columns were used in series, with THF as the eluent, at a flow rate of  $1 \text{ mL min}^{-1}$ , on a Polymer laboratories PL GPC-50 instrument at  $35^\circ\text{C}$ . The light scattering detector was a triple-angle detector (Dawn 8, Wyatt Technology), and the data were analyzed using Astra V version 5.3.4.18. The refractive angle increment for polylactide ( $\text{dn/dc}$ ) in THF was  $0.042 \text{ mL g}^{-1}$ .<sup>8</sup>

### General procedure for lactide polymerization

To a rapidly stirred solution of *rac*-lactide (288 mg, 2 mmol) in THF, in a vial in the glovebox, was added the appropriate quantity of a solution of the initiator, in tetrahydrofuran; the overall concentration of *rac*-lactide was therefore kept at 1 M. Aliquots of the reaction mixture were taken at regular intervals, precipitated in hexane and quenched in air. The solvent was allowed to evaporate slowly, in air, yielding a crude product which was analyzed by  $^1\text{H}$  NMR spectroscopy (to determine % conversion) and by GPC (to determine the  $M_n$  and PDI). The probability of syndiotactic linkages between monomer units ( $P_s$ ) is determined from the homonuclear decoupled  $^1\text{H}$  NMR spectrum:  $\delta$  5.14 and 5.22 ppm in  $\text{CDCl}_3$  for heterotactic PLA.<sup>9</sup>

### Synthesis of 38

At 0°C, bromine (2 mL, 38.83 mmol) was added into a solution of 2-tert-butyl-4-methoxyphenol (7.00 g, 38.83 mmol) in dichloromethane (200 mL), leading to immediate liberation of  $\text{HBr(g)}$  and the formation of a pale yellow solution. Stirring was continued at room temperature for 48h. Dichloromethane and  $\text{HBr}$  was evaporated, the residue was taken in  $\text{Et}_2\text{O}$  (200 mL), washed with an aqueous solution of  $\text{Na}_2\text{CO}_3$  (1M, 200 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated again. The product was purified by chromatography (eluent  $\text{Et}_2\text{O}$ /petroleum ether = 2.5/97.5).

**38** (7.15g, 71%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.88 (d,  $^4J_{\text{H,H}} = 3.0$  Hz, 1H,  $\text{C}_{\text{phenyl}}\text{H}$ ), 6.84 (d,  $^4J_{\text{H,H}} = 3.0$  Hz, 1H,  $\text{C}_{\text{phenyl}}\text{H}$ ), 5.42 (s, 1H, OH), 3.74 (s, 3H, O- $\text{CH}_3$ ), 1.38 (s, 9H,  $\text{C}^{\text{IV}}(\text{CH}_3)_3$ ).

### Synthesis of 39

$n\text{-BuLi}$  (1.6M in hexanes, 34.5 mL, 55.2 mmol) was added into a solution of **S1** (7.15 g, 27.6 mmol) in  $\text{Et}_2\text{O}$  (70 mL) at -78°C. After the addition, the cold bath was removed, an yellowish solution was obtained and stirring was continued at room temperature for 2h.  $\text{ClPPh}_2$  (4.95 mL, 27.6 mmol) was added giving immediately a white suspension. After overnight stirring at room temperature, the solid was isolated by filtration under inert atmosphere and was then put into 80 mL of  $\text{Et}_2\text{O}$ . An aqueous solution (40 mL) of  $\text{HBF}_4$  (1 M) was added, giving a biphasic system with the total disappearance of the solid. The organic phase was washed with  $\text{H}_2\text{O}$  (40 mL), dried over  $\text{MgSO}_4$ . The solvent was isolated, giving the product as a yellow viscous oil (8.4 g, 84%).

**39**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -28.3 (s,  $P^{\text{III}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.36 (m, 10H,  $\text{CH}(\text{PPh}_2)$ ), 6.94 (d,  $^4J_{\text{H,H}} = 3.0$  Hz, 1H,  $\text{C}_b\text{H}$ ), 6.49 (d,  $^2J_{\text{P,H}} = 10.0$  Hz, 1H, OH), 6.35 (dd,  $^3J_{\text{P,H}} = 5.0$  Hz,  $^4J_{\text{H,H}} = 3.0$  Hz, 1H,  $\text{C}_d\text{H}$ ), 3.58 (s, 3H, O- $\text{CH}_3$ ), 1.41 (s, 9H,  $\text{C}^{\text{IV}}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  152.9 (d,  $^2J_{\text{P,C}} = 3.0$  Hz,  $\text{C}^{\text{IV}}\text{-OH}$ ), 152.6 (d,  $^3J_{\text{P,C}} = 19.0$  Hz,  $\text{C}^{\text{IV}}\text{-OMe}$ ), 137.9 (d,  $J_{\text{P,C}} = 1.5$  Hz,  $\text{C}^{\text{IV}}$ ), 135.0 (d,  $J_{\text{P,C}} = 1.5$  Hz,  $\text{C}^{\text{IV}}$ ), 133.5 (d,  $^{2/3}J_{\text{P,C}} = 19.0$  Hz,  $m\text{-or } o\text{-CH}(\text{PPh}_2)$ ), 129.1 (s,  $p\text{-CH}(\text{PPh}_2)$ ), 128.8 (d,  $^{2/3}J_{\text{P,C}} = 7.5$  Hz,  $m\text{-or } o\text{-CH}(\text{PPh}_2)$ ), 121.3 (d,  $J_{\text{P,C}} = 1.0$  Hz,  $\text{C}^{\text{IV}}$ ), 116.7 (s,  $\text{C}_b\text{H}$ ), 115.2 (d,  $^2J_{\text{P,C}} = 3.0$  Hz,  $\text{C}_d\text{H}$ ), 55.5 (s, O- $\text{CH}_3$ ), 35.2 (s,  $\text{C}_{\text{c,a}}^{\text{IV}}\text{-C}^{\text{IV}}(\text{CH}_3)_3$ ), 29.6 (s,  $\text{C}_{\text{c,a}}^{\text{IV}}\text{-C}^{\text{IV}}(\text{CH}_3)_3$ ).



### Synthesis of 41

At -40°C, AlCl<sub>3</sub> (93.3 mg, 0.7 mmol) was added into a solution of the unsubstituted phosphasalen ligand **29** (490 mg, 0.7 mmol) in THF (20 mL), giving a cloudy solution which quickly turned into a white slurry. Stirring was continued at room temperature. After 2h, KOEt (58.9 mg, 0.7 mmol) was added, inducing the slow dissolution of the solid. After 20h, a cloudy solution was obtained. The insoluble salts were removed by centrifugation. THF was evaporated in vacuum, giving an ivory solid, which was then recrystallised in toluene (2 mL). The product was isolated as white solid. (350 mg, 73%)

**41.** <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 35.1 (s, P<sup>V</sup>); <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 8.04 (vddt, <sup>4</sup>J<sub>H,H</sub>=<sup>4</sup>J<sub>H,H</sub>=1.5 Hz, <sup>3</sup>J<sub>H,H</sub>=6.7 Hz, <sup>3</sup>J<sub>P,H</sub>=11.9 Hz, 4 H, *o*-CH(PPh<sub>2</sub>)), 7.55-7.35 (m, br, 16 H, CH(PPh<sub>2</sub>)), 7.12 (dddd, <sup>3</sup>J<sub>H,H</sub>=8.7 Hz, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, <sup>4</sup>J<sub>H,H</sub>=1.7 Hz, <sup>5</sup>J<sub>P,H</sub>=1.2 Hz, 2H, C<sub>b</sub>H), 6.79 (ddd, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, <sup>4</sup>J<sub>H,H</sub>=1.7 Hz, <sup>3</sup>J<sub>P,H</sub>=15.0 Hz, 2H, C<sub>d</sub>H), 6.73 (ddd, <sup>3</sup>J<sub>H,H</sub>=8.7 Hz, <sup>4</sup>J<sub>H,H</sub>=1.0 Hz, <sup>4</sup>J<sub>P,H</sub>=5.7 Hz, 2H, C<sub>a</sub>H), 6.36 (dddd, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, <sup>4</sup>J<sub>H,H</sub>=1.0 Hz, <sup>4</sup>J<sub>P,H</sub>=3.2 Hz, 2H, C<sub>c</sub>H), 3.57 (q, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>), 2.93 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 2.48 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 0.87 (t, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 170.2 (d, <sup>3</sup>J<sub>P,C</sub>=3.0 Hz, C<sup>IV</sup>-O), 134.3 (d, <sup>3</sup>J<sub>P,C</sub>=10.4 Hz, *o*-CH(PPh<sub>2</sub>)), 134.2 (s, C<sub>b</sub>H), 133.9 (d, <sup>3</sup>J<sub>P,C</sub>=8.9 Hz, *o*-CH(PPh<sub>2</sub>)), 132.7 (d, <sup>5</sup>J<sub>P,C</sub>=1.8 Hz, *p*-CH(PPh<sub>2</sub>)), 132.5 (d, <sup>5</sup>J<sub>P,C</sub>=2.2 Hz, *p*-CH(PPh<sub>2</sub>)), 132.0 (d, <sup>3</sup>J<sub>P,C</sub>=11.5 Hz, C<sub>d</sub>H), 130.3 (d, <sup>1</sup>J<sub>P,C</sub>=90.2 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 129.5 (d, <sup>1</sup>J<sub>P,C</sub>=89.2 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 129.3 (d, <sup>4</sup>J<sub>P,C</sub>=11.8 Hz, *m*-CH(PPh<sub>2</sub>)), 129.1 (d, <sup>4</sup>J<sub>P,C</sub>=14.0 Hz, *m*-CH(PPh<sub>2</sub>)), 124.0 (d, <sup>4</sup>J<sub>P,C</sub>=9.4 Hz, C<sub>a</sub>H), 114.7 (d, <sup>4</sup>J<sub>P,C</sub>=14.4 Hz, C<sub>c</sub>H), 108.1 (d, <sup>1</sup>J<sub>P,C</sub>=116.1 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 58.3 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 51.3 (d, <sup>1</sup>J<sub>P,C</sub>=13.8 Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 21.8 (s, O-CH<sub>2</sub>-CH<sub>3</sub>). Anal. Calcd for C<sub>40</sub>H<sub>37</sub>AlN<sub>2</sub>O<sub>3</sub>P<sub>2</sub>: C, 70.38; H, 5.46; N, 4.10. Found: C, 70.50; H, 5.39; N, 4.00.

### Synthesis of 42.

**42** was synthesised using the same method as **41**, except that tBuOK (78.6 mg, 0.7 mmol) was used instead of KOEt. The product was purified by crystallisation in toluene (2 mL) and isolated as white solid. (420 mg, 84%).

**42.** <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 35.1 (s, P<sup>V</sup>); <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 8.07 (vddt, <sup>4</sup>J<sub>H,H</sub>=<sup>4</sup>J<sub>H,H</sub>=1.5 Hz, <sup>3</sup>J<sub>H,H</sub>=6.7 Hz, <sup>3</sup>J<sub>P,H</sub>=12.0 Hz, 4 H, *o*-CH(PPh<sub>2</sub>)), 7.62-7.41 (m, 16 H, CH(PPh<sub>2</sub>)), 7.19 (dddd, <sup>3</sup>J<sub>H,H</sub>=8.7 Hz, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, <sup>4</sup>J<sub>H,H</sub>=1.7 Hz, <sup>5</sup>J<sub>P,H</sub>=1.1 Hz, 2H, C<sub>b</sub>H), 6.86 (ddd, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, <sup>4</sup>J<sub>H,H</sub>=1.7 Hz, <sup>3</sup>J<sub>P,H</sub>=15.2 Hz, 2H, C<sub>d</sub>H), 6.77 (ddd, <sup>3</sup>J<sub>H,H</sub>=8.7 Hz, <sup>4</sup>J<sub>H,H</sub>=1.0 Hz, <sup>4</sup>J<sub>P,H</sub>=5.6 Hz, 2H, C<sub>a</sub>H), 6.41 (dddd, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, <sup>4</sup>J<sub>H,H</sub>=1.0 Hz, <sup>4</sup>J<sub>P,H</sub>=3.0 Hz, 2H, C<sub>c</sub>H), 3.03 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 2.56 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.03 (s, 9H, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 170.1 (d, <sup>3</sup>J<sub>P,C</sub>=3.1 Hz, C<sup>IV</sup>-O), 134.4 (d, <sup>3</sup>J<sub>P,C</sub>=10.0 Hz, *o*-CH(PPh<sub>2</sub>)), 134.1 (d, <sup>5</sup>J<sub>P,C</sub>=1.6 Hz, C<sub>b</sub>H), 133.8 (d, <sup>3</sup>J<sub>P,C</sub>=9.6 Hz, *o*-CH(PPh<sub>2</sub>)), 132.6 (d, <sup>5</sup>J<sub>P,C</sub>=3.7 Hz, *p*-CH(PPh<sub>2</sub>)), 132.5 (d, <sup>5</sup>J<sub>P,C</sub>=2.8 Hz, *p*-CH(PPh<sub>2</sub>)), 132.2 (d, <sup>3</sup>J<sub>P,C</sub>=12.4 Hz, C<sub>d</sub>H), 130.4 (d, <sup>1</sup>J<sub>P,C</sub>=90.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 129.9 (d, <sup>1</sup>J<sub>P,C</sub>=92.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 129.2 (d, <sup>4</sup>J<sub>P,C</sub>=11.4 Hz, *m*-CH(PPh<sub>2</sub>)), 129.1 (d, <sup>4</sup>J<sub>P,C</sub>=10.9 Hz, *m*-CH(PPh<sub>2</sub>)), 124.2 (d, <sup>4</sup>J<sub>P,C</sub>=9.4 Hz, C<sub>a</sub>H), 114.6 (d, <sup>4</sup>J<sub>P,C</sub>=14.4 Hz, C<sub>c</sub>H), 107.0 (d, <sup>1</sup>J<sub>P,C</sub>=115.5 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 46.0 (d, <sup>1</sup>J<sub>P,C</sub>=14.7 Hz, <sup>1</sup>J<sub>P,C</sub>=1.7 Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 34.1 (s, O-

$C^{IV}(CH_3)_3$ ). Anal. Calcd for  $C_{42}H_{41}AlN_2O_3P_2$ : C, 70.98; H, 5.81; N, 3.94. Found: C, 70.84; H, 5.72; N, 3.83.

### Synthesis of 43

$[YCl_3(THF)_{3.5}]$  (313 mg, 0.7 mmol) was added to a solution of the unsubstituted phosphasalen ligand **29** (491 mg, 0.7 mmol), in THF (30 mL) at  $-40\text{ }^{\circ}\text{C}$ . A white slurry was formed after 2 min, stirring was continued at room temperature for 1 h. Potassium ethoxide (59 mg, 0.7 mmol) was added, giving a cloudy solution after 7 h. The solid was removed by centrifugation and the filtrate was evaporated to give an ivory solid. Crystallization from toluene yielded the product as colorless crystals (430 mg, 0.59 mmol, 84%)

**43:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  29.3 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  7.77-7.24 (m, b, 20H,  $\text{CH}(\text{PPh}_2)$ ), 7.09 (dddd,  $^3J_{\text{H,H}}=8.7\text{ Hz}$ ,  $^3J_{\text{H,H}}=7.0\text{ Hz}$ ,  $^4J_{\text{H,H}}=1.7\text{ Hz}$ ,  $^5J_{\text{P,H}}=1.2\text{ Hz}$ , 2H,  $\text{C}_b\text{H}$ ), 6.79 (ddd,  $^3J_{\text{H,H}}=7.7\text{ Hz}$ ,  $^4J_{\text{H,H}}=1.7\text{ Hz}$ ,  $^3J_{\text{P,H}}=13.9\text{ Hz}$ , 2H,  $\text{C}_d\text{H}$ ), 6.52 (ddd,  $^3J_{\text{H,H}}=8.7\text{ Hz}$ ,  $^4J_{\text{H,H}}=0.7\text{ Hz}$ ,  $^4J_{\text{P,H}}=8.3\text{ Hz}$ , 2H,  $\text{C}_a\text{H}$ ), 6.31 (dddd,  $^3J_{\text{H,H}}=7.7\text{ Hz}$ ,  $^3J_{\text{H,H}}=7.0\text{ Hz}$ ,  $^4J_{\text{H,H}}=0.7\text{ Hz}$ ,  $^4J_{\text{P,H}}=3.5\text{ Hz}$ , 2H,  $\text{C}_c\text{H}$ ), 3.42 (br, 2H,  $\text{O}-\text{CH}_2-\text{CH}_3$ ), 3.08 (br, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 2.84 (b, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 1.01 (br, 1H,  $\text{O}-\text{CH}_2-\text{CH}_3$ ); 0.62 (b, 2H,  $\text{O}-\text{CH}_2-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  172.1 (d,  $^3J_{\text{P,C}}=2.3\text{ Hz}$ ,  $\text{C}^{IV}-\text{O}$ ), 172.0 (d,  $^3J_{\text{P,C}}=2.7\text{ Hz}$ ,  $\text{C}^{IV}-\text{O}$ ), 134.0 (s,  $p-\text{CH}(\text{PPh}_2)$ ), 134.0 (d,  $^{2/3}J_{\text{P,C}}=9.5\text{ Hz}$ ,  $o-$  or  $m-\text{CH}(\text{PPh}_2)$ ), 133.1 (d,  $^4J_{\text{P,C}}=10.9\text{ Hz}$ ,  $\text{C}_b\text{H}$ ), 132.0 (m, b,  $\text{C}_d\text{H}$ ); 131.8 (m, b,  $\text{C}(\text{Ar})$ ), 129.1 (m, b,  $\text{C}(\text{Ar})$ ), 122.7 (d,  $^3J_{\text{P,C}}=7.5\text{ Hz}$ ,  $\text{C}_a\text{H}$ ), 114.9 (d,  $^1J_{\text{P,C}}=113.8\text{ Hz}$ ,  $\text{C}^{IV}-\text{PPh}_2$ ), 113.0 (d,  $^3J_{\text{P,C}}=14.9\text{ Hz}$ ,  $\text{C}_c\text{H}$ ), 51.3 (dd,  $J_{\text{P,C}}=6.3\text{ Hz}$ ,  $J'_{\text{P,C}}=13.1\text{ Hz}$ ,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 68.0 (s,  $\text{O}-\text{CH}_2-\text{CH}_3$ ), 25.1 (s,  $\text{O}-\text{CH}_2-\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{80}\text{H}_{74}\text{N}_4\text{O}_6\text{P}_4\text{Y}_2$ : C, 64.52; H, 5.01; N, 3.76. Found: C, 64.44; H, 5.07; N, 3.72.

### Synthesis of 44

$[YCl_3(THF)_{3.5}]$  (313 mg, 0.7 mmol) was added to a solution of the unsubstituted phosphasalen ligand **29** (491 mg, 0.7 mmol) in THF (50 mL) at  $-40\text{ }^{\circ}\text{C}$ . A white slurry was formed after 2 min, stirring was continued at room temperature for 1 h. Potassium *tert*-butoxide (78.6 mg, 0.7 mmol) was added into the mixture, giving a cloudy solution after 7 h. The solid was removed by centrifugation. The solution was concentrated (to 10 mL). The product precipitated from the solution as a white solid (380 mg, 0.49 mmol, 70 %). Crystals suitable for X-ray diffraction experiments were obtained from a solution of complex **44** in THF/toluene (1/3 volume)

**44:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  30.4 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  7.73-7.30 (m, b, 20H,  $\text{CH}(\text{PPh}_2)$ ), 7.08 (dddd,  $^3J_{\text{H,H}}=8.7\text{ Hz}$ ,  $^3J_{\text{H,H}}=7.0\text{ Hz}$ ,  $^4J_{\text{H,H}}=1.7\text{ Hz}$ ,  $^5J_{\text{P,H}}=1.0\text{ Hz}$ , 2H,  $\text{C}_b\text{H}$ ), 6.53 (ddd,  $^3J_{\text{H,H}}=8.0\text{ Hz}$ ,  $^4J_{\text{H,H}}=1.7\text{ Hz}$ ,  $^3J_{\text{P,H}}=14.6\text{ Hz}$ , 2H,  $\text{C}_d\text{H}$ ), 6.50 (ddd,  $^3J_{\text{H,H}}=8.7\text{ Hz}$ ,  $^4J_{\text{H,H}}=1.0\text{ Hz}$ ,  $^4J_{\text{P,H}}=5.5\text{ Hz}$ , 2H,  $\text{C}_a\text{H}$ ), 6.18 (dddd,  $^3J_{\text{H,H}}=8.0\text{ Hz}$ ,  $^3J_{\text{H,H}}=7.0\text{ Hz}$ ,  $^4J_{\text{H,H}}=1.0\text{ Hz}$ ,  $^4J_{\text{P,H}}=3.5\text{ Hz}$ , 2H,  $\text{C}_c\text{H}$ ), 3.42 (b, 2H,  $\text{O}-\text{CH}_2-\text{CH}_3$ ), 3.22 (b, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 2.99 (b, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ ), 0.88 (b, 9H,  $\text{O}-\text{C}^{IV}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  172.7 (d,  $^3J_{\text{P,C}}=2.3\text{ Hz}$ ,  $\text{C}^{IV}-\text{O}$ ), 172.6 (d,  $^3J_{\text{P,C}}=2.5\text{ Hz}$ ,  $\text{C}^{IV}-\text{O}$ ), 134.0 (d,  $^{2/3}J_{\text{P,C}}=9.2\text{ Hz}$ ,  $o-$  or  $m-\text{CH}(\text{PPh}_2)$ ), 134.0 (d,  $^{2/3}J_{\text{P,C}}=8.6\text{ Hz}$ ,  $o-$  or  $m-\text{CH}(\text{PPh}_2)$ ), 133.1 (d,  $^4J_{\text{P,C}}=12.6\text{ Hz}$ ,  $\text{C}_d\text{H}$ ), 131.8 (d,  $^4J_{\text{P,C}}=2.3\text{ Hz}$ ,  $p-\text{CH}(\text{PPh}_2)$ ), 131.6 (d,  $^1J_{\text{P,C}}=74.6\text{ Hz}$ ,  $\text{C}^{IV}(\text{PPh}_2)$ ), 131.5 (d,  $^4J_{\text{P,C}}=2.8\text{ Hz}$ ,  $\text{C}_b\text{H}$ ), 131.5 (d,  $^1J_{\text{P,C}}=75.0\text{ Hz}$ ,  $\text{C}^{IV}(\text{PPh}_2)$ ),

128.9 (d,  $^{2/3}J_{P,C}=11.5$  Hz, *o*- or *m*-CH(PPh<sub>2</sub>)), 128.7 (d,  $^{2/3}J_{P,C}=10.7$  Hz, *o*- or *m*-CH(PPh<sub>2</sub>)), 122.0 (d,  $^3J_{P,C}=8.0$  Hz, C<sub>a</sub>H), 114.2 (d,  $^1J_{P,C}=121.3$  Hz, C<sup>IV</sup>-P(Ph<sub>2</sub>)), 112.4 (d,  $^3J_{P,C}=15.0$  Hz, C<sub>c</sub>H), 68.0 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 51.9 (dd,  $J_{P,C}=5.2$  Hz,  $J'_{P,C}=15.5$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 32.7 (s, b, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>84</sub>H<sub>82</sub>N<sub>4</sub>O<sub>6</sub>P<sub>4</sub>Y<sub>2</sub>: C, 65.29; H, 5.35; N, 3.63. Found: C, 65.27; H, 5.25; N, 3.76.

### Synthesis of 45

[YCl<sub>3</sub>(THF)<sub>3.5</sub>] (313 mg, 0.7 mmol) was added to a solution of the phosphasalen ligand **36a** (745 mg, 0.7 mmol) in THF (25 mL) at -40°C. After 2 h of stirring at room temperature, potassium *tert*-butoxide (78.6 mg, 0.7 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents were removed from the filtrate yielding a pale yellow oil, which transformed into a white solid after one week of storing at room temperature (680 mg, 0.68 mmol, 97 %).

**45:**  $^{31}P\{^1H\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  30.8 (s, P<sup>V</sup>);  $^1H$  NMR (THF-*d*<sub>8</sub>):  $\delta$  7.57 (d,  $^3J_{H,H}=7.0$  Hz,  $^3J_{P,H}=11.2$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.61 (vt,  $^3J_{H,H}=7.0$  Hz,  $^5J_{P,H}=1.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.43 (vt,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.42 (dd,  $^3J_{H,H}=7.0$  Hz,  $^3J_{P,H}=10.7$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.42 (vt,  $^3J_{H,H}=7.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.34 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz,  $^4J_{P,H}=2.5$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.28 (d,  $^3J_{H,H}=2.5$  Hz, 2H, C<sub>b</sub>H), 6.34 (dd,  $^3J_{H,H}=2.5$  Hz,  $^3J_{P,H}=15.9$  Hz, 2H, C<sub>d</sub>H), 3.31 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.18 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.37 (s, 18H, C<sub>a</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 0.98 (s, 18H, C<sub>c</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 0.68 (s, b, 9H, O-C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}C\{^1H\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  169.7 (d,  $^3J_{P,C}=2.7$  Hz, C<sup>IV</sup>-O), 139.0 (d,  $^3J_{P,C}=8.2$  Hz, C<sub>c</sub><sup>IV</sup>); 134.0 (d,  $^3J_{P,C}=15.4$  Hz, C<sub>a</sub><sup>IV</sup>), 134.1 (d,  $^{2/3}J_{P,C}=8.7$  Hz, *o*-CH(PPh<sub>2</sub>)), 133.5 (d,  $^{2/3}J_{P,C}=8.9$  Hz, *o*-CH(PPh<sub>2</sub>)), 132.7 (d,  $^1J_{P,C}=86.6$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 131.7 (d,  $^1J_{P,C}=89.0$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 131.9 (d,  $^4J_{P,C}=1.7$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.5 (d,  $^4J_{P,C}=1.8$  Hz, *p*-CH(PPh<sub>2</sub>)), 128.9 (d,  $^{2/3}J_{P,C}=9.6$  Hz, *m*-CH(PPh<sub>2</sub>)), 128.8 (d,  $^{2/3}J_{P,C}=10.0$  Hz, *m*-CH(PPh<sub>2</sub>)), 128.3 (s, C<sub>b</sub>H), 127.8 (d,  $^2J_{P,C}=13.9$  Hz, C<sub>d</sub>H), 112.5 (d,  $^1J_{P,C}=122.2$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 47.3 (dd,  $J_{P,C}=7.5$  Hz,  $J'_{P,C}=19.0$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 35.8 (s, C<sub>a</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>+O-C(CH<sub>3</sub>)<sub>3</sub>), 34.3 (s, C<sub>c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 31.7 (s, C<sub>c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>+O-C(CH<sub>3</sub>)<sub>3</sub>), 30.4 (s, C<sub>a</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>58</sub>H<sub>73</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Y: C, 69.87; H, 7.38; N, 2.81. Found: C, 69.55; H, 7.26; N, 2.76.

### Synthesis of 46

At -78°C, bromine (200  $\mu$ L, 3.88 mmol) was added dropwise to a solution of the phenolphosphine (1.516 g, 3.88 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (45 mL). The cold bath was removed and stirring was continued for 1 hour at room temperature. Then the solution was cooled down to -78°C. DABCO (1,4-diazabicyclo[2.2.2]octane, 218 mg, 1.94 mmol) was added, followed by (R,R)-1,2-diaminocyclohexane (222 mg, 1.94 mmol). The cold bath was removed. After 16h, a white slurry was formed. CH<sub>2</sub>Cl<sub>2</sub> was evaporated, 50 mL of THF was added. The insoluble DABCO salt was removed by centrifugation. THF was evaporated and the white solid was washed with Et<sub>2</sub>O (7 mL), dried in vacuum (1.04g, 57%).

**46:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  38.5 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.59 (s, 2H, NH), 7.77 (dd,  $^3J_{\text{H,H}}=7.5$  Hz,  $^3J_{\text{P,H}}=12.8$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.69 (dd,  $^3J_{\text{H,H}}=7.5$  Hz,  $^3J_{\text{P,H}}=14.2$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.70 (s, 1H, OH), 7.69 (s, 1H, OH), 7.50 (vtd,  $^3J_{\text{H,H}}=^3J_{\text{H,H}}=7.5$  Hz,  $^4J_{\text{P,H}}=3.0$  Hz, 2H, *m*-CH(PPh<sub>2</sub>)), 7.63 (vt,  $^3J_{\text{H,H}}=^3J_{\text{H,H}}=7.5$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.40 (vt,  $^3J_{\text{H,H}}=^3J_{\text{H,H}}=7.5$  Hz, 4H, *p*-CH(PPh<sub>2</sub>)), 7.13 (vtd,  $^3J_{\text{H,H}}=^3J_{\text{H,H}}=7.5$  Hz,  $^4J_{\text{P,H}}=3.3$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 6.56 (dd,  $^4J_{\text{H,H}}=2.2$  Hz,  $^5J_{\text{P,H}}=8.0$  Hz, 1H, C<sub>b</sub>H), 6.53 (dd,  $^4J_{\text{H,H}}=2.2$  Hz,  $^5J_{\text{P,H}}=8.0$  Hz, 1H, C<sub>b</sub>H), 6.37 (dd,  $^4J_{\text{H,H}}=2.2$  Hz,  $^3J_{\text{P,H}}=15.6$  Hz, 2H, C<sub>b</sub>H), 3.82 (m, 2H, N-CH-CH-N), 2.05 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.59 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.53 (s, 18H, C<sub>a</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 1.30 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.03 (s, 18H, C<sub>c</sub>-C(CH<sub>3</sub>)<sub>3</sub>), 0.93 (m, 2H, CH<sub>2</sub>(cyclohexane));  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  155.9 (d,  $^3J_{\text{P,C}}=0.9$  Hz, C<sup>IV</sup>-O), 145.7 (d,  $^3J_{\text{P,C}}=8.2$  Hz, C<sub>c,a</sub><sup>IV</sup>); 144.5 (d,  $^3J_{\text{P,C}}=7.0$  Hz, C<sub>a,c</sub><sup>IV</sup>), 135.0-133.0 (m, CH(PPh<sub>2</sub>)), 131.8 (d,  $^4J_{\text{P,C}}=0.9$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.5 (d,  $^4J_{\text{P,C}}=0.9$  Hz, *p*-CH(PPh<sub>2</sub>)), 129.7-128.9 (m, CH(PPh<sub>2</sub>) + C<sub>b</sub>H), 128.6 (d,  $^2J_{\text{P,C}}=12.2$  Hz, C<sub>d</sub>H), 123.0 (d,  $^1J_{\text{P,C}}=109.7$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 121.7 (d,  $^1J_{\text{P,C}}=97.5$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 116.0 (d,  $^1J_{\text{P,C}}=106.2$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 59.0 (m, N-CH-CH-N), 35.6 (s, C<sub>a</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 34.7 (s, C<sub>c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 30.2 (s, CH<sub>2</sub>(cyclohexane)), 30.0 (s, CH<sub>2</sub>(cyclohexane)), 29.8 (s, C<sub>c,a</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (s, C<sub>a,c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 29.5 (s, C<sub>a,c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 29.4 (s, CH<sub>2</sub>(cyclohexane)), 28.8 (s, CH<sub>2</sub>(cyclohexane)). Anal. Calcd for C<sub>58</sub>H<sub>74</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 66.16; H, 7.08; N, 2.66. Found: C, 66.25; H, 6.96; N, 2.56.

### Synthesis of 47

**47** was synthesized using the same protocol as the synthesis of **46**, but using 1,3-diaminopropane (162  $\mu\text{L}$ , 1.942 mmol) instead of (R,R)-1,2-diaminocyclohexane. It was isolated as a white solid (1.5g, 71%)

**47:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  40.4 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.74-7.56 (m, 22H, CH(PPh<sub>2</sub>) + C<sub>b</sub>H), 6.54 (dd,  $^4J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{P,H}}=15.5$  Hz, 2H, C<sub>d</sub>H), 3.37 (vq,  $^3J_{\text{H,H}}=^3J_{\text{P,H}}=7.0$  Hz, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 2.32 (qt,  $^3J_{\text{H,H}}=7.0$  Hz, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.49 (s, b, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.11 (s, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  156.0 (d,  $^3J_{\text{P,C}}=1.0$  Hz, C<sup>IV</sup>-O), 145.4 (d,  $^3J_{\text{P,C}}=13.5$  Hz, C<sub>c,a</sub><sup>IV</sup>), 143.6 (d,  $^3J_{\text{P,C}}=7.0$  Hz, C<sub>a,c</sub><sup>IV</sup>), 134.1 (m, CH(PPh<sub>2</sub>)), 133.7 (d,  $^{2/3}J_{\text{P,C}}=10.0$  Hz, *o*-or *m*-CH(PPh<sub>2</sub>)), 133.4 (d,  $^{2/3}J_{\text{P,C}}=10.0$  Hz, *o*-or *m*-CH(PPh<sub>2</sub>)), 131.9 (d,  $^4J_{\text{P,C}}=0.9$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.6 (d,  $^4J_{\text{P,C}}=0.9$  Hz, *p*-CH(PPh<sub>2</sub>)), 129.7-128.9 (m, CH(PPh<sub>2</sub>) + C<sub>b</sub>H), 128.3 (d,  $^2J_{\text{P,C}}=12.2$  Hz, C<sub>d</sub>H), 122.8 (d,  $^1J_{\text{P,C}}=103.7$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 114.9 (d,  $^1J_{\text{P,C}}=109.1$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 41.9 (m, N-CH<sub>2</sub>), 35.3 (s, C<sub>a/c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 34.5 (s, C<sub>c/a</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 31.0 (s, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 30.6 (s, C<sub>c,a</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (s, C<sub>a,c</sub><sup>IV</sup>-C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>55</sub>H<sub>70</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 65.22; H, 6.97; N, 2.77. Found: C, 65.19; H, 7.03; N, 2.70.

### Synthesis of 48

**48** was synthesized using the same protocol as the synthesis of **46**, but using 1,3-diamino-2,2-dimethylpropane (198 mg, 1.942 mmol) instead of (R,R)-1,2-diaminocyclohexane. It was isolated as a white solid (1.32g, 65%)

**48:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  41.7 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.72 (dd,  $^3J_{\text{H,H}}=7.5$  Hz,  $^3J_{\text{P,H}}=13.0$  Hz, 8H, *o*-CH( $\text{PPh}_2$ )), 7.65 (vt,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.5$  Hz, 4H, *p*-CH( $\text{PPh}_2$ )), 7.56 (s, br, 2H,  $\text{C}_b\text{H}$ ), 7.55 (vtd,  $^4J_{\text{P,H}}=3.0$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.5$  Hz, 8H, *m*-CH( $\text{PPh}_2$ )), 6.73 (d, b,  $^3J_{\text{P,H}}=14.0$  Hz, 2H,  $\text{C}_d\text{H}$ ), 3.17 (s, 2H, NH), 3.14 (d,  $^3J_{\text{P,H}}=9.0$  Hz, 4H, N- $\text{CH}_2$ ), 1.29 (s, b, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 1.10 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 0.74 (s, br, 6H, N- $\text{CH}_2-\text{C}^{\text{IV}}(\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  141.9 (d,  $^3J_{\text{P,C}}=2.5$  Hz,  $\text{C}_{c/a}^{\text{IV}}$ ), 133.9 (s, b, *p*-CH( $\text{PPh}_2$ )), 133.7 (d,  $^{2/3}J_{\text{P,C}}=10.5$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 131.6 (s, b,  $\text{C}_b\text{H}$ ), 129.5 (d,  $^{2/3}J_{\text{P,C}}=13.0$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 128.7 (d,  $^2J_{\text{P,C}}=12.0$  Hz,  $\text{C}_d\text{H}$ ), 50.6 (m,b, N- $\text{CH}_2$ ), 37.06 (t,  $^3J_{\text{P,C}}=8.0$  Hz, N- $\text{CH}_2-\text{C}^{\text{IV}}-\text{CH}_2-\text{N}$ ), 35.2 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 34.6 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 31.3 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 30.6 (s, N- $\text{CH}_2-\text{C}^{\text{IV}}(\text{CH}_3)_2$ ), ( $\text{C}^{\text{IV}}-\text{OH}$ ,  $\text{C}^{\text{IV}}-\text{PPh}_2$ ,  $\text{C}^{\text{IV}}(\text{PPh}_2$  and one of  $\text{C}_{c/a}^{\text{IV}}$ ) were not observed at all, even in increasing the number of acquisition). Anal. Calcd for  $\text{C}_{57}\text{H}_{74}\text{Br}_2\text{N}_2\text{O}_2\text{P}_2$ : C, 65.77; H, 7.17; N, 2.69. Found: C, 65.88; H, 7.08; N, 2.81.

### Synthesis of 49

**49** was synthesized using the same protocol as the synthesis of **46**, but using ortho-phenylenediamine (210 mg, 1.942 mmol) instead of (R,R)-1,2-diaminocyclohexane. It was isolated as a white solid (1.47 g, 72%)

**49:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  38.9 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.88 (d,  $^2J_{\text{P,H}}=8.5$  Hz, 2H, NH), 7.76 (d, 2H,  $^4J_{\text{H,H}}=2.0$  Hz,  $\text{C}_b\text{H}$ ), 7.74 (vt,  $^3J_{\text{P,H}}=^3J_{\text{H,H}}=8.0$  Hz, 4H, *o*-CH( $\text{PPh}_2$ )), 7.73 (vt,  $^3J_{\text{P,H}}=^3J_{\text{H,H}}=8.0$  Hz, 4H, *o*-CH( $\text{PPh}_2$ )), 7.71 (vt,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 4H, *p*-CH( $\text{PPh}_2$ )), 7.56 (vtd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz,  $^4J_{\text{P,H}}=4.0$  Hz, 8H, *m*-CH( $\text{PPh}_2$ )), 7.48 (b, 2H, OH), 6.90 (dd,  $^3J_{\text{P,H}}=16.0$  Hz,  $^4J_{\text{H,H}}=2.0$  Hz,  $\text{C}_d\text{H}$ ), 6.65 (dd,  $^3J_{\text{H,H}}=6.0$  Hz,  $^4J_{\text{H,H}}=3.5$  Hz, 2H,  $\text{C}_f\text{H}$ ), 6.53 (ddd,  $^3J_{\text{H,H}}=6.0$  Hz,  $^4J_{\text{H,H}}=3.5$  Hz,  $^4J_{\text{P,H}}=1.0$  Hz, 2H,  $\text{C}_e\text{H}$ ), 1.33 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 1.15 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  155.8 (d,  $^3J_{\text{P,C}}=2.0$  Hz,  $\text{C}^{\text{IV}}-\text{O}$ ), 145.8 (d,  $^3J_{\text{P,C}}=13$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ), 141.6 (d,  $^3J_{\text{P,C}}=7.5$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ), 134.8 (d,  $^4J_{\text{P,C}}=3.0$  Hz, *p*-CH( $\text{PPh}_2$ )), 133.7 (d,  $^{2/3}J_{\text{P,C}}=11.0$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 132.9 (d,  $^4J_{\text{P,C}}=2.0$  Hz,  $\text{C}_b\text{H}$ ), 132.5 (d,  $^2J_{\text{P,C}}=6.5$  Hz,  $\text{C}^{\text{IV}}-\text{N}$ ), 129.9 (d,  $^{2/3}J_{\text{P,C}}=13.5$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 129.1 (d,  $^2J_{\text{P,C}}=11.5$  Hz,  $\text{C}_d\text{H}$ ), 125.3 (d,  $^4J_{\text{P,C}}=1.0$  Hz,  $\text{C}_f\text{H}$ ), 125.0 (d,  $^3J_{\text{P,C}}=3.0$  Hz,  $\text{C}_e\text{H}$ ), 121.5 (d,  $^1J_{\text{P,C}}=104.5$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 111.0 (d,  $^1J_{\text{P,C}}=110.5$  Hz,  $\text{C}^{\text{IV}}-\text{PPh}_2$ ), 35.1 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 34.8 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 31.2 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 30.7 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{58}\text{H}_{68}\text{Br}_2\text{N}_2\text{O}_2\text{P}_2$ : C, 66.54; H, 6.55; N, 2.68. Found: C, 66.68; H, 6.55; N, 2.58.

### Synthesis of 50

**12** was synthesized using the same protocol as the synthesis of **46**, but using diethylenetriamine (210  $\mu\text{L}$ , 1.942 mmol) instead of (R,R)-1,2-diaminocyclohexane, and tributylamine (463  $\mu\text{L}$ , 1.942 mmol) instead of DABCO as base. It was isolated as a white solid (1.8 g, 78%)

**50:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  41.8 (s,  $P^V$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.74 (m, 2H, CH( $\text{PPh}_2$ )), 7.65 (m, 20H, CH( $\text{PPh}_2$ ) +  $\text{C}_b\text{H}$ ), 6.72 (m, b, 2H, OH or NH), 6.56 (dd,  $^3J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{P,H}}=16.0$  Hz, 2H,  $\text{C}_d\text{H}$ ), 3.70 (s, b, 4H,  $\text{CH}_2-\text{NH}_2-\text{CH}_2$ ), 3.52 (s, b, 4H,  $\text{P}^V-\text{NH}-\text{CH}_2$ ), 2.02 (s, b, 4H, OH or NH), 1.47 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 1.10 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):

$\delta$  155.7 (d,  $^2J_{P,C} = 1.0$  Hz,  $C^{IV}$ -OH), 145.5 (d,  $^3J_{P,C} = 14.0$  Hz,  $C_{c/a}^{IV}$ ), 141.9 (d,  $^3J_{P,C} = 7.0$  Hz,  $C_{c/a}^{IV}$ ), 134.7 (d,  $^4J_{P,C} = 3.0$  Hz,  $p$ -CH(PPh<sub>2</sub>)), 133.5 (d,  $^{2/3}J_{P,C} = 11.5$  Hz,  $m$ -or  $o$ -CH(PPh<sub>2</sub>)), 132.3 (d,  $^4J_{P,C} = 1.5$  Hz,  $C_bH$ ), 130.0 (d,  $^{2/3}J_{P,C} = 13.0$  Hz,  $m$ -or  $o$ -CH(PPh<sub>2</sub>)), 128.6 (d,  $^2J_{P,C} = 12.5$  Hz,  $C_dH$ ), 121.7 (d,  $^1J_{P,C} = 105.0$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 114.5 (d,  $^1J_{P,C} = 98.0$  Hz,  $C^{IV}$ -PPh<sub>2</sub>), 113.1 (d,  $^1J_{P,C} = 107.2$  Hz,  $C^{IV}$ -PPh<sub>2</sub>), 49.0 (d,  $^2J_{P,C} = 9.0$  Hz,  $P^V$ -N-CH<sub>2</sub>), 40.0 (s,  $P^V$ -N-CH<sub>2</sub>-CH<sub>2</sub>), 35.1 (d,  $^4J_{P,C} = 2.0$  Hz,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 34.7 (d,  $^4J_{P,C} = 1.0$  Hz,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 31.2 (s,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 30.6 (s, N-CH<sub>2</sub>- $C^{IV}$ (CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>56</sub>H<sub>74</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>2</sub>P<sub>2</sub>: C, 59.90; H, 6.64; N, 3.74. Found: C, 59.78; H, 7.66.536; N, 3.74.

## Synthesis of 51

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **35b** (316 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}P\{^1H\}$  NMR spectrum which showed only one singlet at +18 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4 h of stirring at room temperature,  $^{31}P\{^1H\}$  NMR spectrum showed the clean formation of a complex with two singlets of equal intensity at 27.5 ppm and 22.6 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (265 mg, 79%).

**51:**  $^{31}P\{^1H\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  27.6 (s,  $P^V$ ), 20.8 (s,  $P^V$ );  $^1H$  NMR (THF-*d*<sub>8</sub>):  $\delta$  7.89 (ddd,  $^3J_{P,H} = 10.6$  Hz,  $^3J_{H,H} = 7.5$  Hz,  $^4J_{H,H} = 1.0$  Hz, 2H,  $o$ -CH(PPh<sub>2</sub>)), 7.75 (ddd,  $^3J_{P,H} = 12.3$  Hz,  $^3J_{H,H} = 7.5$  Hz,  $^4J_{H,H} = 1.0$  Hz, 2H,  $o$ -CH(PPh<sub>2</sub>)), 7.62 (ddd,  $^3J_{P,H} = 11.2$  Hz,  $^3J_{H,H} = 7.5$  Hz,  $^4J_{H,H} = 1.0$  Hz, 2H,  $o$ -CH(PPh<sub>2</sub>)), 7.56 (ddd,  $^3J_{P,H} = 11.0$  Hz,  $^3J_{H,H} = 7.5$  Hz,  $^4J_{H,H} = 1.0$  Hz, 2H,  $o$ -CH(PPh<sub>2</sub>)), 7.51-7.42 (m, 5H,  $p$ -CH(PPh<sub>2</sub>) +  $m$ -CH(PPh<sub>2</sub>)), 7.38 (vtd,  $^4J_{P,H} = 2.2$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 2H,  $m$ -CH(PPh<sub>2</sub>)), 7.32 (vtd,  $^4J_{P,H} = 2.2$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 2H,  $m$ -CH(PPh<sub>2</sub>)), 7.27 (d,  $^4J_{H,H} = 2.0$  Hz, 1H,  $C_bH$ ), 7.21 (d,  $^4J_{H,H} = 2.0$  Hz, 1H,  $C_bH$ ), 7.17 (vtd,  $^4J_{H,H} = 1.0$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 1H,  $p$ -CH(PPh<sub>2</sub>)), 6.84 (dd,  $^4J_{H,H} = 2.0$  Hz,  $^3J_{P,H} = 16.0$  Hz, 1H,  $C_dH$ ), 6.82 (vtd,  $^4J_{P,H} = 2.2$  Hz,  $^3J_{H,H} = ^3J'_{H,H} = 7.5$  Hz, 2H,  $m$ -CH(PPh<sub>2</sub>)), 6.47 (dd,  $^4J_{H,H} = 2.0$  Hz,  $^3J_{P,H} = 16.0$  Hz, 1H,  $C_dH$ ), 4.62 (vqd,  $^3J_{H,H} = ^3J'_{H,H} = ^3J_{P,H} = 9.0$  Hz,  $^4J_{P,H} = 3.0$  Hz, 1H, N-CH-CH-N), 2.97 (vqd,  $^3J_{H,H} = ^3J'_{H,H} = ^3J_{P,H} = 9.0$  Hz,  $^4J_{P,H} = 3.0$  Hz, 1H, N-CH-CH-N), 1.57 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.31 (s, 9H,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 1.12 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.12 (s, b, 9H, O- $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 1.10 (s, 9H,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 1.09 (s, 9H,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 0.96 (s, 9H,  $C_{c,a}^{IV}$ - $C^{IV}$ (CH<sub>3</sub>)<sub>3</sub>), 0.82 (m, 2H, CH<sub>2</sub>(cyclohexane)), 0.66 (m, 1H, CH<sub>2</sub>(cyclohexane)), 0.48 (m, 1H, CH<sub>2</sub>(cyclohexane));  $^{13}C\{^1H\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  168.7 (vt,  $^3J_{P,C} = ^2J_{Y,C} = 2.7$  Hz,  $C^{IV}$ -O), 168.5 (vt,  $^3J_{P,C} = ^2J_{Y,C} = 2.7$  Hz,  $C^{IV}$ -O), 139.5 (d,  $^3J_{P,C} = 8.2$  Hz,  $C_{c,a}^{IV}$ ), 138.8 (d,  $^3J_{P,C} = 7.8$  Hz,  $C_{c,a}^{IV}$ ), 136.7 (d,  $^1J_{P,C} = 82.9$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 136.5 (d,  $^1J_{P,C} = 86.2$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 134.9 (d,  $^{2/3}J_{P,C} = 9.3$  Hz,  $m$ -or  $o$ -CH(PPh<sub>2</sub>)), 134.3 (d,  $^1J_{P,C} = 108.5$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 134.1 (d,  $^3J_{P,C} = 8.2$  Hz,  $C_{c,a}^{IV}$ ), 134.0 (d,  $^2J_{P,C} = 9.2$  Hz,  $C_dH$ ), 133.9 (d,  $^{2/3}J_{P,C} = 9.0$  Hz,  $m$ -or  $o$ -CH(PPh<sub>2</sub>)), 133.8 (d,  $^{2/3}J_{P,C} = 10.0$  Hz,  $m$ -or  $o$ -CH(PPh<sub>2</sub>)), 133.0 (d,  $^1J_{P,C} = 82.1$  Hz,  $C^{IV}$ (PPh<sub>2</sub>)), 132.0 (d,  $^4J_{P,C} = 2.6$  Hz,  $p$ -CH(PPh<sub>2</sub>)), 131.8 (d,  $^4J_{P,C} = 2.1$  Hz,  $p$ -CH(PPh<sub>2</sub>)), 131.6 (d,  $^4J_{P,C} = 2.4$  Hz,  $p$ -CH(PPh<sub>2</sub>)), 130.9 (d,  $^4J_{P,C} = 2.4$  Hz,  $p$ -CH(PPh<sub>2</sub>)),

128.9 (d,  $^2J_{P,C}=11.6$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.7 (d,  $^2J_{P,C}=11.6$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.5 (d,  $^2J_{P,C}=12.1$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.4 (d,  $^2J_{P,C}=12.0$  Hz, C<sub>d</sub>H), 128.1 (d,  $^4J_{P,C}=1.5$  Hz, C<sub>b</sub>H), 128.0 (d,  $^4J_{P,C}=1.5$  Hz, C<sub>b</sub>H), 70.0 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 64.0 (d,  $^2J_{P,C}=7.9$  Hz, N-CH-CH-N), 63.8 (d,  $^2J_{P,C}=8.3$  Hz, N-CH-CH-N), 37.7 (s, CH<sub>2</sub>(cyclohexane ring)), 37.6 (s, CH<sub>2</sub>(cyclohexane ring)), 36.3 (s, CH<sub>2</sub>(cyclohexane ring)), 35.9 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.8 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.6 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.5 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.1 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.8 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.3 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 29.6 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 27.1 (s, CH<sub>2</sub>(cyclohexane ring)). Anal. Calcd for C<sub>62</sub>H<sub>79</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Y: C, 70.84; H, 7.58; N, 2.67. Found: C, 70.66; H, 7.65; N, 2.59.

## Synthesis of 52

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **46** (316 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which showed only one singlet at +18 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4 h of stirring at room temperature,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed the clean formation of a complex with two singlets of equal intensity at 27.5 ppm and 22.6 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (293 g, 87%).

**52:**  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  27.6 (s, P<sup>V</sup>), 20.8 (s, P<sup>V</sup>);  $^1\text{H}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  7.89 (ddd,  $^3J_{P,H}=10.6$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^4J_{H,H}=1.0$  Hz, 2H, *o*-CH(PPh<sub>2</sub>)), 7.75 (ddd,  $^3J_{P,H}=12.3$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^4J_{H,H}=1.0$  Hz, 2H, *o*-CH(PPh<sub>2</sub>)), 7.62 (ddd,  $^3J_{P,H}=11.2$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^4J_{H,H}=1.0$  Hz, 2H, *o*-CH(PPh<sub>2</sub>)), 7.56 (ddd,  $^3J_{P,H}=11.0$  Hz,  $^3J_{H,H}=7.5$  Hz,  $^4J_{H,H}=1.0$  Hz, 2H, *o*-CH(PPh<sub>2</sub>)), 7.51-7.42 (m, 5H, *p*-CH(PPh<sub>2</sub>) + *m*-CH(PPh<sub>2</sub>)), 7.38 (vtd,  $^4J_{P,H}=2.2$  Hz,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz, 2H, *m*-CH(PPh<sub>2</sub>)), 7.32 (vtd,  $^4J_{P,H}=2.2$  Hz,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz, 2H, *m*-CH(PPh<sub>2</sub>)), 7.27 (d,  $^4J_{H,H}=2.0$  Hz, 1H, C<sub>b</sub>H), 7.21 (d,  $^4J_{H,H}=2.0$  Hz, 1H, C<sub>b</sub>H), 7.17 (vtd,  $^4J_{H,H}=1.0$  Hz,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz, 1H, *p*-CH(PPh<sub>2</sub>)), 6.84 (dd,  $^4J_{H,H}=2.0$  Hz,  $^3J_{P,H}=16.0$  Hz, 1H, C<sub>d</sub>H), 6.82 (vtd,  $^4J_{P,H}=2.2$  Hz,  $^3J_{H,H}=^3J'_{H,H}=7.5$  Hz, 2H, *m*-CH(PPh<sub>2</sub>)), 6.47 (dd,  $^4J_{H,H}=2.0$  Hz,  $^3J_{P,H}=16.0$  Hz, 1H, C<sub>d</sub>H), 4.62 (vqd,  $^3J_{H,H}=^3J'_{H,H}=^3J_{P,H}=9.0$  Hz,  $^4J_{P,H}=3.0$  Hz, 1H, N-CH-CH-N), 2.97 (vqd,  $^3J_{H,H}=^3J'_{H,H}=^3J_{P,H}=9.0$  Hz,  $^4J_{P,H}=3.0$  Hz, 1H, N-CH-CH-N), 1.57 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.31 (s, 9H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.12 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.12 (s, b, 9H, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.10 (s, 9H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.09 (s, 9H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 0.96 (s, 9H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 0.82 (m, 2H, CH<sub>2</sub>(cyclohexane)), 0.66 (m, 1H, CH<sub>2</sub>(cyclohexane)), 0.48 (m, 1H, CH<sub>2</sub>(cyclohexane));  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  168.7 (vt,  $^3J_{P,C}=^2J_{Y,C}=2.7$  Hz, C<sup>IV</sup>-O), 168.5 (vt,  $^3J_{P,C}=^2J_{Y,C}=2.7$  Hz, C<sup>IV</sup>-O), 139.5 (d,  $^3J_{P,C}=8.2$  Hz, C<sub>c,a</sub><sup>IV</sup>), 138.8 (d,  $^3J_{P,C}=7.8$  Hz, C<sub>c,a</sub><sup>IV</sup>), 136.7 (d,  $^1J_{P,C}=82.9$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 136.5 (d,  $^1J_{P,C}=86.2$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 134.9 (d,  $^2J_{P,C}=9.3$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 134.3 (d,  $^1J_{P,C}=108.5$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 134.1 (d,  $^3J_{P,C}=8.2$  Hz, C<sub>c,a</sub><sup>IV</sup>), 134.0 (d,  $^2J_{P,C}=9.2$  Hz, C<sub>d</sub>H), 133.9 (d,  $^2J_{P,C}=9.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.8 (d,  $^2J_{P,C}=10.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.0 (d,  $^1J_{P,C}=82.1$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 132.0 (d,  $^4J_{P,C}=2.6$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.8 (d,  $^4J_{P,C}=2.1$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.6 (d,  $^4J_{P,C}=2.4$  Hz, *p*-CH(PPh<sub>2</sub>)), 130.9 (d,  $^4J_{P,C}=2.4$  Hz, *p*-CH(PPh<sub>2</sub>)),

128.9 (d,  $^{2/3}J_{P,C}=11.6$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.7 (d,  $^{2/3}J_{P,C}=11.6$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.5 (d,  $^{2/3}J_{P,C}=12.1$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.4 (d,  $^2J_{P,C}=12.0$  Hz, C<sub>d</sub>H), 128.1 (d,  $^4J_{P,C}=1.5$  Hz, C<sub>b</sub>H), 128.0 (d,  $^4J_{P,C}=1.5$  Hz, C<sub>b</sub>H), 70.0 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 64.0 (d,  $^2J_{P,C}=7.9$  Hz, N-CH-CH-N), 63.8 (d,  $^2J_{P,C}=8.3$  Hz, N-CH-CH-N), 37.7 (s, CH<sub>2</sub>(cyclohexane ring)), 37.6 (s, CH<sub>2</sub>(cyclohexane ring)), 36.3 (s, CH<sub>2</sub>(cyclohexane ring)), 35.9 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.8 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.6 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.5 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.1 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.8 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.3 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 29.6 (s, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 27.1 (s, CH<sub>2</sub>(cyclohexane ring)). Anal. Calcd for C<sub>62</sub>H<sub>79</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Y: C, 70.84; H, 7.58; N, 2.67. Found: C, 70.47; H, 7.97; N, 2.53.

### Synthesis of 53a

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **47** (304 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}P\{^1H\}$  NMR spectrum which showed only one singlet at +23.8 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature,  $^{31}P\{^1H\}$  NMR spectrum showed the clean formation of a complex with one singlet at 36.9 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (240 mg, 74%).

**53a:**  $^{31}P\{^1H\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  33.8 (s);  $^1H$  NMR (THF-*d*<sub>8</sub>):  $\delta$  7.63 (dd,  $^3J_{H,H}=7.0$  Hz,  $^3J_{P,H}=10.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.50 (dd,  $^3J_{H,H}=7.0$  Hz,  $^3J_{P,H}=10.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.48 (vt,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.41 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz,  $^4J_{P,H}=2.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.40 (vt,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.32 (vtd,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz,  $^4J_{P,H}=2.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.29 (d,  $^4J_{H,H}=2.5$  Hz, 2H, C<sub>b</sub>H), 6.37 (dd,  $^4J_{H,H}=2.5$  Hz,  $^3J_{P,H}=15.5$  Hz, 2H, C<sub>d</sub>H), 3.51 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.16 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.90 (m, 1H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.63 (m, 1H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.42 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.09 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.86 (s, 9H, O-C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}C\{^1H\}$  NMR (THF-*d*<sub>8</sub>): 169.3 (d,  $^3J_{P,C}=1.5$  Hz, C<sup>IV</sup>-O), 139.0 (d,  $^3J_{P,C}=8.0$  Hz, C<sub>c,a</sub><sup>IV</sup>), 134.3 (d,  $^{2/3}J_{P,C}=9.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 134.1 (d,  $^{2/3}J_{P,C}=9.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.9 (d,  $^3J_{P,C}=10.5$  Hz, C<sub>c,a</sub><sup>IV</sup>), 132.6 (d,  $^1J_{P,C}=87.8$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 131.9 (d,  $^4J_{P,C}=1.0$  Hz, *p*-CH(PPh<sub>2</sub>)), 131.8 (d,  $^4J_{P,C}=1.0$  Hz, *p*-CH(PPh<sub>2</sub>)), 128.9 (d,  $^{2/3}J_{P,C}=11.5$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.4 (s, C<sub>b</sub>H), 128.1 (d,  $^2J_{P,C}=14.0$  Hz, C<sub>d</sub>H), 113.3 (d,  $^1J_{P,C}=121.0$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 69.8 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 47.1 (d,  $^2J_{P,C}=7.0$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 36.4 (t,  $^3J_{P,C}=9.0$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 34.6 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.9 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.7 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.4 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.4 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>63</sub>H<sub>83</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Y: C, 69.86; H, 7.72; N, 2.59. Found: C, 69.72; H, 7.66; N, 2.67.

### Synthesis of 53b

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **47** (304 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}P\{^1H\}$  NMR spectrum which showed only one singlet at +23.8 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4h



of stirring at room temperature,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed the clean formation of a complex with one singlet at 36.9 ppm. Potassium ethoxide (25.2 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as white solid (240 mg, 74%).

**53b:**  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ ):  $\delta$  34.3 (s);  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  7.66 (dd,  $^3J_{\text{H,H}}=7.0$  Hz,  $^3J_{\text{P,H}}=12.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.48 (vt,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.0$  Hz, 4H, *p*-CH(PPh<sub>2</sub>)), 7.34 (vtd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.0$  Hz,  $^4J_{\text{P,H}}=2.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.33 (d,  $^4J_{\text{H,H}}=2.5$  Hz, 2H, C<sub>b</sub>H), 7.16 (vtd,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.0$  Hz,  $^4J_{\text{P,H}}=2.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 6.73 (dd,  $^4J_{\text{H,H}}=2.5$  Hz,  $^3J_{\text{P,H}}=15.5$  Hz, 2H, C<sub>d</sub>H), 3.27 (m, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>), 3.07 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.05 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.58 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.22 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.16 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.12 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ ): 168.7 (d,  $^3J_{\text{P,C}}=2.5$  Hz, C<sup>IV</sup>-O), 139.1 (d,  $^3J_{\text{P,C}}=8.0$  Hz, C<sub>c,a</sub><sup>IV</sup>), 134.1 (d,  $^{2/3}J_{\text{P,C}}=9.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.9 (d,  $^3J_{\text{P,C}}=14.5$  Hz, C<sub>c,a</sub><sup>IV</sup>), 132.5 (d,  $^1J_{\text{P,C}}=91.5$  Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 131.7 (d,  $^4J_{\text{P,C}}=1.0$  Hz, *p*-CH(PPh<sub>2</sub>)), 128.8 (d,  $^{2/3}J_{\text{P,C}}=11.5$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.2 (s, C<sub>b</sub>H), 127.8 (d,  $^2J_{\text{P,C}}=13.5$  Hz, C<sub>d</sub>H), 114.3 (d,  $^1J_{\text{P,C}}=119.5$  Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 60.9 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 48.5 (d,  $^2J_{\text{P,C}}=6.0$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 35.7 (t,  $^3J_{\text{P,C}}=5.0$  Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 34.3 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 32.0 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 31.8 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.1 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 26.5 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>61</sub>H<sub>79</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Y: C, 69.44; H, 7.55; N, 2.65. Found: C, 69.29; H, 7.52; N, 2.65.

## Synthesis of 54a

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **48** (312 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which showed only one singlet at +22.3 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed the clean formation of a complex with one singlet at 36.5 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (295 mg, 88%).

**54a:**  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ ):  $\delta$  33.4 (s);  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  7.70 (ddd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=8.0$  Hz,  $^3J_{\text{P,H}}=10.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.49 (ddd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=8.0$  Hz,  $^3J_{\text{P,H}}=10.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.42(vtd,  $^4J_{\text{P,H}}=2.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.34 (vtd,  $^4J_{\text{P,H}}=2.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.29 (d,  $^4J_{\text{H,H}}=2.0$  Hz, 2H, C<sub>b</sub>H), 7.15 (vtd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.07 (vtd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 6.43 (dd,  $^4J_{\text{H,H}}=2.0$  Hz,  $^3J_{\text{P,H}}=15.5$  Hz, 2H, C<sub>d</sub>H), 3.39 (d,  $^3J_{\text{P,H}}=12.5$  Hz, 1H, N-CH<sub>2</sub>), 3.34 (d,  $^3J_{\text{P,H}}=12.5$  Hz, 1H, N-CH<sub>2</sub>), 2.85 (d,  $^3J_{\text{P,H}}=12.0$  Hz, 1H, N-CH<sub>2</sub>), 2.79 (d,  $^3J_{\text{P,H}}=12.5$  Hz, 1H, N-CH<sub>2</sub>), 1.36 (s, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.02 (s, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 0.80 (s, 9H, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 0.62 (s, 3H, N-CH<sub>2</sub>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>2</sub>), 0.50 (s, 3H, N-CH<sub>2</sub>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>2</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ ): 168.8 (d,  $^3J_{\text{P,C}}=2.5$  Hz, C<sup>IV</sup>-O), 168.7 (d,  $^3J_{\text{P,C}}=2.5$  Hz,

$C^{IV}-O$ ), 137.9 (d,  $^3J_{P,C}=7.7$  Hz,  $C_{c,a}^{IV}$ ), 133.8 (d,  $^{2/3}J_{P,C}=8.5$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.6 (d,  $^{2/3}J_{P,C}=8.5$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 132.8 (d,  $^1J_{P,C}=97.0$  Hz,  $C^{IV}(PPh_2)$ ), 131.7 (d,  $^1J_{P,C}=87.4$  Hz,  $C^{IV}(PPh_2)$ ), 130.9 (s, *p*-CH(PPh<sub>2</sub>)), 130.8 (s, *p*-CH(PPh<sub>2</sub>)), 127.9 (d,  $^{2/3}J_{P,C}=11.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.8 (d,  $^{2/3}J_{P,C}=11.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 127.5 (s,  $C_bH$ ), 127.5 (d,  $^2J_{P,C}=12.5$  Hz,  $C_dH$ ), 112.4 (d,  $^1J_{P,C}=121.0$  Hz,  $C^{IV}-PPh_2$ ), 69.2 (s, O- $C^{IV}(CH_3)_3$ ), 58.1 (d,  $^2J_{P,C}=7.5$  Hz, N-CH<sub>2</sub>), 38.1 (t,  $^3J_{P,C}=12.5$  Hz, N-CH<sub>2</sub>- $C^{IV}-CH_2-N$ ), 35.1 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 33.7 (s, O- $C^{IV}(CH_3)_3$ ), 33.5 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 31.0 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 29.6 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 26.1 (s,  $C^{IV}(CH_3)_2$ ), 25.2 (s, N-CH<sub>2</sub>- $C^{IV}(CH_3)_2$ ). Anal. Calcd for C<sub>65</sub>H<sub>86</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Y: C, 70.32; H, 7.81; N, 2.52. Found: C, 70.40; H, 7.74; N, 2.61.

### Synthesis of 54b

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **48** (312 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}P\{^1H\}$  NMR spectrum which showed only one singlet at +22.3 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature,  $^{31}P\{^1H\}$  NMR spectrum showed the clean formation of a complex with one singlet at 36.5 ppm. Potassium ethoxide (25.2 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as white solid (265 mg, 81%).

**54b:**  $^{31}P\{^1H\}$  NMR (THF-*d*<sub>8</sub>):  $\delta$  33.4 (s);  $^1H$  NMR (THF-*d*<sub>8</sub>):  $\delta$  7.75 (ddd,  $^4J_{H,H}=1.5$  Hz,  $^3J_{H,H}=7.0$  Hz,  $^3J_{P,H}=11.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.58 (ddd,  $^4J_{H,H}=1.5$  Hz,  $^3J_{H,H}=7.0$  Hz,  $^3J_{P,H}=11.5$  Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.45 (m, 8H, *m*-CH(PPh<sub>2</sub>) + *p*-CH(PPh<sub>2</sub>)), 7.35 (d,  $^4J_{H,H}=2.0$  Hz, 2H,  $C_bH$ ), 7.33 (vtd,  $^4J_{P,H}=2.5$  Hz,  $^3J_{H,H}=^3J'_{H,H}=7.0$  Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 6.77 (dd,  $^4J_{H,H}=2.0$  Hz,  $^3J_{P,H}=15.0$  Hz, 2H,  $C_dH$ ), 4.03 (t,  $^3J_{H,H}=6.0$  Hz, 1H, O-CH<sub>2</sub>-CH<sub>3</sub>), 4.01 (t,  $^3J_{H,H}=6.0$  Hz, 1H, O-CH<sub>2</sub>-CH<sub>3</sub>), 3.69 (d,  $^3J_{P,H}=15.0$  Hz, 1H, N-CH<sub>2</sub>), 3.64 (d,  $^3J_{P,H}=15.0$  Hz, 1H, N-CH<sub>2</sub>), 2.68 (d,  $^3J_{P,H}=12.5$  Hz, 1H, N-CH<sub>2</sub>), 2.61 (d,  $^3J_{P,H}=12.5$  Hz, 1H, N-CH<sub>2</sub>), 1.29 (s, 18H,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 1.19 (s, 18H,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 0.90 (m, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>), 0.46 (s, 3H, N-CH<sub>2</sub>- $C^{IV}(CH_3)_2$ ), 0.44 (s, 3H, N-CH<sub>2</sub>- $C^{IV}(CH_3)_2$ );  $^{13}C\{^1H\}$  NMR (THF-*d*<sub>8</sub>): 169.1 (d,  $^3J_{P,C}=2.5$  Hz,  $C^{IV}-O$ ), 169.0 (d,  $^3J_{P,C}=2.5$  Hz,  $C^{IV}-O$ ), 139.0 (d,  $^3J_{P,C}=7.5$  Hz,  $C_{c,a}^{IV}$ ), 134.8 (d,  $^{2/3}J_{P,C}=9.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 134.3 (d,  $^{2/3}J_{P,C}=9.0$  Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 134.0 (d,  $^3J_{P,C}=14.5$  Hz,  $C_{c,a}^{IV}$ ), 133.1 (d,  $^1J_{P,C}=88.5$  Hz,  $C^{IV}(PPh_2)$ ), 131.7 (d,  $^1J_{P,C}=90.5$  Hz,  $C^{IV}(PPh_2)$ ), 131.7 (s, *p*-CH(PPh<sub>2</sub>)+ $C_bH$ ), 127.9 (d,  $^2J_{P,C}=13.0$  Hz,  $C_dH$ ), 114.4 (d,  $^1J_{P,C}=120.0$  Hz,  $C^{IV}-PPh_2$ ), 61.6 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 58.2 (d,  $^2J_{P,C}=7.5$  Hz, N-CH<sub>2</sub>), 37.5 (t,  $^3J_{P,C}=12.5$  Hz, N-CH<sub>2</sub>- $C^{IV}-CH_2-N$ ), 34.9 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 33.5 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 31.3 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 30.9 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 29.3 (s,  $C_{c,a}^{IV}-C^{IV}(CH_3)_3$ ), 26.2 (s,  $C^{IV}(CH_3)_2$ ), 22.3 (s, N-CH<sub>2</sub>- $C^{IV}(CH_3)_2$ ). Anal. Calcd for C<sub>63</sub>H<sub>82</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Y: C, 69.92; H, 7.64; N, 2.59. Found: C, 69.96; H, 7.66; N, 2.65.

### Synthesis of 55

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **49** (314 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified

by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which showed only one singlet at +13.2 ppm. Insoluble potassium salt was removed by centrifugation.  $[\text{YCl}_3(\text{THF})_{3.5}]$  (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed the clean formation of a complex with one singlet at 27.3 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (290 mg, 87%).

**55:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  24.9 (s);  $^1\text{H}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  7.71 (ddd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=8.0$  Hz,  $^3J_{\text{P,H}}=12.0$  Hz, 4H, *o*-CH( $\text{PPh}_2$ )), 7.58 (ddd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=8.0$  Hz,  $^3J_{\text{P,H}}=12.0$  Hz, 4H, *o*-CH( $\text{PPh}_2$ )), 7.58 (vtvt,  $^4J_{\text{H,H}}=^5J_{\text{P,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 2H, *p*-CH( $\text{PPh}_2$ )), 7.51 (vtd,  $^4J_{\text{P,H}}=3.0$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 4H, *m*-CH( $\text{PPh}_2$ )), 7.45 (vtvt,  $^4J_{\text{H,H}}=^5J_{\text{P,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 2H, *p*-CH( $\text{PPh}_2$ )), 7.31 (d,  $^4J_{\text{H,H}}=3.0$  Hz, 2H,  $\text{C}_b\text{H}$ ), 7.30 (vtd,  $^4J_{\text{P,H}}=3.0$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=8.0$  Hz, 4H, *m*-CH( $\text{PPh}_2$ )), 6.37 (dd,  $^4J_{\text{H,H}}=3.0$  Hz,  $^3J_{\text{P,H}}=15.5$  Hz, 2H,  $\text{C}_d\text{H}$ ), 6.27 (ddd,  $^3J_{\text{H,H}}=6.0$  Hz,  $^4J_{\text{H,H}}=3.5$  Hz,  $^4J_{\text{P,H}}=3.0$  Hz, 2H,  $\text{C}_e\text{H}$ ), 6.01 (dd,  $^3J_{\text{H,H}}=6.0$  Hz,  $^4J_{\text{H,H}}=3.5$  Hz, 2H,  $\text{C}_f\text{H}$ ), 1.27 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 1.04 (s, 18H,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 0.56 (b, 9H,  $\text{O}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ): 169.7 (s,  $\text{C}^{\text{IV}}-\text{O}$ ), 144.8 (dd,  $^2J_{\text{P,C}}=19.0$  Hz,  $^3J_{\text{P,C}}=4.0$  Hz,  $\text{C}^{\text{IV}}-\text{N}$ ), 139.0 (d,  $^3J_{\text{P,C}}=7.5$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ), 134.4 (d,  $^3J_{\text{P,C}}=16.0$  Hz,  $\text{C}_{c,a}^{\text{IV}}$ ), 134.0 (d,  $^{2/3}J_{\text{P,C}}=10.0$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 132.3 (s, *p*-CH( $\text{PPh}_2$ )), 132.0 (s, *p*-CH( $\text{PPh}_2$ )), 132.0 (d,  $^1J_{\text{P,C}}=88.5$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 131.1 (d,  $^1J_{\text{P,C}}=87.0$  Hz,  $\text{C}^{\text{IV}}(\text{PPh}_2)$ ), 129.3 (d,  $^{2/3}J_{\text{P,C}}=11.5$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 128.8 (s,  $\text{C}_b\text{H}$ ), 128.7 (d,  $^{2/3}J_{\text{P,C}}=11.5$  Hz, *m*-or *o*-CH( $\text{PPh}_2$ )), 128.4 (d,  $^2J_{\text{P,C}}=14.0$  Hz,  $\text{C}_d\text{H}$ ), 122.2 (d,  $^3J_{\text{P,C}}=10.0$  Hz,  $\text{C}_e\text{H}$ ), 118.3 (s,  $\text{C}_f\text{H}$ ), 114.8 (d,  $^1J_{\text{P,C}}=124.0$  Hz,  $\text{C}^{\text{IV}}-\text{PPh}_2$ ), 35.7 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 34.3 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 33.9 (b,  $\text{O}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 31.8 (s, (b,  $\text{O}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 31.7 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ), 30.3 (s,  $\text{C}_{c,a}^{\text{IV}}-\text{C}^{\text{IV}}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{66}\text{H}_{80}\text{N}_2\text{O}_4\text{P}_2\text{Y}$ : C, 71.02; H, 7.22; N, 2.51. Found: C, 70.85; H, 7.43; N, 2.55.

### Synthesis of 56a

KHMDS (300 mg, 1.5 mmol) was added into a slurry of **50** (350 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which showed only one singlet at +24.2 ppm. Insoluble potassium salt was removed by centrifugation.  $[\text{YCl}_3(\text{THF})_{3.5}]$  (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed the clean formation of a complex with one singlet at 35.0 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (260 mg, 83%).

**56a:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  33.6 (s);  $^1\text{H}$  NMR ( $\text{THF}-d_8$ ):  $\delta$  7.60 (ddd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=7.0$  Hz,  $^3J_{\text{P,H}}=11.5$  Hz, 4H, *o*-CH( $\text{PPh}_2$ )), 7.57 (ddd,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=7.0$  Hz,  $^3J_{\text{P,H}}=11.5$  Hz, 4H, *o*-CH( $\text{PPh}_2$ )), 7.50 (tvq,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=7.0$  Hz,  $^5J_{\text{P,H}}=1.5$  Hz, 2H, *p*-CH( $\text{PPh}_2$ )), 7.42 (vtd,  $^4J_{\text{P,H}}=2.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.0$  Hz, 4H, *m*-CH( $\text{PPh}_2$ )), 7.40 (tvq,  $^4J_{\text{H,H}}=1.5$  Hz,  $^3J_{\text{H,H}}=7.0$  Hz,  $^5J_{\text{P,H}}=1.5$  Hz, 2H, *p*-CH( $\text{PPh}_2$ )), 7.24 (vtd,  $^4J_{\text{P,H}}=2.5$  Hz,  $^3J_{\text{H,H}}=^3J'_{\text{H,H}}=7.0$  Hz, 4H, *m*-

*CH*(PPh<sub>2</sub>)), 7.21 (d, <sup>4</sup>J<sub>H,H</sub>= 2.0 Hz, 2H, C<sub>b</sub>H), 6.59 (dd, <sup>4</sup>J<sub>H,H</sub>=2.0 Hz, <sup>3</sup>J<sub>P,H</sub> = 15.5 Hz, 2H, C<sub>d</sub>H), 3.24 (m, 4H, P=N-CH<sub>2</sub>-CH<sub>2</sub>), 2.93 (m, 2H, P=N-CH<sub>2</sub>-CH<sub>2</sub>), 2.58 (m, 2H, P=N-CH<sub>2</sub>-CH<sub>2</sub>), 1.15 (s, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.10 0.80 (s, 9H, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 1.09 (s, 18H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): 169.1 (d, <sup>3</sup>J<sub>P,C</sub>= 3.0 Hz, C<sup>IV</sup>-O), 169.0 (d, <sup>3</sup>J<sub>P,C</sub>= 3.0 Hz, C<sup>IV</sup>-O), 139.9 (d, <sup>3</sup>J<sub>P,C</sub>=8.0 Hz, C<sub>c,a</sub><sup>IV</sup>), 133.8 (d, <sup>2/3</sup>J<sub>P,C</sub>= 9.5 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.7 (d, <sup>2/3</sup>J<sub>P,C</sub>= 9.5 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.6 (d, <sup>3</sup>J<sub>P,C</sub>=8.0 Hz, C<sub>c,a</sub><sup>IV</sup>), 133.3 (d, <sup>1</sup>J<sub>P,C</sub>=87.5 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 132.1 (d, <sup>1</sup>J<sub>P,C</sub>=90.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 131.8 (d, <sup>4</sup>J<sub>P,C</sub>= 2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 131.6 (<sup>4</sup>J<sub>P,C</sub>= 2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 128.9 (d, <sup>2/3</sup>J<sub>P,C</sub>= 11.0 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.8 (d, <sup>2/3</sup>J<sub>P,C</sub>= 11.0 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.2 (d, <sup>4</sup>J<sub>P,C</sub>= 2.5 Hz, C<sub>b</sub>H), 127.5 (d, <sup>2</sup>J<sub>P,C</sub>=12.5 Hz, C<sub>d</sub>H), 111.8 (d, <sup>1</sup>J<sub>P,C</sub>=118.0 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 69.7 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 54.0 (d, <sup>2</sup>J<sub>P,C</sub>=16.0 Hz, P<sup>IV</sup>-N-CH<sub>2</sub>), 48.6 (d, <sup>3</sup>J<sub>P,C</sub>=5.0 Hz, P<sup>IV</sup>-N-CH<sub>2</sub>-CH<sub>2</sub>), 35.8 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 35.2 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 34.3 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.8 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.2 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>60</sub>H<sub>78</sub>N<sub>3</sub>O<sub>3</sub>P<sub>2</sub>Y: C, 69.28; H, 7.56; N, 4.04. Found: C, 69.16; H, 7.64; N, 3.95.

### Synthesis of 56b

KHMDS (300 mg, 1.5 mmol) was added into a slurry of **50** (350 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by <sup>31</sup>P{<sup>1</sup>H} NMR spectrum which showed only one singlet at +24.2 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3.5</sub>] (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature, <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed the clean formation of a complex with one singlet at 35.0 ppm. Potassium ethoxide (25.2 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (265 mg, 87%).

**56b:** <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 34.2 (s); <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 7.61 (ddd, <sup>4</sup>J<sub>H,H</sub>=1.5 Hz, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, <sup>3</sup>J<sub>P,H</sub>=9.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.55 (ddd, <sup>4</sup>J<sub>H,H</sub>=1.5 Hz, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, <sup>3</sup>J<sub>P,H</sub>=9.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.49 (tt, <sup>4</sup>J<sub>H,H</sub>=1.5 Hz, <sup>3</sup>J<sub>H,H</sub>= 8.0 Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.39 (vtd, <sup>4</sup>J<sub>P,H</sub>=2.5 Hz, <sup>3</sup>J<sub>H,H</sub>= <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.37 (tt, <sup>4</sup>J<sub>H,H</sub>=1.5 Hz, <sup>3</sup>J<sub>H,H</sub>= 8.0 Hz, 2H, *p*-CH(PPh<sub>2</sub>)), 7.22 (vtd, <sup>4</sup>J<sub>P,H</sub>=2.5 Hz, <sup>3</sup>J<sub>H,H</sub>= <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4H, *m*-CH(PPh<sub>2</sub>)), 7.21 (d, <sup>4</sup>J<sub>H,H</sub>= 2.0 Hz, 2H, C<sub>b</sub>H), 6.65 (dd, <sup>4</sup>J<sub>H,H</sub>=2.0 Hz, <sup>3</sup>J<sub>P,H</sub> = 15.5 Hz, 2H, C<sub>d</sub>H), 3.96 (m, 1H, O-CH<sub>2</sub>-CH<sub>3</sub>), 3.32 (m, 1H, O-CH<sub>2</sub>-CH<sub>3</sub>), 3.27 (m, 4H, P=N-CH<sub>2</sub>), 2.83 (m, 2H, P=N-CH<sub>2</sub>-CH<sub>2</sub>), 2.58 (m, 2H, P=N-CH<sub>2</sub>-CH<sub>2</sub>), 1.12 (s, 36H, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 0.90 (m, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): 168.9 (d, <sup>3</sup>J<sub>P,C</sub>= 3.0 Hz, C<sup>IV</sup>-O), 168.8 (d, <sup>3</sup>J<sub>P,C</sub>= 3.0 Hz, C<sup>IV</sup>-O), 139.9 (d, <sup>3</sup>J<sub>P,C</sub>=7.5 Hz, C<sub>c,a</sub><sup>IV</sup>), 133.7 (d, <sup>2/3</sup>J<sub>P,C</sub>= 8.0 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.6 (d, <sup>2/3</sup>J<sub>P,C</sub>= 8.0 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 133.5 (d, <sup>3</sup>J<sub>P,C</sub>=8.0 Hz, C<sub>c,a</sub><sup>IV</sup>), 133.3 (d, <sup>1</sup>J<sub>P,C</sub>=83.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 131.8 (<sup>4</sup>J<sub>P,C</sub>= 2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 131.6 (d, <sup>1</sup>J<sub>P,C</sub>=88.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 131.6 (d, <sup>4</sup>J<sub>P,C</sub>= 2.5 Hz, *p*-CH(PPh<sub>2</sub>)), 128.9 (d, <sup>2/3</sup>J<sub>P,C</sub>= 11.0 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.8 (d, <sup>2/3</sup>J<sub>P,C</sub>= 11.0 Hz, *m*-or *o*-CH(PPh<sub>2</sub>)), 128.3 (d, <sup>4</sup>J<sub>P,C</sub>= 2.0 Hz, C<sub>b</sub>H), 127.2 (d, <sup>2</sup>J<sub>P,C</sub>=12.5 Hz, C<sub>d</sub>H), 113.0 (d, <sup>1</sup>J<sub>P,C</sub>=119.0 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 62.5 (s, O-CH<sub>2</sub>-CH<sub>3</sub>), 53.7 (d, <sup>2</sup>J<sub>P,C</sub>=16.0 Hz, P<sup>IV</sup>-N-CH<sub>2</sub>), 48.8 (d, <sup>3</sup>J<sub>P,C</sub>=5.0 Hz, P<sup>IV</sup>-N-CH<sub>2</sub>-CH<sub>2</sub>), 35.7 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 34.3 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 31.9 (s, C<sub>c,a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 29.9

(s,  $C_{c,a}^{IV}$ - $C^{IV}(CH_3)_3$ ), 23.3 (s, O-CH<sub>2</sub>-CH<sub>3</sub>). Anal. Calcd for C<sub>58</sub>H<sub>74</sub>N<sub>3</sub>O<sub>3</sub>P<sub>2</sub>Y: C, 68.83; H, 7.37; N, 4.74. Found: C, 68.14; H, 7.54; N, 4.27.

### Synthesis of 57

At -78°C, bromine (300 µL, 5.825 mmol) was added dropwise to a solution of the phenolphosphine **39** (2.018 g, 5.825 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The cold bath was removed and stirring was continued for 2 hours at room temperature. Then the solution was cooled down to -78°C. Tributylamine (1.39 mL, 5.825 mmol) was added, followed by ethylenediamine (195 µL, 2.913 mmol). The cold bath was removed. After 16h, a cloudy solution was formed. CH<sub>2</sub>Cl<sub>2</sub> was evaporated and the residue was washed with THF (5x10 mL) to remove tributylamonium salt. The product was isolated as a white solid and dried under vacuum (1.9 g, 69%).

**57:** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 40.1 (s,  $P^V$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.66 (t, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, 4H, *p*-CH(PPh<sub>2</sub>)), 7.63 (dd, <sup>3</sup>J<sub>P,H</sub>=12.5 Hz, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, 8H, *o*-CH(PPh<sub>2</sub>)), 7.53 (vtd, <sup>4</sup>J<sub>P,H</sub>=3.5 Hz, <sup>3</sup>J<sub>H,H</sub>=<sup>3</sup>J'<sub>H,H</sub>=8.0 Hz, 8H, *m*-CH(PPh<sub>2</sub>)), 7.17 (d, <sup>4</sup>J<sub>H,H</sub>=2.5 Hz, 2H, C<sub>b</sub>H), 5.95 (dd, <sup>3</sup>J<sub>P,H</sub>=16.5 Hz, <sup>4</sup>J<sub>H,H</sub>=2.5 Hz, 2H, C<sub>d</sub>H), 3.66 (dd, <sup>3</sup>J<sub>P,H</sub>=6.5 Hz, <sup>4</sup>J<sub>P,H</sub>=2.0 Hz, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.50 (s, 6H, -OCH<sub>3</sub>), 1.50 (s, 18H, C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 154.4 (C<sup>IV</sup>-O or C<sub>c,a</sub><sup>IV</sup>), 151.8 (weak, C<sup>IV</sup>-O or C<sub>c,a</sub><sup>IV</sup>), 145.7 (C<sup>IV</sup>-O or C<sub>c,a</sub><sup>IV</sup>), 134.3 (s, *p*-CH(PPh<sub>2</sub>)), 133.6 (d, <sup>2</sup>J<sub>P,C</sub>=9.0 Hz, *o*-CH(PPh<sub>2</sub>)), 129.7 (d, <sup>3</sup>J<sub>P,C</sub>=13.5 Hz, *m*-CH(PPh<sub>2</sub>)), 122.1 (d, <sup>1</sup>J<sub>P,C</sub>=105 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 121.2 (s, C<sub>b</sub>H), 116.0 (d, <sup>1</sup>J<sub>P,C</sub>=120 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 115.0 (d, <sup>2</sup>J<sub>P,C</sub>=13.5 Hz, C<sub>d</sub>H), 55.6 (s, O-CH<sub>3</sub>), 44.2 (dd, <sup>2</sup>J<sub>P,C</sub>=7.5 Hz, <sup>3</sup>J<sub>P,C</sub>=1.0 Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 35.4 (s, C<sub>a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.3 (s, b, C<sub>a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>48</sub>H<sub>56</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C, 60.90; H, 5.96; N, 2.96. Found: C, 60.71; H, 6.02; N, 3.02.

### Synthesis of 58

KHMDS (240 mg, 1.2 mmol) was added into a slurry of **57** (295 mg, 0.3 mmol) in THF (20 mL). After 4h, a cloudy solution was yielded. The completion of the deprotonation was verified by <sup>31</sup>P{<sup>1</sup>H} NMR spectrum which showed only one singlet at +20.3 ppm. Insoluble potassium salt was removed by centrifugation. [YCl<sub>3</sub>(THF)<sub>3,5</sub>] (134.3 mg, 0.3 mmol) was added. After 4h of stirring at room temperature, <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed the clean formation of a complex with one singlet at 31.5 ppm. Potassium *tert*-butoxide (33.7 mg, 0.3 mmol) was added into the mixture, giving a cloudy solution. Stirring was continued for 7 h and the solid was removed by centrifugation. The solvents was evaporated in vacuum and the residue was recrystallised in cyclohexane (5 mL), giving the product as colorless crystals (250 mg, 88%).

**58:** <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 31.6 (s); <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 7.63 (dd, <sup>3</sup>J<sub>P,H</sub>=11.5 Hz, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.54 (m, 2H, *p*-CH(PPh<sub>2</sub>)), 7.48 (m, 5H, *p*-CH(PPh<sub>2</sub>) + *m*-CH(PPh<sub>2</sub>)), 7.40 (dd, <sup>3</sup>J<sub>P,H</sub>=11.5 Hz, <sup>3</sup>J<sub>H,H</sub>=7.0 Hz, 4H, *o*-CH(PPh<sub>2</sub>)), 7.39 (vt, <sup>3</sup>J<sub>H,H</sub>=<sup>3</sup>J'<sub>H,H</sub>=7.0 Hz, 1H, *m*-CH(PPh<sub>2</sub>)), 6.92 (d, <sup>4</sup>J<sub>H,H</sub>=3.0 Hz, 2H, C<sub>b</sub>H), 5.94 (dd, <sup>3</sup>J<sub>P,H</sub>=15.5 Hz, <sup>4</sup>J<sub>H,H</sub>=3.0 Hz, 2H, C<sub>d</sub>H), 3.35 (s, 6H, -OCH<sub>3</sub>), 3.31 (m,b, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.18 (m,b, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.39 (s, 18H, C<sub>a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 0.84 (s, b, 9H, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): 166.8 (s, C<sup>IV</sup>-O), 148.2 (d, <sup>3</sup>J<sub>P,C</sub>=20.0 Hz, C<sub>c</sub><sup>IV</sup>), 141.1 (d, <sup>3</sup>J<sub>P,C</sub>=9.5 Hz, C<sub>a</sub><sup>IV</sup>), 134.1 (d, <sup>2</sup>J<sub>P,C</sub>=9.0 Hz, *o*-

CH(PPh<sub>2</sub>)), 133.6 (d, <sup>2</sup>J<sub>P,C</sub> = 9.0 Hz, *o*-CH(PPh<sub>2</sub>)), 132.3 (d, <sup>1</sup>J<sub>P,C</sub> = 88.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 132.0 (d, <sup>4</sup>J<sub>P,C</sub> = 1.5 Hz, *p*-CH(PPh<sub>2</sub>)), 131.7 (d, <sup>1</sup>J<sub>P,C</sub> = 90.0 Hz, C<sup>IV</sup>(PPh<sub>2</sub>)), 131.7 (d, <sup>4</sup>J<sub>P,C</sub> = 1.5 Hz, *p*-CH(PPh<sub>2</sub>)), 129.0 (d, <sup>3</sup>J<sub>P,C</sub> = 10.5 Hz, *m*-CH(PPh<sub>2</sub>)), 128.9 (d, <sup>3</sup>J<sub>P,C</sub> = 10.5 Hz, *m*-CH(PPh<sub>2</sub>)), 120.3 (d, <sup>4</sup>J<sub>P,C</sub> = 1.0 Hz, C<sub>b</sub>H), 114.2 (d, <sup>2</sup>J<sub>P,C</sub> = 14.5 Hz, C<sub>d</sub>H), 111.6 (d, <sup>1</sup>J<sub>P,C</sub> = 123.0 Hz, C<sup>IV</sup>-PPh<sub>2</sub>), 55.5 (s, O-CH<sub>3</sub>), 52.1 (dd, <sup>2/3</sup>J<sub>P,C</sub> = 6.5 Hz, <sup>3/3</sup>J<sub>P,C</sub> = 18.0 Hz, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 35.7 (s, C<sub>a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 33.3 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 30.2 (s, C<sub>a</sub><sup>IV</sup>-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>), 26.0 (s, O-C<sup>IV</sup>(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>52</sub>H<sub>61</sub>N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>Y: C, 66.10; H, 6.51; N, 2.96. Found: C, 65.89; H, 6.42; N, 2.85.

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## Crystallographic Data

### Chapter 1

#### *Compound 2a*

Table 1. Crystal data for pa058

|   |  |
|---|--|
| Compound                                    | pa058  |
| Molecular formula                           | C <sub>22</sub> H <sub>25</sub> NPS, BF <sub>4</sub> |
| Molecular weight                            | 453.27   |
| Crystal habit                               | Colorless Block                                      |
| Crystal dimensions(mm)                      | 0.30x0.12x0.08                                       |
| Crystal system                              | orthorhombic   |
| Space group                                 | Pbca   |
| a(Å)  | 15.666(1)  |
| b(Å)  | 16.486(1)  |
| c(Å)  | 17.614(1)  |
| $\alpha(^{\circ})$                          | 90.00  |
| $\beta(^{\circ})$                           | 90.00  |
| $\gamma(^{\circ})$                          | 90.00  |
| V(Å <sup>3</sup> )                          | 4549.2(5)  |
| Z   | 8  |
| d(g·cm <sup>-3</sup> )                      | 1.324  |
| F(000)                                      | 1888   |
| $\mu$ (cm <sup>-1</sup> )                   | 0.254  |
| Absorption corrections                      | multi-scan ; 0.9278 min, 0.9800 max                  |
| Diffractometer                              | KappaCCD   |
| X-ray source                                | MoK $\alpha$   |
| $\lambda$ (Å)                               | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans                                  |
| Maximum $\theta$                            | 27.45  |
| HKL ranges                                  | -20 16 ; -17 20 ; -15 22                             |
| Reflections measured                        | 21003  |
| Unique data                                 | 5177   |
| Rint  | 0.0258   |
| Reflections used                            | 3908   |
| Criterion                                   | I > 2 $\sigma$ (I)                                   |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | mixed  |
| Parameters refined                          | 280  |
| Reflections / parameter                     | 13   |
| wR2   | 0.1107   |
| R1  | 0.0382   |
| Weights a, b                                | 0.0541 ; 1.0556                                      |
| GoF   | 1.066  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.348(0.045) / -0.514(0.045)                         |



## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa058

| atom  | x       | y       | z       | U(eq) |
|-------|---------|---------|---------|-------|
| S(1)  | 4444(1) | 1284(1) | 4211(1) | 45(1) |
| P(1)  | 5259(1) | 2165(1) | 5734(1) | 26(1) |
| F(1)  | 4080(1) | 3504(1) | 7281(1) | 43(1) |
| F(2)  | 4001(1) | 4263(1) | 6219(1) | 44(1) |
| F(3)  | 2926(1) | 4301(1) | 7080(1) | 55(1) |
| F(4)  | 4203(1) | 4873(1) | 7360(1) | 56(1) |
| N(1)  | 5511(1) | 2754(1) | 6438(1) | 29(1) |
| C(1)  | 5059(1) | 2702(1) | 4858(1) | 30(1) |
| C(2)  | 4697(1) | 2337(1) | 4213(1) | 34(1) |
| C(3)  | 4524(1) | 2814(1) | 3576(1) | 42(1) |
| C(4)  | 4726(1) | 3632(1) | 3574(1) | 47(1) |
| C(5)  | 5073(1) | 3997(1) | 4207(1) | 43(1) |
| C(6)  | 5228(1) | 3536(1) | 4848(1) | 35(1) |
| C(7)  | 4259(1) | 1706(1) | 5991(1) | 28(1) |
| C(8)  | 4210(1) | 924(1)  | 6289(1) | 38(1) |
| C(9)  | 3423(1) | 607(1)  | 6484(1) | 45(1) |
| C(10) | 2687(1) | 1053(1) | 6380(1) | 42(1) |
| C(11) | 2734(1) | 1821(1) | 6078(1) | 41(1) |
| C(12) | 3519(1) | 2155(1) | 5883(1) | 34(1) |
| C(13) | 6095(1) | 1439(1) | 5595(1) | 32(1) |
| C(14) | 6525(1) | 1387(1) | 4902(1) | 38(1) |
| C(15) | 7229(1) | 878(1)  | 4839(1) | 51(1) |
| C(16) | 7490(2) | 423(1)  | 5451(2) | 58(1) |
| C(17) | 7059(1) | 458(1)  | 6135(1) | 52(1) |
| C(18) | 6362(1) | 969(1)  | 6214(1) | 38(1) |
| C(19) | 6329(1) | 3141(1) | 6700(1) | 35(1) |
| C(20) | 7037(1) | 3083(1) | 6112(1) | 46(1) |
| C(21) | 6600(2) | 2725(1) | 7434(1) | 55(1) |
| C(22) | 6135(1) | 4035(1) | 6858(1) | 42(1) |
| B(1)  | 3797(1) | 4248(1) | 6983(1) | 33(1) |

U(eq) is defined as 1/3 the trace of the  $U_{ij}$  tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles (deg) for pa058

|              |          |              |          |
|--------------|----------|--------------|----------|
| S(1)-C(2)    | 1.781(2) | S(1)-H(1S)   | 1.34(2)  |
| P(1)-N(1)    | 1.623(1) | P(1)-C(13)   | 1.791(2) |
| P(1)-C(7)    | 1.797(2) | P(1)-C(1)    | 1.807(2) |
| F(1)-B(1)    | 1.406(2) | F(2)-B(1)    | 1.384(2) |
| F(3)-B(1)    | 1.378(2) | F(4)-B(1)    | 1.382(2) |
| N(1)-C(19)   | 1.505(2) | N(1)-H(1N)   | 0.900(1) |
| C(1)-C(6)    | 1.400(2) | C(1)-C(2)    | 1.405(2) |
| C(2)-C(3)    | 1.396(2) | C(3)-C(4)    | 1.385(3) |
| C(3)-H(3)    | 0.9500   | C(4)-C(5)    | 1.378(3) |
| C(4)-H(4)    | 0.9500   | C(5)-C(6)    | 1.383(2) |
| C(5)-H(5)    | 0.9500   | C(6)-H(6)    | 0.9500   |
| C(7)-C(12)   | 1.389(2) | C(7)-C(8)    | 1.395(2) |
| C(8)-C(9)    | 1.383(3) | C(8)-H(8)    | 0.9500   |
| C(9)-C(10)   | 1.380(3) | C(9)-H(9)    | 0.9500   |
| C(10)-C(11)  | 1.374(3) | C(10)-H(10)  | 0.9500   |
| C(11)-C(12)  | 1.391(3) | C(11)-H(11)  | 0.9500   |
| C(12)-H(12)  | 0.9500   | C(13)-C(14)  | 1.396(2) |
| C(13)-C(18)  | 1.401(2) | C(14)-C(15)  | 1.390(3) |
| C(14)-H(14)  | 0.9500   | C(15)-C(16)  | 1.376(3) |
| C(15)-H(15)  | 0.9500   | C(16)-C(17)  | 1.383(3) |
| C(16)-H(16)  | 0.9500   | C(17)-C(18)  | 1.387(3) |
| C(17)-H(17)  | 0.9500   | C(18)-H(18)  | 0.9500   |
| C(19)-C(20)  | 1.520(3) | C(19)-C(21)  | 1.524(3) |
| C(19)-C(22)  | 1.531(2) | C(20)-H(20A) | 0.9800   |
| C(20)-H(20B) | 0.9800   | C(20)-H(20C) | 0.9800   |
| C(21)-H(21A) | 0.9800   | C(21)-H(21B) | 0.9800   |
| C(21)-H(21C) | 0.9800   | C(22)-H(22A) | 0.9800   |
| C(22)-H(22B) | 0.9800   | C(22)-H(22C) | 0.9800   |

|                    |           |                    |           |
|--------------------|-----------|--------------------|-----------|
| C(2)-S(1)-H(1S)    | 97(1)     | N(1)-P(1)-C(13)    | 109.06(8) |
| N(1)-P(1)-C(7)     | 105.72(7) | C(13)-P(1)-C(7)    | 113.01(7) |
| N(1)-P(1)-C(1)     | 113.66(7) | C(13)-P(1)-C(1)    | 109.75(8) |
| C(7)-P(1)-C(1)     | 105.64(8) | C(19)-N(1)-P(1)    | 134.1(1)  |
| C(19)-N(1)-H(1N)   | 113(1)    | P(1)-N(1)-H(1N)    | 113(1)    |
| C(6)-C(1)-C(2)     | 119.2(2)  | C(6)-C(1)-P(1)     | 117.3(1)  |
| C(2)-C(1)-P(1)     | 123.4(1)  | C(3)-C(2)-C(1)     | 119.1(2)  |
| C(3)-C(2)-S(1)     | 120.3(1)  | C(1)-C(2)-S(1)     | 120.6(1)  |
| C(4)-C(3)-C(2)     | 120.4(2)  | C(4)-C(3)-H(3)     | 119.8     |
| C(2)-C(3)-H(3)     | 119.8     | C(5)-C(4)-C(3)     | 120.8(2)  |
| C(5)-C(4)-H(4)     | 119.6     | C(3)-C(4)-H(4)     | 119.6     |
| C(4)-C(5)-C(6)     | 119.4(2)  | C(4)-C(5)-H(5)     | 120.3     |
| C(6)-C(5)-H(5)     | 120.3     | C(5)-C(6)-C(1)     | 121.0(2)  |
| C(5)-C(6)-H(6)     | 119.5     | C(1)-C(6)-H(6)     | 119.5     |
| C(12)-C(7)-C(8)    | 119.9(2)  | C(12)-C(7)-P(1)    | 118.0(1)  |
| C(8)-C(7)-P(1)     | 122.1(1)  | C(9)-C(8)-C(7)     | 119.5(2)  |
| C(7)-C(8)-H(8)     | 120.3     | C(7)-C(8)-H(8)     | 120.3     |
| C(10)-C(9)-C(8)    | 120.7(2)  | C(10)-C(9)-H(9)    | 119.7     |
| C(8)-C(9)-H(9)     | 119.7     | C(11)-C(10)-C(9)   | 119.9(2)  |
| C(11)-C(10)-H(10)  | 120.1     | C(9)-C(10)-H(10)   | 120.1     |
| C(10)-C(11)-C(12)  | 120.5(2)  | C(10)-C(11)-H(11)  | 119.7     |
| C(12)-C(11)-H(11)  | 119.7     | C(7)-C(12)-C(11)   | 119.6(2)  |
| C(7)-C(12)-H(12)   | 120.2     | C(11)-C(12)-H(12)  | 120.2     |
| C(14)-C(13)-C(18)  | 120.2(2)  | C(14)-C(13)-P(1)   | 120.9(1)  |
| C(18)-C(13)-P(1)   | 118.7(1)  | C(15)-C(14)-C(13)  | 119.3(2)  |
| C(15)-C(14)-H(14)  | 120.3     | C(13)-C(14)-H(14)  | 120.3     |
| C(16)-C(15)-C(14)  | 120.2(2)  | C(16)-C(15)-H(15)  | 119.9     |
| C(14)-C(15)-H(15)  | 119.9     | C(15)-C(16)-C(17)  | 121.0(2)  |
| C(15)-C(16)-H(16)  | 119.5     | C(17)-C(16)-H(16)  | 119.5     |
| C(16)-C(17)-C(18)  | 119.8(2)  | C(16)-C(17)-H(17)  | 120.1     |
| C(18)-C(17)-H(17)  | 120.1     | C(17)-C(18)-C(13)  | 119.5(2)  |
| C(17)-C(18)-H(18)  | 120.2     | C(13)-C(18)-H(18)  | 120.2     |
| N(1)-C(19)-C(20)   | 112.7(2)  | N(1)-C(19)-C(21)   | 107.9(1)  |
| C(20)-C(19)-C(21)  | 110.2(2)  | N(1)-C(19)-C(22)   | 107.2(1)  |
| C(20)-C(19)-C(22)  | 109.2(2)  | C(21)-C(19)-C(22)  | 109.5(2)  |
| C(19)-C(20)-H(20A) | 109.5     | C(19)-C(20)-H(20B) | 109.5     |

# Appendix 1. Crystallographic data

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| H(20A)-C(20)-H(20B) | 109.5    | C(19)-C(20)-H(20C)  | 109.5    |
| H(20A)-C(20)-H(20C) | 109.5    | H(20B)-C(20)-H(20C) | 109.5    |
| C(19)-C(21)-H(21A)  | 109.5    | C(19)-C(21)-H(21B)  | 109.5    |
| H(21A)-C(21)-H(21B) | 109.5    | C(19)-C(21)-H(21C)  | 109.5    |
| H(21A)-C(21)-H(21C) | 109.5    | H(21B)-C(21)-H(21C) | 109.5    |
| C(19)-C(22)-H(22A)  | 109.5    | C(19)-C(22)-H(22B)  | 109.5    |
| H(22A)-C(22)-H(22B) | 109.5    | C(19)-C(22)-H(22C)  | 109.5    |
| H(22A)-C(22)-H(22C) | 109.5    | H(22B)-C(22)-H(22C) | 109.5    |
| F(3)-B(1)-F(4)      | 110.4(2) | F(3)-B(1)-F(2)      | 110.4(2) |
| F(4)-B(1)-F(2)      | 110.4(2) | F(3)-B(1)-F(1)      | 108.7(2) |
| F(4)-B(1)-F(1)      | 109.0(2) | F(2)-B(1)-F(1)      | 107.8(2) |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa058

| atom  | U11   | U22   | U33   | U23    | U13    | U12    |
|-------|-------|-------|-------|--------|--------|--------|
| S(1)  | 63(1) | 32(1) | 39(1) | -2(1)  | -11(1) | -5(1)  |
| P(1)  | 28(1) | 23(1) | 27(1) | 2(1)   | 2(1)   | -2(1)  |
| F(1)  | 47(1) | 40(1) | 42(1) | 9(1)   | 2(1)   | 12(1)  |
| F(2)  | 48(1) | 51(1) | 33(1) | 7(1)   | 2(1)   | -9(1)  |
| F(3)  | 33(1) | 57(1) | 76(1) | 21(1)  | 11(1)  | 10(1)  |
| F(4)  | 66(1) | 46(1) | 58(1) | -18(1) | 8(1)   | -8(1)  |
| N(1)  | 24(1) | 32(1) | 31(1) | -3(1)  | 1(1)   | -3(1)  |
| C(1)  | 33(1) | 27(1) | 29(1) | 3(1)   | 3(1)   | 0(1)   |
| C(2)  | 41(1) | 30(1) | 31(1) | 0(1)   | 2(1)   | 0(1)   |
| C(3)  | 57(1) | 39(1) | 31(1) | 1(1)   | -2(1)  | 4(1)   |
| C(4)  | 65(1) | 41(1) | 35(1) | 12(1)  | 3(1)   | 4(1)   |
| C(5)  | 55(1) | 29(1) | 46(1) | 9(1)   | 5(1)   | -2(1)  |
| C(6)  | 40(1) | 28(1) | 36(1) | 2(1)   | 4(1)   | -3(1)  |
| C(7)  | 31(1) | 27(1) | 27(1) | -1(1)  | 1(1)   | -4(1)  |
| C(8)  | 34(1) | 32(1) | 47(1) | 9(1)   | -2(1)  | -3(1)  |
| C(9)  | 43(1) | 38(1) | 55(1) | 15(1)  | 0(1)   | -13(1) |
| C(10) | 32(1) | 45(1) | 49(1) | 3(1)   | 5(1)   | -10(1) |
| C(11) | 31(1) | 42(1) | 49(1) | 1(1)   | 4(1)   | 2(1)   |
| C(12) | 35(1) | 28(1) | 40(1) | 3(1)   | 4(1)   | 0(1)   |
| C(13) | 30(1) | 26(1) | 39(1) | -1(1)  | 3(1)   | 0(1)   |
| C(14) | 38(1) | 33(1) | 44(1) | -2(1)  | 7(1)   | -3(1)  |
| C(15) | 45(1) | 46(1) | 61(1) | -10(1) | 20(1)  | 1(1)   |
| C(16) | 46(1) | 45(1) | 84(2) | -3(1)  | 8(1)   | 15(1)  |
| C(17) | 45(1) | 40(1) | 69(2) | 10(1)  | 0(1)   | 10(1)  |
| C(18) | 34(1) | 32(1) | 47(1) | 5(1)   | 2(1)   | 0(1)   |
| C(19) | 28(1) | 37(1) | 39(1) | 0(1)   | -5(1)  | -7(1)  |
| C(20) | 29(1) | 45(1) | 64(1) | -6(1)  | 7(1)   | -6(1)  |
| C(21) | 52(1) | 59(1) | 55(1) | 12(1)  | -22(1) | -18(1) |
| C(22) | 34(1) | 42(1) | 51(1) | -12(1) | -3(1)  | -8(1)  |
| B(1)  | 32(1) | 31(1) | 36(1) | 4(1)   | 4(1)   | 2(1)   |

The anisotropic displacement factor exponent takes the form  

$$2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa058

| atom   | x        | y        | z        | U(eq) |
|--------|----------|----------|----------|-------|
| H(1S)  | 4330(20) | 1220(10) | 3460(10) | 67    |
| H(1N)  | 5052(8)  | 2920(10) | 6700(10) | 43    |
| H(3)   | 4267     | 2576     | 3142     | 51    |
| H(4)   | 4623     | 3944     | 3131     | 56    |
| H(5)   | 5204     | 4559     | 4202     | 52    |
| H(6)   | 5454     | 3790     | 5289     | 42    |
| H(8)   | 4714     | 611      | 6358     | 46    |
| H(9)   | 3389     | 76       | 6692     | 54    |
| H(10)  | 2149     | 829      | 6516     | 50    |
| H(11)  | 2226     | 2125     | 6003     | 49    |
| H(12)  | 3547     | 2687     | 5677     | 41    |
| H(14)  | 6338     | 1697     | 4478     | 46    |
| H(15)  | 7530     | 845      | 4372     | 61    |
| H(16)  | 7975     | 81       | 5403     | 70    |
| H(17)  | 7239     | 131      | 6549     | 62    |
| H(18)  | 6067     | 1001     | 6684     | 45    |
| H(20A) | 7200     | 2514     | 6045     | 69    |
| H(20B) | 7532     | 3395     | 6286     | 69    |
| H(20C) | 6833     | 3303     | 5628     | 69    |
| H(21A) | 6136     | 2760     | 7806     | 83    |
| H(21B) | 7109     | 2994     | 7637     | 83    |
| H(21C) | 6730     | 2154     | 7331     | 83    |
| H(22A) | 5965     | 4303     | 6384     | 64    |
| H(22B) | 6646     | 4300     | 7062     | 64    |
| H(22C) | 5669     | 4075     | 7228     | 64    |

## Appendix 1. Crystallographic data

*Monodeprotonation from 2a*

Table 1. Crystal data for pa069

|   |  |
|---|--|
| Compound                                      | pa069                                  |
| Molecular formula                             | $\text{C}_{22}\text{H}_{24}\text{NPS}$ |
| Molecular weight                              | 365.45                                 |
| Crystal habit                                 | Pale Yellow Plate                      |
| Crystal dimensions(mm)                        | 0.20x0.16x0.04                         |
| Crystal system                                | monoclinic                             |
| Space group                                   | $P2_1/c$                               |
| a( $\text{\AA}$ )                             | 10.459(1)                              |
| b( $\text{\AA}$ )                             | 10.181(1)                              |
| c( $\text{\AA}$ )                             | 18.909(1)                              |
| $\alpha(^{\circ})$                            | 90.00                                  |
| $\beta(^{\circ})$                             | 109.043(3)                             |
| $\gamma(^{\circ})$                            | 90.00                                  |
| V( $\text{\AA}^3$ )                           | 1903.3(3)                              |
| Z   | 4                                      |
| d(g-cm $^{-3}$ )                              | 1.275                                  |
| F(000)  | 776                                    |
| $\mu(\text{cm}^{-1})$                         | 0.258                                  |
| Absorption corrections                        | multi-scan ; 0.9501 min, 0.9897 max    |
| Diffractionmeter                              | KappaCCD                               |
| X-ray source                                  | MoK $\alpha$                           |
| $\lambda(\text{\AA})$                         | 0.71069                                |
| Monochromator                                 | graphite                               |
| T (K)   | 150.0(1)                               |
| Scan mode                                     | phi and omega scans                    |
| Maximum $\theta$                              | 30.02                                  |
| HKL ranges                                    | -13 14 ; -14 12 ; -26 26               |
| Reflections measured                          | 15481                                  |
| Unique data                                   | 5554                                   |
| Rint  | 0.0306                                 |
| Reflections used                              | 3919                                   |
| Criterion                                     | $I > 2\sigma(I)$                       |
| Refinement type                               | Fsqd                                   |
| Hydrogen atoms                                | mixed                                  |
| Parameters refined                            | 229                                    |
| Reflections / parameter                       | 17                                     |
| wR2   | 0.0964                                 |
| R1  | 0.0379                                 |
| Weights a, b                                  | 0.0402 ; 0.2099                        |
| GoF   | 1.028                                  |
| difference peak / hole (e $\text{\AA}^{-3}$ ) | 0.340(0.055) / -0.350(0.055)           |

## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa069

| atom  | x        | y        | z        | U(eq) |
|-------|----------|----------|----------|-------|
| S(1)  | 2019(1)  | -4073(1) | -2994(1) | 23(1) |
| P(1)  | 1923(1)  | -5253(1) | -1341(1) | 18(1) |
| N(1)  | 454(1)   | -5271(1) | -1999(1) | 19(1) |
| C(1)  | 3131(1)  | -5776(1) | -1775(1) | 19(1) |
| C(2)  | 3151(1)  | -5240(2) | -2470(1) | 19(1) |
| C(3)  | 4183(1)  | -5720(2) | -2730(1) | 23(1) |
| C(4)  | 5095(2)  | -6661(2) | -2358(1) | 27(1) |
| C(5)  | 5049(2)  | -7182(2) | -1688(1) | 29(1) |
| C(6)  | 4074(2)  | -6733(2) | -1401(1) | 25(1) |
| C(7)  | 1898(1)  | -6432(2) | -636(1)  | 20(1) |
| C(8)  | 2729(2)  | -6289(2) | 111(1)   | 24(1) |
| C(9)  | 2718(2)  | -7250(2) | 629(1)   | 27(1) |
| C(10) | 1906(2)  | -8346(2) | 418(1)   | 28(1) |
| C(11) | 1098(2)  | -8504(2) | -324(1)  | 27(1) |
| C(12) | 1104(1)  | -7555(2) | -847(1)  | 23(1) |
| C(13) | -912(1)  | -4768(2) | -2027(1) | 21(1) |
| C(14) | -1347(2) | -5351(2) | -1397(1) | 26(1) |
| C(15) | -1865(2) | -5258(2) | -2781(1) | 30(1) |
| C(16) | -933(2)  | -3266(2) | -2005(1) | 27(1) |
| C(17) | 2499(1)  | -3720(2) | -858(1)  | 20(1) |
| C(18) | 1899(2)  | -3203(2) | -357(1)  | 25(1) |
| C(19) | 2319(2)  | -2008(2) | -9(1)    | 29(1) |
| C(20) | 3345(2)  | -1319(2) | -159(1)  | 30(1) |
| C(21) | 3956(2)  | -1828(2) | -646(1)  | 29(1) |
| C(22) | 3539(1)  | -3023(2) | -995(1)  | 24(1) |

U(eq) is defined as 1/3 the trace of the  $U_{ij}$  tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for pa069

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| S(1)-C(2)         | 1.741(2)  | P(1)-N(1)         | 1.631(1)  |
| P(1)-C(1)         | 1.797(1)  | P(1)-C(7)         | 1.799(1)  |
| P(1)-C(17)        | 1.809(2)  | N(1)-C(13)        | 1.502(2)  |
| C(1)-C(6)         | 1.402(2)  | C(1)-C(2)         | 1.428(2)  |
| C(2)-C(3)         | 1.412(2)  | C(3)-C(4)         | 1.372(2)  |
| C(4)-C(5)         | 1.389(2)  | C(5)-C(6)         | 1.381(2)  |
| C(7)-C(12)        | 1.393(2)  | C(7)-C(8)         | 1.405(2)  |
| C(8)-C(9)         | 1.387(2)  | C(9)-C(10)        | 1.380(2)  |
| C(10)-C(11)       | 1.390(2)  | C(11)-C(12)       | 1.385(2)  |
| C(13)-C(14)       | 1.526(2)  | C(13)-C(16)       | 1.530(2)  |
| C(13)-C(15)       | 1.532(2)  | C(17)-C(22)       | 1.393(2)  |
| C(17)-C(18)       | 1.399(2)  | C(18)-C(19)       | 1.384(2)  |
| C(19)-C(20)       | 1.386(2)  | C(20)-C(21)       | 1.382(2)  |
| C(21)-C(22)       | 1.385(2)  |                   |           |
|                   |           |                   |           |
| N(1)-P(1)-C(1)    | 106.02(6) | N(1)-P(1)-C(7)    | 108.63(6) |
| C(1)-P(1)-C(7)    | 108.84(7) | N(1)-P(1)-C(17)   | 118.04(6) |
| C(1)-P(1)-C(17)   | 108.56(6) | C(7)-P(1)-C(17)   | 106.51(6) |
| C(13)-N(1)-P(1)   | 132.2(1)  | C(6)-C(1)-C(2)    | 120.7(1)  |
| C(6)-C(1)-P(1)    | 117.3(1)  | C(2)-C(1)-P(1)    | 122.0(1)  |
| C(3)-C(2)-C(1)    | 115.5(1)  | C(3)-C(2)-S(1)    | 119.5(1)  |
| C(1)-C(2)-S(1)    | 125.0(1)  | C(4)-C(3)-C(2)    | 123.0(1)  |
| C(3)-C(4)-C(5)    | 120.6(1)  | C(6)-C(5)-C(4)    | 118.8(1)  |
| C(5)-C(6)-C(1)    | 121.3(1)  | C(12)-C(7)-C(8)   | 119.2(1)  |
| C(12)-C(7)-P(1)   | 119.1(1)  | C(8)-C(7)-P(1)    | 121.5(1)  |
| C(9)-C(8)-C(7)    | 119.5(1)  | C(10)-C(9)-C(8)   | 120.8(1)  |
| C(9)-C(10)-C(11)  | 120.0(1)  | C(12)-C(11)-C(10) | 119.8(2)  |
| C(11)-C(12)-C(7)  | 120.6(1)  | N(1)-C(13)-C(14)  | 111.2(1)  |
| N(1)-C(13)-C(16)  | 111.2(1)  | C(14)-C(13)-C(16) | 110.9(1)  |
| N(1)-C(13)-C(15)  | 104.1(1)  | C(14)-C(13)-C(15) | 109.2(1)  |
| C(16)-C(13)-C(15) | 109.9(1)  | C(22)-C(17)-C(18) | 119.0(1)  |
| C(22)-C(17)-P(1)  | 119.8(1)  | C(18)-C(17)-P(1)  | 121.2(1)  |
| C(19)-C(18)-C(17) | 120.6(1)  | C(18)-C(19)-C(20) | 119.7(1)  |
| C(21)-C(20)-C(19) | 120.2(2)  | C(20)-C(21)-C(22) | 120.4(2)  |
| C(21)-C(22)-C(17) | 120.2(1)  |                   |           |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa069

| atom  | U11   | U22   | U33   | U23   | U13   | U12   |
|-------|-------|-------|-------|-------|-------|-------|
| S(1)  | 25(1) | 25(1) | 23(1) | 5(1)  | 11(1) | 3(1)  |
| P(1)  | 20(1) | 18(1) | 17(1) | 0(1)  | 8(1)  | 1(1)  |
| N(1)  | 20(1) | 23(1) | 17(1) | 1(1)  | 9(1)  | 1(1)  |
| C(1)  | 19(1) | 20(1) | 19(1) | -2(1) | 7(1)  | -1(1) |
| C(2)  | 20(1) | 20(1) | 19(1) | -3(1) | 6(1)  | -3(1) |
| C(3)  | 22(1) | 29(1) | 21(1) | -3(1) | 10(1) | -3(1) |
| C(4)  | 22(1) | 34(1) | 29(1) | -5(1) | 12(1) | 2(1)  |
| C(5)  | 25(1) | 31(1) | 29(1) | 1(1)  | 8(1)  | 9(1)  |
| C(6)  | 27(1) | 29(1) | 21(1) | 2(1)  | 9(1)  | 4(1)  |
| C(7)  | 22(1) | 20(1) | 19(1) | 1(1)  | 9(1)  | 3(1)  |
| C(8)  | 28(1) | 24(1) | 21(1) | 0(1)  | 9(1)  | 1(1)  |
| C(9)  | 33(1) | 30(1) | 19(1) | 4(1)  | 10(1) | 8(1)  |
| C(10) | 34(1) | 26(1) | 28(1) | 9(1)  | 17(1) | 8(1)  |
| C(11) | 28(1) | 22(1) | 33(1) | 4(1)  | 13(1) | 1(1)  |
| C(12) | 26(1) | 21(1) | 23(1) | 0(1)  | 10(1) | 2(1)  |
| C(13) | 19(1) | 23(1) | 23(1) | 2(1)  | 9(1)  | 3(1)  |
| C(14) | 26(1) | 26(1) | 30(1) | 4(1)  | 15(1) | 4(1)  |
| C(15) | 23(1) | 37(1) | 27(1) | 0(1)  | 6(1)  | -1(1) |
| C(16) | 30(1) | 25(1) | 29(1) | 5(1)  | 13(1) | 6(1)  |
| C(17) | 21(1) | 20(1) | 17(1) | 0(1)  | 4(1)  | 1(1)  |
| C(18) | 27(1) | 26(1) | 24(1) | -2(1) | 11(1) | 0(1)  |
| C(19) | 31(1) | 30(1) | 26(1) | -7(1) | 8(1)  | 4(1)  |
| C(20) | 30(1) | 24(1) | 30(1) | -8(1) | 1(1)  | 0(1)  |
| C(21) | 28(1) | 26(1) | 32(1) | -3(1) | 8(1)  | -6(1) |
| C(22) | 25(1) | 24(1) | 22(1) | -1(1) | 8(1)  | -1(1) |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa069

| atom   | x          | y          | z          | U(eq) |
|--------|------------|------------|------------|-------|
| H(1N)  | 643        | -4995      | -2398      | 23    |
| H(3)   | 4249       | -5375      | -3184      | 28    |
| H(4)   | 5763       | -6958      | -2561      | 33    |
| H(5)   | 5678       | -7835      | -1432      | 35    |
| H(6)   | 4040       | -7079      | -941       | 30    |
| H(8)   | 3294       | -5540      | 261        | 29    |
| H(9)   | 3277       | -7154      | 1135       | 32    |
| H(10)  | 1898       | -8992      | 779        | 33    |
| H(11)  | 543        | -9261      | -471       | 32    |
| H(12)  | 561        | -7671      | -1355      | 28    |
| H(14A) | -1350      | -6311      | -1430.9999 | 39    |
| H(14B) | -2258      | -5040      | -1444      | 39    |
| H(14C) | -713       | -5075      | -913.0001  | 39    |
| H(15A) | -1562.0001 | -4921      | -3185      | 44    |
| H(15B) | -2785      | -4947      | -2851.0002 | 44    |
| H(15C) | -1857      | -6221      | -2788      | 44    |
| H(16A) | -384.0000  | -2961      | -1507      | 41    |
| H(16B) | -1866      | -2961      | -2115      | 41    |
| H(16C) | -562       | -2913.9998 | -2380      | 41    |
| H(18)  | 1196       | -3675      | -254       | 30    |
| H(19)  | 1907       | -1662      | 330        | 35    |
| H(20)  | 3629       | -494.0000  | 74         | 36    |
| H(21)  | 4665       | -1356      | -741.9999  | 34    |
| H(22)  | 3964       | -3368      | -1329      | 29    |

**Complex 3a'**

Table 1. Crystal data for pa074

|   |  |
|---|--|
| Compound                                    | pa074  |
| Molecular formula                           | 2(C <sub>40</sub> H <sub>38</sub> BrNP <sub>2</sub> PdS),CH <sub>2</sub> Cl <sub>2</sub> |
| Molecular weight                            | 855.49   |
| Crystal habit                               | orange plate   |
| Crystal dimensions(mm)                      | 0.22x0.20x0.12   |
| Crystal system                              | triclinic  |
| Space group                                 | P -1   |
| a(Å)  | 9.798(1)   |
| b(Å)  | 9.884(1)   |
| c(Å)  | 20.216(1)  |
| α(°)  | 87.730(1)  |
| β(°)  | 83.800(1)  |
| γ(°)  | 72.090(1)  |
| V(Å <sup>3</sup> )                          | 1852.0(3)  |
| Z   | 2  |
| d(g·cm <sup>-3</sup> )                      | 1.534  |
| F(000)                                      | 866  |
| μ(cm <sup>-1</sup> )                        | 1.825  |
| Absorption corrections                      | multi-scan ; 0.6896 min, 0.8107 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71073  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 30.02  |
| HKL ranges                                  | -13 13 ; -12 13 ; -28 27   |
| Reflections measured                        | 23799  |
| Unique data                                 | 10763  |
| Rint  | 0.0199   |
| Reflections used                            | 9318   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | mixed  |
| Parameters refined                          | 445  |
| Reflections / parameter                     | 20   |
| wR2   | 0.1442   |
| R1  | 0.0456   |
| Weights a, b                                | 0.0790 ; 4.4523  |
| GoF   | 1.033  |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.076(0.131) / -2.924(0.131)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa074

| atom  | x        | y        | z       | U(eq) |
|-------|----------|----------|---------|-------|
| Pd(1) | 1518(1)  | 1604(1)  | 2415(1) | 17(1) |
| Br(1) | 3427(1)  | -346(1)  | 2886(1) | 38(1) |
| S(1)  | 32(1)    | 3508(1)  | 1904(1) | 25(1) |
| P(1)  | -1134(1) | 2435(1)  | 3430(1) | 19(1) |
| P(2)  | 2722(1)  | 784(1)   | 1418(1) | 17(1) |
| N(1)  | 543(3)   | 2333(3)  | 3374(1) | 21(1) |
| C(1)  | -2269(4) | 3805(3)  | 2936(2) | 23(1) |
| C(2)  | 1302(6)  | 2795(5)  | 4454(2) | 45(1) |
| C(3)  | -4597(4) | 5551(4)  | 2788(2) | 33(1) |
| C(4)  | -3978(4) | 6095(4)  | 2235(2) | 30(1) |
| C(5)  | -2552(4) | 5466(3)  | 2013(2) | 25(1) |
| C(6)  | -1669(3) | 4277(3)  | 2340(2) | 21(1) |
| C(7)  | -1270(4) | 761(4)   | 3168(2) | 22(1) |
| C(8)  | -2535(5) | 673(5)   | 2948(2) | 40(1) |
| C(9)  | -2657(6) | -635(6)  | 2801(3) | 57(1) |
| C(10) | -1531(6) | -1854(5) | 2866(3) | 55(1) |
| C(11) | -255(5)  | -1785(4) | 3082(2) | 42(1) |
| C(12) | -130(4)  | -483(4)  | 3240(2) | 28(1) |
| C(13) | -1971(4) | 2628(4)  | 4285(2) | 25(1) |
| C(14) | -1720(4) | 1404(4)  | 4677(2) | 33(1) |
| C(15) | -2210(5) | 1491(5)  | 5348(2) | 45(1) |
| C(16) | -2969(6) | 2786(6)  | 5633(2) | 49(1) |
| C(17) | -3240(5) | 4011(5)  | 5251(2) | 41(1) |
| C(18) | -2746(4) | 3946(4)  | 4578(2) | 32(1) |
| C(19) | 1142(4)  | 3296(4)  | 3735(2) | 27(1) |
| C(20) | 2625(6)  | 3217(7)  | 3399(3) | 64(2) |
| C(21) | -3746(4) | 4420(4)  | 3134(2) | 29(1) |
| C(22) | 201(6)   | 4841(5)  | 3725(3) | 53(1) |
| C(23) | 4490(3)  | 1056(3)  | 1372(2) | 21(1) |
| C(24) | 5790(4)  | 50(4)    | 1158(2) | 28(1) |
| C(25) | 7072(4)  | 386(5)   | 1136(2) | 38(1) |
| C(26) | 7068(4)  | 1729(5)  | 1321(2) | 37(1) |
| C(27) | 5769(4)  | 2737(4)  | 1538(2) | 31(1) |
| C(28) | 4493(4)  | 2398(4)  | 1569(2) | 24(1) |
| C(29) | 1950(3)  | 1694(3)  | 676(1)  | 19(1) |
| C(30) | 714(4)   | 1446(4)  | 491(2)  | 25(1) |
| C(31) | 29(4)    | 2179(4)  | -40(2)  | 30(1) |
| C(32) | 558(4)   | 3188(4)  | -389(2) | 31(1) |
| C(33) | 1783(4)  | 3428(4)  | -213(2) | 31(1) |
| C(34) | 2484(4)  | 2686(4)  | 318(2)  | 25(1) |
| C(35) | 2950(3)  | -1063(3) | 1221(2) | 21(1) |
| C(36) | 3683(4)  | -1637(4) | 613(2)  | 27(1) |
| C(37) | 3813(4)  | -3037(4) | 455(2)  | 33(1) |
| C(38) | 3185(5)  | -3840(4) | 893(2)  | 36(1) |
| C(39) | 2424(5)  | -3268(4) | 1479(2) | 35(1) |
| C(40) | 2295(4)  | -1870(4) | 1652(2) | 27(1) |
| Cl(1) | 3749(4)  | 2179(5)  | 5717(2) | 90(1) |
| Cl(2) | 5288(4)  | 60(6)    | 4719(2) | 84(1) |
| C(41) | 4630(20) | 430(20)  | 5560(7) | 72(4) |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths (Å) and angles (deg) for pa074

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| Pd(1)-N(1)        | 2.116(2)  | Pd(1)-P(2)        | 2.2676(8) |
| Pd(1)-S(1)        | 2.283(1)  | Pd(1)-Br(1)       | 2.4781(6) |
| S(1)-C(6)         | 1.757(3)  | P(1)-N(1)         | 1.608(3)  |
| P(1)-C(7)         | 1.803(3)  | P(1)-C(1)         | 1.809(3)  |
| P(1)-C(13)        | 1.823(3)  | P(2)-C(23)        | 1.825(3)  |
| P(2)-C(35)        | 1.825(3)  | P(2)-C(29)        | 1.829(3)  |
| N(1)-C(19)        | 1.507(4)  | C(1)-C(21)        | 1.406(5)  |
| C(1)-C(6)         | 1.409(4)  | C(2)-C(19)        | 1.526(6)  |
| C(3)-C(4)         | 1.384(6)  | C(3)-C(21)        | 1.387(5)  |
| C(4)-C(5)         | 1.376(5)  | C(5)-C(6)         | 1.416(4)  |
| C(7)-C(8)         | 1.390(5)  | C(7)-C(12)        | 1.399(5)  |
| C(8)-C(9)         | 1.381(6)  | C(9)-C(10)        | 1.374(8)  |
| C(10)-C(11)       | 1.390(7)  | C(11)-C(12)       | 1.382(5)  |
| C(13)-C(14)       | 1.390(5)  | C(13)-C(18)       | 1.408(5)  |
| C(14)-C(15)       | 1.386(5)  | C(15)-C(16)       | 1.380(7)  |
| C(16)-C(17)       | 1.381(7)  | C(17)-C(18)       | 1.391(5)  |
| C(19)-C(20)       | 1.517(6)  | C(19)-C(22)       | 1.523(6)  |
| C(23)-C(24)       | 1.391(4)  | C(23)-C(28)       | 1.401(4)  |
| C(24)-C(25)       | 1.390(5)  | C(25)-C(26)       | 1.392(6)  |
| C(26)-C(27)       | 1.393(6)  | C(27)-C(28)       | 1.385(5)  |
| C(29)-C(34)       | 1.392(4)  | C(29)-C(30)       | 1.399(4)  |
| C(30)-C(31)       | 1.385(5)  | C(31)-C(32)       | 1.395(5)  |
| C(32)-C(33)       | 1.377(6)  | C(33)-C(34)       | 1.396(5)  |
| C(35)-C(40)       | 1.396(5)  | C(35)-C(36)       | 1.402(4)  |
| C(36)-C(37)       | 1.397(5)  | C(37)-C(38)       | 1.385(6)  |
| C(38)-C(39)       | 1.372(6)  | C(39)-C(40)       | 1.404(5)  |
| Cl(1)-C(41)       | 1.70(2)   | Cl(2)-C(41)#2     | 0.74(1)   |
| Cl(2)-Cl(2)#2     | 1.23(1)   | Cl(2)-C(41)       | 1.76(2)   |
| N(1)-Pd(1)-P(2)   | 175.78(8) | N(1)-Pd(1)-S(1)   | 92.53(8)  |
| P(2)-Pd(1)-S(1)   | 90.51(3)  | N(1)-Pd(1)-Br(1)  | 91.97(8)  |
| P(2)-Pd(1)-Br(1)  | 84.65(3)  | S(1)-Pd(1)-Br(1)  | 171.51(3) |
| C(6)-S(1)-Pd(1)   | 115.4(1)  | N(1)-P(1)-C(7)    | 108.3(2)  |
| N(1)-P(1)-C(1)    | 116.5(2)  | C(7)-P(1)-C(1)    | 106.7(2)  |
| N(1)-P(1)-C(13)   | 112.7(1)  | C(7)-P(1)-C(13)   | 104.2(2)  |
| C(1)-P(1)-C(13)   | 107.6(2)  | C(23)-P(2)-C(35)  | 109.2(2)  |
| C(23)-P(2)-C(29)  | 104.0(1)  | C(35)-P(2)-C(29)  | 101.0(1)  |
| C(23)-P(2)-Pd(1)  | 107.9(1)  | C(35)-P(2)-Pd(1)  | 117.1(1)  |
| C(29)-P(2)-Pd(1)  | 116.7(1)  | C(19)-N(1)-P(1)   | 124.3(2)  |
| C(19)-N(1)-Pd(1)  | 118.7(2)  | P(1)-N(1)-Pd(1)   | 109.3(1)  |
| C(21)-C(1)-C(6)   | 118.8(3)  | C(21)-C(1)-P(1)   | 121.4(3)  |
| C(6)-C(1)-P(1)    | 119.7(2)  | C(4)-C(3)-C(21)   | 119.3(3)  |
| C(5)-C(4)-C(3)    | 119.9(3)  | C(4)-C(5)-C(6)    | 122.1(3)  |
| C(1)-C(6)-C(5)    | 117.7(3)  | C(1)-C(6)-S(1)    | 128.3(2)  |
| C(5)-C(6)-S(1)    | 113.8(2)  | C(8)-C(7)-C(12)   | 119.4(3)  |
| C(8)-C(7)-P(1)    | 120.9(3)  | C(12)-C(7)-P(1)   | 119.5(2)  |
| C(9)-C(8)-C(7)    | 120.0(4)  | C(10)-C(9)-C(8)   | 120.5(4)  |
| C(9)-C(10)-C(11)  | 120.3(4)  | C(12)-C(11)-C(10) | 119.6(4)  |
| C(11)-C(12)-C(7)  | 120.2(4)  | C(14)-C(13)-C(18) | 119.0(3)  |
| C(14)-C(13)-P(1)  | 117.1(3)  | C(18)-C(13)-P(1)  | 123.6(3)  |
| C(15)-C(14)-C(13) | 120.2(4)  | C(16)-C(15)-C(14) | 120.6(4)  |
| C(15)-C(16)-C(17) | 120.0(4)  | C(16)-C(17)-C(18) | 120.2(4)  |
| C(17)-C(18)-C(13) | 119.9(4)  | N(1)-C(19)-C(20)  | 108.9(3)  |
| N(1)-C(19)-C(22)  | 112.3(3)  | C(20)-C(19)-C(22) | 108.1(4)  |
| N(1)-C(19)-C(2)   | 109.9(3)  | C(20)-C(19)-C(2)  | 108.2(4)  |
| C(22)-C(19)-C(2)  | 109.4(4)  | C(3)-C(21)-C(1)   | 121.8(3)  |
| C(24)-C(23)-C(28) | 119.2(3)  | C(24)-C(23)-P(2)  | 125.1(2)  |
| C(28)-C(23)-P(2)  | 115.6(2)  | C(25)-C(24)-C(23) | 120.0(3)  |
| C(24)-C(25)-C(26) | 120.6(4)  | C(25)-C(26)-C(27) | 119.6(3)  |
| C(28)-C(27)-C(26) | 119.9(3)  | C(27)-C(28)-C(23) | 120.7(3)  |
| C(34)-C(29)-C(30) | 118.9(3)  | C(34)-C(29)-P(2)  | 122.8(2)  |
| C(30)-C(29)-P(2)  | 118.2(2)  | C(31)-C(30)-C(29) | 120.6(3)  |
| C(30)-C(31)-C(32) | 120.2(3)  | C(33)-C(32)-C(31) | 119.6(3)  |
| C(32)-C(33)-C(34) | 120.5(3)  | C(29)-C(34)-C(33) | 120.3(3)  |
| C(40)-C(35)-C(36) | 119.8(3)  | C(40)-C(35)-P(2)  | 119.9(2)  |

## Appendix 1. Crystallographic data

|                       |          |                     |          |
|-----------------------|----------|---------------------|----------|
| C(36)-C(35)-P(2)      | 120.1(2) | C(37)-C(36)-C(35)   | 119.8(3) |
| C(38)-C(37)-C(36)     | 119.9(3) | C(39)-C(38)-C(37)   | 120.6(3) |
| C(38)-C(39)-C(40)     | 120.5(4) | C(35)-C(40)-C(39)   | 119.3(3) |
| C(41)#2-Cl(2)-Cl(2)#2 | 125(2)   | C(41)#2-Cl(2)-C(41) | 145(1)   |
| Cl(2)#2-Cl(2)-C(41)   | 20.0(5)  | Cl(1)-C(41)-Cl(2)   | 114.2(8) |

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Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z                      2: -x, -y, -z

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa074

| atom  | U11    | U22    | U33   | U23    | U13    | U12     |
|-------|--------|--------|-------|--------|--------|---------|
| Pd(1) | 16(1)  | 18(1)  | 15(1) | -1(1)  | 0(1)   | -5(1)   |
| Br(1) | 31(1)  | 45(1)  | 33(1) | 4(1)   | -4(1)  | -3(1)   |
| S(1)  | 27(1)  | 22(1)  | 20(1) | 4(1)   | 5(1)   | -1(1)   |
| P(1)  | 18(1)  | 23(1)  | 15(1) | 0(1)   | 1(1)   | -5(1)   |
| P(2)  | 16(1)  | 17(1)  | 17(1) | -2(1)  | 1(1)   | -5(1)   |
| N(1)  | 20(1)  | 27(1)  | 17(1) | -6(1)  | 2(1)   | -9(1)   |
| C(1)  | 23(2)  | 23(1)  | 19(1) | 0(1)   | -2(1)  | -2(1)   |
| C(2)  | 62(3)  | 48(2)  | 36(2) | 2(2)   | -22(2) | -26(2)  |
| C(3)  | 26(2)  | 34(2)  | 27(2) | -7(1)  | -3(1)  | 6(1)    |
| C(4)  | 32(2)  | 23(2)  | 30(2) | -2(1)  | -9(1)  | 1(1)    |
| C(5)  | 31(2)  | 20(1)  | 23(2) | 1(1)   | -4(1)  | -4(1)   |
| C(6)  | 24(2)  | 17(1)  | 19(1) | -2(1)  | -1(1)  | -3(1)   |
| C(7)  | 25(2)  | 26(2)  | 19(1) | 3(1)   | -4(1)  | -12(1)  |
| C(8)  | 37(2)  | 39(2)  | 50(2) | 14(2)  | -21(2) | -18(2)  |
| C(9)  | 60(3)  | 57(3)  | 76(4) | 17(3)  | -40(3) | -40(3)  |
| C(10) | 72(4)  | 39(2)  | 69(3) | 5(2)   | -23(3) | -34(2)  |
| C(11) | 48(2)  | 28(2)  | 53(3) | 5(2)   | -6(2)  | -18(2)  |
| C(12) | 26(2)  | 26(2)  | 32(2) | 2(1)   | -1(1)  | -11(1)  |
| C(13) | 20(1)  | 35(2)  | 18(1) | 1(1)   | 1(1)   | -5(1)   |
| C(14) | 38(2)  | 36(2)  | 20(2) | 5(1)   | 1(1)   | -8(2)   |
| C(15) | 56(3)  | 52(3)  | 21(2) | 9(2)   | 4(2)   | -13(2)  |
| C(16) | 53(3)  | 66(3)  | 19(2) | 0(2)   | 7(2)   | -10(2)  |
| C(17) | 38(2)  | 48(2)  | 27(2) | -11(2) | 4(2)   | -2(2)   |
| C(18) | 30(2)  | 36(2)  | 23(2) | -3(1)  | 1(1)   | -1(1)   |
| C(19) | 31(2)  | 31(2)  | 24(2) | -7(1)  | 0(1)   | -15(1)  |
| C(20) | 50(3)  | 107(5) | 56(3) | -46(3) | 20(2)  | -56(3)  |
| C(21) | 25(2)  | 35(2)  | 21(2) | -1(1)  | 0(1)   | -1(1)   |
| C(22) | 68(3)  | 26(2)  | 71(3) | -3(2)  | -23(3) | -20(2)  |
| C(23) | 17(1)  | 24(1)  | 21(1) | -3(1)  | 0(1)   | -7(1)   |
| C(24) | 22(2)  | 30(2)  | 31(2) | -9(1)  | 2(1)   | -5(1)   |
| C(25) | 19(2)  | 49(2)  | 45(2) | -15(2) | 4(1)   | -7(2)   |
| C(26) | 25(2)  | 55(2)  | 38(2) | -12(2) | 4(1)   | -22(2)  |
| C(27) | 31(2)  | 38(2)  | 29(2) | -5(1)  | 0(1)   | -20(2)  |
| C(28) | 21(2)  | 26(2)  | 26(2) | -5(1)  | 2(1)   | -9(1)   |
| C(29) | 19(1)  | 19(1)  | 17(1) | -3(1)  | 0(1)   | -4(1)   |
| C(30) | 20(2)  | 29(2)  | 25(2) | 1(1)   | -1(1)  | -7(1)   |
| C(31) | 23(2)  | 37(2)  | 29(2) | -1(1)  | -7(1)  | -5(1)   |
| C(32) | 34(2)  | 30(2)  | 24(2) | 4(1)   | -7(1)  | -1(1)   |
| C(33) | 43(2)  | 29(2)  | 23(2) | 6(1)   | -5(1)  | -12(2)  |
| C(34) | 31(2)  | 25(2)  | 22(1) | 0(1)   | -2(1)  | -11(1)  |
| C(35) | 22(1)  | 17(1)  | 23(1) | -1(1)  | -3(1)  | -5(1)   |
| C(36) | 27(2)  | 25(2)  | 28(2) | -6(1)  | 1(1)   | -7(1)   |
| C(37) | 32(2)  | 27(2)  | 38(2) | -14(2) | -4(2)  | -4(1)   |
| C(38) | 43(2)  | 20(2)  | 46(2) | -3(1)  | -18(2) | -7(2)   |
| C(39) | 46(2)  | 23(2)  | 39(2) | 7(1)   | -13(2) | -16(2)  |
| C(40) | 32(2)  | 25(2)  | 26(2) | 2(1)   | -5(1)  | -13(1)  |
| Cl(1) | 78(2)  | 91(3)  | 80(2) | 15(2)  | -22(2) | 6(2)    |
| Cl(2) | 67(2)  | 123(4) | 73(2) | -17(2) | -16(2) | -38(2)  |
| C(41) | 90(10) | 90(10) | 53(8) | 12(7)  | -22(7) | -60(10) |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa074

| atom   | x          | y     | z    | U(eq) |
|--------|------------|-------|------|-------|
| H(2A)  | 345        | 2922  | 4692 | 68    |
| H(2B)  | 1796       | 3353  | 4671 | 68    |
| H(2C)  | 1866       | 1788  | 4462 | 68    |
| H(3)   | -5594      | 5948  | 2930 | 39    |
| H(4)   | -4538      | 6901  | 2008 | 36    |
| H(5)   | -2147      | 5841  | 1627 | 30    |
| H(8)   | -3314      | 1513  | 2897 | 47    |
| H(9)   | -3527      | -692  | 2655 | 69    |
| H(10)  | -1624.0001 | -2748 | 2761 | 66    |
| H(11)  | 527        | -2628 | 3122 | 50    |
| H(12)  | 732        | -433  | 3398 | 33    |
| H(14)  | -1210      | 506   | 4484 | 39    |
| H(15)  | -2023      | 652   | 5613 | 54    |
| H(16)  | -3305      | 2834  | 6093 | 58    |
| H(17)  | -3765      | 4901  | 5448 | 49    |
| H(18)  | -2931      | 4791  | 4317 | 38    |
| H(20A) | 3210       | 2219  | 3345 | 96    |
| H(20B) | 3094       | 3703  | 3673 | 96    |
| H(20C) | 2531       | 3679  | 2961 | 96    |
| H(21)  | -4173      | 4052  | 3516 | 35    |
| H(22A) | -13        | 5123  | 3268 | 79    |
| H(22B) | 713        | 5447  | 3890 | 79    |
| H(22C) | -701       | 4946  | 4009 | 79    |
| H(24)  | 5802       | -866  | 1027 | 34    |
| H(25)  | 7957       | -308  | 995  | 46    |
| H(26)  | 7946       | 1956  | 1298 | 45    |
| H(27)  | 5759       | 3656  | 1665 | 37    |
| H(28)  | 3612       | 3082  | 1726 | 29    |
| H(30)  | 341        | 768   | 730  | 30    |
| H(31)  | -802       | 1993  | -166 | 36    |
| H(32)  | 77         | 3705  | -747 | 38    |
| H(33)  | 2153       | 4105  | -454 | 37    |
| H(34)  | 3328       | 2858  | 435  | 30    |
| H(36)  | 4091       | -1076 | 308  | 32    |
| H(37)  | 4330       | -3439 | 48   | 39    |
| H(38)  | 3282       | -4795 | 787  | 43    |
| H(39)  | 1980       | -3824 | 1770 | 41    |
| H(40)  | 1769       | -1478 | 2059 | 32    |
| H(41A) | 3959       | -129  | 5698 | 86    |
| H(41B) | 5445       | 108   | 5836 | 86    |



**Complex 14**

Table 1. Crystal data for pa321

|   |  |
|---|--|
| Compound                                    | pa321  |
| Molecular formula                           | C <sub>38</sub> H <sub>34</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Molecular weight                            | 833.49   |
| Crystal habit                               | Green Block  |
| Crystal dimensions(mm)                      | 0.20x0.10x0.08   |
| Crystal system                              | monoclinic   |
| Space group                                 | P2 <sub>1</sub> /c   |
| a(Å)  | 9.002(1)   |
| b(Å)  | 17.784(1)  |
| c(Å)  | 12.158(1)  |
| α(°)  | 90.00  |
| β(°)  | 113.901(2)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 1779.5(3)  |
| Z   | 2  |
| d(g·cm <sup>-3</sup> )                      | 1.556  |
| F(000)                                      | 852  |
| μ(cm <sup>-1</sup> )                        | 1.321  |
| Absorption corrections                      | multi-scan ; 0.7780 min, 0.9017 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 30.03  |
| HKL ranges                                  | -12 12 ; -25 22 ; -17 17   |
| Reflections measured                        | 15358  |
| Unique data                                 | 5174   |
| Rint  | 0.0338   |
| Reflections used                            | 4305   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 217  |
| Reflections / parameter                     | 19   |
| wR2   | 0.1050   |
| R1  | 0.0452   |
| Weights a, b                                | 0.0362 ; 3.8823  |
| GoF   | 1.066  |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.082(0.094) / -0.639(0.094)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa321

| atom  | x        | y        | z       | U(eq) |
|-------|----------|----------|---------|-------|
| Co(1) | 4924(1)  | -4499(1) | 4054(1) | 20(1) |
| Cl(1) | 6161(1)  | -4733(1) | 2811(1) | 26(1) |
| S(1)  | 3153(1)  | -5505(1) | 3944(1) | 21(1) |
| P(1)  | 1442(1)  | -4012(1) | 3464(1) | 18(1) |
| N(1)  | 3303(2)  | -3728(1) | 3981(2) | 19(1) |
| C(1)  | 1448(3)  | -4967(2) | 3984(2) | 23(1) |
| C(2)  | 219(3)   | -3472(2) | 4032(2) | 21(1) |
| C(3)  | 593(3)   | -3508(2) | 5267(2) | 26(1) |
| C(4)  | -368(4)  | -3133(2) | 5737(3) | 31(1) |
| C(5)  | -1691(4) | -2713(2) | 4981(3) | 33(1) |
| C(6)  | -2036(4) | -2656(2) | 3774(3) | 32(1) |
| C(7)  | -1092(3) | -3037(2) | 3286(2) | 25(1) |
| C(8)  | 465(3)   | -4044(2) | 1846(2) | 21(1) |
| C(9)  | -1134(3) | -4298(2) | 1261(3) | 27(1) |
| C(10) | -1830(4) | -4347(2) | 7(3)    | 32(1) |
| C(11) | -959(4)  | -4130(2) | -646(3) | 32(1) |
| C(12) | 628(4)   | -3879(2) | -71(2)  | 30(1) |
| C(13) | 1344(3)  | -3842(2) | 1175(2) | 23(1) |
| C(14) | 3700(3)  | -2952(2) | 4274(2) | 19(1) |
| C(15) | 3459(4)  | -2407(2) | 3393(3) | 27(1) |
| C(16) | 3884(4)  | -1662(2) | 3711(3) | 33(1) |
| C(17) | 4538(4)  | -1451(2) | 4910(3) | 31(1) |
| C(18) | 4779(3)  | -1987(2) | 5789(3) | 29(1) |
| C(19) | 4370(3)  | -2733(2) | 5479(2) | 25(1) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa321

|                      |           |                     |           |
|----------------------|-----------|---------------------|-----------|
| Co(1)-N(1)           | 1.977(2)  | Co(1)-Cl(1)         | 2.2501(7) |
| Co(1)-S(1)#3         | 2.3465(7) | Co(1)-S(1)          | 2.3643(8) |
| Co(1)-Co(1)#3        | 2.8689(7) | S(1)-C(1)           | 1.827(3)  |
| S(1)-Co(1)#3         | 2.3465(7) | P(1)-N(1)           | 1.613(2)  |
| P(1)-C(2)            | 1.797(3)  | P(1)-C(8)           | 1.801(3)  |
| P(1)-C(1)            | 1.812(3)  | N(1)-C(14)          | 1.435(3)  |
| C(1)-H(1A)           | 0.9900    | C(1)-H(1B)          | 0.9900    |
| C(2)-C(7)            | 1.395(4)  | C(2)-C(3)           | 1.401(4)  |
| C(3)-C(4)            | 1.386(4)  | C(3)-H(3)           | 0.9500    |
| C(4)-C(5)            | 1.390(5)  | C(4)-H(4)           | 0.9500    |
| C(5)-C(6)            | 1.376(4)  | C(5)-H(5)           | 0.9500    |
| C(6)-C(7)            | 1.393(4)  | C(6)-H(6)           | 0.9500    |
| C(7)-H(7)            | 0.9500    | C(8)-C(13)          | 1.394(4)  |
| C(8)-C(9)            | 1.397(4)  | C(9)-C(10)          | 1.396(4)  |
| C(9)-H(9)            | 0.9500    | C(10)-C(11)         | 1.378(5)  |
| C(10)-H(10)          | 0.9500    | C(11)-C(12)         | 1.386(4)  |
| C(11)-H(11)          | 0.9500    | C(12)-C(13)         | 1.387(4)  |
| C(12)-H(12)          | 0.9500    | C(13)-H(13)         | 0.9500    |
| C(14)-C(19)          | 1.394(4)  | C(14)-C(15)         | 1.395(4)  |
| C(15)-C(16)          | 1.389(4)  | C(15)-H(15)         | 0.9500    |
| C(16)-C(17)          | 1.384(4)  | C(16)-H(16)         | 0.9500    |
| C(17)-C(18)          | 1.382(5)  | C(17)-H(17)         | 0.9500    |
| C(18)-C(19)          | 1.388(4)  | C(18)-H(18)         | 0.9500    |
| C(19)-H(19)          | 0.9500    |                     |           |
|                      |           |                     |           |
| N(1)-Co(1)-Cl(1)     | 130.91(7) | N(1)-Co(1)-S(1)#3   | 105.40(6) |
| Cl(1)-Co(1)-S(1)#3   | 109.84(3) | N(1)-Co(1)-S(1)     | 93.08(7)  |
| Cl(1)-Co(1)-S(1)     | 109.14(3) | S(1)#3-Co(1)-S(1)   | 104.97(2) |
| N(1)-Co(1)-Co(1)#3   | 105.16(7) | Cl(1)-Co(1)-Co(1)#3 | 123.22(3) |
| S(1)#3-Co(1)-Co(1)#3 | 52.77(2)  | S(1)-Co(1)-Co(1)#3  | 52.20(2)  |
| C(1)-S(1)-Co(1)#3    | 104.2(1)  | C(1)-S(1)-Co(1)     | 99.0(1)   |
| Co(1)#3-S(1)-Co(1)   | 75.04(2)  | N(1)-P(1)-C(2)      | 112.6(1)  |
| N(1)-P(1)-C(8)       | 114.0(1)  | C(2)-P(1)-C(8)      | 109.4(1)  |
| N(1)-P(1)-C(1)       | 107.5(1)  | C(2)-P(1)-C(1)      | 106.4(1)  |
| C(8)-P(1)-C(1)       | 106.4(1)  | C(14)-N(1)-P(1)     | 120.8(2)  |
| C(14)-N(1)-Co(1)     | 123.4(2)  | P(1)-N(1)-Co(1)     | 115.6(1)  |
| P(1)-C(1)-S(1)       | 111.5(1)  | P(1)-C(1)-H(1A)     | 109.3     |
| S(1)-C(1)-H(1A)      | 109.3     | P(1)-C(1)-H(1B)     | 109.3     |
| S(1)-C(1)-H(1B)      | 109.3     | H(1A)-C(1)-H(1B)    | 108.0     |
| C(7)-C(2)-C(3)       | 119.7(2)  | C(7)-C(2)-P(1)      | 122.3(2)  |
| C(3)-C(2)-P(1)       | 118.0(2)  | C(4)-C(3)-C(2)      | 120.0(3)  |
| C(4)-C(3)-H(3)       | 120.0     | C(2)-C(3)-H(3)      | 120.0     |
| C(3)-C(4)-C(5)       | 119.8(3)  | C(3)-C(4)-H(4)      | 120.1     |
| C(5)-C(4)-H(4)       | 120.1     | C(6)-C(5)-C(4)      | 120.5(3)  |
| C(6)-C(5)-H(5)       | 119.8     | C(4)-C(5)-H(5)      | 119.8     |
| C(5)-C(6)-C(7)       | 120.4(3)  | C(5)-C(6)-H(6)      | 119.8     |
| C(7)-C(6)-H(6)       | 119.8     | C(6)-C(7)-C(2)      | 119.6(3)  |
| C(6)-C(7)-H(7)       | 120.2     | C(2)-C(7)-H(7)      | 120.2     |
| C(13)-C(8)-C(9)      | 119.8(2)  | C(13)-C(8)-P(1)     | 119.3(2)  |
| C(9)-C(8)-P(1)       | 120.9(2)  | C(10)-C(9)-C(8)     | 119.4(3)  |
| C(10)-C(9)-H(9)      | 120.3     | C(8)-C(9)-H(9)      | 120.3     |
| C(11)-C(10)-C(9)     | 120.2(3)  | C(11)-C(10)-H(10)   | 119.9     |
| C(9)-C(10)-H(10)     | 119.9     | C(10)-C(11)-C(12)   | 120.7(3)  |
| C(10)-C(11)-H(11)    | 119.6     | C(12)-C(11)-H(11)   | 119.6     |
| C(11)-C(12)-C(13)    | 119.6(3)  | C(11)-C(12)-H(12)   | 120.2     |
| C(13)-C(12)-H(12)    | 120.2     | C(12)-C(13)-C(8)    | 120.3(3)  |
| C(12)-C(13)-H(13)    | 119.9     | C(8)-C(13)-H(13)    | 119.9     |
| C(19)-C(14)-C(15)    | 118.7(3)  | C(19)-C(14)-N(1)    | 119.2(2)  |
| C(15)-C(14)-N(1)     | 122.1(2)  | C(16)-C(15)-C(14)   | 120.6(3)  |
| C(16)-C(15)-H(15)    | 119.7     | C(14)-C(15)-H(15)   | 119.7     |
| C(17)-C(16)-C(15)    | 120.3(3)  | C(17)-C(16)-H(16)   | 119.9     |
| C(15)-C(16)-H(16)    | 119.9     | C(18)-C(17)-C(16)   | 119.6(3)  |
| C(18)-C(17)-H(17)    | 120.2     | C(16)-C(17)-H(17)   | 120.2     |
| C(17)-C(18)-C(19)    | 120.5(3)  | C(17)-C(18)-H(18)   | 119.7     |
| C(19)-C(18)-H(18)    | 119.7     | C(18)-C(19)-C(14)   | 120.4(3)  |

C(18)-C(19)-H(19) 119.8 C(14)-C(19)-H(19) 119.8

-----  
 Estimated standard deviations are given in the parenthesis.  
 Symmetry operators ::  
 1: x, y, z 2: -x, y+1/2, -z+1/2 3: -x, -y, -z  
 4: x, -y-1/2, z-1/2

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa321

| atom  | U11   | U22   | U33   | U23    | U13   | U12   |
|-------|-------|-------|-------|--------|-------|-------|
| Co(1) | 19(1) | 20(1) | 20(1) | 1(1)   | 7(1)  | 1(1)  |
| Cl(1) | 32(1) | 28(1) | 25(1) | 2(1)   | 19(1) | 2(1)  |
| S(1)  | 21(1) | 19(1) | 21(1) | -1(1)  | 5(1)  | 0(1)  |
| P(1)  | 17(1) | 19(1) | 17(1) | 0(1)   | 6(1)  | 0(1)  |
| N(1)  | 17(1) | 19(1) | 20(1) | -1(1)  | 6(1)  | 0(1)  |
| C(1)  | 19(1) | 22(1) | 28(1) | 4(1)   | 7(1)  | 0(1)  |
| C(2)  | 18(1) | 21(1) | 24(1) | -2(1)  | 9(1)  | -2(1) |
| C(3)  | 28(1) | 25(1) | 26(1) | 1(1)   | 13(1) | 1(1)  |
| C(4)  | 39(2) | 31(2) | 29(1) | -6(1)  | 21(1) | -6(1) |
| C(5)  | 31(1) | 30(2) | 44(2) | -13(1) | 22(1) | -4(1) |
| C(6)  | 25(1) | 30(2) | 37(2) | -8(1)  | 8(1)  | 5(1)  |
| C(7)  | 25(1) | 24(1) | 24(1) | -3(1)  | 8(1)  | 2(1)  |
| C(8)  | 20(1) | 20(1) | 18(1) | -2(1)  | 5(1)  | 2(1)  |
| C(9)  | 22(1) | 28(1) | 27(1) | -5(1)  | 7(1)  | 2(1)  |
| C(10) | 23(1) | 34(2) | 30(1) | -9(1)  | 1(1)  | 5(1)  |
| C(11) | 36(2) | 33(2) | 20(1) | -4(1)  | 4(1)  | 9(1)  |
| C(12) | 36(2) | 34(2) | 21(1) | 0(1)   | 11(1) | 8(1)  |
| C(13) | 25(1) | 23(1) | 21(1) | -2(1)  | 9(1)  | 1(1)  |
| C(14) | 16(1) | 18(1) | 22(1) | -1(1)  | 7(1)  | 1(1)  |
| C(15) | 35(1) | 22(1) | 24(1) | -2(1)  | 11(1) | -2(1) |
| C(16) | 42(2) | 21(1) | 37(2) | 2(1)   | 18(1) | -4(1) |
| C(17) | 27(1) | 23(1) | 45(2) | -10(1) | 17(1) | -6(1) |
| C(18) | 21(1) | 32(2) | 30(1) | -12(1) | 7(1)  | -1(1) |
| C(19) | 22(1) | 27(1) | 23(1) | -2(1)  | 6(1)  | 0(1)  |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa321

| atom  | x     | y          | z     | U(eq) |
|-------|-------|------------|-------|-------|
| H(1A) | 416   | -5217.0005 | 3470  | 28    |
| H(1B) | 1517  | -4957      | 4818  | 28    |
| H(3)  | 1506  | -3790      | 5783  | 31    |
| H(4)  | -124  | -3162      | 6572  | 37    |
| H(5)  | -2363 | -2464      | 5301  | 39    |
| H(6)  | -2922 | -2354      | 3270  | 39    |
| H(7)  | -1339 | -3001      | 2450  | 30    |
| H(9)  | -1741 | -4437      | 1711  | 32    |
| H(10) | -2908 | -4530      | -397  | 38    |
| H(11) | -1452 | -4153      | -1500 | 38    |
| H(12) | 1222  | -3732.9998 | -528  | 36    |
| H(13) | 2438  | -3678      | 1573  | 28    |
| H(15) | 2999  | -2546      | 2568  | 33    |
| H(16) | 3726  | -1297      | 3104  | 39    |
| H(17) | 4820  | -939.9999  | 5126  | 37    |
| H(18) | 5228  | -1843      | 6612  | 35    |
| H(19) | 4548  | -3097      | 6091  | 30    |

**Complex 15**

Table 1. Crystal data for pa163

|   |                                       |
|---|---------------------------------------|
| Compound                                    | pa163                                 |
| Molecular formula                           | C <sub>27</sub> H <sub>29</sub> NPRhS |
| Molecular weight                            | 533.45                                |
| Crystal habit                               | Yellow Block                          |
| Crystal dimensions(mm)                      | 0.16x0.12x0.08                        |
| Crystal system                              | monoclinic                            |
| Space group                                 | P2 <sub>1</sub> /c                    |
| a(Å)  | 15.329(1)                             |
| b(Å)  | 10.354(1)                             |
| c(Å)  | 15.839(1)                             |
| α(°)  | 90.00                                 |
| β(°)  | 112.885(1)                            |
| γ(°)  | 90.00                                 |
| V(Å <sup>3</sup> )                          | 2316.0(3)                             |
| Z   | 4                                     |
| d(g·cm <sup>-3</sup> )                      | 1.530                                 |
| F(000)                                      | 1096                                  |
| μ(cm <sup>-1</sup> )                        | 0.912                                 |
| Absorption corrections                      | multi-scan ; 0.8678 min, 0.9306 max   |
| Diffractionmeter                            | KappaCCD                              |
| X-ray source                                | MoKα                                  |
| λ(Å)  | 0.71069                               |
| Monochromator                               | graphite                              |
| T (K)                                       | 150.0(1)                              |
| Scan mode                                   | phi and omega scans                   |
| Maximum θ                                   | 27.48                                 |
| HKL ranges                                  | -19 14 ; -13 12 ; -20 20              |
| Reflections measured                        | 14478                                 |
| Unique data                                 | 5290                                  |
| Rint  | 0.0453                                |
| Reflections used                            | 3973                                  |
| Criterion                                   | I > 2σ(I)                             |
| Refinement type                             | Fsqd                                  |
| Hydrogen atoms                              | constr                                |
| Parameters refined                          | 280                                   |
| Reflections / parameter                     | 14                                    |
| wR2   | 0.1087                                |
| R1  | 0.0407                                |
| Weights a, b                                | 0.0583 ; 0.0000                       |
| GoF   | 1.040                                 |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.213(0.101) / -0.831(0.101)          |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa163

| atom  | x       | y        | z       | U(eq) |
|-------|---------|----------|---------|-------|
| Rh(1) | 3075(1) | -350(1)  | 6884(1) | 24(1) |
| S(1)  | 2803(1) | -1963(1) | 5786(1) | 31(1) |
| P(1)  | 2055(1) | 412(1)   | 4803(1) | 24(1) |
| N(1)  | 2235(2) | 905(2)   | 5823(2) | 24(1) |
| C(1)  | 1862(2) | -1292(3) | 4779(2) | 29(1) |
| C(2)  | 1978(2) | 2214(3)  | 5911(2) | 26(1) |
| C(3)  | 1252(2) | 2469(3)  | 6198(2) | 36(1) |
| C(4)  | 937(3)  | 3716(4)  | 6230(2) | 47(1) |
| C(5)  | 1367(3) | 4741(3)  | 5986(3) | 46(1) |
| C(6)  | 2102(3) | 4519(3)  | 5717(2) | 41(1) |
| C(7)  | 2410(2) | 3259(3)  | 5682(2) | 32(1) |
| C(8)  | 1025(2) | 1217(3)  | 3981(2) | 27(1) |
| C(9)  | 129(2)  | 829(4)   | 3903(2) | 35(1) |
| C(10) | -665(2) | 1506(4)  | 3364(2) | 42(1) |
| C(11) | -567(2) | 2602(4)  | 2902(2) | 41(1) |
| C(12) | 306(3)  | 3001(4)  | 2972(2) | 42(1) |
| C(13) | 1113(2) | 2303(3)  | 3512(2) | 34(1) |
| C(14) | 3010(2) | 688(3)   | 4425(2) | 27(1) |
| C(15) | 2893(2) | 348(3)   | 3532(2) | 33(1) |
| C(16) | 3623(3) | 525(3)   | 3237(2) | 37(1) |
| C(17) | 4470(2) | 1051(4)  | 3826(2) | 40(1) |
| C(18) | 4593(2) | 1389(3)  | 4707(2) | 37(1) |
| C(19) | 3870(2) | 1199(3)  | 5014(2) | 32(1) |
| C(20) | 3141(2) | 939(3)   | 7977(2) | 32(1) |
| C(21) | 3888(2) | 1169(3)  | 7716(2) | 31(1) |
| C(22) | 4906(2) | 702(4)   | 8227(2) | 41(1) |
| C(23) | 4966(2) | -705(4)  | 8495(2) | 39(1) |
| C(24) | 4168(2) | -1502(3) | 7838(2) | 32(1) |
| C(25) | 3313(2) | -1761(3) | 7935(2) | 29(1) |
| C(26) | 3034(2) | -1212(4) | 8678(2) | 41(1) |
| C(27) | 3237(3) | 225(4)   | 8842(2) | 42(1) |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

Table 3. Bond lengths (Å) and angles (deg) for pal63

|                   |          |                   |           |
|-------------------|----------|-------------------|-----------|
| Rh(1)-N(1)        | 2.118(2) | Rh(1)-C(21)       | 2.118(3)  |
| Rh(1)-C(24)       | 2.133(3) | Rh(1)-C(25)       | 2.138(3)  |
| Rh(1)-C(20)       | 2.157(3) | Rh(1)-S(1)        | 2.3291(8) |
| S(1)-C(1)         | 1.821(3) | P(1)-N(1)         | 1.613(2)  |
| P(1)-C(1)         | 1.788(3) | P(1)-C(14)        | 1.808(3)  |
| P(1)-C(8)         | 1.812(3) | N(1)-C(2)         | 1.432(4)  |
| C(1)-H(1A)        | 0.9900   | C(1)-H(1B)        | 0.9900    |
| C(2)-C(3)         | 1.382(4) | C(2)-C(7)         | 1.389(4)  |
| C(3)-C(4)         | 1.386(5) | C(3)-H(3)         | 0.9500    |
| C(4)-C(5)         | 1.381(5) | C(4)-H(4)         | 0.9500    |
| C(5)-C(6)         | 1.370(6) | C(5)-H(5)         | 0.9500    |
| C(6)-C(7)         | 1.396(5) | C(6)-H(6)         | 0.9500    |
| C(7)-H(7)         | 0.9500   | C(8)-C(13)        | 1.383(4)  |
| C(8)-C(9)         | 1.390(4) | C(9)-C(10)        | 1.376(5)  |
| C(9)-H(9)         | 0.9500   | C(10)-C(11)       | 1.390(5)  |
| C(10)-H(10)       | 0.9500   | C(11)-C(12)       | 1.363(5)  |
| C(11)-H(11)       | 0.9500   | C(12)-C(13)       | 1.401(5)  |
| C(12)-H(12)       | 0.9500   | C(13)-H(13)       | 0.9500    |
| C(14)-C(19)       | 1.390(4) | C(14)-C(15)       | 1.400(4)  |
| C(15)-C(16)       | 1.382(5) | C(15)-H(15)       | 0.9500    |
| C(16)-C(17)       | 1.383(5) | C(16)-H(16)       | 0.9500    |
| C(17)-C(18)       | 1.379(5) | C(17)-H(17)       | 0.9500    |
| C(18)-C(19)       | 1.386(4) | C(18)-H(18)       | 0.9500    |
| C(19)-H(19)       | 0.9500   | C(20)-C(21)       | 1.381(4)  |
| C(20)-C(27)       | 1.513(5) | C(20)-H(20)       | 0.9500    |
| C(21)-C(22)       | 1.530(4) | C(21)-H(21)       | 0.9500    |
| C(22)-C(23)       | 1.510(5) | C(22)-H(22A)      | 0.9900    |
| C(22)-H(22B)      | 0.9900   | C(23)-C(24)       | 1.507(5)  |
| C(23)-H(23A)      | 0.9900   | C(23)-H(23B)      | 0.9900    |
| C(24)-C(25)       | 1.403(4) | C(24)-H(24)       | 0.9500    |
| C(25)-C(26)       | 1.510(5) | C(25)-H(25)       | 0.9500    |
| C(26)-C(27)       | 1.521(5) | C(26)-H(26A)      | 0.9900    |
| C(26)-H(26B)      | 0.9900   | C(27)-H(27A)      | 0.9900    |
| C(27)-H(27B)      | 0.9900   |                   |           |
| N(1)-Rh(1)-C(21)  | 93.9(1)  | N(1)-Rh(1)-C(24)  | 166.8(1)  |
| C(21)-Rh(1)-C(24) | 82.2(1)  | N(1)-Rh(1)-C(25)  | 154.7(1)  |
| C(21)-Rh(1)-C(25) | 98.1(1)  | C(24)-Rh(1)-C(25) | 38.4(1)   |
| N(1)-Rh(1)-C(20)  | 94.7(1)  | C(21)-Rh(1)-C(20) | 37.7(1)   |
| C(24)-Rh(1)-C(20) | 89.9(1)  | C(25)-Rh(1)-C(20) | 81.8(1)   |
| N(1)-Rh(1)-S(1)   | 88.32(7) | C(21)-Rh(1)-S(1)  | 152.6(1)  |
| C(24)-Rh(1)-S(1)  | 89.5(1)  | C(25)-Rh(1)-S(1)  | 91.1(1)   |
| C(20)-Rh(1)-S(1)  | 169.1(1) | C(1)-S(1)-Rh(1)   | 103.4(1)  |
| N(1)-P(1)-C(1)    | 107.2(1) | N(1)-P(1)-C(14)   | 115.9(1)  |
| C(1)-P(1)-C(14)   | 107.3(2) | N(1)-P(1)-C(8)    | 109.6(1)  |
| C(1)-P(1)-C(8)    | 110.4(1) | C(14)-P(1)-C(8)   | 106.3(1)  |
| C(2)-N(1)-P(1)    | 116.8(2) | C(2)-N(1)-Rh(1)   | 127.5(2)  |
| P(1)-N(1)-Rh(1)   | 114.5(1) | P(1)-C(1)-S(1)    | 106.8(2)  |
| P(1)-C(1)-H(1A)   | 110.4    | S(1)-C(1)-H(1A)   | 110.4     |
| P(1)-C(1)-H(1B)   | 110.4    | S(1)-C(1)-H(1B)   | 110.4     |
| H(1A)-C(1)-H(1B)  | 108.6    | C(3)-C(2)-C(7)    | 117.6(3)  |
| C(3)-C(2)-N(1)    | 120.0(3) | C(7)-C(2)-N(1)    | 122.3(3)  |
| C(2)-C(3)-C(4)    | 121.8(3) | C(2)-C(3)-H(3)    | 119.1     |
| C(4)-C(3)-H(3)    | 119.1    | C(5)-C(4)-C(3)    | 119.6(4)  |
| C(5)-C(4)-H(4)    | 120.2    | C(3)-C(4)-H(4)    | 120.2     |
| C(6)-C(5)-C(4)    | 119.9(3) | C(6)-C(5)-H(5)    | 120.1     |
| C(4)-C(5)-H(5)    | 120.1    | C(5)-C(6)-C(7)    | 120.1(3)  |
| C(5)-C(6)-H(6)    | 120.0    | C(7)-C(6)-H(6)    | 120.0     |
| C(2)-C(7)-C(6)    | 121.0(3) | C(2)-C(7)-H(7)    | 119.5     |
| C(6)-C(7)-H(7)    | 119.5    | C(13)-C(8)-C(9)   | 119.2(3)  |
| C(13)-C(8)-P(1)   | 121.3(2) | C(9)-C(8)-P(1)    | 119.0(2)  |
| C(10)-C(9)-C(8)   | 120.8(3) | C(10)-C(9)-H(9)   | 119.6     |
| C(8)-C(9)-H(9)    | 119.6    | C(9)-C(10)-C(11)  | 119.5(3)  |
| C(9)-C(10)-H(10)  | 120.2    | C(11)-C(10)-H(10) | 120.2     |
| C(12)-C(11)-C(10) | 120.5(3) | C(12)-C(11)-H(11) | 119.7     |

|                     |          |                    |          |
|---------------------|----------|--------------------|----------|
| C(10)-C(11)-H(11)   | 119.7    | C(11)-C(12)-C(13)  | 120.0(3) |
| C(11)-C(12)-H(12)   | 120.0    | C(13)-C(12)-H(12)  | 120.0    |
| C(8)-C(13)-C(12)    | 120.0(3) | C(8)-C(13)-H(13)   | 120.0    |
| C(12)-C(13)-H(13)   | 120.0    | C(19)-C(14)-C(15)  | 119.3(3) |
| C(19)-C(14)-P(1)    | 121.1(2) | C(15)-C(14)-P(1)   | 119.5(2) |
| C(16)-C(15)-C(14)   | 120.4(3) | C(16)-C(15)-H(15)  | 119.8    |
| C(14)-C(15)-H(15)   | 119.8    | C(15)-C(16)-C(17)  | 119.7(3) |
| C(15)-C(16)-H(16)   | 120.2    | C(17)-C(16)-H(16)  | 120.2    |
| C(18)-C(17)-C(16)   | 120.4(3) | C(18)-C(17)-H(17)  | 119.8    |
| C(16)-C(17)-H(17)   | 119.8    | C(17)-C(18)-C(19)  | 120.3(3) |
| C(17)-C(18)-H(18)   | 119.8    | C(19)-C(18)-H(18)  | 119.8    |
| C(18)-C(19)-C(14)   | 119.8(3) | C(18)-C(19)-H(19)  | 120.1    |
| C(14)-C(19)-H(19)   | 120.1    | C(21)-C(20)-C(27)  | 123.8(3) |
| C(21)-C(20)-Rh(1)   | 69.6(2)  | C(27)-C(20)-Rh(1)  | 112.5(2) |
| C(21)-C(20)-H(20)   | 118.1    | C(27)-C(20)-H(20)  | 118.1    |
| Rh(1)-C(20)-H(20)   | 87.9     | C(20)-C(21)-C(22)  | 125.5(3) |
| C(20)-C(21)-Rh(1)   | 72.7(2)  | C(22)-C(21)-Rh(1)  | 109.1(2) |
| C(20)-C(21)-H(21)   | 117.3    | C(22)-C(21)-H(21)  | 117.3    |
| Rh(1)-C(21)-H(21)   | 88.2     | C(23)-C(22)-C(21)  | 113.1(3) |
| C(23)-C(22)-H(22A)  | 109.0    | C(21)-C(22)-H(22A) | 109.0    |
| C(23)-C(22)-H(22B)  | 109.0    | C(21)-C(22)-H(22B) | 109.0    |
| H(22A)-C(22)-H(22B) | 107.8    | C(24)-C(23)-C(22)  | 112.9(3) |
| C(24)-C(23)-H(23A)  | 109.0    | C(22)-C(23)-H(23A) | 109.0    |
| C(24)-C(23)-H(23B)  | 109.0    | C(22)-C(23)-H(23B) | 109.0    |
| H(23A)-C(23)-H(23B) | 107.8    | C(25)-C(24)-C(23)  | 124.8(3) |
| C(25)-C(24)-Rh(1)   | 71.0(2)  | C(23)-C(24)-Rh(1)  | 112.7(2) |
| C(25)-C(24)-H(24)   | 117.6    | C(23)-C(24)-H(24)  | 117.6    |
| Rh(1)-C(24)-H(24)   | 86.2     | C(24)-C(25)-C(26)  | 125.0(3) |
| C(24)-C(25)-Rh(1)   | 70.6(2)  | C(26)-C(25)-Rh(1)  | 109.6(2) |
| C(24)-C(25)-H(25)   | 117.5    | C(26)-C(25)-H(25)  | 117.5    |
| Rh(1)-C(25)-H(25)   | 89.8     | C(25)-C(26)-C(27)  | 113.6(3) |
| C(25)-C(26)-H(26A)  | 108.9    | C(27)-C(26)-H(26A) | 108.9    |
| C(25)-C(26)-H(26B)  | 108.9    | C(27)-C(26)-H(26B) | 108.9    |
| H(26A)-C(26)-H(26B) | 107.7    | C(20)-C(27)-C(26)  | 112.4(3) |
| C(20)-C(27)-H(27A)  | 109.1    | C(26)-C(27)-H(27A) | 109.1    |
| C(20)-C(27)-H(27B)  | 109.1    | C(26)-C(27)-H(27B) | 109.1    |
| H(27A)-C(27)-H(27B) | 107.8    |                    |          |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pal63

| atom  | U11   | U22   | U33   | U23   | U13   | U12   |
|-------|-------|-------|-------|-------|-------|-------|
| Rh(1) | 27(1) | 20(1) | 24(1) | 2(1)  | 10(1) | 1(1)  |
| S(1)  | 40(1) | 21(1) | 31(1) | -1(1) | 11(1) | 3(1)  |
| P(1)  | 25(1) | 21(1) | 24(1) | 0(1)  | 9(1)  | -1(1) |
| N(1)  | 28(1) | 18(1) | 27(1) | 0(1)  | 11(1) | 1(1)  |
| C(1)  | 32(2) | 23(2) | 30(2) | 0(1)  | 9(1)  | 0(1)  |
| C(2)  | 27(2) | 25(2) | 21(1) | 0(1)  | 5(1)  | -1(1) |
| C(3)  | 40(2) | 29(2) | 45(2) | -2(2) | 22(2) | 0(2)  |
| C(4)  | 52(2) | 46(2) | 47(2) | -2(2) | 25(2) | 15(2) |
| C(5)  | 72(3) | 23(2) | 44(2) | -3(2) | 25(2) | 13(2) |
| C(6)  | 69(3) | 20(2) | 36(2) | 3(2)  | 20(2) | -1(2) |
| C(7)  | 42(2) | 25(2) | 32(2) | 0(2)  | 15(1) | -2(2) |
| C(8)  | 31(2) | 29(2) | 22(1) | -1(1) | 11(1) | 1(1)  |
| C(9)  | 33(2) | 37(2) | 33(2) | 4(2)  | 12(1) | -2(2) |
| C(10) | 27(2) | 59(3) | 38(2) | 3(2)  | 11(2) | 2(2)  |
| C(11) | 34(2) | 54(2) | 31(2) | -1(2) | 7(1)  | 17(2) |
| C(12) | 51(2) | 40(2) | 35(2) | 6(2)  | 17(2) | 5(2)  |
| C(13) | 31(2) | 33(2) | 37(2) | 5(2)  | 14(1) | 2(2)  |
| C(14) | 30(2) | 24(2) | 29(2) | 1(1)  | 13(1) | 2(1)  |
| C(15) | 36(2) | 28(2) | 35(2) | 2(1)  | 15(2) | 4(2)  |
| C(16) | 50(2) | 33(2) | 36(2) | 8(2)  | 26(2) | 10(2) |
| C(17) | 38(2) | 34(2) | 57(2) | 17(2) | 29(2) | 11(2) |
| C(18) | 30(2) | 30(2) | 51(2) | 7(2)  | 15(2) | 1(2)  |
| C(19) | 33(2) | 29(2) | 34(2) | 2(2)  | 12(1) | 4(2)  |
| C(20) | 40(2) | 31(2) | 23(1) | -5(1) | 10(1) | 4(2)  |
| C(21) | 36(2) | 26(2) | 27(2) | -3(1) | 7(1)  | -2(2) |
| C(22) | 35(2) | 37(2) | 44(2) | -2(2) | 7(2)  | -4(2) |
| C(23) | 34(2) | 41(2) | 37(2) | 4(2)  | 7(2)  | 6(2)  |
| C(24) | 36(2) | 29(2) | 29(2) | 7(1)  | 10(1) | 10(2) |
| C(25) | 32(2) | 26(2) | 27(2) | 7(1)  | 10(1) | 2(1)  |
| C(26) | 43(2) | 49(2) | 33(2) | 10(2) | 17(2) | 3(2)  |
| C(27) | 50(2) | 47(2) | 32(2) | 1(2)  | 20(2) | 8(2)  |

The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U(11) + \dots + 2hka^* b^* U(12)]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pal63

| atom   | x     | y       | z    | U(eq) |
|--------|-------|---------|------|-------|
| H(1A)  | 1882  | -1672   | 4213 | 35    |
| H(1B)  | 1235  | -1480   | 4797 | 35    |
| H(3)   | 960   | 1771    | 6379 | 43    |
| H(4)   | 428   | 3865    | 6418 | 56    |
| H(5)   | 1154  | 5598    | 6005 | 55    |
| H(6)   | 2402  | 5223    | 5553 | 50    |
| H(7)   | 2924  | 3115    | 5500 | 39    |
| H(9)   | 64    | 87      | 4227 | 42    |
| H(10)  | -1275 | 1226    | 3308 | 50    |
| H(11)  | -1113 | 3076    | 2533 | 49    |
| H(12)  | 367   | 3752    | 2655 | 50    |
| H(13)  | 1720  | 2575    | 3556 | 40    |
| H(15)  | 2308  | -6.0000 | 3125 | 40    |
| H(16)  | 3543  | 286     | 2632 | 45    |
| H(17)  | 4970  | 1180    | 3623 | 48    |
| H(18)  | 5176  | 1755    | 5105 | 44    |
| H(19)  | 3963  | 1417    | 5626 | 39    |
| H(20)  | 2532  | 1247    | 7592 | 39    |
| H(21)  | 3759  | 1658    | 7173 | 38    |
| H(22A) | 5265  | 837     | 7834 | 49    |
| H(22B) | 5208  | 1230    | 8787 | 49    |
| H(23A) | 5576  | -1062   | 8523 | 47    |
| H(23B) | 4958  | -774    | 9116 | 47    |
| H(24)  | 4250  | -1856   | 7320 | 38    |
| H(25)  | 2877  | -2323   | 7501 | 35    |
| H(26A) | 3380  | -1683   | 9256 | 49    |
| H(26B) | 2349  | -1361   | 8509 | 49    |
| H(27A) | 2791  | 602     | 9090 | 50    |
| H(27B) | 3887  | 342     | 9306 | 50    |

**Complex 17**

Table 1. Crystal data for pa136

|   |   |
|---|---|
| Compound                                    | pa136   |
| Molecular formula                           | C <sub>37</sub> H <sub>32</sub> ClNP <sub>2</sub> PdS |
| Molecular weight                            | 726.49  |
| Crystal habit                               | Orange Block  |
| Crystal dimensions(mm)                      | 0.14x0.12x0.10  |
| Crystal system                              | monoclinic  |
| Space group                                 | P2 <sub>1</sub> /c                                    |
| a(Å)  | 9.612(1)  |
| b(Å)  | 16.430(1)   |
| c(Å)  | 21.208(1)   |
| α(°)  | 90.00   |
| β(°)  | 102.9220(10)  |
| γ(°)  | 90.00   |
| V(Å <sup>3</sup> )                          | 3264.5(4)   |
| Z   | 4   |
| d(g·cm <sup>-3</sup> )                      | 1.478   |
| F(000)                                      | 1480  |
| μ(cm <sup>-1</sup> )                        | 0.840   |
| Absorption corrections                      | multi-scan ; 0.8915 min, 0.9207 max                   |
| Diffractionmeter                            | KappaCCD  |
| X-ray source                                | MoKα  |
| λ(Å)  | 0.71069   |
| Monochromator                               | graphite  |
| T (K)                                       | 150.0(1)  |
| Scan mode                                   | phi and omega scans                                   |
| Maximum θ                                   | 27.47   |
| HKL ranges                                  | -9 12 ; -21 19 ; -27 27                               |
| Reflections measured                        | 23979   |
| Unique data                                 | 7391  |
| Rint  | 0.0449  |
| Reflections used                            | 4991  |
| Criterion                                   | I > 2σ(I)   |
| Refinement type                             | Fsqd  |
| Hydrogen atoms                              | constr  |
| Parameters refined                          | 388   |
| Reflections / parameter                     | 12  |
| wR2   | 0.0970  |
| R1  | 0.0405  |
| Weights a, b                                | 0.0465 ; 0.0000                                       |
| GoF   | 0.956   |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.938(0.090) / -0.626(0.090)                          |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa136

| atom  | x        | y        | z       | U(eq) |
|-------|----------|----------|---------|-------|
| Pd(1) | 8406(1)  | 1829(1)  | 4144(1) | 23(1) |
| Cl(1) | 8917(1)  | 2153(1)  | 3122(1) | 21(1) |
| S(1)  | 7289(1)  | 1681(1)  | 4983(1) | 33(1) |
| P(3)  | 6208(1)  | 453(1)   | 3970(1) | 26(1) |
| P(4)  | 9152(1)  | 3078(1)  | 4509(1) | 22(1) |
| N(1)  | 7755(3)  | 643(1)   | 3847(1) | 26(1) |
| C(1)  | 6323(4)  | 723(2)   | 4803(2) | 34(1) |
| C(2)  | 4779(3)  | 1044(2)  | 3490(2) | 28(1) |
| C(3)  | 3373(4)  | 926(2)   | 3543(2) | 37(1) |
| C(4)  | 2280(4)  | 1371(2)  | 3170(2) | 47(1) |
| C(5)  | 2590(4)  | 1958(2)  | 2754(2) | 47(1) |
| C(6)  | 3973(4)  | 2088(2)  | 2706(2) | 40(1) |
| C(7)  | 5079(4)  | 1630(2)  | 3061(2) | 30(1) |
| C(8)  | 5736(4)  | -611(2)  | 3867(2) | 28(1) |
| C(9)  | 6653(4)  | -1165(2) | 4249(2) | 41(1) |
| C(10) | 6319(5)  | -1983(2) | 4219(2) | 54(1) |
| C(11) | 5087(4)  | -2261(2) | 3817(2) | 49(1) |
| C(12) | 4185(4)  | -1724(2) | 3415(2) | 37(1) |
| C(13) | 4513(4)  | -902(2)  | 3449(2) | 32(1) |
| C(14) | 8429(3)  | 139(2)   | 3457(2) | 27(1) |
| C(15) | 7788(4)  | -81(2)   | 2832(2) | 34(1) |
| C(16) | 8472(5)  | -606(2)  | 2483(2) | 47(1) |
| C(17) | 9814(5)  | -910(2)  | 2757(2) | 47(1) |
| C(18) | 10460(4) | -689(2)  | 3388(2) | 47(1) |
| C(19) | 9783(4)  | -175(2)  | 3735(2) | 38(1) |
| C(20) | 8831(3)  | 3349(2)  | 5299(2) | 24(1) |
| C(21) | 7981(3)  | 4005(2)  | 5380(2) | 28(1) |
| C(22) | 7725(4)  | 4178(2)  | 5987(2) | 34(1) |
| C(23) | 8308(4)  | 3688(2)  | 6513(2) | 36(1) |
| C(24) | 9141(4)  | 3036(2)  | 6433(2) | 33(1) |
| C(25) | 9413(3)  | 2860(2)  | 5835(2) | 28(1) |
| C(26) | 8209(3)  | 3850(2)  | 3962(2) | 26(1) |
| C(27) | 6752(4)  | 3750(2)  | 3727(2) | 32(1) |
| C(28) | 5968(4)  | 4339(2)  | 3335(2) | 43(1) |
| C(29) | 6652(4)  | 5029(2)  | 3168(2) | 43(1) |
| C(30) | 8097(4)  | 5120(2)  | 3385(2) | 41(1) |
| C(31) | 8874(4)  | 4536(2)  | 3785(2) | 32(1) |
| C(32) | 11054(3) | 3292(2)  | 4602(2) | 26(1) |
| C(33) | 11759(4) | 3836(2)  | 5073(2) | 29(1) |
| C(34) | 13194(4) | 3995(2)  | 5144(2) | 34(1) |
| C(35) | 13959(4) | 3624(2)  | 4751(2) | 43(1) |
| C(36) | 13257(4) | 3095(3)  | 4278(2) | 63(1) |
| C(37) | 11821(4) | 2928(2)  | 4208(2) | 47(1) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pal36

|                  |           |                  |           |
|------------------|-----------|------------------|-----------|
| Pd(1)-N(1)       | 2.100(2)  | Pd(1)-P(4)       | 2.2528(8) |
| Pd(1)-S(1)       | 2.289(1)  | Pd(1)-Cl(1)      | 2.3869(7) |
| S(1)-C(1)        | 1.824(3)  | P(3)-N(1)        | 1.597(3)  |
| P(3)-C(2)        | 1.799(3)  | P(3)-C(1)        | 1.801(3)  |
| P(3)-C(8)        | 1.808(3)  | P(4)-C(26)       | 1.818(3)  |
| P(4)-C(20)       | 1.825(3)  | P(4)-C(32)       | 1.829(3)  |
| N(1)-C(14)       | 1.424(4)  | C(1)-H(1A)       | 0.9900    |
| C(1)-H(1B)       | 0.9900    | C(2)-C(3)        | 1.394(5)  |
| C(2)-C(7)        | 1.398(4)  | C(3)-C(4)        | 1.376(5)  |
| C(3)-H(3)        | 0.9500    | C(4)-C(5)        | 1.383(6)  |
| C(4)-H(4)        | 0.9500    | C(5)-C(6)        | 1.372(5)  |
| C(5)-H(5)        | 0.9500    | C(6)-C(7)        | 1.380(5)  |
| C(6)-H(6)        | 0.9500    | C(7)-H(7)        | 0.9500    |
| C(8)-C(13)       | 1.388(4)  | C(8)-C(9)        | 1.393(5)  |
| C(9)-C(10)       | 1.379(5)  | C(9)-H(9)        | 0.9500    |
| C(10)-C(11)      | 1.374(5)  | C(10)-H(10)      | 0.9500    |
| C(11)-C(12)      | 1.387(5)  | C(11)-H(11)      | 0.9500    |
| C(12)-C(13)      | 1.386(4)  | C(12)-H(12)      | 0.9500    |
| C(13)-H(13)      | 0.9500    | C(14)-C(15)      | 1.380(4)  |
| C(14)-C(19)      | 1.401(5)  | C(15)-C(16)      | 1.394(5)  |
| C(15)-H(15)      | 0.9500    | C(16)-C(17)      | 1.384(5)  |
| C(16)-H(16)      | 0.9500    | C(17)-C(18)      | 1.392(5)  |
| C(17)-H(17)      | 0.9500    | C(18)-C(19)      | 1.375(5)  |
| C(18)-H(18)      | 0.9500    | C(19)-H(19)      | 0.9500    |
| C(20)-C(21)      | 1.386(4)  | C(20)-C(25)      | 1.402(4)  |
| C(21)-C(22)      | 1.393(4)  | C(21)-H(21)      | 0.9500    |
| C(22)-C(23)      | 1.386(5)  | C(22)-H(22)      | 0.9500    |
| C(23)-C(24)      | 1.371(5)  | C(23)-H(23)      | 0.9500    |
| C(24)-C(25)      | 1.382(4)  | C(24)-H(24)      | 0.9500    |
| C(25)-H(25)      | 0.9500    | C(26)-C(27)      | 1.387(4)  |
| C(26)-C(31)      | 1.387(4)  | C(27)-C(28)      | 1.384(5)  |
| C(27)-H(27)      | 0.9500    | C(28)-C(29)      | 1.395(5)  |
| C(28)-H(28)      | 0.9500    | C(29)-C(30)      | 1.370(5)  |
| C(29)-H(29)      | 0.9500    | C(30)-C(31)      | 1.384(5)  |
| C(30)-H(30)      | 0.9500    | C(31)-H(31)      | 0.9500    |
| C(32)-C(37)      | 1.369(5)  | C(32)-C(33)      | 1.398(4)  |
| C(33)-C(34)      | 1.379(4)  | C(33)-H(33)      | 0.9500    |
| C(34)-C(35)      | 1.371(5)  | C(34)-H(34)      | 0.9500    |
| C(35)-C(36)      | 1.384(5)  | C(35)-H(35)      | 0.9500    |
| C(36)-C(37)      | 1.383(5)  | C(36)-H(36)      | 0.9500    |
| C(37)-H(37)      | 0.9500    |                  |           |
| N(1)-Pd(1)-P(4)  | 177.26(7) | N(1)-Pd(1)-S(1)  | 88.52(7)  |
| P(4)-Pd(1)-S(1)  | 89.87(3)  | N(1)-Pd(1)-Cl(1) | 92.45(7)  |
| P(4)-Pd(1)-Cl(1) | 89.73(3)  | S(1)-Pd(1)-Cl(1) | 163.28(3) |
| C(1)-S(1)-Pd(1)  | 103.6(1)  | N(1)-P(3)-C(2)   | 115.0(2)  |
| N(1)-P(3)-C(1)   | 104.9(2)  | C(2)-P(3)-C(1)   | 107.1(2)  |
| N(1)-P(3)-C(8)   | 112.8(1)  | C(2)-P(3)-C(8)   | 108.3(2)  |
| C(1)-P(3)-C(8)   | 108.4(2)  | C(26)-P(4)-C(20) | 104.6(1)  |
| C(26)-P(4)-C(32) | 106.1(1)  | C(20)-P(4)-C(32) | 103.0(1)  |
| C(26)-P(4)-Pd(1) | 110.0(1)  | C(20)-P(4)-Pd(1) | 115.6(1)  |
| C(32)-P(4)-Pd(1) | 116.5(1)  | C(14)-N(1)-P(3)  | 122.8(2)  |
| C(14)-N(1)-Pd(1) | 124.8(2)  | P(3)-N(1)-Pd(1)  | 111.0(1)  |
| P(3)-C(1)-S(1)   | 109.5(2)  | P(3)-C(1)-H(1A)  | 109.8     |
| S(1)-C(1)-H(1A)  | 109.8     | P(3)-C(1)-H(1B)  | 109.8     |
| S(1)-C(1)-H(1B)  | 109.8     | H(1A)-C(1)-H(1B) | 108.2     |
| C(3)-C(2)-C(7)   | 119.5(3)  | C(3)-C(2)-P(3)   | 120.7(3)  |
| C(7)-C(2)-P(3)   | 119.8(3)  | C(4)-C(3)-C(2)   | 120.6(4)  |
| C(4)-C(3)-H(3)   | 119.7     | C(2)-C(3)-H(3)   | 119.7     |
| C(3)-C(4)-C(5)   | 119.4(4)  | C(3)-C(4)-H(4)   | 120.3     |
| C(5)-C(4)-H(4)   | 120.3     | C(6)-C(5)-C(4)   | 120.4(4)  |
| C(6)-C(5)-H(5)   | 119.8     | C(4)-C(5)-H(5)   | 119.8     |
| C(5)-C(6)-C(7)   | 121.0(4)  | C(5)-C(6)-H(6)   | 119.5     |
| C(7)-C(6)-H(6)   | 119.5     | C(6)-C(7)-C(2)   | 119.0(3)  |
| C(7)-C(7)-H(7)   | 120.5     | C(2)-C(7)-H(7)   | 120.5     |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(13)-C(8)-C(9)   | 118.8(3) | C(13)-C(8)-P(3)   | 124.3(2) |
| C(9)-C(8)-P(3)    | 116.9(3) | C(10)-C(9)-C(8)   | 119.9(3) |
| C(10)-C(9)-H(9)   | 120.0    | C(8)-C(9)-H(9)    | 120.0    |
| C(11)-C(10)-C(9)  | 120.8(4) | C(11)-C(10)-H(10) | 119.6    |
| C(9)-C(10)-H(10)  | 119.6    | C(10)-C(11)-C(12) | 120.2(3) |
| C(10)-C(11)-H(11) | 119.9    | C(12)-C(11)-H(11) | 119.9    |
| C(13)-C(12)-C(11) | 118.9(3) | C(13)-C(12)-H(12) | 120.5    |
| C(11)-C(12)-H(12) | 120.5    | C(12)-C(13)-C(8)  | 121.3(3) |
| C(12)-C(13)-H(13) | 119.4    | C(8)-C(13)-H(13)  | 119.4    |
| C(15)-C(14)-C(19) | 118.7(3) | C(15)-C(14)-N(1)  | 123.2(3) |
| C(19)-C(14)-N(1)  | 118.1(3) | C(14)-C(15)-C(16) | 120.7(3) |
| C(14)-C(15)-H(15) | 119.7    | C(16)-C(15)-H(15) | 119.7    |
| C(17)-C(16)-C(15) | 120.5(4) | C(17)-C(16)-H(16) | 119.8    |
| C(15)-C(16)-H(16) | 119.8    | C(16)-C(17)-C(18) | 118.9(4) |
| C(16)-C(17)-H(17) | 120.6    | C(18)-C(17)-H(17) | 120.6    |
| C(19)-C(18)-C(17) | 120.8(4) | C(19)-C(18)-H(18) | 119.6    |
| C(17)-C(18)-H(18) | 119.6    | C(18)-C(19)-C(14) | 120.5(4) |
| C(18)-C(19)-H(19) | 119.7    | C(14)-C(19)-H(19) | 119.7    |
| C(21)-C(20)-C(25) | 119.0(3) | C(21)-C(20)-P(4)  | 121.9(2) |
| C(25)-C(20)-P(4)  | 119.0(2) | C(20)-C(21)-C(22) | 120.2(3) |
| C(20)-C(21)-H(21) | 119.9    | C(22)-C(21)-H(21) | 119.9    |
| C(23)-C(22)-C(21) | 120.1(3) | C(23)-C(22)-H(22) | 119.9    |
| C(21)-C(22)-H(22) | 119.9    | C(24)-C(23)-C(22) | 119.8(3) |
| C(24)-C(23)-H(23) | 120.1    | C(22)-C(23)-H(23) | 120.1    |
| C(23)-C(24)-C(25) | 120.9(3) | C(23)-C(24)-H(24) | 119.6    |
| C(25)-C(24)-H(24) | 119.6    | C(24)-C(25)-C(20) | 120.0(3) |
| C(24)-C(25)-H(25) | 120.0    | C(20)-C(25)-H(25) | 120.0    |
| C(27)-C(26)-C(31) | 119.2(3) | C(27)-C(26)-P(4)  | 117.7(2) |
| C(31)-C(26)-P(4)  | 123.0(3) | C(28)-C(27)-C(26) | 120.2(3) |
| C(28)-C(27)-H(27) | 119.9    | C(26)-C(27)-H(27) | 119.9    |
| C(27)-C(28)-C(29) | 119.8(4) | C(27)-C(28)-H(28) | 120.1    |
| C(29)-C(28)-H(28) | 120.1    | C(30)-C(29)-C(28) | 120.2(3) |
| C(30)-C(29)-H(29) | 119.9    | C(28)-C(29)-H(29) | 119.9    |
| C(29)-C(30)-C(31) | 119.8(3) | C(29)-C(30)-H(30) | 120.1    |
| C(31)-C(30)-H(30) | 120.1    | C(30)-C(31)-C(26) | 120.7(3) |
| C(30)-C(31)-H(31) | 119.6    | C(26)-C(31)-H(31) | 119.6    |
| C(37)-C(32)-C(33) | 118.4(3) | C(37)-C(32)-P(4)  | 120.8(3) |
| C(33)-C(32)-P(4)  | 120.9(2) | C(34)-C(33)-C(32) | 120.8(3) |
| C(34)-C(33)-H(33) | 119.6    | C(32)-C(33)-H(33) | 119.6    |
| C(35)-C(34)-C(33) | 120.6(3) | C(35)-C(34)-H(34) | 119.7    |
| C(33)-C(34)-H(34) | 119.7    | C(34)-C(35)-C(36) | 118.6(3) |
| C(34)-C(35)-H(35) | 120.7    | C(36)-C(35)-H(35) | 120.7    |
| C(37)-C(36)-C(35) | 121.0(4) | C(37)-C(36)-H(36) | 119.5    |
| C(35)-C(36)-H(36) | 119.5    | C(32)-C(37)-C(36) | 120.6(3) |
| C(32)-C(37)-H(37) | 119.7    | C(36)-C(37)-H(37) | 119.7    |



## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pal36

| atom  | U11   | U22    | U33   | U23    | U13   | U12    |
|-------|-------|--------|-------|--------|-------|--------|
| Pd(1) | 25(1) | 23(1)  | 22(1) | -1(1)  | 6(1)  | -3(1)  |
| Cl(1) | 23(1) | 23(1)  | 18(1) | -3(1)  | 9(1)  | -5(1)  |
| S(1)  | 40(1) | 37(1)  | 25(1) | -5(1)  | 13(1) | -13(1) |
| P(3)  | 27(1) | 24(1)  | 27(1) | 1(1)   | 8(1)  | -3(1)  |
| P(4)  | 23(1) | 23(1)  | 21(1) | 0(1)   | 4(1)  | -2(1)  |
| N(1)  | 26(2) | 21(1)  | 33(2) | -4(1)  | 8(1)  | -1(1)  |
| C(1)  | 37(2) | 38(2)  | 29(2) | 0(2)   | 10(2) | -13(2) |
| C(2)  | 27(2) | 25(2)  | 31(2) | -7(1)  | 5(2)  | 0(1)   |
| C(3)  | 30(2) | 32(2)  | 52(2) | -8(2)  | 15(2) | 1(2)   |
| C(4)  | 28(2) | 44(2)  | 66(3) | -12(2) | 8(2)  | 3(2)   |
| C(5)  | 41(3) | 40(2)  | 52(3) | -9(2)  | -7(2) | 12(2)  |
| C(6)  | 47(3) | 31(2)  | 37(2) | 2(2)   | -1(2) | 1(2)   |
| C(7)  | 31(2) | 28(2)  | 30(2) | -2(2)  | 3(2)  | -5(2)  |
| C(8)  | 28(2) | 24(2)  | 34(2) | 2(1)   | 13(2) | -2(1)  |
| C(9)  | 33(2) | 37(2)  | 50(2) | 7(2)   | -1(2) | -3(2)  |
| C(10) | 48(3) | 30(2)  | 77(3) | 17(2)  | 2(2)  | 2(2)   |
| C(11) | 52(3) | 25(2)  | 69(3) | 4(2)   | 10(2) | -5(2)  |
| C(12) | 27(2) | 30(2)  | 53(2) | -4(2)  | 10(2) | -7(2)  |
| C(13) | 29(2) | 28(2)  | 37(2) | 1(2)   | 6(2)  | 0(2)   |
| C(14) | 29(2) | 22(2)  | 34(2) | 2(1)   | 12(2) | -4(1)  |
| C(15) | 41(2) | 31(2)  | 32(2) | 0(2)   | 12(2) | 5(2)   |
| C(16) | 69(3) | 38(2)  | 35(2) | 1(2)   | 15(2) | 3(2)   |
| C(17) | 60(3) | 28(2)  | 61(3) | -1(2)  | 34(2) | 5(2)   |
| C(18) | 36(2) | 37(2)  | 71(3) | -3(2)  | 19(2) | 6(2)   |
| C(19) | 29(2) | 37(2)  | 48(2) | -6(2)  | 7(2)  | 0(2)   |
| C(20) | 26(2) | 24(2)  | 24(2) | -3(1)  | 8(2)  | -7(1)  |
| C(21) | 31(2) | 25(2)  | 26(2) | -1(1)  | 4(2)  | 0(1)   |
| C(22) | 38(2) | 32(2)  | 35(2) | -6(2)  | 14(2) | 1(2)   |
| C(23) | 47(2) | 40(2)  | 24(2) | -8(2)  | 12(2) | -8(2)  |
| C(24) | 42(2) | 34(2)  | 20(2) | 4(2)   | 2(2)  | -6(2)  |
| C(25) | 28(2) | 27(2)  | 28(2) | -1(1)  | 2(2)  | -1(1)  |
| C(26) | 30(2) | 26(2)  | 21(2) | -1(1)  | 7(2)  | 0(1)   |
| C(27) | 30(2) | 32(2)  | 32(2) | 3(2)   | 2(2)  | -3(2)  |
| C(28) | 41(2) | 43(2)  | 40(2) | 5(2)   | -2(2) | 3(2)   |
| C(29) | 56(3) | 39(2)  | 27(2) | 6(2)   | -4(2) | 8(2)   |
| C(30) | 57(3) | 32(2)  | 31(2) | 7(2)   | 3(2)  | -6(2)  |
| C(31) | 30(2) | 32(2)  | 31(2) | 2(2)   | 2(2)  | -5(2)  |
| C(32) | 25(2) | 25(2)  | 28(2) | 2(1)   | 7(2)  | -3(1)  |
| C(33) | 30(2) | 23(2)  | 33(2) | 0(1)   | 7(2)  | 0(1)   |
| C(34) | 30(2) | 26(2)  | 40(2) | -1(2)  | -1(2) | -6(2)  |
| C(35) | 25(2) | 62(3)  | 42(2) | -2(2)  | 7(2)  | -13(2) |
| C(36) | 34(3) | 111(4) | 47(3) | -32(3) | 18(2) | -15(2) |
| C(37) | 27(2) | 79(3)  | 38(2) | -28(2) | 11(2) | -15(2) |

The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U(11) + \dots + 2hka^*b^*U(12)]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pal36

| atom  | x     | y          | z    | U(eq) |
|-------|-------|------------|------|-------|
| H(1A) | 6825  | 288        | 5089 | 41    |
| H(1B) | 5351  | 780        | 4883 | 41    |
| H(3)  | 3168  | 536        | 3840 | 45    |
| H(4)  | 1320  | 1276       | 3198 | 56    |
| H(5)  | 1842  | 2273       | 2500 | 57    |
| H(6)  | 4172  | 2499       | 2424 | 48    |
| H(7)  | 6029  | 1712       | 3015 | 36    |
| H(9)  | 7506  | -980       | 4530 | 50    |
| H(10) | 6950  | -2358      | 4479 | 65    |
| H(11) | 4851  | -2823      | 3814 | 59    |
| H(12) | 3356  | -1917      | 3121 | 44    |
| H(13) | 3890  | -530       | 3182 | 38    |
| H(15) | 6871  | 128        | 2637 | 41    |
| H(16) | 8014  | -757       | 2054 | 56    |
| H(17) | 10287 | -1263.0001 | 2518 | 56    |
| H(18) | 11379 | -895.9999  | 3582 | 56    |
| H(19) | 10237 | -31        | 4165 | 46    |
| H(21) | 7572  | 4339       | 5019 | 33    |
| H(22) | 7149  | 4631       | 6041 | 41    |
| H(23) | 8132  | 3805       | 6926 | 44    |
| H(24) | 9537  | 2701       | 6793 | 40    |
| H(25) | 9995  | 2407       | 5786 | 34    |
| H(27) | 6291  | 3276       | 3836 | 38    |
| H(28) | 4968  | 4274       | 3180 | 51    |
| H(29) | 6114  | 5437       | 2903 | 52    |
| H(30) | 8564  | 5583       | 3261 | 49    |
| H(31) | 9873  | 4605       | 3940 | 38    |
| H(33) | 11243 | 4099       | 5349 | 35    |
| H(34) | 13657 | 4365       | 5468 | 40    |
| H(35) | 14950 | 3729       | 4802 | 52    |
| H(36) | 13770 | 2843       | 3996 | 75    |
| H(37) | 11362 | 2557       | 3884 | 57    |

**Complex 18**

Table 1. Crystal data for pa118

|   |  |
|---|--|
| Compound                                    | pa118  |
| Molecular formula                           | C <sub>38</sub> H <sub>34</sub> N <sub>2</sub> NiP <sub>2</sub> S <sub>2</sub> |
| Molecular weight                            | 703.44   |
| Crystal habit                               | blue plate   |
| Crystal dimensions(mm)                      | 0.20x0.12x0.02   |
| Crystal system                              | monoclinic   |
| Space group                                 | C2/c   |
| a(Å)  | 12.469(1)  |
| b(Å)  | 25.716(1)  |
| c(Å)  | 11.930(1)  |
| α(°)  | 90.00  |
| β(°)  | 121.135(1)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 3274.3(4)  |
| Z   | 4  |
| d(g·cm <sup>-3</sup> )                      | 1.427  |
| F(000)                                      | 1464   |
| μ(cm <sup>-1</sup> )                        | 0.849  |
| Absorption corrections                      | multi-scan ; 0.8485 min, 0.9832 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 27.46  |
| HKL ranges                                  | -12 16 ; -33 30 ; -15 15   |
| Reflections measured                        | 14046  |
| Unique data                                 | 3756   |
| Rint  | 0.0294   |
| Reflections used                            | 3025   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 204  |
| Reflections / parameter                     | 14   |
| wR2   | 0.0689   |
| R1  | 0.0283   |
| Weights a, b                                | 0.0263 ; 1.7209  |
| GoF   | 1.039  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.333(0.050) / -0.330(0.050)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa118

| atom  | x       | y       | z       | U(eq) |
|-------|---------|---------|---------|-------|
| Ni(1) | 0       | 2014(1) | 2500    | 20(1) |
| S(1)  | 1284(1) | 2646(1) | 2723(1) | 23(1) |
| P(1)  | 2570(1) | 1691(1) | 3077(1) | 20(1) |
| N(1)  | 1340(1) | 1497(1) | 3075(1) | 23(1) |
| C(1)  | 2845(1) | 2350(1) | 3633(2) | 24(1) |
| C(2)  | 2381(2) | 1685(1) | 1472(2) | 26(1) |
| C(3)  | 1425(2) | 1395(1) | 491(2)  | 40(1) |
| C(4)  | 1308(2) | 1367(1) | -731(2) | 60(1) |
| C(5)  | 2142(3) | 1623(1) | -967(2) | 57(1) |
| C(6)  | 3098(2) | 1904(1) | 5(2)    | 49(1) |
| C(7)  | 3228(2) | 1939(1) | 1230(2) | 35(1) |
| C(8)  | 3905(1) | 1286(1) | 4092(2) | 21(1) |
| C(9)  | 4484(2) | 1318(1) | 5453(2) | 26(1) |
| C(10) | 5453(2) | 984(1)  | 6244(2) | 29(1) |
| C(11) | 5855(2) | 616(1)  | 5696(2) | 31(1) |
| C(12) | 5299(2) | 584(1)  | 4347(2) | 30(1) |
| C(13) | 4324(2) | 917(1)  | 3543(2) | 26(1) |
| C(14) | 1423(1) | 1055(1) | 3836(2) | 25(1) |
| C(15) | 1464(2) | 555(1)  | 3435(2) | 43(1) |
| C(16) | 1559(2) | 129(1)  | 4198(3) | 61(1) |
| C(17) | 1595(2) | 197(1)  | 5358(3) | 60(1) |
| C(18) | 1553(2) | 688(1)  | 5763(2) | 53(1) |
| C(19) | 1478(2) | 1118(1) | 5022(2) | 36(1) |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

Table 3. Bond lengths (Å) and angles (deg) for pall8

|                   |           |                     |           |
|-------------------|-----------|---------------------|-----------|
| Ni(1)-N(1)#2      | 1.961(1)  | Ni(1)-N(1)          | 1.961(1)  |
| Ni(1)-S(1)        | 2.1996(5) | Ni(1)-S(1)#2        | 2.1996(5) |
| S(1)-C(1)         | 1.834(2)  | P(1)-N(1)           | 1.612(1)  |
| P(1)-C(1)         | 1.787(2)  | P(1)-C(8)           | 1.800(2)  |
| P(1)-C(2)         | 1.805(2)  | N(1)-C(14)          | 1.424(2)  |
| C(1)-H(1A)        | 0.9900    | C(1)-H(1B)          | 0.9900    |
| C(2)-C(3)         | 1.379(3)  | C(2)-C(7)           | 1.393(2)  |
| C(3)-C(4)         | 1.389(3)  | C(3)-H(3)           | 0.9500    |
| C(4)-C(5)         | 1.378(3)  | C(4)-H(4)           | 0.9500    |
| C(5)-C(6)         | 1.363(3)  | C(5)-H(5)           | 0.9500    |
| C(6)-C(7)         | 1.388(3)  | C(6)-H(6)           | 0.9500    |
| C(7)-H(7)         | 0.9500    | C(8)-C(9)           | 1.397(2)  |
| C(8)-C(13)        | 1.398(2)  | C(9)-C(10)          | 1.381(2)  |
| C(9)-H(9)         | 0.9500    | C(10)-C(11)         | 1.383(2)  |
| C(10)-H(10)       | 0.9500    | C(11)-C(12)         | 1.387(2)  |
| C(11)-H(11)       | 0.9500    | C(12)-C(13)         | 1.388(2)  |
| C(12)-H(12)       | 0.9500    | C(13)-H(13)         | 0.9500    |
| C(14)-C(15)       | 1.383(3)  | C(14)-C(19)         | 1.391(2)  |
| C(15)-C(16)       | 1.389(3)  | C(15)-H(15)         | 0.9500    |
| C(16)-C(17)       | 1.374(4)  | C(16)-H(16)         | 0.9500    |
| C(17)-C(18)       | 1.364(4)  | C(17)-H(17)         | 0.9500    |
| C(18)-C(19)       | 1.388(3)  | C(18)-H(18)         | 0.9500    |
| C(19)-H(19)       | 0.9500    |                     |           |
|                   |           |                     |           |
| N(1)#2-Ni(1)-N(1) | 94.61(8)  | N(1)#2-Ni(1)-S(1)   | 168.20(4) |
| N(1)-Ni(1)-S(1)   | 91.38(4)  | N(1)#2-Ni(1)-S(1)#2 | 91.38(4)  |
| N(1)-Ni(1)-S(1)#2 | 168.20(4) | S(1)-Ni(1)-S(1)#2   | 84.62(2)  |
| C(1)-S(1)-Ni(1)   | 104.35(5) | N(1)-P(1)-C(1)      | 107.16(7) |
| N(1)-P(1)-C(8)    | 111.73(7) | C(1)-P(1)-C(8)      | 111.47(8) |
| N(1)-P(1)-C(2)    | 113.17(8) | C(1)-P(1)-C(2)      | 107.27(8) |
| C(8)-P(1)-C(2)    | 106.02(7) | C(14)-N(1)-P(1)     | 119.4(1)  |
| C(14)-N(1)-Ni(1)  | 122.2(2)  | P(1)-N(1)-Ni(1)     | 115.35(8) |
| P(1)-C(1)-S(1)    | 103.46(8) | P(1)-C(1)-H(1A)     | 111.1     |
| S(1)-C(1)-H(1A)   | 111.1     | P(1)-C(1)-H(1B)     | 111.1     |
| S(1)-C(1)-H(1B)   | 111.1     | H(1A)-C(1)-H(1B)    | 109.0     |
| C(3)-C(2)-C(7)    | 119.5(2)  | C(3)-C(2)-P(1)      | 119.2(1)  |
| C(7)-C(2)-P(1)    | 121.2(1)  | C(2)-C(3)-C(4)      | 119.7(2)  |
| C(2)-C(3)-H(3)    | 120.2     | C(4)-C(3)-H(3)      | 120.2     |
| C(5)-C(4)-C(3)    | 120.6(2)  | C(5)-C(4)-H(4)      | 119.7     |
| C(3)-C(4)-H(4)    | 119.7     | C(6)-C(5)-C(4)      | 120.0(2)  |
| C(6)-C(5)-H(5)    | 120.0     | C(4)-C(5)-H(5)      | 120.0     |
| C(5)-C(6)-C(7)    | 120.3(2)  | C(5)-C(6)-H(6)      | 119.9     |
| C(7)-C(6)-H(6)    | 119.9     | C(6)-C(7)-C(2)      | 120.0(2)  |
| C(6)-C(7)-H(7)    | 120.0     | C(2)-C(7)-H(7)      | 120.0     |
| C(9)-C(8)-C(13)   | 119.4(2)  | C(9)-C(8)-P(1)      | 119.3(1)  |
| C(13)-C(8)-P(1)   | 121.1(1)  | C(10)-C(9)-C(8)     | 120.1(2)  |
| C(10)-C(9)-H(9)   | 120.0     | C(8)-C(9)-H(9)      | 120.0     |
| C(9)-C(10)-C(11)  | 120.4(2)  | C(9)-C(10)-H(10)    | 119.8     |
| C(11)-C(10)-H(10) | 119.8     | C(10)-C(11)-C(12)   | 120.2(2)  |
| C(10)-C(11)-H(11) | 119.9     | C(12)-C(11)-H(11)   | 119.9     |
| C(11)-C(12)-C(13) | 119.9(2)  | C(11)-C(12)-H(12)   | 120.0     |
| C(13)-C(12)-H(12) | 120.0     | C(12)-C(13)-C(8)    | 120.0(2)  |
| C(12)-C(13)-H(13) | 120.0     | C(8)-C(13)-H(13)    | 120.0     |
| C(15)-C(14)-C(19) | 118.0(2)  | C(15)-C(14)-N(1)    | 121.7(2)  |
| C(19)-C(14)-N(1)  | 120.3(2)  | C(14)-C(15)-C(16)   | 120.9(2)  |
| C(14)-C(15)-H(15) | 119.6     | C(16)-C(15)-H(15)   | 119.6     |
| C(17)-C(16)-C(15) | 120.5(2)  | C(17)-C(16)-H(16)   | 119.8     |
| C(15)-C(16)-H(16) | 119.8     | C(18)-C(17)-C(16)   | 119.2(2)  |
| C(18)-C(17)-H(17) | 120.4     | C(16)-C(17)-H(17)   | 120.4     |
| C(17)-C(18)-C(19) | 121.0(2)  | C(17)-C(18)-H(18)   | 119.5     |
| C(19)-C(18)-H(18) | 119.5     | C(18)-C(19)-C(14)   | 120.5(2)  |
| C(18)-C(19)-H(19) | 119.8     | C(14)-C(19)-H(19)   | 119.8     |

-----  
 Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z                      2: -x, y, -z+1/2                      3: x+1/2, y+1/2, z  
 4: -x+1/2, y+1/2, -z+1/2    5: -x, -y, -z                      6: x, -y, z-1/2  
 7: -x+1/2, -y+1/2, -z        8: x+1/2, -y+1/2, z-1/2

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pall18

| atom  | U11   | U22   | U33    | U23   | U13   | U12   |
|-------|-------|-------|--------|-------|-------|-------|
| Ni(1) | 18(1) | 20(1) | 23(1)  | 0     | 12(1) | 0     |
| S(1)  | 22(1) | 22(1) | 26(1)  | 1(1)  | 14(1) | 0(1)  |
| P(1)  | 19(1) | 24(1) | 21(1)  | -1(1) | 12(1) | 0(1)  |
| N(1)  | 20(1) | 22(1) | 31(1)  | 4(1)  | 15(1) | 1(1)  |
| C(1)  | 21(1) | 25(1) | 27(1)  | -1(1) | 14(1) | -2(1) |
| C(2)  | 27(1) | 28(1) | 24(1)  | 3(1)  | 15(1) | 9(1)  |
| C(3)  | 41(1) | 45(1) | 28(1)  | -3(1) | 14(1) | 3(1)  |
| C(4)  | 79(2) | 59(2) | 27(1)  | -7(1) | 17(1) | 10(1) |
| C(5)  | 93(2) | 55(2) | 33(1)  | 12(1) | 40(1) | 33(1) |
| C(6)  | 67(2) | 53(2) | 52(1)  | 24(1) | 49(1) | 32(1) |
| C(7)  | 36(1) | 42(1) | 37(1)  | 10(1) | 25(1) | 11(1) |
| C(8)  | 18(1) | 23(1) | 26(1)  | 1(1)  | 13(1) | -1(1) |
| C(9)  | 23(1) | 29(1) | 27(1)  | -2(1) | 14(1) | 1(1)  |
| C(10) | 26(1) | 36(1) | 25(1)  | 2(1)  | 13(1) | 2(1)  |
| C(11) | 25(1) | 31(1) | 34(1)  | 7(1)  | 14(1) | 5(1)  |
| C(12) | 30(1) | 28(1) | 37(1)  | -1(1) | 21(1) | 4(1)  |
| C(13) | 27(1) | 28(1) | 26(1)  | -2(1) | 16(1) | 0(1)  |
| C(14) | 16(1) | 25(1) | 34(1)  | 4(1)  | 13(1) | 1(1)  |
| C(15) | 51(1) | 28(1) | 70(2)  | 3(1)  | 46(1) | 4(1)  |
| C(16) | 59(2) | 27(1) | 120(2) | 20(1) | 63(2) | 12(1) |
| C(17) | 37(1) | 57(2) | 87(2)  | 46(2) | 35(1) | 16(1) |
| C(18) | 41(1) | 73(2) | 36(1)  | 25(1) | 14(1) | 1(1)  |
| C(19) | 32(1) | 42(1) | 28(1)  | 4(1)  | 11(1) | -4(1) |

The anisotropic displacement factor exponent takes the form  

$$\frac{1}{2} \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pall18

| atom  | x    | y    | z     | U(eq) |
|-------|------|------|-------|-------|
| H(1A) | 3430 | 2523 | 3425  | 29    |
| H(1B) | 3192 | 2369 | 4589  | 29    |
| H(3)  | 850  | 1216 | 649   | 48    |
| H(4)  | 647  | 1169 | -1409 | 72    |
| H(5)  | 2050 | 1605 | -1808 | 68    |
| H(6)  | 3678 | 2077 | -157  | 59    |
| H(7)  | 3894 | 2136 | 1904  | 42    |
| H(9)  | 4212 | 1570 | 5835  | 31    |
| H(10) | 5845 | 1008 | 7169  | 35    |
| H(11) | 6515 | 385  | 6246  | 37    |
| H(12) | 5583 | 334  | 3974  | 36    |
| H(13) | 3941 | 895  | 2619  | 31    |
| H(15) | 1427 | 501  | 2628  | 52    |
| H(16) | 1599 | -212 | 3914  | 73    |
| H(17) | 1648 | -95  | 5873  | 71    |
| H(18) | 1575 | 737  | 6564  | 64    |
| H(19) | 1465 | 1456 | 5328  | 43    |

## Chapter 2

## Complex 24a

Table 1. Crystal data for pa209

|   |  |
|---|--|
| Compound                                    | pa209  |
| Molecular formula                           | C <sub>30</sub> H <sub>39</sub> Br <sub>2</sub> LiNNiO <sub>3</sub> P <sub>4</sub> C <sub>4</sub> H <sub>8</sub> O |
| Molecular weight                            | 790.17   |
| Crystal habit                               | Blue Block   |
| Crystal dimensions(mm)                      | 0.28x0.20x0.18   |
| Crystal system                              | monoclinic   |
| Space group                                 | P2 <sub>1</sub> /c   |
| a(Å)  | 9.169(1)   |
| b(Å)  | 23.772(1)  |
| c(Å)  | 18.710(1)  |
| α(°)  | 90.00  |
| β(°)  | 118.751(3)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 3575.4(5)  |
| Z   | 4  |
| d(g·cm <sup>-3</sup> )                      | 1.468  |
| F(000)                                      | 1624   |
| μ(cm <sup>-1</sup> )                        | 2.859  |
| Absorption corrections                      | multi-scan ; 0.5016 min, 0.6272 max  |
| Diffractometer                              | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 27.48  |
| HKL ranges                                  | -9 11 ; -30 30 ; -24 22  |
| Reflections measured                        | 19718  |
| Unique data                                 | 8125   |
| Rint  | 0.0338   |
| Reflections used                            | 5770   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 400  |
| Reflections / parameter                     | 14   |
| wR2   | 0.1014   |
| R1  | 0.0389   |
| Weights a, b                                | 0.0467 ; 0.3463  |
| GoF   | 1.041  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.989(0.075) / -0.554(0.075)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa209

| atom  | x         | y        | z       | U(eq)  |
|-------|-----------|----------|---------|--------|
| Br(1) | -7289(1)  | -2595(1) | 2740(1) | 42(1)  |
| Br(2) | -3219(1)  | -2283(1) | 2708(1) | 43(1)  |
| Ni(1) | -5837(1)  | -1875(1) | 2382(1) | 31(1)  |
| P(1)  | -7228(1)  | -723(1)  | 1708(1) | 25(1)  |
| O(1)  | -7473(2)  | -1930(1) | 1228(1) | 33(1)  |
| O(2)  | -8232(3)  | -3237(1) | 703(1)  | 46(1)  |
| O(3)  | -11016(3) | -2546(1) | 692(1)  | 42(1)  |
| N(1)  | -5864(3)  | -1049(1) | 2498(1) | 26(1)  |
| C(1)  | -7465(3)  | -1586(1) | 667(2)  | 28(1)  |
| C(2)  | -7654(4)  | -1797(1) | -70(2)  | 33(1)  |
| C(3)  | -7656(4)  | -1442(1) | -654(2) | 37(1)  |
| C(4)  | -7476(4)  | -867(1)  | -521(2) | 35(1)  |
| C(5)  | -7313(3)  | -649(1)  | 195(2)  | 30(1)  |
| C(6)  | -7298(3)  | -998(1)  | 801(2)  | 25(1)  |
| C(7)  | -6894(3)  | 27(1)    | 1685(2) | 27(1)  |
| C(8)  | -8048(4)  | 426(1)   | 1634(2) | 34(1)  |
| C(9)  | -7703(4)  | 998(1)   | 1643(2) | 41(1)  |
| C(10) | -6228(4)  | 1176(1)  | 1701(2) | 38(1)  |
| C(11) | -5068(4)  | 781(1)   | 1745(2) | 35(1)  |
| C(12) | -5396(4)  | 213(1)   | 1734(2) | 30(1)  |
| C(13) | -9328(3)  | -809(1)  | 1562(2) | 27(1)  |
| C(14) | -9548(4)  | -1048(1) | 2186(2) | 33(1)  |
| C(15) | -11121(4) | -1117(1) | 2093(2) | 41(1)  |
| C(16) | -12497(4) | -949(1)  | 1380(2) | 40(1)  |
| C(17) | -12301(4) | -719(1)  | 761(2)  | 42(1)  |
| C(18) | -10717(4) | -653(1)  | 845(2)  | 36(1)  |
| C(19) | -4859(4)  | -824(1)  | 3357(2) | 30(1)  |
| C(20) | -3143(4)  | -657(1)  | 3496(2) | 43(1)  |
| C(21) | -5671(4)  | -329(1)  | 3555(2) | 46(1)  |
| C(22) | -4656(4)  | -1305(1) | 3942(2) | 40(1)  |
| C(23) | -9304(5)  | -3419(2) | -119(2) | 61(1)  |
| C(24) | -8171(6)  | -3637(2) | -419(3) | 86(2)  |
| C(25) | -6776(6)  | -3889(2) | 334(3)  | 72(1)  |
| C(26) | -6649(5)  | -3514(2) | 1010(2) | 60(1)  |
| C(27) | -11904(4) | -2182(2) | 1(2)    | 52(1)  |
| C(28) | -13654(4) | -2128(2) | -131(2) | 50(1)  |
| C(29) | -13653(4) | -2466(2) | 557(2)  | 50(1)  |
| C(30) | -11846(4) | -2507(1) | 1178(2) | 44(1)  |
| Li(1) | -8641(7)  | -2594(2) | 1198(3) | 38(1)  |
| O(4)  | -50(6)    | -4011(2) | 1990(3) | 149(2) |
| C(31) | -1730(7)  | -4048(2) | 1245(3) | 117(2) |
| C(32) | -1898(6)  | -4503(2) | 770(2)  | 69(1)  |
| C(33) | -543(8)   | -4778(3) | 1097(4) | 128(2) |
| C(34) | 510(7)    | -4624(2) | 1996(4) | 127(2) |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa209

|              |           |              |          |
|--------------|-----------|--------------|----------|
| Br(1)-Ni(1)  | 2.4526(5) | Br(1)-Li(1)  | 2.535(5) |
| Br(2)-Ni(1)  | 2.3799(5) | Ni(1)-O(1)   | 1.954(2) |
| Ni(1)-N(1)   | 1.977(2)  | Ni(1)-Li(1)  | 2.994(5) |
| P(1)-N(1)    | 1.602(2)  | P(1)-C(6)    | 1.792(3) |
| P(1)-C(7)    | 1.813(3)  | P(1)-C(13)   | 1.822(3) |
| O(1)-C(1)    | 1.332(3)  | O(1)-Li(1)   | 1.893(5) |
| O(2)-C(23)   | 1.437(4)  | O(2)-C(26)   | 1.439(4) |
| O(2)-Li(1)   | 1.915(6)  | O(3)-C(27)   | 1.439(4) |
| O(3)-C(30)   | 1.441(4)  | O(3)-Li(1)   | 1.915(6) |
| N(1)-C(19)   | 1.515(3)  | C(1)-C(2)    | 1.398(4) |
| C(1)-C(6)    | 1.415(4)  | C(2)-C(3)    | 1.381(4) |
| C(2)-H(2)    | 0.9500    | C(3)-C(4)    | 1.384(4) |
| C(3)-H(3)    | 0.9500    | C(4)-C(5)    | 1.376(4) |
| C(4)-H(4)    | 0.9500    | C(5)-C(6)    | 1.400(4) |
| C(5)-H(5)    | 0.9500    | C(7)-C(8)    | 1.389(4) |
| C(7)-C(12)   | 1.403(4)  | C(8)-C(9)    | 1.396(4) |
| C(8)-H(8)    | 0.9500    | C(9)-C(10)   | 1.371(4) |
| C(9)-H(9)    | 0.9500    | C(10)-C(11)  | 1.392(4) |
| C(10)-H(10)  | 0.9500    | C(11)-C(12)  | 1.382(4) |
| C(11)-H(11)  | 0.9500    | C(12)-H(12)  | 0.9500   |
| C(13)-C(18)  | 1.384(4)  | C(13)-C(14)  | 1.398(4) |
| C(14)-C(15)  | 1.377(4)  | C(14)-H(14)  | 0.9500   |
| C(15)-C(16)  | 1.382(5)  | C(15)-H(15)  | 0.9500   |
| C(16)-C(17)  | 1.369(5)  | C(16)-H(16)  | 0.9500   |
| C(17)-C(18)  | 1.394(4)  | C(17)-H(17)  | 0.9500   |
| C(18)-H(18)  | 0.9500    | C(19)-C(20)  | 1.519(4) |
| C(19)-C(21)  | 1.531(4)  | C(19)-C(22)  | 1.533(4) |
| C(20)-H(20A) | 0.9800    | C(20)-H(20B) | 0.9800   |
| C(20)-H(20C) | 0.9800    | C(21)-H(21A) | 0.9800   |
| C(21)-H(21B) | 0.9800    | C(21)-H(21C) | 0.9800   |
| C(22)-H(22A) | 0.9800    | C(22)-H(22B) | 0.9800   |
| C(22)-H(22C) | 0.9800    | C(23)-C(24)  | 1.491(5) |
| C(23)-H(23A) | 0.9900    | C(23)-H(23B) | 0.9900   |
| C(24)-C(25)  | 1.499(6)  | C(24)-H(24A) | 0.9900   |
| C(24)-H(24B) | 0.9900    | C(25)-C(26)  | 1.504(5) |
| C(25)-H(25A) | 0.9900    | C(25)-H(25B) | 0.9900   |
| C(26)-H(26A) | 0.9900    | C(26)-H(26B) | 0.9900   |
| C(27)-C(28)  | 1.507(5)  | C(27)-H(27A) | 0.9900   |
| C(27)-H(27B) | 0.9900    | C(28)-C(29)  | 1.516(5) |
| C(28)-H(28A) | 0.9900    | C(28)-H(28B) | 0.9900   |
| C(29)-C(30)  | 1.500(5)  | C(29)-H(29A) | 0.9900   |
| C(29)-H(29B) | 0.9900    | C(30)-H(30A) | 0.9900   |
| C(30)-H(30B) | 0.9900    | O(4)-C(31)   | 1.503(6) |
| O(4)-C(34)   | 1.544(7)  | C(31)-C(32)  | 1.362(6) |
| C(31)-H(31A) | 0.9900    | C(31)-H(31B) | 0.9900   |
| C(32)-C(33)  | 1.271(7)  | C(32)-H(32A) | 0.9900   |
| C(32)-H(32B) | 0.9900    | C(33)-C(34)  | 1.528(8) |
| C(33)-H(33A) | 0.9900    | C(33)-H(33B) | 0.9900   |
| C(34)-H(34A) | 0.9900    | C(34)-H(34B) | 0.9900   |

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| Ni(1)-Br(1)-Li(1) | 73.8(1)   | O(1)-Ni(1)-N(1)   | 98.30(8)  |
| O(1)-Ni(1)-Br(2)  | 113.52(6) | N(1)-Ni(1)-Br(2)  | 116.17(7) |
| O(1)-Ni(1)-Br(1)  | 91.47(6)  | N(1)-Ni(1)-Br(1)  | 128.82(7) |
| Br(2)-Ni(1)-Br(1) | 104.99(2) | O(1)-Ni(1)-Li(1)  | 38.2(1)   |
| N(1)-Ni(1)-Li(1)  | 126.6(1)  | Br(2)-Ni(1)-Li(1) | 111.0(1)  |
| Br(1)-Ni(1)-Li(1) | 54.4(1)   | N(1)-P(1)-C(6)    | 110.7(1)  |
| N(1)-P(1)-C(7)    | 115.6(1)  | C(6)-P(1)-C(7)    | 105.4(1)  |
| N(1)-P(1)-C(13)   | 112.6(1)  | C(6)-P(1)-C(13)   | 105.3(1)  |
| C(7)-P(1)-C(13)   | 106.6(1)  | C(1)-O(1)-Li(1)   | 134.9(2)  |
| C(1)-O(1)-Ni(1)   | 122.5(2)  | Li(1)-O(1)-Ni(1)  | 102.2(2)  |
| C(23)-O(2)-C(26)  | 109.2(3)  | C(23)-O(2)-Li(1)  | 124.4(3)  |
| C(26)-O(2)-Li(1)  | 124.6(3)  | C(27)-O(3)-C(30)  | 106.6(2)  |
| C(27)-O(3)-Li(1)  | 119.8(3)  | C(30)-O(3)-Li(1)  | 120.8(2)  |
| C(19)-N(1)-P(1)   | 127.9(2)  | C(19)-N(1)-Ni(1)  | 115.7(2)  |
| P(1)-N(1)-Ni(1)   | 115.1(1)  | O(1)-C(1)-C(2)    | 120.8(2)  |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| O(1)-C(1)-C(6)      | 120.6(2) | C(2)-C(1)-C(6)      | 118.6(3) |
| C(3)-C(2)-C(1)      | 121.0(3) | C(3)-C(2)-H(2)      | 119.5    |
| C(1)-C(2)-H(2)      | 119.5    | C(2)-C(3)-C(4)      | 120.4(3) |
| C(2)-C(3)-H(3)      | 119.8    | C(4)-C(3)-H(3)      | 119.8    |
| C(5)-C(4)-C(3)      | 119.6(3) | C(5)-C(4)-H(4)      | 120.2    |
| C(3)-C(4)-H(4)      | 120.2    | C(4)-C(5)-C(6)      | 121.3(3) |
| C(4)-C(5)-H(5)      | 119.3    | C(6)-C(5)-H(5)      | 119.3    |
| C(5)-C(6)-C(1)      | 119.0(2) | C(5)-C(6)-P(1)      | 122.2(2) |
| C(1)-C(6)-P(1)      | 118.7(2) | C(8)-C(7)-C(12)     | 118.6(2) |
| C(8)-C(7)-P(1)      | 122.7(2) | C(12)-C(7)-P(1)     | 118.7(2) |
| C(7)-C(8)-C(9)      | 120.3(3) | C(7)-C(8)-H(8)      | 119.9    |
| C(9)-C(8)-H(8)      | 119.9    | C(10)-C(9)-C(8)     | 120.7(3) |
| C(10)-C(9)-H(9)     | 119.6    | C(8)-C(9)-H(9)      | 119.6    |
| C(9)-C(10)-C(11)    | 119.6(3) | C(9)-C(10)-H(10)    | 120.2    |
| C(11)-C(10)-H(10)   | 120.2    | C(12)-C(11)-C(10)   | 120.3(3) |
| C(12)-C(11)-H(11)   | 119.9    | C(10)-C(11)-H(11)   | 119.9    |
| C(11)-C(12)-C(7)    | 120.5(3) | C(11)-C(12)-H(12)   | 119.7    |
| C(7)-C(12)-H(12)    | 119.7    | C(18)-C(13)-C(14)   | 119.0(3) |
| C(18)-C(13)-P(1)    | 121.9(2) | C(14)-C(13)-P(1)    | 119.1(2) |
| C(15)-C(14)-C(13)   | 120.4(3) | C(15)-C(14)-H(14)   | 119.8    |
| C(13)-C(14)-H(14)   | 119.8    | C(14)-C(15)-C(16)   | 120.2(3) |
| C(14)-C(15)-H(15)   | 119.9    | C(16)-C(15)-H(15)   | 119.9    |
| C(17)-C(16)-C(15)   | 120.1(3) | C(17)-C(16)-H(16)   | 120.0    |
| C(15)-C(16)-H(16)   | 120.0    | C(16)-C(17)-C(18)   | 120.3(3) |
| C(16)-C(17)-H(17)   | 119.9    | C(18)-C(17)-H(17)   | 119.9    |
| C(13)-C(18)-C(17)   | 120.1(3) | C(13)-C(18)-H(18)   | 119.9    |
| C(17)-C(18)-H(18)   | 119.9    | N(1)-C(19)-C(20)    | 109.0(2) |
| N(1)-C(19)-C(21)    | 114.2(2) | C(20)-C(19)-C(21)   | 110.0(3) |
| N(1)-C(19)-C(22)    | 107.3(2) | C(20)-C(19)-C(22)   | 108.2(2) |
| C(21)-C(19)-C(22)   | 107.9(2) | C(19)-C(20)-H(20A)  | 109.5    |
| C(19)-C(20)-H(20B)  | 109.5    | H(20A)-C(20)-H(20B) | 109.5    |
| C(19)-C(20)-H(20C)  | 109.5    | H(20A)-C(20)-H(20C) | 109.5    |
| H(20B)-C(20)-H(20C) | 109.5    | C(19)-C(21)-H(21A)  | 109.5    |
| C(19)-C(21)-H(21B)  | 109.5    | H(21A)-C(21)-H(21B) | 109.5    |
| C(19)-C(21)-H(21C)  | 109.5    | H(21A)-C(21)-H(21C) | 109.5    |
| H(21B)-C(21)-H(21C) | 109.5    | C(19)-C(22)-H(22A)  | 109.5    |
| C(19)-C(22)-H(22B)  | 109.5    | H(22A)-C(22)-H(22B) | 109.5    |
| C(19)-C(22)-H(22C)  | 109.5    | H(22A)-C(22)-H(22C) | 109.5    |
| H(22B)-C(22)-H(22C) | 109.5    | O(2)-C(23)-C(24)    | 105.4(3) |
| O(2)-C(23)-H(23A)   | 110.7    | C(24)-C(23)-H(23A)  | 110.7    |
| O(2)-C(23)-H(23B)   | 110.7    | C(24)-C(23)-H(23B)  | 110.7    |
| H(23A)-C(23)-H(23B) | 108.8    | C(23)-C(24)-C(25)   | 102.6(3) |
| C(23)-C(24)-H(24A)  | 111.2    | C(25)-C(24)-H(24A)  | 111.2    |
| C(23)-C(24)-H(24B)  | 111.2    | C(25)-C(24)-H(24B)  | 111.2    |
| H(24A)-C(24)-H(24B) | 109.2    | C(24)-C(25)-C(26)   | 103.9(3) |
| C(24)-C(25)-H(25A)  | 111.0    | C(26)-C(25)-H(25A)  | 111.0    |
| C(24)-C(25)-H(25B)  | 111.0    | C(26)-C(25)-H(25B)  | 111.0    |
| H(25A)-C(25)-H(25B) | 109.0    | O(2)-C(26)-C(25)    | 106.3(3) |
| O(2)-C(26)-H(26A)   | 110.5    | C(25)-C(26)-H(26A)  | 110.5    |
| O(2)-C(26)-H(26B)   | 110.5    | C(25)-C(26)-H(26B)  | 110.5    |
| H(26A)-C(26)-H(26B) | 108.7    | O(3)-C(27)-C(28)    | 107.2(3) |
| O(3)-C(27)-H(27A)   | 110.3    | C(28)-C(27)-H(27A)  | 110.3    |
| O(3)-C(27)-H(27B)   | 110.3    | C(28)-C(27)-H(27B)  | 110.3    |
| H(27A)-C(27)-H(27B) | 108.5    | C(27)-C(28)-C(29)   | 104.5(3) |
| C(27)-C(28)-H(28A)  | 110.9    | C(29)-C(28)-H(28A)  | 110.9    |
| C(27)-C(28)-H(28B)  | 110.9    | C(29)-C(28)-H(28B)  | 110.9    |
| H(28A)-C(28)-H(28B) | 108.9    | C(30)-C(29)-C(28)   | 104.0(3) |
| C(30)-C(29)-H(29A)  | 111.0    | C(28)-C(29)-H(29A)  | 111.0    |
| C(30)-C(29)-H(29B)  | 111.0    | C(28)-C(29)-H(29B)  | 111.0    |
| H(29A)-C(29)-H(29B) | 109.0    | O(3)-C(30)-C(29)    | 103.8(3) |
| O(3)-C(30)-H(30A)   | 111.0    | C(29)-C(30)-H(30A)  | 111.0    |
| O(3)-C(30)-H(30B)   | 111.0    | C(29)-C(30)-H(30B)  | 111.0    |
| H(30A)-C(30)-H(30B) | 109.0    | O(1)-Li(1)-O(3)     | 117.3(3) |
| O(1)-Li(1)-O(2)     | 116.1(3) | O(3)-Li(1)-O(2)     | 104.4(3) |
| O(1)-Li(1)-Br(1)    | 90.4(2)  | O(3)-Li(1)-Br(1)    | 112.3(2) |
| O(2)-Li(1)-Br(1)    | 116.5(2) | O(1)-Li(1)-Ni(1)    | 39.6(1)  |
| O(2)-Li(1)-Ni(1)    | 134.4(2) | O(2)-Li(1)-Ni(1)    | 121.0(2) |
| Br(1)-Li(1)-Ni(1)   | 51.9(1)  | C(31)-O(4)-C(34)    | 98.1(4)  |

# Appendix 1. Crystallographic data

|                    |          |                     |       |
|--------------------|----------|---------------------|-------|
| C(32)-C(31)-O(4)   | 113.3(5) | C(32)-C(31)-H(31A)  | 108.9 |
| O(4)-C(31)-H(31A)  | 108.9    | C(32)-C(31)-H(31B)  | 108.9 |
| O(4)-C(31)-H(31B)  | 108.9    | H(31A)-C(31)-H(31B) | 107.7 |
| C(33)-C(32)-C(31)  | 108.5(4) | C(33)-C(32)-H(32A)  | 110.0 |
| C(31)-C(32)-H(32A) | 110.0    | C(33)-C(32)-H(32B)  | 110.0 |
| C(31)-C(32)-H(32B) | 110.0    | H(32A)-C(32)-H(32B) | 108.4 |
| C(32)-C(33)-C(34)  | 111.1(5) | C(32)-C(33)-H(33A)  | 109.4 |
| C(34)-C(33)-H(33A) | 109.4    | C(32)-C(33)-H(33B)  | 109.4 |
| C(34)-C(33)-H(33B) | 109.4    | H(33A)-C(33)-H(33B) | 108.0 |
| C(33)-C(34)-O(4)   | 100.8(4) | C(33)-C(34)-H(34A)  | 111.6 |
| O(4)-C(34)-H(34A)  | 111.6    | C(33)-C(34)-H(34B)  | 111.6 |
| O(4)-C(34)-H(34B)  | 111.6    | H(34A)-C(34)-H(34B) | 109.4 |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa209

| atom  | U11    | U22    | U33    | U23    | U13    | U12    |
|-------|--------|--------|--------|--------|--------|--------|
| Br(1) | 35(1)  | 52(1)  | 30(1)  | 11(1)  | 9(1)   | -8(1)  |
| Br(2) | 40(1)  | 44(1)  | 49(1)  | 5(1)   | 26(1)  | 3(1)   |
| Ni(1) | 33(1)  | 27(1)  | 26(1)  | 4(1)   | 9(1)   | 0(1)   |
| P(1)  | 23(1)  | 25(1)  | 25(1)  | 1(1)   | 12(1)  | 1(1)   |
| O(1)  | 40(1)  | 28(1)  | 24(1)  | 3(1)   | 10(1)  | -3(1)  |
| O(2)  | 38(1)  | 45(1)  | 43(1)  | -12(1) | 10(1)  | 0(1)   |
| O(3)  | 34(1)  | 53(1)  | 34(1)  | 2(1)   | 11(1)  | 6(1)   |
| N(1)  | 26(1)  | 26(1)  | 22(1)  | -1(1)  | 9(1)   | 0(1)   |
| C(1)  | 23(1)  | 30(2)  | 28(2)  | 2(1)   | 9(1)   | 2(1)   |
| C(2)  | 35(2)  | 30(2)  | 28(2)  | -3(1)  | 11(1)  | 6(1)   |
| C(3)  | 39(2)  | 46(2)  | 25(2)  | -1(1)  | 15(1)  | 12(2)  |
| C(4)  | 37(2)  | 44(2)  | 28(2)  | 9(1)   | 18(1)  | 7(1)   |
| C(5)  | 27(2)  | 32(2)  | 28(2)  | 4(1)   | 11(1)  | 4(1)   |
| C(6)  | 21(1)  | 28(1)  | 24(2)  | 3(1)   | 9(1)   | 4(1)   |
| C(7)  | 30(2)  | 27(1)  | 24(2)  | -1(1)  | 14(1)  | 0(1)   |
| C(8)  | 31(2)  | 33(2)  | 39(2)  | 2(1)   | 18(1)  | 2(1)   |
| C(9)  | 42(2)  | 28(2)  | 53(2)  | 3(2)   | 22(2)  | 5(1)   |
| C(10) | 46(2)  | 29(2)  | 35(2)  | 0(1)   | 17(2)  | -5(1)  |
| C(11) | 37(2)  | 35(2)  | 31(2)  | 1(1)   | 16(1)  | -7(1)  |
| C(12) | 31(2)  | 30(1)  | 30(2)  | 1(1)   | 15(1)  | 1(1)   |
| C(13) | 28(2)  | 23(1)  | 31(2)  | 0(1)   | 16(1)  | 2(1)   |
| C(14) | 33(2)  | 37(2)  | 29(2)  | -2(1)  | 16(1)  | -3(1)  |
| C(15) | 44(2)  | 47(2)  | 44(2)  | -2(2)  | 30(2)  | -8(2)  |
| C(16) | 31(2)  | 34(2)  | 63(2)  | -7(2)  | 30(2)  | -1(1)  |
| C(17) | 25(2)  | 36(2)  | 57(2)  | 6(2)   | 15(2)  | 1(1)   |
| C(18) | 32(2)  | 33(2)  | 41(2)  | 10(2)  | 16(2)  | 3(1)   |
| C(19) | 31(2)  | 33(2)  | 21(2)  | 0(1)   | 8(1)   | -2(1)  |
| C(20) | 33(2)  | 52(2)  | 34(2)  | 1(2)   | 9(2)   | -8(2)  |
| C(21) | 51(2)  | 47(2)  | 31(2)  | -11(2) | 12(2)  | 3(2)   |
| C(22) | 49(2)  | 43(2)  | 25(2)  | -2(1)  | 16(2)  | -6(2)  |
| C(23) | 51(2)  | 69(2)  | 44(2)  | -22(2) | 8(2)   | 0(2)   |
| C(24) | 93(4)  | 106(4) | 58(3)  | -8(3)  | 35(3)  | 33(3)  |
| C(25) | 79(3)  | 79(3)  | 65(3)  | 1(2)   | 39(3)  | 26(2)  |
| C(26) | 41(2)  | 69(2)  | 57(2)  | -1(2)  | 15(2)  | 9(2)   |
| C(27) | 49(2)  | 65(2)  | 38(2)  | 7(2)   | 16(2)  | 12(2)  |
| C(28) | 41(2)  | 51(2)  | 40(2)  | -8(2)  | 5(2)   | 2(2)   |
| C(29) | 35(2)  | 59(2)  | 50(2)  | -5(2)  | 15(2)  | 2(2)   |
| C(30) | 42(2)  | 45(2)  | 44(2)  | 1(2)   | 20(2)  | 4(2)   |
| Li(1) | 37(3)  | 38(3)  | 34(3)  | -2(2)  | 12(2)  | -3(2)  |
| O(4)  | 117(4) | 157(4) | 148(4) | -6(3)  | 44(3)  | 12(3)  |
| C(31) | 105(4) | 78(3)  | 81(4)  | -12(3) | -25(3) | 23(3)  |
| C(32) | 80(3)  | 64(3)  | 38(2)  | -5(2)  | 8(2)   | -16(2) |
| C(33) | 81(4)  | 145(6) | 135(6) | -81(5) | 34(4)  | -21(4) |
| C(34) | 65(3)  | 111(5) | 161(6) | 49(4)  | 20(4)  | 52(3)  |

The anisotropic displacement factor exponent takes the form  

$$\frac{1}{2} \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

Table 5. Hydrogen Coordinates (Å x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa209

| atom   | x           | y          | z         | U(eq) |
|--------|-------------|------------|-----------|-------|
| H(2)   | -7783       | -2190      | -170.0000 | 39    |
| H(3)   | -7781.9995  | -1593      | -1151     | 44    |
| H(4)   | -7465       | -624       | -922.0001 | 42    |
| H(5)   | -7208       | -254       | 280       | 36    |
| H(8)   | -9077       | 308        | 1592      | 41    |
| H(9)   | -8500       | 1267       | 1609      | 50    |
| H(10)  | -6000       | 1567       | 1712      | 46    |
| H(11)  | -4047       | 903        | 1782      | 42    |
| H(12)  | -4601       | -54        | 1759      | 36    |
| H(14)  | -8606       | -1162      | 2678      | 39    |
| H(15)  | -11260.9990 | -1282      | 2518      | 49    |
| H(16)  | -13580      | -993       | 1320      | 48    |
| H(17)  | -13250      | -604       | 272       | 50    |
| H(18)  | -10589      | -500       | 409       | 43    |
| H(20A) | -2643       | -974       | 3356      | 64    |
| H(20B) | -2439       | -557       | 4071      | 64    |
| H(20C) | -3239.0002  | -333       | 3153      | 64    |
| H(21A) | -5695.0005  | 0          | 3233      | 69    |
| H(21B) | -5029       | -239       | 4137      | 69    |
| H(21C) | -6810       | -429       | 3422      | 69    |
| H(22A) | -5756.0005  | -1437      | 3836      | 60    |
| H(22B) | -4032       | -1172      | 4506      | 60    |
| H(22C) | -4052       | -1615.9999 | 3859      | 60    |
| H(23A) | -9976       | -3101      | -460      | 73    |
| H(23B) | -10065      | -3719      | -130      | 73    |
| H(24A) | -7768       | -3328.9998 | -635      | 103   |
| H(24B) | -8731       | -3924      | -849      | 103   |
| H(25A) | -5727       | -3886      | 305       | 87    |
| H(25B) | -7037       | -4280      | 413       | 87    |
| H(26A) | -6408       | -3740.0002 | 1499      | 72    |
| H(26B) | -5748       | -3235      | 1158      | 72    |
| H(27A) | -11913      | -2343      | -488      | 63    |
| H(27B) | -11364      | -1808      | 109       | 63    |
| H(28A) | -14466      | -2284      | -666.9999 | 60    |
| H(28B) | -13936      | -1729.0001 | -103      | 60    |
| H(29A) | -14290      | -2270      | 785       | 60    |
| H(29B) | -14138      | -2843.9998 | 366       | 60    |
| H(30A) | -11478      | -2169      | 1530      | 53    |
| H(30B) | -11629      | -2845      | 1523      | 53    |
| H(31A) | -2594       | -4064      | 1418      | 141   |
| H(31B) | -1922       | -3702      | 917       | 141   |
| H(32A) | -2822       | -4743      | 721       | 83    |
| H(32B) | -2152       | -4379      | 217       | 83    |
| H(33A) | 93          | -4698      | 806       | 154   |
| H(33B) | -791        | -5186      | 1049      | 154   |
| H(34A) | 1715        | -4647      | 2174      | 152   |
| H(34B) | 250         | -4866      | 2350      | 152   |

**Complex 24b'**

Table 1. Crystal data for pa278

|   |   |
|---|---|
| Compound                                    | pa278   |
| Molecular formula                           | C <sub>35</sub> H <sub>49</sub> Br <sub>1.70</sub> Cl <sub>0.31</sub> LiNNiO <sub>4</sub> P |
| Molecular weight                            | 790.63  |
| Crystal habit                               | Blue Block  |
| Crystal dimensions(mm)                      | 0.28x0.14x0.10  |
| Crystal system                              | monoclinic  |
| Space group                                 | P2 <sub>1</sub> /c  |
| a(Å)  | 9.793(1)  |
| b(Å)  | 17.973(1)   |
| c(Å)  | 22.786(1)   |
| α(°)  | 90.00   |
| β(°)  | 114.646(3)  |
| γ(°)  | 90.00   |
| V(Å <sup>3</sup> )                          | 3645.2(5)   |
| Z   | 4   |
| d(g·cm <sup>-3</sup> )                      | 1.441   |
| F(000)                                      | 1634  |
| μ(cm <sup>-1</sup> )                        | 2.493   |
| Absorption corrections                      | multi-scan ; 0.5419 min, 0.7886 max   |
| Diffractionmeter                            | KappaCCD  |
| X-ray source                                | MoKα  |
| λ(Å)  | 0.71069   |
| Monochromator                               | graphite  |
| T (K)                                       | 150.0(1)  |
| Scan mode                                   | phi and omega scans   |
| Maximum θ                                   | 27.46   |
| HKL ranges                                  | -12 8 ; -17 23 ; -19 29   |
| Reflections measured                        | 18906   |
| Unique data                                 | 8073  |
| Rint  | 0.0453  |
| Reflections used                            | 6116  |
| Criterion                                   | I > 2σ(I)   |
| Refinement type                             | Fsqd  |
| Hydrogen atoms                              | constr  |
| Parameters refined                          | 417   |
| Reflections / parameter                     | 14  |
| wR2   | 0.1001  |
| R1  | 0.0500  |
| Weights a, b                                | 0.0262 ; 7.8434   |
| GoF   | 1.091   |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.584(0.083) / -0.427(0.083)  |



## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa278

| atom   | x        | y         | z         | U(eq) |
|--------|----------|-----------|-----------|-------|
| Br(1A) | -1094(1) | -2664(1)  | -2592(1)  | 43(1) |
| Cl(1B) | -660(30) | -2560(10) | -2490(10) | 43(1) |
| Br(2A) | 3187(2)  | -1972(1)  | -2420(1)  | 41(1) |
| Cl(2B) | 3350(20) | -2123(8)  | -2433(8)  | 41(1) |
| Ni(1)  | 993(1)   | -2724(1)  | -2885(1)  | 26(1) |
| P(1)   | 413(1)   | -3491(1)  | -4150(1)  | 21(1) |
| O(1)   | 1591(3)  | -3781(1)  | -2727(1)  | 28(1) |
| O(2)   | 3563(3)  | -5082(2)  | -1660(1)  | 47(1) |
| O(3)   | 3147(3)  | -3621(1)  | -1157(1)  | 36(1) |
| O(4)   | 5224(3)  | -3795(2)  | -1905(1)  | 51(1) |
| N(1)   | 324(3)   | -2703(1)  | -3834(1)  | 23(1) |
| C(1)   | -152(4)  | -4224(2)  | -3765(2)  | 23(1) |
| C(2)   | 525(4)   | -4264(2)  | -3080(2)  | 27(1) |
| C(3)   | 52(4)    | -4835(2)  | -2787(2)  | 33(1) |
| C(4)   | -1022(4) | -5345(2)  | -3148(2)  | 34(1) |
| C(5)   | -1667(4) | -5306(2)  | -3818(2)  | 31(1) |
| C(6)   | -1224(4) | -4753(2)  | -4122(2)  | 27(1) |
| C(7)   | -830(4)  | -3519(2)  | -5006(2)  | 24(1) |
| C(8)   | -2383(4) | -3447(2)  | -5193(2)  | 29(1) |
| C(9)   | -3352(4) | -3432(2)  | -5841(2)  | 35(1) |
| C(10)  | -2797(5) | -3468(2)  | -6308(2)  | 39(1) |
| C(11)  | -1277(5) | -3541(2)  | -6131(2)  | 38(1) |
| C(12)  | -283(4)  | -3572(2)  | -5477(2)  | 29(1) |
| C(13)  | 2258(4)  | -3717(2)  | -4107(2)  | 27(1) |
| C(14)  | 2657(4)  | -4449(2)  | -4182(2)  | 34(1) |
| C(15)  | 4063(5)  | -4593(2)  | -4168(2)  | 43(1) |
| C(16)  | 5075(4)  | -4026(2)  | -4085(2)  | 39(1) |
| C(17)  | 4698(4)  | -3309(2)  | -4007(2)  | 38(1) |
| C(18)  | 3303(4)  | -3152(2)  | -4016(2)  | 34(1) |
| C(19)  | 471(4)   | -2015(2)  | -4168(2)  | 26(1) |
| C(20)  | -677(4)  | -1402(2)  | -4238(2)  | 28(1) |
| C(21)  | -2270(4) | -1702(2)  | -4567(2)  | 38(1) |
| C(22)  | -417(4)  | -1059(2)  | -3589(2)  | 34(1) |
| C(23)  | -435(5)  | -799(2)   | -4663(2)  | 39(1) |
| C(24)  | 3581(6)  | -5678(2)  | -2086(2)  | 59(1) |
| C(25)  | 4435(7)  | -6292(3)  | -1660(3)  | 80(2) |
| C(26)  | 5390(8)  | -5956(4)  | -1052(3)  | 88(2) |
| C(27)  | 4601(5)  | -5254(2)  | -1015(2)  | 49(1) |
| C(28)  | 1779(5)  | -3731(2)  | -1080(2)  | 44(1) |
| C(29)  | 1574(5)  | -3068(2)  | -722(2)   | 44(1) |
| C(30)  | 2572(5)  | -2478(2)  | -829(2)   | 43(1) |
| C(31)  | 3831(5)  | -2938(2)  | -846(2)   | 41(1) |
| C(32)  | 6692(5)  | -3721(3)  | -1415(2)  | 55(1) |
| C(33)  | 7664(6)  | -4190(4)  | -1623(3)  | 79(2) |
| C(34)  | 6783(6)  | -4323(3)  | -2330(2)  | 57(1) |
| C(35)  | 5420(6)  | -3833(4)  | -2492(2)  | 70(2) |
| Li(1)  | 3286(7)  | -4010(3)  | -1928(3)  | 33(1) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles (deg) for pa278

|              |           |              |          |
|--------------|-----------|--------------|----------|
| Br(1A)-Ni(1) | 2.4020(8) | Cl(1B)-Ni(1) | 2.17(2)  |
| Br(2A)-Ni(1) | 2.381(2)  | Cl(2B)-Ni(1) | 2.36(2)  |
| Ni(1)-O(1)   | 1.975(2)  | Ni(1)-N(1)   | 1.981(3) |
| P(1)-N(1)    | 1.607(3)  | P(1)-C(1)    | 1.794(3) |
| P(1)-C(13)   | 1.815(4)  | P(1)-C(7)    | 1.820(3) |
| O(1)-C(2)    | 1.338(4)  | O(1)-Li(1)   | 1.930(7) |
| O(2)-C(27)   | 1.429(5)  | O(2)-C(24)   | 1.451(5) |
| O(2)-Li(1)   | 2.006(7)  | O(3)-C(28)   | 1.436(5) |
| O(3)-C(31)   | 1.437(4)  | O(3)-Li(1)   | 1.945(7) |
| O(4)-C(32)   | 1.411(5)  | O(4)-C(35)   | 1.431(5) |
| O(4)-Li(1)   | 1.917(7)  | N(1)-C(19)   | 1.490(4) |
| C(1)-C(6)    | 1.398(5)  | C(1)-C(2)    | 1.419(5) |
| C(2)-C(3)    | 1.405(5)  | C(3)-C(4)    | 1.379(5) |
| C(3)-H(3)    | 0.9500    | C(4)-C(5)    | 1.390(5) |
| C(4)-H(4)    | 0.9500    | C(5)-C(6)    | 1.382(5) |
| C(5)-H(5)    | 0.9500    | C(6)-H(6)    | 0.9500   |
| C(7)-C(12)   | 1.389(5)  | C(7)-C(8)    | 1.403(5) |
| C(8)-C(9)    | 1.382(5)  | C(8)-H(8)    | 0.9500   |
| C(9)-C(10)   | 1.385(6)  | C(9)-H(9)    | 0.9500   |
| C(10)-C(11)  | 1.376(6)  | C(10)-H(10)  | 0.9500   |
| C(11)-C(12)  | 1.401(5)  | C(11)-H(11)  | 0.9500   |
| C(12)-H(12)  | 0.9500    | C(13)-C(18)  | 1.394(5) |
| C(13)-C(14)  | 1.402(5)  | C(14)-C(15)  | 1.388(5) |
| C(14)-H(14)  | 0.9500    | C(15)-C(16)  | 1.379(6) |
| C(15)-H(15)  | 0.9500    | C(16)-C(17)  | 1.372(6) |
| C(16)-H(16)  | 0.9500    | C(17)-C(18)  | 1.388(5) |
| C(17)-H(17)  | 0.9500    | C(18)-H(18)  | 0.9500   |
| C(19)-C(20)  | 1.534(5)  | C(19)-H(19A) | 0.9900   |
| C(19)-H(19B) | 0.9900    | C(20)-C(21)  | 1.520(5) |
| C(20)-C(22)  | 1.524(5)  | C(20)-C(23)  | 1.536(5) |
| C(21)-H(21A) | 0.9800    | C(21)-H(21B) | 0.9800   |
| C(21)-H(21C) | 0.9800    | C(22)-H(22A) | 0.9800   |
| C(22)-H(22B) | 0.9800    | C(22)-H(22C) | 0.9800   |
| C(23)-H(23A) | 0.9800    | C(23)-H(23B) | 0.9800   |
| C(23)-H(23C) | 0.9800    | C(24)-C(25)  | 1.478(7) |
| C(24)-H(24A) | 0.9900    | C(24)-H(24B) | 0.9900   |
| C(25)-C(26)  | 1.441(8)  | C(25)-H(25A) | 0.9900   |
| C(25)-H(25B) | 0.9900    | C(26)-C(27)  | 1.500(7) |
| C(26)-H(26A) | 0.9900    | C(26)-H(26B) | 0.9900   |
| C(27)-H(27A) | 0.9900    | C(27)-H(27B) | 0.9900   |
| C(28)-C(29)  | 1.504(6)  | C(28)-H(28A) | 0.9900   |
| C(28)-H(28B) | 0.9900    | C(29)-C(30)  | 1.528(6) |
| C(29)-H(29A) | 0.9900    | C(29)-H(29B) | 0.9900   |
| C(30)-C(31)  | 1.498(6)  | C(30)-H(30A) | 0.9900   |
| C(30)-H(30B) | 0.9900    | C(31)-H(31A) | 0.9900   |
| C(31)-H(31B) | 0.9900    | C(32)-C(33)  | 1.489(7) |
| C(32)-H(32A) | 0.9900    | C(32)-H(32B) | 0.9900   |
| C(33)-C(34)  | 1.497(7)  | C(33)-H(33A) | 0.9900   |
| C(33)-H(33B) | 0.9900    | C(34)-C(35)  | 1.510(7) |
| C(34)-H(34A) | 0.9900    | C(34)-H(34B) | 0.9900   |
| C(35)-H(35A) | 0.9900    | C(35)-H(35B) | 0.9900   |

|                     |           |                     |           |
|---------------------|-----------|---------------------|-----------|
| O(1)-Ni(1)-N(1)     | 98.9(1)   | O(1)-Ni(1)-Cl(1B)   | 105.9(7)  |
| N(1)-Ni(1)-Cl(1B)   | 119.0(7)  | O(1)-Ni(1)-Cl(2B)   | 101.5(3)  |
| N(1)-Ni(1)-Cl(2B)   | 106.6(4)  | Cl(1B)-Ni(1)-Cl(2B) | 121.0(8)  |
| O(1)-Ni(1)-Br(2A)   | 108.69(8) | N(1)-Ni(1)-Br(2A)   | 107.5(1)  |
| Cl(1B)-Ni(1)-Br(2A) | 115.2(7)  | Cl(2B)-Ni(1)-Br(2A) | 7.7(3)    |
| O(1)-Ni(1)-Br(1A)   | 102.43(7) | N(1)-Ni(1)-Br(1A)   | 111.73(8) |
| Cl(1B)-Ni(1)-Br(1A) | 9.3(7)    | Cl(2B)-Ni(1)-Br(1A) | 130.3(3)  |
| Br(2A)-Ni(1)-Br(1A) | 124.39(4) | N(1)-P(1)-C(1)      | 110.1(2)  |
| N(1)-P(1)-C(13)     | 114.4(2)  | C(1)-P(1)-C(13)     | 108.2(2)  |
| N(1)-P(1)-C(7)      | 111.6(2)  | C(1)-P(1)-C(7)      | 107.4(2)  |
| C(13)-P(1)-C(7)     | 104.9(2)  | C(2)-O(1)-Li(1)     | 125.3(3)  |
| C(2)-O(1)-Ni(1)     | 114.6(2)  | Li(1)-O(1)-Ni(1)    | 116.7(2)  |
| C(27)-O(2)-C(24)    | 109.1(3)  | C(27)-O(2)-Li(1)    | 117.9(3)  |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(24)-O(2)-Li(1)    | 122.9(3) | C(28)-O(3)-C(31)    | 108.9(3) |
| C(28)-O(3)-Li(1)    | 118.8(3) | C(31)-O(3)-Li(1)    | 123.9(3) |
| C(32)-O(4)-C(35)    | 104.8(4) | C(32)-O(4)-Li(1)    | 135.3(3) |
| C(35)-O(4)-Li(1)    | 118.9(3) | C(19)-N(1)-P(1)     | 117.9(2) |
| C(19)-N(1)-Ni(1)    | 121.0(2) | P(1)-N(1)-Ni(1)     | 114.6(2) |
| C(6)-C(1)-C(2)      | 119.9(3) | C(6)-C(1)-P(1)      | 121.6(3) |
| C(2)-C(1)-P(1)      | 118.4(2) | O(1)-C(2)-C(3)      | 121.2(3) |
| O(1)-C(2)-C(1)      | 121.2(3) | C(3)-C(2)-C(1)      | 117.6(3) |
| C(4)-C(3)-C(2)      | 121.6(3) | C(4)-C(3)-H(3)      | 119.2    |
| C(2)-C(3)-H(3)      | 119.2    | C(3)-C(4)-C(5)      | 120.3(3) |
| C(3)-C(4)-H(4)      | 119.8    | C(5)-C(4)-H(4)      | 119.8    |
| C(6)-C(5)-C(4)      | 119.6(3) | C(6)-C(5)-H(5)      | 120.2    |
| C(4)-C(5)-H(5)      | 120.2    | C(5)-C(6)-C(1)      | 120.9(3) |
| C(5)-C(6)-H(6)      | 119.6    | C(1)-C(6)-H(6)      | 119.6    |
| C(12)-C(7)-C(8)     | 119.3(3) | C(12)-C(7)-P(1)     | 122.0(3) |
| C(8)-C(7)-P(1)      | 118.7(3) | C(9)-C(8)-C(7)      | 120.1(4) |
| C(9)-C(8)-H(8)      | 120.0    | C(7)-C(8)-H(8)      | 120.0    |
| C(8)-C(9)-C(10)     | 120.3(4) | C(8)-C(9)-H(9)      | 119.8    |
| C(10)-C(9)-H(9)     | 119.8    | C(11)-C(10)-C(9)    | 120.2(3) |
| C(11)-C(10)-H(10)   | 119.9    | C(9)-C(10)-H(10)    | 119.9    |
| C(10)-C(11)-C(12)   | 120.1(4) | C(10)-C(11)-H(11)   | 119.9    |
| C(12)-C(11)-H(11)   | 119.9    | C(7)-C(12)-C(11)    | 119.9(3) |
| C(7)-C(12)-H(12)    | 120.0    | C(11)-C(12)-H(12)   | 120.0    |
| C(18)-C(13)-C(14)   | 118.5(3) | C(18)-C(13)-P(1)    | 119.8(3) |
| C(14)-C(13)-P(1)    | 121.7(3) | C(15)-C(14)-C(13)   | 119.8(3) |
| C(15)-C(14)-H(14)   | 120.1    | C(13)-C(14)-H(14)   | 120.1    |
| C(16)-C(15)-C(14)   | 121.0(4) | C(16)-C(15)-H(15)   | 119.5    |
| C(14)-C(15)-H(15)   | 119.5    | C(17)-C(16)-C(15)   | 119.7(4) |
| C(17)-C(16)-H(16)   | 120.2    | C(15)-C(16)-H(16)   | 120.2    |
| C(16)-C(17)-C(18)   | 120.3(4) | C(16)-C(17)-H(17)   | 119.8    |
| C(18)-C(17)-H(17)   | 119.8    | C(17)-C(18)-C(13)   | 120.7(3) |
| C(17)-C(18)-H(18)   | 119.6    | C(13)-C(18)-H(18)   | 119.6    |
| N(1)-C(19)-C(20)    | 115.2(3) | N(1)-C(19)-H(19A)   | 108.5    |
| C(20)-C(19)-H(19A)  | 108.5    | N(1)-C(19)-H(19B)   | 108.5    |
| C(20)-C(19)-H(19B)  | 108.5    | H(19A)-C(19)-H(19B) | 107.5    |
| C(21)-C(20)-C(22)   | 110.1(3) | C(21)-C(20)-C(19)   | 110.7(3) |
| C(22)-C(20)-C(19)   | 111.8(3) | C(21)-C(20)-C(23)   | 109.7(3) |
| C(22)-C(20)-C(23)   | 108.6(3) | C(19)-C(20)-C(23)   | 105.9(3) |
| C(20)-C(21)-H(21A)  | 109.5    | C(20)-C(21)-H(21B)  | 109.5    |
| H(21A)-C(21)-H(21B) | 109.5    | C(20)-C(21)-H(21C)  | 109.5    |
| H(21A)-C(21)-H(21C) | 109.5    | H(21B)-C(21)-H(21C) | 109.5    |
| C(20)-C(22)-H(22A)  | 109.5    | C(20)-C(22)-H(22B)  | 109.5    |
| H(22A)-C(22)-H(22B) | 109.5    | C(20)-C(22)-H(22C)  | 109.5    |
| H(22A)-C(22)-H(22C) | 109.5    | H(22B)-C(22)-H(22C) | 109.5    |
| C(20)-C(23)-H(23A)  | 109.5    | C(20)-C(23)-H(23B)  | 109.5    |
| H(23A)-C(23)-H(23B) | 109.5    | C(20)-C(23)-H(23C)  | 109.5    |
| H(23A)-C(23)-H(23C) | 109.5    | H(23B)-C(23)-H(23C) | 109.5    |
| O(2)-C(24)-C(25)    | 105.8(4) | O(2)-C(24)-H(24A)   | 110.6    |
| C(25)-C(24)-H(24A)  | 110.6    | O(2)-C(24)-H(24B)   | 110.6    |
| C(25)-C(24)-H(24B)  | 110.6    | H(24A)-C(24)-H(24B) | 108.7    |
| C(26)-C(25)-C(24)   | 106.3(5) | C(26)-C(25)-H(25A)  | 110.5    |
| C(24)-C(25)-H(25A)  | 110.5    | C(26)-C(25)-H(25B)  | 110.5    |
| C(24)-C(25)-H(25B)  | 110.5    | H(25A)-C(25)-H(25B) | 108.7    |
| C(25)-C(26)-C(27)   | 105.3(4) | C(25)-C(26)-H(26A)  | 110.7    |
| C(27)-C(26)-H(26A)  | 110.7    | C(25)-C(26)-H(26B)  | 110.7    |
| C(27)-C(26)-H(26B)  | 110.7    | H(26A)-C(26)-H(26B) | 108.8    |
| O(2)-C(27)-C(26)    | 106.6(4) | O(2)-C(27)-H(27A)   | 110.4    |
| C(26)-C(27)-H(27A)  | 110.4    | O(2)-C(27)-H(27B)   | 110.4    |
| C(26)-C(27)-H(27B)  | 110.4    | H(27A)-C(27)-H(27B) | 108.6    |
| O(3)-C(28)-C(29)    | 107.5(3) | O(3)-C(28)-H(28A)   | 110.2    |
| C(29)-C(28)-H(28A)  | 110.2    | O(3)-C(28)-H(28B)   | 110.2    |
| C(29)-C(28)-H(28B)  | 110.2    | H(28A)-C(28)-H(28B) | 108.5    |
| C(28)-C(29)-C(30)   | 102.9(3) | C(28)-C(29)-H(29A)  | 111.2    |
| C(30)-C(29)-H(29A)  | 111.2    | C(28)-C(29)-H(29B)  | 111.2    |
| C(30)-C(29)-H(29B)  | 111.2    | H(29A)-C(29)-H(29B) | 109.1    |
| C(31)-C(30)-C(29)   | 102.2(3) | C(31)-C(30)-H(30A)  | 111.3    |
| C(29)-C(30)-H(30A)  | 111.3    | C(31)-C(30)-H(30B)  | 111.3    |
| C(29)-C(30)-H(30B)  | 111.3    | H(30A)-C(30)-H(30B) | 109.2    |

|                    |          |                     |          |
|--------------------|----------|---------------------|----------|
| O(3)-C(31)-C(30)   | 105.3(3) | O(3)-C(31)-H(31A)   | 110.7    |
| C(30)-C(31)-H(31A) | 110.7    | O(3)-C(31)-H(31B)   | 110.7    |
| C(30)-C(31)-H(31B) | 110.7    | H(31A)-C(31)-H(31B) | 108.8    |
| O(4)-C(32)-C(33)   | 105.7(4) | O(4)-C(32)-H(32A)   | 110.6    |
| C(33)-C(32)-H(32A) | 110.6    | O(4)-C(32)-H(32B)   | 110.6    |
| C(33)-C(32)-H(32B) | 110.6    | H(32A)-C(32)-H(32B) | 108.7    |
| C(32)-C(33)-C(34)  | 106.0(4) | C(32)-C(33)-H(33A)  | 110.5    |
| C(34)-C(33)-H(33A) | 110.5    | C(32)-C(33)-H(33B)  | 110.5    |
| C(34)-C(33)-H(33B) | 110.5    | H(33A)-C(33)-H(33B) | 108.7    |
| C(33)-C(34)-C(35)  | 103.0(4) | C(33)-C(34)-H(34A)  | 111.2    |
| C(35)-C(34)-H(34A) | 111.2    | C(33)-C(34)-H(34B)  | 111.2    |
| C(35)-C(34)-H(34B) | 111.2    | H(34A)-C(34)-H(34B) | 109.1    |
| O(4)-C(35)-C(34)   | 104.4(4) | O(4)-C(35)-H(35A)   | 110.9    |
| C(34)-C(35)-H(35A) | 110.9    | O(4)-C(35)-H(35B)   | 110.9    |
| C(34)-C(35)-H(35B) | 110.9    | H(35A)-C(35)-H(35B) | 108.9    |
| O(4)-Li(1)-O(1)    | 115.8(3) | O(4)-Li(1)-O(3)     | 110.1(3) |
| O(1)-Li(1)-O(3)    | 114.8(3) | O(4)-Li(1)-O(2)     | 100.3(3) |
| O(1)-Li(1)-O(2)    | 116.5(3) | O(3)-Li(1)-O(2)     | 97.1(3)  |

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa278

| atom   | U11   | U22    | U33    | U23    | U13   | U12    |
|--------|-------|--------|--------|--------|-------|--------|
| Br(1A) | 41(1) | 46(1)  | 51(1)  | 5(1)   | 30(1) | 3(1)   |
| Cl(1B) | 41(1) | 46(1)  | 51(1)  | 5(1)   | 30(1) | 3(1)   |
| Br(2A) | 28(1) | 46(1)  | 42(1)  | -7(1)  | 7(1)  | -4(1)  |
| Cl(2B) | 28(1) | 46(1)  | 42(1)  | -7(1)  | 7(1)  | -4(1)  |
| Ni(1)  | 29(1) | 26(1)  | 23(1)  | -1(1)  | 11(1) | 1(1)   |
| P(1)   | 22(1) | 21(1)  | 22(1)  | 0(1)   | 10(1) | 0(1)   |
| O(1)   | 28(1) | 25(1)  | 29(1)  | 3(1)   | 9(1)  | 1(1)   |
| O(2)   | 55(2) | 34(2)  | 41(2)  | 1(1)   | 10(1) | 9(1)   |
| O(3)   | 36(2) | 32(1)  | 45(2)  | -6(1)  | 23(1) | -3(1)  |
| O(4)   | 31(2) | 86(2)  | 35(2)  | 11(2)  | 13(1) | 12(2)  |
| N(1)   | 25(1) | 20(1)  | 24(1)  | 1(1)   | 12(1) | 1(1)   |
| C(1)   | 25(2) | 19(2)  | 26(2)  | 1(1)   | 13(1) | 2(1)   |
| C(2)   | 27(2) | 23(2)  | 31(2)  | 1(1)   | 13(2) | 2(1)   |
| C(3)   | 41(2) | 31(2)  | 31(2)  | 7(2)   | 19(2) | 4(2)   |
| C(4)   | 41(2) | 25(2)  | 45(2)  | 8(2)   | 26(2) | 1(2)   |
| C(5)   | 31(2) | 22(2)  | 42(2)  | -2(2)  | 17(2) | -3(1)  |
| C(6)   | 31(2) | 23(2)  | 29(2)  | -1(1)  | 13(2) | 2(1)   |
| C(7)   | 26(2) | 18(2)  | 24(2)  | -1(1)  | 8(1)  | -1(1)  |
| C(8)   | 24(2) | 26(2)  | 36(2)  | -2(2)  | 10(2) | 4(1)   |
| C(9)   | 28(2) | 26(2)  | 37(2)  | -6(2)  | 2(2)  | 2(1)   |
| C(10)  | 45(2) | 34(2)  | 26(2)  | -2(2)  | 3(2)  | 7(2)   |
| C(11)  | 47(2) | 41(2)  | 25(2)  | 1(2)   | 14(2) | 2(2)   |
| C(12)  | 32(2) | 27(2)  | 27(2)  | 0(1)   | 10(2) | -1(1)  |
| C(13)  | 25(2) | 28(2)  | 25(2)  | 1(1)   | 8(1)  | 2(1)   |
| C(14)  | 28(2) | 29(2)  | 47(2)  | -10(2) | 16(2) | -1(2)  |
| C(15)  | 38(2) | 34(2)  | 60(3)  | -8(2)  | 23(2) | 7(2)   |
| C(16)  | 28(2) | 47(2)  | 47(2)  | -1(2)  | 21(2) | 5(2)   |
| C(17)  | 31(2) | 38(2)  | 52(2)  | 1(2)   | 23(2) | -4(2)  |
| C(18)  | 28(2) | 27(2)  | 49(2)  | 0(2)   | 18(2) | 0(1)   |
| C(19)  | 31(2) | 23(2)  | 26(2)  | -2(1)  | 15(2) | -3(1)  |
| C(20)  | 33(2) | 22(2)  | 26(2)  | 2(1)   | 10(2) | 3(1)   |
| C(21)  | 36(2) | 30(2)  | 43(2)  | -2(2)  | 12(2) | 7(2)   |
| C(22)  | 43(2) | 27(2)  | 35(2)  | -3(2)  | 18(2) | 4(2)   |
| C(23)  | 54(3) | 27(2)  | 37(2)  | 6(2)   | 20(2) | 4(2)   |
| C(24)  | 73(3) | 40(3)  | 60(3)  | -10(2) | 24(3) | 10(2)  |
| C(25)  | 75(4) | 50(3)  | 100(5) | -7(3)  | 22(4) | 27(3)  |
| C(26)  | 83(4) | 93(5)  | 81(4)  | 29(4)  | 29(4) | 48(4)  |
| C(27)  | 47(3) | 46(3)  | 48(3)  | 14(2)  | 12(2) | 1(2)   |
| C(28)  | 44(2) | 40(2)  | 60(3)  | -5(2)  | 34(2) | -6(2)  |
| C(29)  | 46(2) | 47(2)  | 47(2)  | -4(2)  | 27(2) | 4(2)   |
| C(30)  | 46(2) | 38(2)  | 42(2)  | -6(2)  | 14(2) | 2(2)   |
| C(31)  | 38(2) | 39(2)  | 42(2)  | -14(2) | 13(2) | -9(2)  |
| C(32)  | 40(2) | 62(3)  | 59(3)  | -12(2) | 15(2) | -12(2) |
| C(33)  | 41(3) | 128(5) | 62(4)  | 13(4)  | 15(3) | 27(3)  |
| C(34)  | 55(3) | 68(3)  | 62(3)  | -6(3)  | 37(3) | -2(2)  |
| C(35)  | 43(3) | 128(5) | 41(3)  | 8(3)   | 20(2) | 11(3)  |
| Li(1)  | 35(3) | 35(3)  | 30(3)  | 3(3)   | 15(3) | 7(3)   |

The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U(11) + \dots + 2hka^*b^*U(12)]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa278

| atom   | x     | y          | z          | U(eq) |
|--------|-------|------------|------------|-------|
| H(3)   | 482   | -4871      | -2329      | 40    |
| H(4)   | -1323 | -5725      | -2937      | 41    |
| H(5)   | -2407 | -5658      | -4065      | 37    |
| H(6)   | -1654 | -4731      | -4580      | 32    |
| H(8)   | -2768 | -3407.9998 | -4875      | 35    |
| H(9)   | -4404 | -3397.0002 | -5966      | 42    |
| H(10)  | -3466 | -3441.9998 | -6752      | 47    |
| H(11)  | -901  | -3569      | -6452.9995 | 45    |
| H(12)  | 765   | -3630      | -5356      | 35    |
| H(14)  | 1966  | -4844      | -4244      | 41    |
| H(15)  | 4332  | -5090      | -4215      | 52    |
| H(16)  | 6029  | -4132      | -4081      | 47    |
| H(17)  | 5396  | -2918      | -3948      | 46    |
| H(18)  | 3055  | -2654      | -3959      | 41    |
| H(19A) | 376   | -2153      | -4604      | 31    |
| H(19B) | 1492  | -1810      | -3926.9998 | 31    |
| H(21A) | -2425 | -2082      | -4292      | 56    |
| H(21B) | -2426 | -1922      | -4983      | 56    |
| H(21C) | -2986 | -1295      | -4637      | 56    |
| H(22A) | -1111 | -641       | -3656      | 51    |
| H(22B) | 621   | -879       | -3376      | 51    |
| H(22C) | -592  | -1435      | -3316      | 51    |
| H(23A) | -1128 | -384.0000  | -4716      | 59    |
| H(23B) | -626  | -1008      | -5087      | 59    |
| H(23C) | 602   | -618       | -4457      | 59    |
| H(24A) | 4077  | -5511.9995 | -2364      | 70    |
| H(24B) | 2545  | -5838.9995 | -2366      | 70    |
| H(25A) | 3743  | -6654.0005 | -1600      | 96    |
| H(25B) | 5047  | -6555      | -1848      | 96    |
| H(26A) | 6391  | -5843      | -1038      | 105   |
| H(26B) | 5516  | -6292      | -688.9999  | 105   |
| H(27A) | 4063  | -5327      | -736       | 59    |
| H(27B) | 5333  | -4844      | -834.0001  | 59    |
| H(28A) | 1841  | -4192      | -833       | 52    |
| H(28B) | 917   | -3775      | -1507      | 52    |
| H(29A) | 1911  | -3177.9998 | -257       | 53    |
| H(29B) | 512   | -2906      | -903       | 53    |
| H(30A) | 2031  | -2210      | -1241      | 52    |
| H(30B) | 2942  | -2115      | -470.0000  | 52    |
| H(31A) | 4315  | -2681      | -1094      | 49    |
| H(31B) | 4599  | -3034      | -404.0000  | 49    |
| H(32A) | 6734  | -3896      | -996       | 67    |
| H(32B) | 7020  | -3195      | -1368.9999 | 67    |
| H(33A) | 7901  | -4667      | -1384      | 95    |
| H(33B) | 8616  | -3929      | -1542      | 95    |
| H(34A) | 6493  | -4853      | -2419      | 69    |
| H(34B) | 7363  | -4174      | -2578.0002 | 69    |
| H(35A) | 5596  | -3332      | -2628      | 84    |
| H(35B) | 4527  | -4055      | -2843      | 84    |

**Complex 26a**

Table 1. Crystal data for pa874bis

|   |  |
|---|--|
| Compound                                    | pa874bis   |
| Molecular formula                           | C <sub>40</sub> H <sub>38</sub> BrNNiOP <sub>2</sub> , C <sub>4</sub> H <sub>8</sub> O |
| Molecular weight                            | 821.38   |
| Crystal habit                               | Dark Green Block   |
| Crystal dimensions(mm)                      | 0.22x0.18x0.16   |
| Crystal system                              | Triclinic  |
| Space group                                 | P -1   |
| a(Å)  | 9.656(1)   |
| b(Å)  | 12.252(1)  |
| c(Å)  | 17.162(1)  |
| α(°)  | 92.016(1)  |
| β(°)  | 96.257(1)  |
| γ(°)  | 99.969(1)  |
| V(Å <sup>3</sup> )                          | 1984.8(3)  |
| Z   | 2  |
| d(g·cm <sup>-3</sup> )                      | 1.374  |
| F(000)                                      | 852  |
| μ(cm <sup>-1</sup> )                        | 1.613  |
| Absorption corrections                      | multi-scan ; 0.7179 min, 0.7824 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 25.01  |
| HKL ranges                                  | -9 11 ; -14 14 ; -17 20  |
| Reflections measured                        | 18156  |
| Unique data                                 | 6780   |
| Rint  | 0.0531   |
| Reflections used                            | 5658   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 418  |
| Reflections / parameter                     | 13   |
| wR2   | 0.1372   |
| R1  | 0.0565   |
| Weights a, b                                | 0.0568 ; 4.3728  |
| GoF   | 1.072  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.831(0.084) / -0.450(0.084)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa874bis

| atom  | x        | y        | z       | U(eq) |
|-------|----------|----------|---------|-------|
| Br(1) | -321(1)  | 7523(1)  | 3561(1) | 59(1) |
| Ni(1) | 1392(1)  | 8146(1)  | 2709(1) | 36(1) |
| P(1)  | 3885(1)  | 10026(1) | 2925(1) | 33(1) |
| P(2)  | 737(1)   | 6873(1)  | 1643(1) | 35(1) |
| O(1)  | 883(3)   | 9389(2)  | 2166(2) | 38(1) |
| N(1)  | 3433(4)  | 8702(3)  | 2991(2) | 35(1) |
| C(1)  | 3155(4)  | 10423(3) | 1992(2) | 34(1) |
| C(2)  | 1710(4)  | 10038(3) | 1749(2) | 34(1) |
| C(3)  | 1131(5)  | 10399(4) | 1026(3) | 39(1) |
| C(4)  | 1954(5)  | 11094(4) | 585(3)  | 43(1) |
| C(5)  | 3369(5)  | 11486(4) | 840(3)  | 43(1) |
| C(6)  | 3960(5)  | 11166(4) | 1543(3) | 39(1) |
| C(7)  | 5788(4)  | 10486(4) | 3004(3) | 36(1) |
| C(8)  | 6550(5)  | 11015(4) | 3683(3) | 42(1) |
| C(9)  | 8011(5)  | 11224(4) | 3767(3) | 51(1) |
| C(10) | 8733(5)  | 10916(4) | 3172(3) | 54(1) |
| C(11) | 7989(5)  | 10395(4) | 2482(3) | 47(1) |
| C(12) | 6525(5)  | 10187(4) | 2402(3) | 41(1) |
| C(13) | 3227(4)  | 10879(4) | 3639(2) | 35(1) |
| C(14) | 3537(5)  | 12029(4) | 3606(3) | 42(1) |
| C(15) | 2985(5)  | 12707(4) | 4108(3) | 47(1) |
| C(16) | 2129(5)  | 12243(4) | 4644(3) | 45(1) |
| C(17) | 1810(5)  | 11107(4) | 4676(3) | 45(1) |
| C(18) | 2343(5)  | 10423(4) | 4170(2) | 39(1) |
| C(19) | 4239(5)  | 7987(4)  | 3512(3) | 39(1) |
| C(20) | 4300(6)  | 8339(5)  | 4372(3) | 60(1) |
| C(21) | 5756(6)  | 7981(5)  | 3324(3) | 60(1) |
| C(22) | 3443(6)  | 6815(4)  | 3366(4) | 66(2) |
| C(23) | 1534(5)  | 7391(4)  | 782(2)  | 38(1) |
| C(24) | 812(5)   | 7224(4)  | 29(3)   | 45(1) |
| C(25) | 1465(5)  | 7666(5)  | -594(3) | 54(1) |
| C(26) | 2803(5)  | 8286(5)  | -479(3) | 53(1) |
| C(27) | 3529(5)  | 8461(4)  | 267(3)  | 47(1) |
| C(28) | 2889(5)  | 8005(4)  | 895(3)  | 40(1) |
| C(29) | -1163(4) | 6597(4)  | 1335(2) | 38(1) |
| C(30) | -1896(5) | 5580(4)  | 1016(3) | 50(1) |
| C(31) | -3323(6) | 5421(5)  | 802(3)  | 60(1) |
| C(32) | -4057(5) | 6287(5)  | 883(3)  | 58(1) |
| C(33) | -3338(5) | 7307(5)  | 1190(3) | 52(1) |
| C(34) | -1904(5) | 7472(4)  | 1415(3) | 43(1) |
| C(35) | 1184(4)  | 5498(4)  | 1743(3) | 38(1) |
| C(36) | 1971(5)  | 5036(4)  | 1233(3) | 44(1) |
| C(37) | 2299(5)  | 3998(4)  | 1355(3) | 50(1) |
| C(38) | 1846(6)  | 3411(4)  | 1979(3) | 52(1) |
| C(39) | 1066(6)  | 3864(4)  | 2488(3) | 51(1) |
| C(40) | 742(5)   | 4902(4)  | 2384(3) | 46(1) |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa874bis

|                  |           |                  |           |
|------------------|-----------|------------------|-----------|
| Br(1)-Ni(1)      | 2.3712(7) | Ni(1)-O(1)       | 1.921(3)  |
| Ni(1)-N(1)       | 1.971(3)  | Ni(1)-P(2)       | 2.321(1)  |
| P(1)-N(1)        | 1.616(4)  | P(1)-C(1)        | 1.796(4)  |
| P(1)-C(7)        | 1.815(4)  | P(1)-C(13)       | 1.819(4)  |
| P(2)-C(35)       | 1.819(4)  | P(2)-C(29)       | 1.822(4)  |
| P(2)-C(23)       | 1.824(4)  | O(1)-C(2)        | 1.314(5)  |
| N(1)-C(19)       | 1.522(5)  | C(1)-C(6)        | 1.400(6)  |
| C(1)-C(2)        | 1.406(6)  | C(2)-C(3)        | 1.422(6)  |
| C(3)-C(4)        | 1.368(7)  | C(3)-H(3)        | 0.9500    |
| C(4)-C(5)        | 1.384(7)  | C(4)-H(4)        | 0.9500    |
| C(5)-C(6)        | 1.377(6)  | C(5)-H(5)        | 0.9500    |
| C(6)-H(6)        | 0.9500    | C(7)-C(8)        | 1.383(6)  |
| C(7)-C(12)       | 1.390(6)  | C(8)-C(9)        | 1.379(7)  |
| C(8)-H(8)        | 0.9500    | C(9)-C(10)       | 1.375(7)  |
| C(9)-H(9)        | 0.9500    | C(10)-C(11)      | 1.390(7)  |
| C(10)-H(10)      | 0.9500    | C(11)-C(12)      | 1.383(6)  |
| C(11)-H(11)      | 0.9500    | C(12)-H(12)      | 0.9500    |
| C(13)-C(18)      | 1.382(6)  | C(13)-C(14)      | 1.393(6)  |
| C(14)-C(15)      | 1.385(6)  | C(14)-H(14)      | 0.9500    |
| C(15)-C(16)      | 1.375(7)  | C(15)-H(15)      | 0.9500    |
| C(16)-C(17)      | 1.377(7)  | C(16)-H(16)      | 0.9500    |
| C(17)-C(18)      | 1.384(6)  | C(17)-H(17)      | 0.9500    |
| C(18)-H(18)      | 0.9500    | C(19)-C(22)      | 1.505(7)  |
| C(19)-C(20)      | 1.516(7)  | C(19)-C(21)      | 1.534(7)  |
| C(20)-H(20A)     | 0.9800    | C(20)-H(20B)     | 0.9800    |
| C(20)-H(20C)     | 0.9800    | C(21)-H(21A)     | 0.9800    |
| C(21)-H(21B)     | 0.9800    | C(21)-H(21C)     | 0.9800    |
| C(22)-H(22A)     | 0.9800    | C(22)-H(22B)     | 0.9800    |
| C(22)-H(22C)     | 0.9800    | C(23)-C(28)      | 1.382(6)  |
| C(23)-C(24)      | 1.390(6)  | C(24)-C(25)      | 1.380(7)  |
| C(24)-H(24)      | 0.9500    | C(25)-C(26)      | 1.371(7)  |
| C(25)-H(25)      | 0.9500    | C(26)-C(27)      | 1.382(7)  |
| C(26)-H(26)      | 0.9500    | C(27)-C(28)      | 1.387(6)  |
| C(27)-H(27)      | 0.9500    | C(28)-H(28)      | 0.9500    |
| C(29)-C(30)      | 1.384(7)  | C(29)-C(34)      | 1.399(6)  |
| C(30)-C(31)      | 1.365(7)  | C(30)-H(30)      | 0.9500    |
| C(31)-C(32)      | 1.386(8)  | C(31)-H(31)      | 0.9500    |
| C(32)-C(33)      | 1.377(8)  | C(32)-H(32)      | 0.9500    |
| C(33)-C(34)      | 1.374(7)  | C(33)-H(33)      | 0.9500    |
| C(34)-H(34)      | 0.9500    | C(35)-C(36)      | 1.387(6)  |
| C(35)-C(40)      | 1.407(6)  | C(36)-C(37)      | 1.380(6)  |
| C(36)-H(36)      | 0.9500    | C(37)-C(38)      | 1.379(7)  |
| C(37)-H(37)      | 0.9500    | C(38)-C(39)      | 1.376(7)  |
| C(38)-H(38)      | 0.9500    | C(39)-C(40)      | 1.374(7)  |
| C(39)-H(39)      | 0.9500    | C(40)-H(40)      | 0.9500    |
| O(1)-Ni(1)-N(1)  | 99.4(1)   | O(1)-Ni(1)-P(2)  | 95.6(1)   |
| N(1)-Ni(1)-P(2)  | 117.2(1)  | O(1)-Ni(1)-Br(1) | 109.7(1)  |
| N(1)-Ni(1)-Br(1) | 127.8(1)  | P(2)-Ni(1)-Br(1) | 102.25(4) |
| N(1)-P(1)-C(7)   | 109.8(2)  | N(1)-P(1)-C(13)  | 113.2(2)  |
| C(1)-P(1)-C(7)   | 107.2(2)  | N(1)-P(1)-C(13)  | 115.1(2)  |
| C(1)-P(1)-C(13)  | 104.3(2)  | C(7)-P(1)-C(13)  | 106.7(2)  |
| C(35)-P(2)-C(29) | 103.9(2)  | C(35)-P(2)-C(23) | 104.8(2)  |
| C(29)-P(2)-C(23) | 105.0(2)  | C(35)-P(2)-Ni(1) | 117.8(1)  |
| C(29)-P(2)-Ni(1) | 113.2(2)  | C(23)-P(2)-Ni(1) | 111.0(2)  |
| C(2)-O(1)-Ni(1)  | 125.1(3)  | C(19)-N(1)-P(1)  | 125.3(3)  |
| C(19)-N(1)-Ni(1) | 116.5(3)  | P(1)-N(1)-Ni(1)  | 113.7(2)  |
| C(6)-C(1)-C(2)   | 120.3(4)  | C(6)-C(1)-P(1)   | 121.5(3)  |
| C(2)-C(1)-P(1)   | 118.0(3)  | O(1)-C(2)-C(1)   | 123.0(4)  |
| O(1)-C(2)-C(3)   | 119.5(4)  | C(1)-C(2)-C(3)   | 117.4(4)  |
| C(4)-C(3)-C(2)   | 121.1(4)  | C(4)-C(3)-H(3)   | 119.5     |
| C(2)-C(3)-H(3)   | 119.5     | C(3)-C(4)-C(5)   | 120.8(4)  |
| C(3)-C(4)-H(4)   | 119.6     | C(5)-C(4)-H(4)   | 119.6     |
| C(6)-C(5)-C(4)   | 119.7(4)  | C(6)-C(5)-H(5)   | 120.1     |
| C(4)-C(5)-H(5)   | 120.1     | C(5)-C(6)-C(1)   | 120.6(4)  |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(5)-C(6)-H(6)      | 119.7    | C(1)-C(6)-H(6)      | 119.7    |
| C(8)-C(7)-C(12)     | 118.6(4) | C(8)-C(7)-P(1)      | 121.9(3) |
| C(12)-C(7)-P(1)     | 119.0(3) | C(9)-C(8)-C(7)      | 120.8(4) |
| C(9)-C(8)-H(8)      | 119.6    | C(7)-C(8)-H(8)      | 119.6    |
| C(10)-C(9)-C(8)     | 120.3(5) | C(10)-C(9)-H(9)     | 119.8    |
| C(8)-C(9)-H(9)      | 119.8    | C(9)-C(10)-C(11)    | 119.8(4) |
| C(9)-C(10)-H(10)    | 120.1    | C(11)-C(10)-H(10)   | 120.1    |
| C(12)-C(11)-C(10)   | 119.5(4) | C(12)-C(11)-H(11)   | 120.3    |
| C(10)-C(11)-H(11)   | 120.3    | C(11)-C(12)-C(7)    | 120.9(4) |
| C(7)-C(12)-H(12)    | 119.5    | C(7)-C(12)-H(12)    | 119.5    |
| C(18)-C(13)-C(14)   | 119.2(4) | C(18)-C(13)-P(1)    | 122.1(3) |
| C(14)-C(13)-P(1)    | 118.5(3) | C(15)-C(14)-C(13)   | 120.4(4) |
| C(15)-C(14)-H(14)   | 119.8    | C(13)-C(14)-H(14)   | 119.8    |
| C(16)-C(15)-C(14)   | 119.9(5) | C(16)-C(15)-H(15)   | 120.1    |
| C(14)-C(15)-H(15)   | 120.1    | C(15)-C(16)-C(17)   | 120.1(4) |
| C(15)-C(16)-H(16)   | 120.0    | C(17)-C(16)-H(16)   | 120.0    |
| C(16)-C(17)-C(18)   | 120.4(4) | C(16)-C(17)-H(17)   | 119.8    |
| C(18)-C(17)-H(17)   | 119.8    | C(13)-C(18)-C(17)   | 120.1(4) |
| C(13)-C(18)-H(18)   | 120.0    | C(17)-C(18)-H(18)   | 120.0    |
| C(22)-C(19)-C(20)   | 109.5(4) | C(22)-C(19)-N(1)    | 106.3(3) |
| C(20)-C(19)-N(1)    | 111.3(4) | C(22)-C(19)-C(21)   | 107.0(4) |
| C(20)-C(19)-C(21)   | 108.4(4) | N(1)-C(19)-C(21)    | 114.2(4) |
| C(19)-C(20)-H(20A)  | 109.5    | C(19)-C(20)-H(20B)  | 109.5    |
| H(20A)-C(20)-H(20B) | 109.5    | C(19)-C(20)-H(20C)  | 109.5    |
| H(20A)-C(20)-H(20C) | 109.5    | H(20B)-C(20)-H(20C) | 109.5    |
| C(19)-C(21)-H(21A)  | 109.5    | C(19)-C(21)-H(21B)  | 109.5    |
| H(21A)-C(21)-H(21B) | 109.5    | C(19)-C(21)-H(21C)  | 109.5    |
| H(21A)-C(21)-H(21C) | 109.5    | H(21B)-C(21)-H(21C) | 109.5    |
| C(19)-C(22)-H(22A)  | 109.5    | C(19)-C(22)-H(22B)  | 109.5    |
| H(22A)-C(22)-H(22B) | 109.5    | C(19)-C(22)-H(22C)  | 109.5    |
| H(22A)-C(22)-H(22C) | 109.5    | H(22B)-C(22)-H(22C) | 109.5    |
| C(28)-C(23)-C(24)   | 119.5(4) | C(28)-C(23)-P(2)    | 118.0(3) |
| C(24)-C(23)-P(2)    | 122.4(4) | C(25)-C(24)-C(23)   | 119.5(5) |
| C(25)-C(24)-H(24)   | 120.3    | C(23)-C(24)-H(24)   | 120.3    |
| C(26)-C(25)-C(24)   | 120.9(4) | C(26)-C(25)-H(25)   | 119.5    |
| C(24)-C(25)-H(25)   | 119.5    | C(25)-C(26)-C(27)   | 120.1(4) |
| C(27)-C(26)-H(26)   | 119.9    | C(27)-C(26)-H(26)   | 119.9    |
| C(26)-C(27)-C(28)   | 119.3(5) | C(26)-C(27)-H(27)   | 120.3    |
| C(28)-C(27)-H(27)   | 120.3    | C(23)-C(28)-C(27)   | 120.6(4) |
| C(23)-C(28)-H(28)   | 119.7    | C(27)-C(28)-H(28)   | 119.7    |
| C(30)-C(29)-C(34)   | 118.8(4) | C(30)-C(29)-P(2)    | 123.5(4) |
| C(34)-C(29)-P(2)    | 117.7(3) | C(31)-C(30)-C(29)   | 120.8(5) |
| C(31)-C(30)-H(30)   | 119.6    | C(29)-C(30)-H(30)   | 119.6    |
| C(30)-C(31)-C(32)   | 120.3(5) | C(30)-C(31)-H(31)   | 119.8    |
| C(32)-C(31)-H(31)   | 119.8    | C(33)-C(32)-C(31)   | 119.4(5) |
| C(33)-C(32)-H(32)   | 120.3    | C(31)-C(32)-H(32)   | 120.3    |
| C(34)-C(33)-C(32)   | 120.7(5) | C(34)-C(33)-H(33)   | 119.7    |
| C(33)-C(33)-H(33)   | 119.7    | C(33)-C(34)-C(29)   | 119.9(5) |
| C(33)-C(34)-H(34)   | 120.0    | C(29)-C(34)-H(34)   | 120.0    |
| C(36)-C(35)-C(40)   | 119.2(4) | C(36)-C(35)-P(2)    | 123.0(3) |
| C(40)-C(35)-P(2)    | 117.8(3) | C(37)-C(36)-C(35)   | 119.9(5) |
| C(37)-C(36)-H(36)   | 120.0    | C(35)-C(36)-H(36)   | 120.0    |
| C(38)-C(37)-C(36)   | 120.6(5) | C(38)-C(37)-H(37)   | 119.7    |
| C(36)-C(37)-H(37)   | 119.7    | C(39)-C(38)-C(37)   | 119.9(5) |
| C(39)-C(38)-H(38)   | 120.1    | C(37)-C(38)-H(38)   | 120.1    |
| C(40)-C(39)-C(38)   | 120.5(5) | C(40)-C(39)-H(39)   | 119.7    |
| C(38)-C(39)-H(39)   | 119.7    | C(39)-C(40)-C(35)   | 119.9(5) |
| C(39)-C(40)-H(40)   | 120.1    | C(35)-C(40)-H(40)   | 120.1    |

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa874bis

| atom  | U11   | U22   | U33   | U23   | U13    | U12   |
|-------|-------|-------|-------|-------|--------|-------|
| Br(1) | 63(1) | 63(1) | 53(1) | 5(1)  | 29(1)  | 4(1)  |
| Ni(1) | 37(1) | 41(1) | 30(1) | 6(1)  | 5(1)   | 9(1)  |
| P(1)  | 33(1) | 41(1) | 27(1) | 5(1)  | 3(1)   | 11(1) |
| P(2)  | 34(1) | 40(1) | 32(1) | 5(1)  | 4(1)   | 11(1) |
| O(1)  | 36(2) | 41(2) | 40(2) | 10(1) | 4(1)   | 11(1) |
| N(1)  | 34(2) | 43(2) | 28(2) | 8(2)  | 0(1)   | 10(2) |
| C(1)  | 38(2) | 39(2) | 26(2) | 4(2)  | 2(2)   | 12(2) |
| C(2)  | 39(2) | 40(2) | 27(2) | 3(2)  | 5(2)   | 16(2) |
| C(3)  | 37(2) | 44(2) | 37(2) | 3(2)  | -3(2)  | 12(2) |
| C(4)  | 51(3) | 51(3) | 32(2) | 9(2)  | 2(2)   | 23(2) |
| C(5)  | 53(3) | 50(3) | 34(2) | 17(2) | 14(2)  | 23(2) |
| C(6)  | 37(2) | 45(3) | 36(2) | 8(2)  | 6(2)   | 11(2) |
| C(7)  | 31(2) | 41(2) | 38(2) | 10(2) | 4(2)   | 10(2) |
| C(8)  | 45(3) | 43(3) | 39(2) | 10(2) | 7(2)   | 10(2) |
| C(9)  | 41(3) | 55(3) | 54(3) | 6(2)  | -6(2)  | 6(2)  |
| C(10) | 35(3) | 66(3) | 64(3) | 18(3) | 5(2)   | 15(2) |
| C(11) | 44(3) | 55(3) | 50(3) | 13(2) | 16(2)  | 20(2) |
| C(12) | 41(2) | 48(3) | 38(2) | 9(2)  | 7(2)   | 18(2) |
| C(13) | 35(2) | 42(2) | 30(2) | 4(2)  | 2(2)   | 14(2) |
| C(14) | 43(3) | 51(3) | 35(2) | 11(2) | 7(2)   | 13(2) |
| C(15) | 53(3) | 49(3) | 43(3) | 7(2)  | 8(2)   | 22(2) |
| C(16) | 43(3) | 57(3) | 39(2) | -2(2) | 3(2)   | 22(2) |
| C(17) | 39(2) | 63(3) | 35(2) | 2(2)  | 8(2)   | 13(2) |
| C(18) | 41(2) | 47(3) | 32(2) | 6(2)  | 2(2)   | 12(2) |
| C(19) | 37(2) | 44(2) | 37(2) | 11(2) | 0(2)   | 14(2) |
| C(20) | 68(3) | 78(4) | 37(3) | 10(3) | -2(2)  | 30(3) |
| C(21) | 59(3) | 70(4) | 59(3) | 21(3) | 14(3)  | 31(3) |
| C(22) | 65(4) | 51(3) | 76(4) | 19(3) | -20(3) | 11(3) |
| C(23) | 41(2) | 44(2) | 35(2) | 6(2)  | 7(2)   | 20(2) |
| C(24) | 42(3) | 59(3) | 35(2) | 8(2)  | 5(2)   | 12(2) |
| C(25) | 53(3) | 83(4) | 28(2) | 14(2) | 3(2)   | 19(3) |
| C(26) | 50(3) | 75(4) | 43(3) | 24(3) | 17(2)  | 22(3) |
| C(27) | 43(3) | 54(3) | 47(3) | 7(2)  | 14(2)  | 15(2) |
| C(28) | 40(2) | 49(3) | 35(2) | 3(2)  | 8(2)   | 18(2) |
| C(29) | 36(2) | 54(3) | 26(2) | 7(2)  | 5(2)   | 11(2) |
| C(30) | 41(3) | 54(3) | 52(3) | -4(2) | 0(2)   | 3(2)  |
| C(31) | 49(3) | 67(4) | 59(3) | -8(3) | -2(2)  | 1(3)  |
| C(32) | 34(3) | 89(4) | 49(3) | -2(3) | 1(2)   | 7(3)  |
| C(33) | 44(3) | 75(4) | 43(3) | 8(3)  | 7(2)   | 26(3) |
| C(34) | 41(3) | 53(3) | 37(2) | 4(2)  | 5(2)   | 9(2)  |
| C(35) | 37(2) | 41(2) | 38(2) | 4(2)  | 0(2)   | 9(2)  |
| C(36) | 50(3) | 44(3) | 40(2) | 5(2)  | 4(2)   | 16(2) |
| C(37) | 55(3) | 51(3) | 46(3) | 0(2)  | 1(2)   | 21(2) |
| C(38) | 60(3) | 44(3) | 54(3) | 8(2)  | -5(2)  | 17(2) |
| C(39) | 64(3) | 43(3) | 44(3) | 10(2) | 1(2)   | 9(2)  |
| C(40) | 51(3) | 46(3) | 43(3) | 6(2)  | 5(2)   | 11(2) |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa874bis

| atom   | x          | y     | z         | U(eq) |
|--------|------------|-------|-----------|-------|
| H(3)   | 158        | 10152 | 845       | 47    |
| H(4)   | 1550       | 11311 | 98        | 51    |
| H(5)   | 3929       | 11973 | 532       | 52    |
| H(6)   | 4924       | 11452 | 1726      | 47    |
| H(8)   | 6062       | 11237 | 4096      | 50    |
| H(9)   | 8520       | 11583 | 4239      | 61    |
| H(10)  | 9739       | 11059 | 3233      | 65    |
| H(11)  | 8482       | 10183 | 2067      | 57    |
| H(12)  | 6014       | 9835  | 1929      | 49    |
| H(14)  | 4132       | 12350 | 3237      | 50    |
| H(15)  | 3197       | 13490 | 4081      | 56    |
| H(16)  | 1759       | 12707 | 4992      | 54    |
| H(17)  | 1219       | 10790 | 5047      | 54    |
| H(18)  | 2102       | 9640  | 4188      | 47    |
| H(20A) | 4762       | 9118  | 4461      | 89    |
| H(20B) | 4839       | 7874  | 4692      | 89    |
| H(20C) | 3336       | 8254  | 4520      | 89    |
| H(21A) | 5747       | 7832  | 2759      | 90    |
| H(21B) | 6143       | 7402  | 3610      | 90    |
| H(21C) | 6345       | 8705  | 3483      | 90    |
| H(22A) | 2466       | 6784  | 3482      | 99    |
| H(22B) | 3903       | 6324  | 3705      | 99    |
| H(22C) | 3441       | 6575  | 2815      | 99    |
| H(24)  | -123.0000  | 6809  | -56.0000  | 54    |
| H(25)  | 980        | 7539  | -1111     | 65    |
| H(26)  | 3231       | 8596  | -913.0001 | 64    |
| H(27)  | 4458       | 8888  | 348       | 56    |
| H(28)  | 3387       | 8117  | 1408      | 48    |
| H(30)  | -1400      | 4985  | 946       | 60    |
| H(31)  | -3815      | 4713  | 595       | 73    |
| H(32)  | -5049      | 6178  | 729       | 70    |
| H(33)  | -3837.0002 | 7903  | 1246      | 63    |
| H(34)  | -1417      | 8180  | 1625      | 52    |
| H(36)  | 2285       | 5432  | 801       | 52    |
| H(37)  | 2842       | 3685  | 1005      | 60    |
| H(38)  | 2071       | 2694  | 2056      | 63    |
| H(39)  | 750        | 3456  | 2915      | 61    |
| H(40)  | 220        | 5215  | 2744      | 55    |

Chapter 3

Compound 28

Table 1. Crystal data for pa370

|   |   |
|---|---|
| Compound                                    | pa370   |
| Molecular formula                           | C <sub>38</sub> H <sub>36</sub> N <sub>2</sub> O <sub>2</sub> P <sub>2</sub> ,2(CHCl <sub>3</sub> ) <sub>2</sub> (Br) |
| Molecular weight                            | 1015.20   |
| Crystal habit                               | Colorless Block   |
| Crystal dimensions(mm)                      | 0.60x0.58x0.54  |
| Crystal system                              | monoclinic  |
| Space group                                 | P2 <sub>1</sub> /c  |
| a(Å)  | 13.347(1)   |
| b(Å)  | 11.074(1)   |
| c(Å)  | 15.874(1)   |
| α(°)  | 90.00   |
| β(°)  | 111.514(1)  |
| γ(°)  | 90.00   |
| V(Å <sup>3</sup> )                          | 2182.8(3)   |
| Z   | 2   |
| d(g·cm <sup>-3</sup> )                      | 1.545   |
| F(000)                                      | 1024  |
| μ(cm <sup>-1</sup> )                        | 2.334   |
| Absorption corrections                      | multi-scan ; 0.3348 min, 0.3654 max   |
| Diffractometer                              | KappaCCD  |
| X-ray source                                | MoKα  |
| λ(Å)  | 0.71069   |
| Monochromator                               | graphite  |
| T (K)                                       | 150.0(1)  |
| Scan mode                                   | phi and omega scans   |
| Maximum θ                                   | 30.01   |
| HKL ranges                                  | -18 18 ; -14 15 ; -20 22  |
| Reflections measured                        | 14803   |
| Unique data                                 | 6278  |
| Rint  | 0.0242  |
| Reflections used                            | 5351  |
| Criterion                                   | I > 2σ(I)   |
| Refinement type                             | Fsqd  |
| Hydrogen atoms                              | mixed   |
| Parameters refined                          | 251   |
| Reflections / parameter                     | 21  |
| wR2   | 0.0860  |
| R1  | 0.0388  |
| Weights a, b                                | 0.0261 ; 3.1298   |
| GoF   | 1.078   |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.157(0.074) / -0.748(0.074)  |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa370

| atom  | x        | y        | z       | U(eq) |
|-------|----------|----------|---------|-------|
| P(1)  | 1655(1)  | 6312(1)  | 4350(1) | 20(1) |
| O(1)  | -477(1)  | 7410(2)  | 3992(1) | 27(1) |
| C(1A) | 143(2)   | 4759(2)  | 4609(2) | 21(1) |
| N(1A) | 1260(2)  | 5114(2)  | 4730(2) | 31(1) |
| C(1B) | 490(10)  | 5320(10) | 5301(8) | 21(1) |
| N(1B) | 1260(2)  | 5114(2)  | 4730(2) | 31(1) |
| C(2)  | 670(2)   | 6710(2)  | 3270(2) | 22(1) |
| C(3)  | 867(2)   | 6480(2)  | 2477(2) | 26(1) |
| C(4)  | 82(2)    | 6708(2)  | 1635(2) | 32(1) |
| C(5)  | -910(2)  | 7165(2)  | 1580(2) | 32(1) |
| C(6)  | -1115(2) | 7405(2)  | 2360(2) | 29(1) |
| C(7)  | -329(2)  | 7185(2)  | 3206(2) | 23(1) |
| C(8)  | 1971(2)  | 7587(2)  | 5097(2) | 24(1) |
| C(9)  | 1647(2)  | 8761(2)  | 4806(2) | 30(1) |
| C(10) | 2003(2)  | 9713(3)  | 5409(2) | 37(1) |
| C(11) | 2684(2)  | 9498(3)  | 6299(2) | 39(1) |
| C(13) | 3001(2)  | 8342(3)  | 6591(2) | 40(1) |
| C(14) | 2648(2)  | 7379(3)  | 5995(2) | 34(1) |
| C(15) | 2879(2)  | 5897(2)  | 4207(1) | 21(1) |
| C(16) | 3684(2)  | 6756(2)  | 4322(2) | 24(1) |
| C(17) | 4594(2)  | 6441(2)  | 4142(2) | 28(1) |
| C(18) | 4699(2)  | 5292(2)  | 3844(2) | 28(1) |
| C(19) | 3905(2)  | 4434(2)  | 3734(2) | 31(1) |
| C(20) | 2992(2)  | 4734(2)  | 3918(2) | 28(1) |
| Cl(1) | 2323(1)  | -633(1)  | 2815(1) | 44(1) |
| Cl(2) | 4611(1)  | -613(1)  | 3190(1) | 56(1) |
| Cl(3) | 3704(1)  | 961(1)   | 4194(1) | 62(1) |
| C(21) | 3489(2)  | 270(3)   | 3142(2) | 43(1) |
| Br(1) | 2838(1)  | 2041(1)  | 1115(1) | 28(1) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa370

|                      |          |                      |          |
|----------------------|----------|----------------------|----------|
| P(1)-N(1A)           | 1.623(2) | P(1)-C(15)           | 1.790(2) |
| P(1)-C(2)            | 1.790(2) | P(1)-C(8)            | 1.792(2) |
| O(1)-C(7)            | 1.355(3) | O(1)-H(10)           | 0.8400   |
| C(1A)-N(1A)          | 1.485(3) | C(1A)-C(1A)#3        | 1.524(5) |
| C(1A)-H(1A1)         | 0.9900   | C(1A)-H(1A2)         | 0.9900   |
| N(1A)-H(1NA)         | 0.75(2)  | N(1A)-H(1NB)         | 0.75(2)  |
| C(1B)-C(1B)#3        | 1.48(2)  | C(1B)-H(1B1)         | 0.9900   |
| C(1B)-H(1B2)         | 0.9900   | C(2)-C(3)            | 1.401(3) |
| C(2)-C(7)            | 1.402(3) | C(3)-C(4)            | 1.387(3) |
| C(3)-H(3)            | 0.9500   | C(4)-C(5)            | 1.391(3) |
| C(4)-H(4)            | 0.9500   | C(5)-C(6)            | 1.388(3) |
| C(5)-H(5)            | 0.9500   | C(6)-C(7)            | 1.389(3) |
| C(6)-H(6)            | 0.9500   | C(8)-C(9)            | 1.395(3) |
| C(8)-C(14)           | 1.399(3) | C(9)-C(10)           | 1.385(4) |
| C(9)-H(9)            | 0.9500   | C(10)-C(11)          | 1.391(4) |
| C(10)-H(10)          | 0.9500   | C(11)-C(13)          | 1.375(4) |
| C(11)-H(11)          | 0.9500   | C(13)-C(14)          | 1.388(4) |
| C(13)-H(13)          | 0.9500   | C(14)-H(14)          | 0.9500   |
| C(15)-C(20)          | 1.393(3) | C(15)-C(16)          | 1.396(3) |
| C(16)-C(17)          | 1.391(3) | C(16)-H(16)          | 0.9500   |
| C(17)-C(18)          | 1.383(4) | C(17)-H(17)          | 0.9500   |
| C(18)-C(19)          | 1.386(4) | C(18)-H(18)          | 0.9500   |
| C(19)-C(20)          | 1.393(3) | C(19)-H(19)          | 0.9500   |
| C(20)-H(20)          | 0.9500   | Cl(1)-C(21)          | 1.760(3) |
| Cl(2)-C(21)          | 1.767(3) | Cl(3)-C(21)          | 1.762(3) |
| C(21)-H(21)          | 1.0000   |                      |          |
|                      |          |                      |          |
| N(1A)-P(1)-C(15)     | 105.8(1) | N(1A)-P(1)-C(2)      | 109.4(1) |
| C(15)-P(1)-C(2)      | 109.0(1) | N(1A)-P(1)-C(8)      | 115.3(1) |
| C(15)-P(1)-C(8)      | 106.4(1) | C(2)-P(1)-C(8)       | 110.6(1) |
| C(7)-O(1)-H(10)      | 109.6    | N(1A)-C(1A)-C(1A)#3  | 110.0(3) |
| N(1A)-C(1A)-H(1A1)   | 109.7    | C(1A)#3-C(1A)-H(1A1) | 109.7    |
| N(1A)-C(1A)-H(1A2)   | 109.7    | C(1A)#3-C(1A)-H(1A2) | 109.7    |
| H(1A1)-C(1A)-H(1A2)  | 108.2    | C(1A)-N(1A)-P(1)     | 128.0(2) |
| C(1A)-N(1A)-H(1NA)   | 114(1)   | P(1)-N(1A)-H(1NA)    | 118(1)   |
| C(1A)-N(1A)-H(1NB)   | 114(1)   | P(1)-N(1A)-H(1NB)    | 118(1)   |
| H(1NA)-N(1A)-H(1NB)  | 0(3)     | C(1B)#3-C(1B)-H(1B1) | 111.9    |
| C(1B)#3-C(1B)-H(1B2) | 111.9    | H(1B1)-C(1B)-H(1B2)  | 109.6    |
| C(3)-C(2)-C(7)       | 119.4(2) | C(3)-C(2)-P(1)       | 120.1(2) |
| C(7)-C(2)-P(1)       | 120.5(2) | C(4)-C(3)-C(2)       | 120.6(2) |
| C(4)-C(3)-H(3)       | 119.7    | C(2)-C(3)-H(3)       | 119.7    |
| C(3)-C(4)-C(5)       | 119.4(2) | C(3)-C(4)-H(4)       | 120.3    |
| C(5)-C(4)-H(4)       | 120.3    | C(6)-C(5)-C(4)       | 120.6(2) |
| C(6)-C(5)-H(5)       | 119.7    | C(4)-C(5)-H(5)       | 119.7    |
| C(5)-C(6)-C(7)       | 120.2(2) | C(5)-C(6)-H(6)       | 119.9    |
| C(7)-C(6)-H(6)       | 119.9    | O(1)-C(7)-C(6)       | 123.0(2) |
| O(1)-C(7)-C(2)       | 117.2(2) | C(6)-C(7)-C(2)       | 119.8(2) |
| C(9)-C(8)-C(14)      | 119.8(2) | C(9)-C(8)-P(1)       | 123.1(2) |
| C(14)-C(8)-P(1)      | 116.9(2) | C(10)-C(9)-C(8)      | 119.6(2) |
| C(10)-C(9)-H(9)      | 120.2    | C(8)-C(9)-H(9)       | 120.2    |
| C(9)-C(10)-C(11)     | 120.2(3) | C(9)-C(10)-H(10)     | 119.9    |
| C(11)-C(10)-H(10)    | 119.9    | C(13)-C(11)-C(10)    | 120.5(3) |
| C(13)-C(11)-H(11)    | 119.8    | C(10)-C(11)-H(11)    | 119.8    |
| C(11)-C(13)-C(14)    | 120.0(2) | C(11)-C(13)-H(13)    | 120.0    |
| C(14)-C(13)-H(13)    | 120.0    | C(13)-C(14)-C(8)     | 119.9(3) |
| C(13)-C(14)-H(14)    | 120.0    | C(8)-C(14)-H(14)     | 120.0    |
| C(20)-C(15)-C(16)    | 120.2(2) | C(20)-C(15)-P(1)     | 119.5(2) |
| C(16)-C(15)-P(1)     | 120.2(2) | C(17)-C(16)-C(15)    | 119.4(2) |
| C(17)-C(16)-H(16)    | 120.3    | C(15)-C(16)-H(16)    | 120.3    |
| C(18)-C(17)-C(16)    | 120.5(2) | C(18)-C(17)-H(17)    | 119.8    |
| C(16)-C(17)-H(17)    | 119.8    | C(17)-C(18)-C(19)    | 120.3(2) |
| C(17)-C(18)-H(18)    | 119.8    | C(19)-C(18)-H(18)    | 119.8    |
| C(18)-C(19)-C(20)    | 119.8(2) | C(18)-C(19)-H(19)    | 120.1    |
| C(20)-C(19)-H(19)    | 120.1    | C(19)-C(20)-C(15)    | 119.8(2) |
| C(19)-C(20)-H(20)    | 120.1    | C(15)-C(20)-H(20)    | 120.1    |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Cl(1)-C(21)-Cl(3) | 110.2(2) | Cl(1)-C(21)-Cl(2) | 110.0(2) |
| Cl(3)-C(21)-Cl(2) | 111.0(2) | Cl(1)-C(21)-H(21) | 108.5    |
| Cl(3)-C(21)-H(21) | 108.5    | Cl(2)-C(21)-H(21) | 108.5    |

-----  
 Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z                      2: -x, y+1/2, -z+1/2                      3: -x, -y, -z  
 4: x, -y-1/2, z-1/2



## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa370

| atom  | U11   | U22   | U33   | U23    | U13   | U12    |
|-------|-------|-------|-------|--------|-------|--------|
| P(1)  | 15(1) | 26(1) | 22(1) | 4(1)   | 10(1) | 0(1)   |
| O(1)  | 19(1) | 37(1) | 28(1) | 2(1)   | 11(1) | 3(1)   |
| C(1A) | 19(1) | 22(1) | 24(1) | -1(1)  | 10(1) | -6(1)  |
| N(1A) | 18(1) | 36(1) | 42(1) | 19(1)  | 15(1) | 6(1)   |
| C(1B) | 19(1) | 22(1) | 24(1) | -1(1)  | 10(1) | -6(1)  |
| N(1B) | 18(1) | 36(1) | 42(1) | 19(1)  | 15(1) | 6(1)   |
| C(2)  | 18(1) | 24(1) | 23(1) | 4(1)   | 8(1)  | -1(1)  |
| C(3)  | 23(1) | 33(1) | 25(1) | 2(1)   | 11(1) | 3(1)   |
| C(4)  | 33(1) | 39(1) | 23(1) | 3(1)   | 10(1) | 3(1)   |
| C(5)  | 29(1) | 39(1) | 25(1) | 5(1)   | 5(1)  | 4(1)   |
| C(6)  | 21(1) | 34(1) | 31(1) | 6(1)   | 7(1)  | 5(1)   |
| C(7)  | 20(1) | 24(1) | 24(1) | 3(1)   | 9(1)  | -1(1)  |
| C(8)  | 21(1) | 32(1) | 22(1) | 1(1)   | 12(1) | -2(1)  |
| C(9)  | 32(1) | 31(1) | 26(1) | 1(1)   | 11(1) | -4(1)  |
| C(10) | 43(1) | 34(1) | 36(1) | -3(1)  | 17(1) | -8(1)  |
| C(11) | 41(1) | 48(2) | 31(1) | -12(1) | 17(1) | -14(1) |
| C(13) | 37(1) | 58(2) | 23(1) | -4(1)  | 9(1)  | -1(1)  |
| C(14) | 32(1) | 46(2) | 23(1) | 1(1)   | 10(1) | 6(1)   |
| C(15) | 15(1) | 27(1) | 20(1) | 3(1)   | 7(1)  | -1(1)  |
| C(16) | 19(1) | 28(1) | 26(1) | 4(1)   | 10(1) | -2(1)  |
| C(17) | 18(1) | 39(1) | 30(1) | 6(1)   | 12(1) | -2(1)  |
| C(18) | 19(1) | 44(1) | 23(1) | 6(1)   | 10(1) | 6(1)   |
| C(19) | 30(1) | 34(1) | 31(1) | -3(1)  | 14(1) | 5(1)   |
| C(20) | 23(1) | 32(1) | 29(1) | -3(1)  | 12(1) | -3(1)  |
| Cl(1) | 44(1) | 46(1) | 41(1) | -1(1)  | 15(1) | -4(1)  |
| Cl(2) | 48(1) | 66(1) | 61(1) | 13(1)  | 27(1) | -2(1)  |
| Cl(3) | 67(1) | 62(1) | 42(1) | -10(1) | 3(1)  | -3(1)  |
| C(21) | 49(2) | 39(2) | 35(1) | 7(1)   | 9(1)  | -5(1)  |
| Br(1) | 21(1) | 31(1) | 34(1) | 1(1)   | 13(1) | 1(1)   |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa370

| atom   | x        | y        | z        | U(eq) |
|--------|----------|----------|----------|-------|
| H(10)  | -1101    | 7679     | 3878     | 41    |
| H(1A1) | 80       | 3868     | 4585     | 25    |
| H(1A2) | -365     | 5088     | 4030     | 25    |
| H(1NA) | 1680(10) | 4720(20) | 5060(10) | 46    |
| H(1B1) | 787      | 4943     | 5908     | 25    |
| H(1B2) | 347      | 6186     | 5362     | 25    |
| H(1NB) | 1680(10) | 4720(20) | 5060(10) | 46    |
| H(3)   | 1544     | 6164     | 2517     | 32    |
| H(4)   | 221      | 6553     | 1099     | 38    |
| H(5)   | -1452    | 7315     | 1004     | 39    |
| H(6)   | -1795    | 7719     | 2315     | 35    |
| H(9)   | 1184     | 8907     | 4198     | 36    |
| H(10)  | 1782     | 10513    | 5213     | 44    |
| H(11)  | 2931     | 10154    | 6707     | 47    |
| H(13)  | 3462     | 8202     | 7201     | 48    |
| H(14)  | 2865     | 6579     | 6197     | 40    |
| H(16)  | 3611     | 7548     | 4523     | 28    |
| H(17)  | 5147     | 7020     | 4224     | 34    |
| H(18)  | 5319     | 5089     | 3714     | 34    |
| H(19)  | 3982     | 3644     | 3533     | 37    |
| H(20)  | 2448     | 4147     | 3847     | 33    |
| H(21)  | 3382     | 916      | 2676     | 51    |

**Complex 30**

Table 1. Crystal data for pa236

|   |   |
|---|---|
| Compound                                    | pa236   |
| Molecular formula                           | C <sub>38</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd <sub>4</sub> (CH <sub>2</sub> Cl <sub>2</sub> ) |
| Molecular weight                            | 1056.70   |
| Crystal habit                               | Orange Block  |
| Crystal dimensions(mm)                      | 0.28x0.18x0.16  |
| Crystal system                              | orthorhombic  |
| Space group                                 | Pna2 <sub>1</sub>   |
| a(Å)  | 23.441(1)   |
| b(Å)  | 10.218(1)   |
| c(Å)  | 19.401(1)   |
| α(°)  | 90.00   |
| β(°)  | 90.00   |
| γ(°)  | 90.00   |
| V(Å <sup>3</sup> )                          | 4646.9(6)   |
| Z   | 4   |
| d(g·cm <sup>-3</sup> )                      | 1.510   |
| F(000)                                      | 2136  |
| μ(cm <sup>-1</sup> )                        | 0.965   |
| Absorption corrections                      | multi-scan ; 0.7738 min, 0.8608 max   |
| Diffractionmeter                            | KappaCCD  |
| X-ray source                                | MoKα  |
| λ(Å)  | 0.71069   |
| Monochromator                               | graphite  |
| T (K)                                       | 150.0(1)  |
| Scan mode                                   | phi and omega scans   |
| Maximum θ                                   | 30.02   |
| HKL ranges                                  | -33 31 ; -10 14 ; -27 20  |
| Reflections measured                        | 44198   |
| Unique data                                 | 12183   |
| Rint  | 0.0323  |
| Reflections used                            | 10068   |
| Criterion                                   | I > 2σ(I)   |
| Refinement type                             | Fsqd  |
| Hydrogen atoms                              | constr  |
| Parameters refined                          | 516   |
| Reflections / parameter                     | 19  |
| wR2   | 0.1165  |
| R1  | 0.0433  |
| Flack's parameter                           | 0.38(2)   |
| Weights a, b                                | 0.0609 ; 1.5094   |
| GoF   | 1.091   |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.835(0.065) / -0.501(0.065)  |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa236

| atom  | x        | y        | z        | U(eq)  |
|-------|----------|----------|----------|--------|
| Pd(1) | -6221(1) | -1849(1) | -3994(1) | 26(1)  |
| P(1)  | -7426(1) | -3000(1) | -4108(1) | 27(1)  |
| P(2)  | -5012(1) | -2965(1) | -3893(1) | 26(1)  |
| O(1)  | -6776(1) | -390(2)  | -4225(1) | 33(1)  |
| O(2)  | -5667(1) | -367(2)  | -3780(1) | 34(1)  |
| N(1)  | -6756(1) | -3343(3) | -4199(2) | 31(1)  |
| N(2)  | -5679(1) | -3319(3) | -3765(2) | 28(1)  |
| C(1)  | -6539(1) | -4557(3) | -3873(3) | 38(1)  |
| C(2)  | -5904(1) | -4579(3) | -4033(3) | 35(1)  |
| C(3)  | -7579(1) | -1649(4) | -4654(2) | 29(1)  |
| C(4)  | -7223(1) | -521(4)  | -4629(2) | 30(1)  |
| C(5)  | -7381(2) | 544(4)   | -5056(2) | 34(1)  |
| C(6)  | -7849(2) | 473(4)   | -5487(2) | 36(1)  |
| C(7)  | -8179(2) | -652(4)  | -5526(2) | 36(1)  |
| C(8)  | -8050(2) | -1705(4) | -5107(2) | 33(1)  |
| C(9)  | -7842(1) | -4375(4) | -4392(2) | 30(1)  |
| C(10) | -7675(2) | -5006(4) | -5012(2) | 38(1)  |
| C(11) | -7992(2) | -6025(5) | -5267(3) | 47(1)  |
| C(12) | -8482(2) | -6438(4) | -4924(2) | 44(1)  |
| C(13) | -8651(2) | -5825(4) | -4323(2) | 39(1)  |
| C(14) | -8337(1) | -4799(3) | -4054(2) | 33(1)  |
| C(15) | -7648(1) | -2638(4) | -3230(2) | 29(1)  |
| C(16) | -7642(2) | -3631(4) | -2732(2) | 36(1)  |
| C(17) | -7800(2) | -3347(5) | -2065(2) | 46(1)  |
| C(18) | -7953(2) | -2097(6) | -1878(2) | 51(1)  |
| C(19) | -7957(2) | -1100(5) | -2375(2) | 45(1)  |
| C(20) | -7805(2) | -1378(4) | -3045(2) | 37(1)  |
| C(21) | -4858(1) | -1586(4) | -3368(2) | 29(1)  |
| C(22) | -5217(1) | -479(3)  | -3381(2) | 28(1)  |
| C(23) | -5070(2) | 580(4)   | -2944(2) | 35(1)  |
| C(24) | -4605(2) | 528(4)   | -2514(2) | 36(1)  |
| C(25) | -4257(2) | -591(4)  | -2491(2) | 36(1)  |
| C(26) | -4384(2) | -1638(4) | -2914(2) | 32(1)  |
| C(27) | -4581(1) | -4330(3) | -3616(2) | 28(1)  |
| C(28) | -4107(1) | -4757(3) | -3982(2) | 31(1)  |
| C(29) | -3797(1) | -5810(4) | -3742(2) | 37(1)  |
| C(30) | -3949(2) | -6435(4) | -3136(2) | 42(1)  |
| C(31) | -4414(2) | -5985(4) | -2759(2) | 39(1)  |
| C(32) | -4729(2) | -4945(4) | -3005(2) | 36(1)  |
| C(33) | -4817(1) | -2599(4) | -4766(2) | 33(1)  |
| C(34) | -4828(2) | -3577(5) | -5279(2) | 37(1)  |
| C(35) | -4695(2) | -3250(5) | -5954(2) | 46(1)  |
| C(36) | -4554(2) | -1986(5) | -6134(2) | 48(1)  |
| C(37) | -4552(2) | -1021(6) | -5636(3) | 58(1)  |
| C(38) | -4687(2) | -1317(4) | -4963(2) | 41(1)  |
| Cl(1) | -6342(1) | -1024(2) | -1954(1) | 86(1)  |
| Cl(2) | -5851(1) | -3470(2) | -1532(1) | 142(1) |
| C(39) | -5811(3) | -2199(6) | -2076(3) | 77(2)  |
| Cl(3) | -6397(1) | 2823(2)  | -2594(1) | 89(1)  |
| Cl(4) | -7408(1) | 2421(1)  | -3425(1) | 63(1)  |
| C(40) | -6821(2) | 1665(5)  | -3008(3) | 60(1)  |
| Cl(5) | -8236(1) | 3021(2)  | -1514(1) | 109(1) |
| Cl(6) | -8775(1) | 671(2)   | -1003(1) | 70(1)  |
| C(41) | -8676(2) | 2360(7)  | -862(3)  | 70(2)  |
| Cl(7) | -9159(1) | -3328(3) | -726(1)  | 144(1) |
| Cl(8) | -9925(1) | -2515(1) | 370(1)   | 66(1)  |
| C(42) | -9247(3) | -3125(6) | 129(3)   | 71(2)  |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa236

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| Pd(1)-N(1)       | 2.014(3) | Pd(1)-N(2)       | 2.017(3) |
| Pd(1)-O(1)       | 2.029(2) | Pd(1)-O(2)       | 2.039(2) |
| P(1)-N(1)        | 1.620(3) | P(1)-C(3)        | 1.777(4) |
| P(1)-C(9)        | 1.795(4) | P(1)-C(15)       | 1.819(4) |
| P(2)-N(2)        | 1.623(3) | P(2)-C(21)       | 1.777(4) |
| P(2)-C(33)       | 1.793(4) | P(2)-C(27)       | 1.804(3) |
| O(1)-C(4)        | 1.314(4) | O(2)-C(22)       | 1.313(4) |
| N(1)-C(1)        | 1.482(5) | N(2)-C(2)        | 1.484(4) |
| C(1)-C(2)        | 1.521(4) | C(1)-H(1A)       | 0.9900   |
| C(1)-H(1B)       | 0.9900   | C(2)-H(2A)       | 0.9900   |
| C(2)-H(2B)       | 0.9900   | C(3)-C(8)        | 1.412(5) |
| C(3)-C(4)        | 1.425(5) | C(4)-C(5)        | 1.417(5) |
| C(5)-C(6)        | 1.381(5) | C(5)-H(5)        | 0.9500   |
| C(6)-C(7)        | 1.388(6) | C(6)-H(6)        | 0.9500   |
| C(7)-C(8)        | 1.383(6) | C(7)-H(7)        | 0.9500   |
| C(8)-H(8)        | 0.9500   | C(9)-C(14)       | 1.402(5) |
| C(9)-C(10)       | 1.420(6) | C(10)-C(11)      | 1.371(6) |
| C(10)-H(10)      | 0.9500   | C(11)-C(12)      | 1.393(6) |
| C(11)-H(11)      | 0.9500   | C(12)-C(13)      | 1.382(6) |
| C(12)-H(12)      | 0.9500   | C(13)-C(14)      | 1.383(5) |
| C(13)-H(13)      | 0.9500   | C(14)-H(14)      | 0.9500   |
| C(15)-C(20)      | 1.387(6) | C(15)-C(16)      | 1.402(6) |
| C(16)-C(17)      | 1.377(6) | C(16)-H(16)      | 0.9500   |
| C(17)-C(18)      | 1.375(7) | C(17)-H(17)      | 0.9500   |
| C(18)-C(19)      | 1.403(7) | C(18)-H(18)      | 0.9500   |
| C(19)-C(20)      | 1.377(6) | C(19)-H(19)      | 0.9500   |
| C(20)-H(20)      | 0.9500   | C(21)-C(22)      | 1.411(5) |
| C(21)-C(26)      | 1.417(5) | C(22)-C(23)      | 1.417(5) |
| C(23)-C(24)      | 1.373(5) | C(23)-H(23)      | 0.9500   |
| C(24)-C(25)      | 1.406(5) | C(24)-H(24)      | 0.9500   |
| C(25)-C(26)      | 1.381(6) | C(25)-H(25)      | 0.9500   |
| C(26)-H(26)      | 0.9500   | C(27)-C(32)      | 1.386(5) |
| C(27)-C(28)      | 1.390(5) | C(28)-C(29)      | 1.380(5) |
| C(28)-H(28)      | 0.9500   | C(29)-C(30)      | 1.384(6) |
| C(29)-H(29)      | 0.9500   | C(30)-C(31)      | 1.392(6) |
| C(30)-H(30)      | 0.9500   | C(31)-C(32)      | 1.378(5) |
| C(31)-H(31)      | 0.9500   | C(32)-H(32)      | 0.9500   |
| C(33)-C(38)      | 1.399(6) | C(33)-C(34)      | 1.410(6) |
| C(34)-C(35)      | 1.387(6) | C(34)-H(34)      | 0.9500   |
| C(35)-C(36)      | 1.378(7) | C(35)-H(35)      | 0.9500   |
| C(36)-C(37)      | 1.380(7) | C(36)-H(36)      | 0.9500   |
| C(37)-C(38)      | 1.378(6) | C(37)-H(37)      | 0.9500   |
| C(38)-H(38)      | 0.9500   | Cl(1)-C(39)      | 1.745(6) |
| Cl(2)-C(39)      | 1.677(6) | C(39)-H(39A)     | 0.9900   |
| C(39)-H(39B)     | 0.9900   | Cl(3)-C(40)      | 1.741(5) |
| Cl(4)-C(40)      | 1.774(5) | C(40)-H(40A)     | 0.9900   |
| C(40)-H(40B)     | 0.9900   | Cl(5)-C(41)      | 1.765(6) |
| Cl(6)-C(41)      | 1.763(7) | C(41)-H(41A)     | 0.9900   |
| C(41)-H(41B)     | 0.9900   | Cl(7)-C(42)      | 1.684(7) |
| Cl(8)-C(42)      | 1.770(6) | C(42)-H(42A)     | 0.9900   |
| C(42)-H(42B)     | 0.9900   |                  |          |
| N(1)-Pd(1)-N(2)  | 82.6(1)  | N(1)-Pd(1)-O(1)  | 96.6(1)  |
| N(2)-Pd(1)-O(1)  | 179.1(1) | N(1)-Pd(1)-O(2)  | 178.7(1) |
| N(2)-Pd(1)-O(2)  | 96.1(1)  | O(1)-Pd(1)-O(2)  | 84.7(1)  |
| N(1)-P(1)-C(3)   | 107.4(2) | N(1)-P(1)-C(9)   | 108.9(2) |
| C(3)-P(1)-C(9)   | 108.4(2) | N(1)-P(1)-C(15)  | 115.0(2) |
| C(3)-P(1)-C(15)  | 110.0(2) | C(9)-P(1)-C(15)  | 106.9(2) |
| N(2)-P(2)-C(21)  | 106.6(2) | N(2)-P(2)-C(33)  | 115.9(2) |
| C(21)-P(2)-C(33) | 108.9(2) | N(2)-P(2)-C(27)  | 108.8(2) |
| C(21)-P(2)-C(27) | 109.1(2) | C(33)-P(2)-C(27) | 107.4(2) |
| C(4)-O(1)-Pd(1)  | 124.6(2) | C(22)-O(2)-Pd(1) | 124.6(2) |
| C(1)-N(1)-P(1)   | 117.9(2) | C(1)-N(1)-Pd(1)  | 109.7(2) |
| P(1)-N(1)-Pd(1)  | 114.7(2) | C(2)-N(2)-P(2)   | 118.8(2) |
| C(2)-N(2)-Pd(1)  | 110.2(2) | P(2)-N(2)-Pd(1)  | 114.0(2) |

|                    |          |                     |          |
|--------------------|----------|---------------------|----------|
| N(1)-C(1)-C(2)     | 105.1(3) | N(1)-C(1)-H(1A)     | 110.7    |
| C(2)-C(1)-H(1A)    | 110.7    | N(1)-C(1)-H(1B)     | 110.7    |
| C(2)-C(1)-H(1B)    | 110.7    | H(1A)-C(1)-H(1B)    | 108.8    |
| N(2)-C(2)-C(1)     | 105.3(3) | N(2)-C(2)-H(2A)     | 110.7    |
| C(1)-C(2)-H(2A)    | 110.7    | N(2)-C(2)-H(2B)     | 110.7    |
| C(1)-C(2)-H(2B)    | 110.7    | H(2A)-C(2)-H(2B)    | 108.8    |
| C(8)-C(3)-C(4)     | 120.9(3) | C(8)-C(3)-P(1)      | 119.8(3) |
| C(4)-C(3)-P(1)     | 119.3(3) | O(1)-C(4)-C(5)      | 118.7(3) |
| O(1)-C(4)-C(3)     | 124.8(3) | C(5)-C(4)-C(3)      | 116.5(3) |
| C(6)-C(5)-C(4)     | 121.5(4) | C(6)-C(5)-H(5)      | 119.3    |
| C(4)-C(5)-H(5)     | 119.3    | C(5)-C(6)-C(7)      | 121.3(4) |
| C(5)-C(6)-H(6)     | 119.3    | C(7)-C(6)-H(6)      | 119.3    |
| C(8)-C(7)-C(6)     | 119.3(4) | C(8)-C(7)-H(7)      | 120.3    |
| C(6)-C(7)-H(7)     | 120.3    | C(7)-C(8)-C(3)      | 120.4(4) |
| C(7)-C(8)-H(8)     | 119.8    | C(3)-C(8)-H(8)      | 119.8    |
| C(14)-C(9)-C(10)   | 118.9(3) | C(14)-C(9)-P(1)     | 123.2(3) |
| C(10)-C(9)-P(1)    | 117.8(3) | C(11)-C(10)-C(9)    | 120.2(4) |
| C(11)-C(10)-H(10)  | 119.9    | C(9)-C(10)-H(10)    | 119.9    |
| C(10)-C(11)-C(12)  | 120.3(4) | C(10)-C(11)-H(11)   | 119.9    |
| C(12)-C(11)-H(11)  | 119.9    | C(13)-C(12)-C(11)   | 120.1(4) |
| C(13)-C(12)-H(12)  | 119.9    | C(11)-C(12)-H(12)   | 119.9    |
| C(12)-C(13)-C(14)  | 120.7(4) | C(12)-C(13)-H(13)   | 119.6    |
| C(14)-C(13)-H(13)  | 119.6    | C(13)-C(14)-C(9)    | 119.9(4) |
| C(13)-C(14)-H(14)  | 120.1    | C(9)-C(14)-H(14)    | 120.1    |
| C(20)-C(15)-C(16)  | 119.7(4) | C(20)-C(15)-P(1)    | 120.5(3) |
| C(16)-C(15)-P(1)   | 119.8(3) | C(17)-C(16)-C(15)   | 119.6(4) |
| C(17)-C(16)-H(16)  | 120.2    | C(15)-C(16)-H(16)   | 120.2    |
| C(18)-C(17)-C(16)  | 120.9(4) | C(18)-C(17)-H(17)   | 119.6    |
| C(16)-C(17)-H(17)  | 119.6    | C(17)-C(18)-C(19)   | 119.7(4) |
| C(17)-C(18)-H(18)  | 120.2    | C(19)-C(18)-H(18)   | 120.2    |
| C(20)-C(19)-C(18)  | 119.8(5) | C(20)-C(19)-H(19)   | 120.1    |
| C(18)-C(19)-H(19)  | 120.1    | C(19)-C(20)-C(15)   | 120.3(4) |
| C(19)-C(20)-H(20)  | 119.8    | C(15)-C(20)-H(20)   | 119.8    |
| C(22)-C(21)-C(26)  | 120.6(3) | C(22)-C(21)-P(2)    | 120.3(3) |
| C(26)-C(21)-P(2)   | 119.1(3) | O(2)-C(22)-C(21)    | 124.1(3) |
| O(2)-C(22)-C(23)   | 118.8(3) | C(21)-C(22)-C(23)   | 117.2(3) |
| C(24)-C(23)-C(22)  | 121.8(3) | C(24)-C(23)-H(23)   | 119.1    |
| C(22)-C(23)-H(23)  | 119.1    | C(23)-C(24)-C(25)   | 120.7(4) |
| C(23)-C(24)-H(24)  | 119.6    | C(25)-C(24)-H(24)   | 119.6    |
| C(26)-C(25)-C(24)  | 119.1(3) | C(26)-C(25)-H(25)   | 120.5    |
| C(24)-C(25)-H(25)  | 120.5    | C(25)-C(26)-C(21)   | 120.6(4) |
| C(25)-C(26)-H(26)  | 119.7    | C(21)-C(26)-H(26)   | 119.7    |
| C(32)-C(27)-C(28)  | 119.6(3) | C(32)-C(27)-P(2)    | 117.8(3) |
| C(28)-C(27)-P(2)   | 122.6(3) | C(29)-C(28)-C(27)   | 119.6(4) |
| C(29)-C(28)-H(28)  | 120.2    | C(27)-C(28)-H(28)   | 120.2    |
| C(28)-C(29)-C(30)  | 120.7(4) | C(28)-C(29)-H(29)   | 119.6    |
| C(30)-C(29)-H(29)  | 119.6    | C(29)-C(30)-C(31)   | 119.7(4) |
| C(29)-C(30)-H(30)  | 120.1    | C(31)-C(30)-H(30)   | 120.1    |
| C(32)-C(31)-C(30)  | 119.5(4) | C(32)-C(31)-H(31)   | 120.3    |
| C(30)-C(31)-H(31)  | 120.3    | C(31)-C(32)-C(27)   | 120.8(3) |
| C(31)-C(32)-H(32)  | 119.6    | C(27)-C(32)-H(32)   | 119.6    |
| C(38)-C(33)-C(34)  | 118.3(4) | C(38)-C(33)-P(2)    | 120.6(3) |
| C(34)-C(33)-P(2)   | 120.9(3) | C(35)-C(34)-C(33)   | 119.5(4) |
| C(35)-C(34)-H(34)  | 120.3    | C(33)-C(34)-H(34)   | 120.3    |
| C(36)-C(35)-C(34)  | 121.2(4) | C(36)-C(35)-H(35)   | 119.4    |
| C(34)-C(35)-H(35)  | 119.4    | C(35)-C(36)-C(37)   | 119.6(4) |
| C(35)-C(36)-H(36)  | 120.2    | C(37)-C(36)-H(36)   | 120.2    |
| C(38)-C(37)-C(36)  | 120.3(5) | C(38)-C(37)-H(37)   | 119.8    |
| C(36)-C(37)-H(37)  | 119.8    | C(37)-C(38)-C(33)   | 121.0(4) |
| C(37)-C(38)-H(38)  | 119.5    | C(33)-C(38)-H(38)   | 119.5    |
| Cl(2)-C(39)-Cl(1)  | 114.1(3) | Cl(2)-C(39)-H(39A)  | 108.7    |
| Cl(1)-C(39)-H(39A) | 108.7    | Cl(2)-C(39)-H(39B)  | 108.7    |
| Cl(1)-C(39)-H(39B) | 108.7    | H(39A)-C(39)-H(39B) | 107.6    |
| Cl(3)-C(40)-Cl(4)  | 110.9(3) | Cl(3)-C(40)-H(40A)  | 109.5    |
| Cl(4)-C(40)-H(40A) | 109.5    | Cl(3)-C(40)-H(40B)  | 109.5    |
| Cl(4)-C(40)-H(40B) | 109.5    | H(40A)-C(40)-H(40B) | 108.0    |
| Cl(6)-C(41)-Cl(5)  | 109.9(3) | Cl(6)-C(41)-H(41A)  | 109.7    |
| Cl(5)-C(41)-H(41A) | 109.7    | Cl(6)-C(41)-H(41B)  | 109.7    |

# Appendix 1. Crystallographic data

|                    |          |                     |       |
|--------------------|----------|---------------------|-------|
| Cl(5)-C(41)-H(41B) | 109.7    | H(41A)-C(41)-H(41B) | 108.2 |
| Cl(7)-C(42)-Cl(8)  | 114.4(4) | Cl(7)-C(42)-H(42A)  | 108.7 |
| Cl(8)-C(42)-H(42A) | 108.7    | Cl(7)-C(42)-H(42B)  | 108.7 |
| Cl(8)-C(42)-H(42B) | 108.7    | H(42A)-C(42)-H(42B) | 107.6 |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa236

| atom  | U11    | U22    | U33    | U23    | U13    | U12    |
|-------|--------|--------|--------|--------|--------|--------|
| Pd(1) | 23(1)  | 25(1)  | 30(1)  | 1(1)   | 1(1)   | 1(1)   |
| P(1)  | 22(1)  | 28(1)  | 31(1)  | 1(1)   | 2(1)   | 0(1)   |
| P(2)  | 22(1)  | 28(1)  | 29(1)  | 1(1)   | 1(1)   | 2(1)   |
| O(1)  | 27(1)  | 28(1)  | 44(2)  | -1(1)  | -4(1)  | 5(1)   |
| O(2)  | 30(1)  | 28(1)  | 44(2)  | 0(1)   | -8(1)  | -1(1)  |
| N(1)  | 20(1)  | 28(2)  | 44(2)  | -1(1)  | -2(1)  | -2(1)  |
| N(2)  | 23(1)  | 24(1)  | 36(2)  | 0(1)   | 4(1)   | 2(1)   |
| C(1)  | 24(1)  | 28(2)  | 62(3)  | 2(2)   | 0(2)   | 0(1)   |
| C(2)  | 30(1)  | 25(2)  | 49(2)  | 1(2)   | 0(2)   | 2(1)   |
| C(3)  | 26(2)  | 30(2)  | 30(2)  | 1(2)   | 4(1)   | 2(1)   |
| C(4)  | 29(2)  | 32(2)  | 30(2)  | -1(2)  | 1(1)   | 3(1)   |
| C(5)  | 32(2)  | 32(2)  | 38(2)  | 5(2)   | 1(1)   | -1(1)  |
| C(6)  | 37(2)  | 41(2)  | 30(2)  | 7(2)   | 3(2)   | 5(2)   |
| C(7)  | 33(2)  | 44(2)  | 30(2)  | 5(2)   | 0(2)   | 3(2)   |
| C(8)  | 23(2)  | 35(2)  | 40(2)  | -3(2)  | 1(1)   | -2(1)  |
| C(9)  | 26(2)  | 31(2)  | 33(2)  | 4(2)   | 0(1)   | -2(1)  |
| C(10) | 35(2)  | 37(2)  | 43(2)  | -5(2)  | 7(2)   | -5(2)  |
| C(11) | 49(2)  | 43(2)  | 50(3)  | -4(2)  | 9(2)   | -3(2)  |
| C(12) | 43(2)  | 39(2)  | 51(3)  | -3(2)  | -5(2)  | -10(2) |
| C(13) | 28(2)  | 41(2)  | 49(2)  | 5(2)   | -4(2)  | -4(2)  |
| C(14) | 24(1)  | 37(2)  | 37(2)  | 1(2)   | 2(2)   | -1(1)  |
| C(15) | 23(2)  | 35(2)  | 28(2)  | 2(2)   | -3(1)  | 0(1)   |
| C(16) | 34(2)  | 42(2)  | 32(2)  | 4(2)   | -4(2)  | -2(2)  |
| C(17) | 41(2)  | 60(3)  | 38(2)  | 10(2)  | -4(2)  | -11(2) |
| C(18) | 37(2)  | 86(4)  | 31(2)  | -9(2)  | 2(2)   | -9(2)  |
| C(19) | 45(2)  | 55(3)  | 37(2)  | -7(2)  | 3(2)   | 2(2)   |
| C(20) | 34(2)  | 42(2)  | 35(2)  | -3(2)  | 2(2)   | 1(2)   |
| C(21) | 25(2)  | 34(2)  | 27(2)  | 2(2)   | 2(1)   | -3(1)  |
| C(22) | 27(2)  | 28(2)  | 28(2)  | 3(2)   | 3(1)   | -4(1)  |
| C(23) | 34(2)  | 27(2)  | 45(2)  | -5(2)  | 1(2)   | 0(1)   |
| C(24) | 30(2)  | 38(2)  | 41(2)  | -11(2) | -3(2)  | 0(1)   |
| C(25) | 31(2)  | 39(2)  | 39(2)  | -2(2)  | -2(2)  | -2(2)  |
| C(26) | 31(2)  | 37(2)  | 27(2)  | 2(2)   | 2(1)   | 2(1)   |
| C(27) | 24(1)  | 27(2)  | 32(2)  | -1(2)  | -1(1)  | 1(1)   |
| C(28) | 24(1)  | 34(2)  | 33(2)  | -4(2)  | 1(2)   | 1(1)   |
| C(29) | 27(2)  | 43(2)  | 41(2)  | -2(2)  | -2(1)  | 5(1)   |
| C(30) | 37(2)  | 39(2)  | 49(3)  | -2(2)  | -7(2)  | 7(2)   |
| C(31) | 44(2)  | 39(2)  | 35(2)  | 4(2)   | 1(2)   | 10(2)  |
| C(32) | 34(2)  | 36(2)  | 36(2)  | -5(2)  | 5(2)   | 7(2)   |
| C(33) | 25(2)  | 38(2)  | 37(2)  | 1(2)   | 2(2)   | 4(1)   |
| C(34) | 32(2)  | 45(2)  | 35(2)  | -6(2)  | -4(2)  | 4(2)   |
| C(35) | 41(2)  | 69(3)  | 28(2)  | -11(2) | -6(2)  | 18(2)  |
| C(36) | 50(2)  | 63(3)  | 31(2)  | 6(2)   | 3(2)   | 14(2)  |
| C(37) | 67(3)  | 60(3)  | 48(3)  | 18(3)  | 8(2)   | 6(3)   |
| C(38) | 47(2)  | 41(2)  | 35(2)  | 4(2)   | 7(2)   | 4(2)   |
| Cl(1) | 82(1)  | 104(1) | 73(1)  | 11(1)  | 12(1)  | 38(1)  |
| Cl(2) | 196(3) | 102(2) | 128(2) | 63(1)  | 99(2)  | 68(2)  |
| C(39) | 95(4)  | 70(4)  | 65(4)  | 10(3)  | 24(3)  | 23(3)  |
| Cl(3) | 98(1)  | 64(1)  | 104(1) | -19(1) | -61(1) | 21(1)  |
| Cl(4) | 49(1)  | 54(1)  | 87(1)  | 6(1)   | -19(1) | -9(1)  |
| C(40) | 68(3)  | 47(3)  | 66(4)  | -2(2)  | -23(3) | 0(2)   |
| Cl(5) | 123(2) | 129(2) | 73(1)  | -4(1)  | -14(1) | -41(1) |
| Cl(6) | 59(1)  | 103(1) | 48(1)  | -11(1) | 1(1)   | 16(1)  |
| C(41) | 77(4)  | 94(5)  | 40(3)  | -5(3)  | -3(2)  | 18(3)  |
| Cl(7) | 113(2) | 240(3) | 79(1)  | 27(2)  | 38(1)  | 32(2)  |
| Cl(8) | 54(1)  | 62(1)  | 82(1)  | -5(1)  | 10(1)  | -6(1)  |
| C(42) | 64(3)  | 76(4)  | 73(4)  | 21(3)  | 4(3)   | 14(3)  |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa236

| atom   | x          | y          | z          | U(eq) |
|--------|------------|------------|------------|-------|
| H(1A)  | -6730      | -5335.9995 | -4069      | 46    |
| H(1B)  | -6605      | -4540      | -3369      | 46    |
| H(2A)  | -5716      | -5327      | -3801      | 42    |
| H(2B)  | -5838.9995 | -4651      | -4535      | 42    |
| H(5)   | -7161      | 1324       | -5044.9995 | 41    |
| H(6)   | -7946      | 1209       | -5762      | 43    |
| H(7)   | -8491      | -697.9999  | -5838.9995 | 43    |
| H(8)   | -8280      | -2471      | -5123      | 39    |
| H(10)  | -7343.9995 | -4723      | -5251      | 46    |
| H(11)  | -7877      | -6451      | -5680      | 57    |
| H(12)  | -8701      | -7141      | -5104      | 53    |
| H(13)  | -8985      | -6111.9995 | -4092.0002 | 47    |
| H(14)  | -8457      | -4382      | -3641      | 39    |
| H(16)  | -7530      | -4494      | -2852.9998 | 44    |
| H(17)  | -7803      | -4023.9998 | -1729.0001 | 56    |
| H(18)  | -8056      | -1910      | -1415      | 61    |
| H(19)  | -8063      | -235.0000  | -2250      | 54    |
| H(20)  | -7808      | -703       | -3382      | 44    |
| H(23)  | -5299      | 1347       | -2949      | 42    |
| H(24)  | -4518      | 1257       | -2229      | 43    |
| H(25)  | -3939      | -626       | -2189      | 44    |
| H(26)  | -4152      | -2400      | -2901      | 38    |
| H(28)  | -3996.9998 | -4327      | -4396      | 37    |
| H(29)  | -3476.0002 | -6111      | -3995.0002 | 44    |
| H(30)  | -3736      | -7167      | -2978      | 50    |
| H(31)  | -4515      | -6393      | -2336      | 47    |
| H(32)  | -5050      | -4646      | -2752      | 43    |
| H(34)  | -4927      | -4451      | -5163      | 45    |
| H(35)  | -4702      | -3910      | -6299      | 55    |
| H(36)  | -4459      | -1781      | -6597      | 58    |
| H(37)  | -4456      | -147       | -5759      | 70    |
| H(38)  | -4692      | -640       | -4628      | 50    |
| H(39A) | -5837      | -2532      | -2555      | 92    |
| H(39B) | -5434      | -1776      | -2022      | 92    |
| H(40A) | -6964      | 1024       | -2666.0002 | 72    |
| H(40B) | -6590      | 1186       | -3352      | 72    |
| H(41A) | -8496      | 2500       | -406.0000  | 84    |
| H(41B) | -9050      | 2810       | -864       | 84    |
| H(42A) | -8951      | -2515      | 299        | 85    |
| H(42B) | -9186      | -3978      | 359        | 85    |

**Complex 31**

Table 1. Crystal data for pa185

|   |  |
|---|--|
| Compound                                      | pa185  |
| Molecular formula                             | $\text{C}_{38}\text{H}_{32}\text{N}_2\text{NiO}_2\text{P}_2\text{CH}_2\text{Cl}_2$ |
| Molecular weight                              | 754.23   |
| Crystal habit                                 | Purple Needle  |
| Crystal dimensions(mm)                        | 0.32x0.10x0.04   |
| Crystal system                                | monoclinic   |
| Space group                                   | Pc   |
| a( $\text{\AA}$ )                             | 14.095(1)  |
| b( $\text{\AA}$ )                             | 9.040(1)   |
| c( $\text{\AA}$ )                             | 16.233(1)  |
| $\alpha(^{\circ})$                            | 90.00  |
| $\beta(^{\circ})$                             | 122.384(4)   |
| $\gamma(^{\circ})$                            | 90.00  |
| V( $\text{\AA}^3$ )                           | 1746.7(3)  |
| Z   | 2  |
| d(g·cm <sup>-3</sup> )                        | 1.434  |
| F(000)  | 780  |
| $\mu(\text{cm}^{-1})$                         | 0.838  |
| Absorption corrections                        | multi-scan ; 0.7753 min, 0.9672 max  |
| Diffractometer                                | KappaCCD   |
| X-ray source                                  | MoK $\alpha$   |
| $\lambda(\text{\AA})$                         | 0.71069  |
| Monochromator                                 | graphite   |
| T (K)   | 150.0(1)   |
| Scan mode                                     | phi and omega scans  |
| Maximum $\theta$                              | 26.00  |
| HKL ranges                                    | -13 17 ; -10 11 ; -19 20   |
| Reflections measured                          | 9847   |
| Unique data                                   | 5021   |
| Rint  | 0.0244   |
| Reflections used                              | 4499   |
| Criterion                                     | I > 2 $\sigma$ (I)   |
| Refinement type                               | Fsqd   |
| Hydrogen atoms                                | constr   |
| Parameters refined                            | 433  |
| Reflections / parameter                       | 10   |
| wR2   | 0.1219   |
| R1  | 0.0449   |
| Flack's parameter                             | 0.022(16)  |
| Weights a, b                                  | 0.0739 ; 0.7114  |
| GoF   | 1.044  |
| difference peak / hole (e $\text{\AA}^{-3}$ ) | 0.909(0.069) / -0.722(0.069)   |

## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa185

| atom  | x        | y         | z        | U(eq)  |
|-------|----------|-----------|----------|--------|
| Ni(1) | 913(1)   | -9383(1)  | -2668(1) | 32(1)  |
| P(2)  | -1253(1) | -10212(1) | -2808(1) | 31(1)  |
| P(3)  | 2546(1)  | -11573(1) | -2605(1) | 32(1)  |
| O(1)  | -137(3)  | -7837(4)  | -3246(3) | 40(1)  |
| O(2)  | 1695(4)  | -8318(4)  | -3102(4) | 57(1)  |
| N(1)  | 83(3)    | -10482(4) | -2259(3) | 33(1)  |
| N(2)  | 2024(4)  | -10855(5) | -2019(3) | 36(1)  |
| C(1)  | 576(4)   | -11954(5) | -1867(4) | 38(1)  |
| C(2)  | 1824(4)  | -11742(6) | -1365(4) | 41(1)  |
| C(3)  | -1491(4) | -8282(5)  | -2830(3) | 29(1)  |
| C(4)  | -872(4)  | -7338(5)  | -3065(4) | 33(1)  |
| C(5)  | -1112(5) | -5799(5)  | -3131(4) | 43(1)  |
| C(6)  | -1890(5) | -5272(6)  | -2941(4) | 42(1)  |
| C(7)  | -2465(5) | -6201(6)  | -2679(4) | 42(1)  |
| C(8)  | -2286(4) | -7705(5)  | -2627(4) | 36(1)  |
| C(9)  | -1810(4) | -11099(5) | -2156(4) | 35(1)  |
| C(10) | -1172(5) | -11027(6) | -1137(4) | 45(1)  |
| C(11) | -1551(6) | -11702(6) | -605(5)  | 54(2)  |
| C(12) | -2569(6) | -12427(7) | -1075(6) | 62(2)  |
| C(13) | -3219(5) | -12487(6) | -2089(5) | 52(2)  |
| C(14) | -2843(4) | -11819(5) | -2621(4) | 38(1)  |
| C(15) | -2065(4) | -10853(5) | -4053(4) | 31(1)  |
| C(16) | -3147(4) | -10288(6) | -4707(4) | 43(1)  |
| C(17) | -3762(5) | -10764(7) | -5661(4) | 48(1)  |
| C(18) | -3326(4) | -11789(6) | -5990(4) | 43(1)  |
| C(19) | -2264(5) | -12351(6) | -5368(4) | 47(1)  |
| C(20) | -1631(5) | -11876(6) | -4405(4) | 40(1)  |
| C(21) | 3011(4)  | -10114(5) | -3031(4) | 32(1)  |
| C(22) | 2528(5)  | -8692(5)  | -3209(4) | 39(1)  |
| C(23) | 2962(5)  | -7592(5)  | -3534(4) | 43(1)  |
| C(24) | 3827(5)  | -7877(6)  | -3681(4) | 43(1)  |
| C(25) | 4290(5)  | -9283(6)  | -3514(4) | 46(1)  |
| C(26) | 3894(5)  | -10369(6) | -3191(4) | 43(1)  |
| C(27) | 3722(4)  | -12758(5) | -1808(4) | 34(1)  |
| C(28) | 4385(4)  | -12397(5) | -824(4)  | 40(1)  |
| C(29) | 5300(4)  | -13269(6) | -167(4)  | 49(1)  |
| C(30) | 5556(5)  | -14517(6) | -535(5)  | 51(2)  |
| C(31) | 4914(5)  | -14857(6) | -1497(5) | 49(1)  |
| C(32) | 4011(5)  | -13983(6) | -2149(4) | 41(1)  |
| C(33) | 1596(4)  | -12746(5) | -3642(4) | 33(1)  |
| C(34) | 1132(5)  | -12268(6) | -4581(4) | 45(1)  |
| C(35) | 399(5)   | -13157(7) | -5347(4) | 51(1)  |
| C(36) | 115(5)   | -14539(6) | -5194(4) | 49(2)  |
| C(37) | 576(4)   | -15040(6) | -4246(4) | 43(1)  |
| C(38) | 1309(4)  | -14151(6) | -3473(4) | 39(1)  |
| Cl(1) | 2951(3)  | -5630(3)  | -217(3)  | 138(1) |
| Cl(2) | 4293(2)  | -276(3)   | -7980(3) | 121(1) |
| C(39) | 3020(10) | -7270(10) | -730(10) | 126(4) |

U(eq) is defined as 1/3 the trace of the  $U_{ij}$  tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles (deg) for pa185

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Ni(1)-O(2)        | 1.863(4) | Ni(1)-O(1)        | 1.881(3) |
| Ni(1)-N(2)        | 1.888(4) | Ni(1)-N(1)        | 1.905(4) |
| P(2)-N(1)         | 1.613(4) | P(2)-C(3)         | 1.774(5) |
| P(2)-C(15)        | 1.804(5) | P(2)-C(9)         | 1.807(5) |
| P(3)-N(2)         | 1.617(4) | P(3)-C(21)        | 1.771(5) |
| P(3)-C(27)        | 1.809(5) | P(3)-C(33)        | 1.827(5) |
| O(1)-C(4)         | 1.301(6) | O(2)-C(22)        | 1.319(6) |
| N(1)-C(1)         | 1.478(6) | N(2)-C(2)         | 1.474(6) |
| C(1)-C(2)         | 1.502(7) | C(3)-C(4)         | 1.410(7) |
| C(3)-C(8)         | 1.425(7) | C(4)-C(5)         | 1.421(7) |
| C(5)-C(6)         | 1.373(8) | C(6)-C(7)         | 1.382(8) |
| C(7)-C(8)         | 1.378(7) | C(9)-C(14)        | 1.391(7) |
| C(9)-C(10)        | 1.398(8) | C(10)-C(11)       | 1.378(8) |
| C(11)-C(12)       | 1.38(1)  | C(12)-C(13)       | 1.39(1)  |
| C(13)-C(14)       | 1.373(8) | C(15)-C(20)       | 1.389(7) |
| C(15)-C(16)       | 1.407(7) | C(16)-C(17)       | 1.377(8) |
| C(17)-C(18)       | 1.368(8) | C(18)-C(19)       | 1.378(8) |
| C(19)-C(20)       | 1.390(8) | C(21)-C(22)       | 1.410(7) |
| C(21)-C(26)       | 1.419(7) | C(22)-C(23)       | 1.409(7) |
| C(23)-C(24)       | 1.387(8) | C(24)-C(25)       | 1.387(8) |
| C(25)-C(26)       | 1.366(8) | C(27)-C(28)       | 1.390(7) |
| C(27)-C(32)       | 1.392(7) | C(28)-C(29)       | 1.397(7) |
| C(29)-C(30)       | 1.41(1)  | C(30)-C(31)       | 1.36(1)  |
| C(31)-C(32)       | 1.386(8) | C(33)-C(34)       | 1.367(7) |
| C(33)-C(38)       | 1.404(7) | C(34)-C(35)       | 1.372(8) |
| C(35)-C(36)       | 1.375(8) | C(36)-C(37)       | 1.387(8) |
| C(37)-C(38)       | 1.378(7) | Cl(1)-C(39)       | 1.72(1)  |
| Cl(2)-C(39)       | 1.66(1)  |                   |          |
|                   |          |                   |          |
| O(2)-Ni(1)-O(1)   | 83.9(2)  | O(2)-Ni(1)-N(2)   | 95.4(2)  |
| O(1)-Ni(1)-N(2)   | 176.3(2) | O(2)-Ni(1)-N(1)   | 178.5(2) |
| O(1)-Ni(1)-N(1)   | 95.4(2)  | N(2)-Ni(1)-N(1)   | 85.4(2)  |
| N(1)-P(2)-C(3)    | 108.2(2) | N(1)-P(2)-C(15)   | 115.0(2) |
| C(3)-P(2)-C(15)   | 107.1(2) | N(1)-P(2)-C(9)    | 110.8(2) |
| C(3)-P(2)-C(9)    | 108.2(2) | C(15)-P(2)-C(9)   | 107.4(2) |
| N(2)-P(3)-C(21)   | 108.1(2) | N(2)-P(3)-C(27)   | 110.4(2) |
| C(21)-P(3)-C(27)  | 109.3(2) | N(2)-P(3)-C(33)   | 115.8(2) |
| C(21)-P(3)-C(33)  | 108.3(2) | C(27)-P(3)-C(33)  | 104.7(2) |
| C(4)-O(1)-Ni(1)   | 130.9(3) | C(22)-O(2)-Ni(1)  | 131.7(3) |
| C(1)-N(1)-P(2)    | 121.0(3) | C(1)-N(1)-Ni(1)   | 112.6(3) |
| P(2)-N(1)-Ni(1)   | 118.8(2) | C(2)-N(2)-P(3)    | 121.9(3) |
| C(2)-N(2)-Ni(1)   | 111.3(3) | P(3)-N(2)-Ni(1)   | 117.2(2) |
| N(1)-C(1)-C(2)    | 105.3(4) | N(2)-C(2)-C(1)    | 107.4(4) |
| C(4)-C(3)-C(8)    | 121.2(4) | C(4)-C(3)-P(2)    | 117.6(3) |
| C(8)-C(3)-P(2)    | 121.2(4) | O(1)-C(4)-C(3)    | 122.3(4) |
| O(1)-C(4)-C(5)    | 120.5(4) | C(3)-C(4)-C(5)    | 117.1(4) |
| C(6)-C(5)-C(4)    | 120.5(5) | C(5)-C(6)-C(7)    | 121.9(5) |
| C(8)-C(7)-C(6)    | 120.1(5) | C(7)-C(8)-C(3)    | 119.2(5) |
| C(14)-C(9)-C(10)  | 119.1(5) | C(14)-C(9)-P(2)   | 123.1(4) |
| C(10)-C(9)-P(2)   | 117.7(4) | C(11)-C(10)-C(9)  | 120.1(6) |
| C(12)-C(11)-C(10) | 120.1(6) | C(11)-C(12)-C(13) | 120.3(6) |
| C(14)-C(13)-C(12) | 119.7(6) | C(13)-C(14)-C(9)  | 120.6(6) |
| C(20)-C(15)-C(16) | 118.0(5) | C(20)-C(15)-P(2)  | 121.3(4) |
| C(16)-C(15)-P(2)  | 120.6(4) | C(17)-C(16)-C(15) | 120.7(5) |
| C(18)-C(17)-C(16) | 120.4(5) | C(17)-C(18)-C(19) | 120.2(5) |
| C(18)-C(19)-C(20) | 120.1(5) | C(15)-C(20)-C(19) | 120.6(5) |
| C(22)-C(21)-C(26) | 119.1(5) | C(22)-C(21)-P(3)  | 121.3(4) |
| C(26)-C(21)-P(3)  | 119.6(4) | O(2)-C(22)-C(23)  | 117.6(4) |
| O(2)-C(22)-C(21)  | 125.0(5) | C(23)-C(22)-C(21) | 117.4(5) |
| C(24)-C(23)-C(22) | 122.1(5) | C(25)-C(24)-C(23) | 120.1(5) |
| C(26)-C(25)-C(24) | 119.2(5) | C(25)-C(26)-C(21) | 122.1(5) |
| C(28)-C(27)-C(32) | 118.9(5) | C(28)-C(27)-P(3)  | 118.5(4) |
| C(32)-C(27)-P(3)  | 122.6(4) | C(27)-C(28)-C(29) | 121.5(5) |
| C(28)-C(29)-C(30) | 118.0(5) | C(31)-C(30)-C(29) | 120.3(5) |
| C(30)-C(31)-C(32) | 121.5(6) | C(31)-C(32)-C(27) | 119.7(5) |

# Appendix 1. Crystallographic data

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(34)-C(33)-C(38) | 119.2(5) | C(34)-C(33)-P(3)  | 121.4(4) |
| C(38)-C(33)-P(3)  | 119.4(4) | C(33)-C(34)-C(35) | 120.2(5) |
| C(34)-C(35)-C(36) | 121.3(5) | C(35)-C(36)-C(37) | 119.2(5) |
| C(38)-C(37)-C(36) | 119.8(5) | C(37)-C(38)-C(33) | 120.2(5) |
| Cl(2)-C(39)-Cl(1) | 116.4(6) |                   |          |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pal85

| atom  | U11    | U22   | U33    | U23    | U13    | U12    |
|-------|--------|-------|--------|--------|--------|--------|
| Ni(1) | 34(1)  | 29(1) | 35(1)  | 3(1)   | 20(1)  | 3(1)   |
| P(2)  | 32(1)  | 29(1) | 33(1)  | 1(1)   | 19(1)  | 2(1)   |
| P(3)  | 31(1)  | 31(1) | 34(1)  | 4(1)   | 17(1)  | 4(1)   |
| O(1)  | 45(2)  | 34(2) | 47(2)  | 9(2)   | 28(2)  | 5(2)   |
| O(2)  | 63(3)  | 37(2) | 100(4) | 20(2)  | 64(3)  | 12(2)  |
| N(1)  | 30(2)  | 28(2) | 39(2)  | 7(2)   | 18(2)  | 4(2)   |
| N(2)  | 41(2)  | 39(2) | 37(2)  | 4(2)   | 28(2)  | 2(2)   |
| C(1)  | 44(3)  | 28(2) | 43(3)  | 9(2)   | 24(3)  | 6(2)   |
| C(2)  | 40(3)  | 48(3) | 36(3)  | 12(2)  | 21(2)  | 12(2)  |
| C(3)  | 37(3)  | 26(2) | 24(2)  | -3(2)  | 15(2)  | -1(2)  |
| C(4)  | 38(3)  | 29(2) | 34(3)  | 2(2)   | 21(2)  | 3(2)   |
| C(5)  | 47(3)  | 32(3) | 51(3)  | -2(2)  | 26(3)  | -3(2)  |
| C(6)  | 53(3)  | 27(2) | 41(3)  | 3(2)   | 22(3)  | 7(2)   |
| C(7)  | 43(3)  | 41(3) | 42(3)  | -1(3)  | 23(2)  | 12(2)  |
| C(8)  | 39(3)  | 35(3) | 32(3)  | 2(2)   | 17(2)  | 11(2)  |
| C(9)  | 37(3)  | 27(2) | 46(3)  | 7(2)   | 26(3)  | 7(2)   |
| C(10) | 51(3)  | 43(3) | 46(3)  | 6(3)   | 31(3)  | 9(2)   |
| C(11) | 80(5)  | 45(3) | 57(4)  | 13(3)  | 50(4)  | 18(3)  |
| C(12) | 84(5)  | 41(3) | 101(6) | 16(3)  | 75(5)  | 13(3)  |
| C(13) | 54(4)  | 41(3) | 78(5)  | 9(3)   | 48(4)  | 8(3)   |
| C(14) | 37(3)  | 35(3) | 49(3)  | 1(2)   | 27(3)  | 4(2)   |
| C(15) | 39(3)  | 26(2) | 36(3)  | -3(2)  | 25(2)  | -4(2)  |
| C(16) | 35(3)  | 47(3) | 45(3)  | -2(3)  | 19(3)  | 5(2)   |
| C(17) | 36(3)  | 58(4) | 43(3)  | -10(3) | 17(3)  | -6(2)  |
| C(18) | 42(3)  | 44(3) | 42(3)  | -6(2)  | 23(3)  | -13(2) |
| C(19) | 57(4)  | 43(3) | 47(3)  | -10(3) | 32(3)  | -4(3)  |
| C(20) | 42(3)  | 39(3) | 42(3)  | 2(2)   | 24(3)  | 7(2)   |
| C(21) | 34(3)  | 27(2) | 34(3)  | -2(2)  | 18(2)  | -3(2)  |
| C(22) | 44(3)  | 33(3) | 45(3)  | -2(2)  | 27(3)  | -2(2)  |
| C(23) | 51(3)  | 30(3) | 55(4)  | 4(2)   | 35(3)  | -1(2)  |
| C(24) | 52(3)  | 41(3) | 44(3)  | 0(2)   | 30(3)  | -5(2)  |
| C(25) | 46(3)  | 57(3) | 47(3)  | 7(3)   | 32(3)  | 1(3)   |
| C(26) | 43(3)  | 42(3) | 48(3)  | 6(3)   | 28(3)  | 8(2)   |
| C(27) | 32(3)  | 33(3) | 37(3)  | -3(2)  | 18(2)  | -1(2)  |
| C(28) | 35(3)  | 33(3) | 45(3)  | 8(2)   | 16(2)  | 1(2)   |
| C(29) | 32(3)  | 52(3) | 46(3)  | 7(3)   | 10(3)  | -3(2)  |
| C(30) | 30(3)  | 41(3) | 61(4)  | 18(3)  | 10(3)  | 5(2)   |
| C(31) | 39(3)  | 38(3) | 63(4)  | 6(3)   | 22(3)  | 5(2)   |
| C(32) | 37(3)  | 37(3) | 42(3)  | 3(2)   | 16(2)  | 7(2)   |
| C(33) | 30(3)  | 34(3) | 36(3)  | 3(2)   | 19(2)  | 5(2)   |
| C(34) | 45(3)  | 39(3) | 38(3)  | 6(2)   | 14(3)  | 3(2)   |
| C(35) | 50(4)  | 53(3) | 35(3)  | 2(3)   | 12(3)  | -4(3)  |
| C(36) | 46(4)  | 44(3) | 41(3)  | -7(3)  | 13(3)  | 0(2)   |
| C(37) | 37(3)  | 33(3) | 46(3)  | -1(3)  | 14(3)  | -3(2)  |
| C(38) | 33(3)  | 42(3) | 36(3)  | 0(2)   | 14(2)  | -4(2)  |
| Cl(1) | 177(3) | 63(1) | 250(4) | -23(2) | 165(3) | -15(1) |
| Cl(2) | 94(2)  | 92(2) | 176(3) | 40(2)  | 72(2)  | 16(1)  |
| C(39) | 125(8) | 86(6) | 109(8) | -33(6) | 23(7)  | 0(6)   |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa185

| atom   | x          | y           | z          | U(eq) |
|--------|------------|-------------|------------|-------|
| H(1A)  | 304        | -12687      | -2400      | 46    |
| H(1B)  | 378        | -12299      | -1399      | 46    |
| H(2A)  | 2121       | -11221      | -736       | 49    |
| H(2B)  | 2205       | -12711.9990 | -1233      | 49    |
| H(5)   | -731       | -5130       | -3308      | 52    |
| H(6)   | -2037.9999 | -4240       | -2991      | 51    |
| H(7)   | -2984.0002 | -5801       | -2536      | 50    |
| H(8)   | -2687      | -8350       | -2457      | 44    |
| H(10)  | -476       | -10512      | -812.0001  | 54    |
| H(11)  | -1109      | -11668      | 87         | 65    |
| H(12)  | -2829      | -12887      | -706       | 75    |
| H(13)  | -3921      | -12988      | -2411      | 62    |
| H(14)  | -3291.0002 | -11849      | -3314      | 46    |
| H(16)  | -3456      | -9570       | -4489      | 52    |
| H(17)  | -4493      | -10378      | -6093.9995 | 57    |
| H(18)  | -3757      | -12115      | -6648      | 51    |
| H(19)  | -1964      | -13063      | -5599      | 57    |
| H(20)  | -894       | -12255      | -3983      | 48    |
| H(23)  | 2652       | -6625       | -3656      | 51    |
| H(24)  | 4104       | -7109       | -3897      | 52    |
| H(25)  | 4875       | -9487       | -3623      | 56    |
| H(26)  | 4220       | -11327      | -3069      | 51    |
| H(28)  | 4211       | -11537      | -594       | 48    |
| H(29)  | 5737       | -13030      | 508        | 58    |
| H(30)  | 6181       | -15121      | -106       | 62    |
| H(31)  | 5088       | -15714      | -1729.9999 | 59    |
| H(32)  | 3592       | -14218      | -2824      | 49    |
| H(34)  | 1318       | -11318.0010 | -4703      | 54    |
| H(35)  | 82         | -12810      | -5995      | 61    |
| H(36)  | -392       | -15144      | -5730.9995 | 59    |
| H(37)  | 388        | -15993      | -4130      | 52    |
| H(38)  | 1621       | -14490      | -2823      | 47    |
| H(39A) | 2554       | -8009       | -653.9999  | 151   |
| H(39B) | 2675       | -7104       | -1436      | 151   |

## Chapter 4

*Complex 37a*

Table 1. Crystal data for pa646

|   |  |
|---|--|
| Compound                                      | pa646  |
| Molecular formula                             | $\text{C}_{54}\text{H}_{64}\text{N}_2\text{NiO}_2\text{P}_2 \cdot 2(\text{C}_7\text{H}_8)$ |
| Molecular weight                              | 1077.99  |
| Crystal habit                                 | Dark Blue Block  |
| Crystal dimensions(mm)                        | 0.22x0.12x0.06   |
| Crystal system                                | monoclinic   |
| Space group                                   | C2/c   |
| a( $\text{\AA}$ )                             | 31.194(1)  |
| b( $\text{\AA}$ )                             | 10.777(1)  |
| c( $\text{\AA}$ )                             | 19.804(1)  |
| $\alpha(^{\circ})$                            | 90.00  |
| $\beta(^{\circ})$                             | 112.805(1)   |
| $\gamma(^{\circ})$                            | 90.00  |
| V( $\text{\AA}^3$ )                           | 6137.2(7)  |
| Z   | 4  |
| d(g·cm <sup>-3</sup> )                        | 1.167  |
| F(000)  | 2304   |
| $\mu(\text{cm}^{-1})$                         | 0.412  |
| Absorption corrections                        | multi-scan ; 0.9148 min, 0.9757 max  |
| Diffractionmeter                              | KappaCCD   |
| X-ray source                                  | MoK $\alpha$   |
| $\lambda(\text{\AA})$                         | 0.71069  |
| Monochromator                                 | graphite   |
| T (K)   | 150.0(1)   |
| Scan mode                                     | phi and omega scans  |
| Maximum $\theta$                              | 27.48  |
| HKL ranges                                    | -38 40 ; -13 13 ; -25 25   |
| Reflections measured                          | 24477  |
| Unique data                                   | 6920   |
| Rint  | 0.0511   |
| Reflections used                              | 5745   |
| Criterion                                     | I > 2 $\sigma$ (I)   |
| Refinement type                               | Fsqd   |
| Hydrogen atoms                                | constr   |
| Parameters refined                            | 346  |
| Reflections / parameter                       | 16   |
| wR2   | 0.1019   |
| R1  | 0.0486   |
| Weights a, b                                  | 0.0267 ; 15.563  |
| GoF   | 1.060  |
| difference peak / hole (e $\text{\AA}^{-3}$ ) | 0.605(0.061) / -0.332(0.061)   |



## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa646

| atom  | x       | y        | z       | U(eq)  |
|-------|---------|----------|---------|--------|
| Ni(1) | 0       | 6409(1)  | 2500    | 17(1)  |
| P(1)  | 507(1)  | 7358(1)  | 4017(1) | 18(1)  |
| O(1)  | 340(1)  | 5126(1)  | 3117(1) | 21(1)  |
| N(1)  | 307(1)  | 7699(2)  | 3154(1) | 19(1)  |
| C(1)  | 73(1)   | 8909(2)  | 2911(1) | 24(1)  |
| C(2)  | 804(1)  | 8692(2)  | 4545(1) | 21(1)  |
| C(3)  | 1224(1) | 9070(2)  | 4510(1) | 28(1)  |
| C(4)  | 1437(1) | 10154(2) | 4861(1) | 33(1)  |
| C(5)  | 1233(1) | 10873(2) | 5231(2) | 38(1)  |
| C(6)  | 815(1)  | 10513(2) | 5260(2) | 40(1)  |
| C(7)  | 601(1)  | 9423(2)  | 4920(1) | 30(1)  |
| C(8)  | 64(1)   | 6925(2)  | 4353(1) | 21(1)  |
| C(9)  | 174(1)  | 6715(2)  | 5100(1) | 25(1)  |
| C(10) | -171(1) | 6372(2)  | 5341(1) | 29(1)  |
| C(11) | -625(1) | 6230(2)  | 4839(1) | 28(1)  |
| C(12) | -735(1) | 6410(2)  | 4100(1) | 28(1)  |
| C(13) | -390(1) | 6764(2)  | 3857(1) | 23(1)  |
| C(14) | 906(1)  | 6119(2)  | 4157(1) | 19(1)  |
| C(15) | 764(1)  | 5156(2)  | 3627(1) | 19(1)  |
| C(16) | 1094(1) | 4194(2)  | 3690(1) | 22(1)  |
| C(17) | 1509(1) | 4200(2)  | 4299(1) | 23(1)  |
| C(18) | 1637(1) | 5102(2)  | 4853(1) | 23(1)  |
| C(19) | 1331(1) | 6075(2)  | 4761(1) | 22(1)  |
| C(20) | 981(1)  | 3176(2)  | 3104(1) | 28(1)  |
| C(21) | 1404(1) | 2343(3)  | 3217(2) | 41(1)  |
| C(22) | 828(1)  | 3751(2)  | 2333(1) | 37(1)  |
| C(23) | 589(1)  | 2347(2)  | 3146(2) | 35(1)  |
| C(24) | 2098(1) | 5054(2)  | 5525(1) | 29(1)  |
| C(25) | 2358(1) | 3836(3)  | 5578(2) | 60(1)  |
| C(26) | 2412(1) | 6117(3)  | 5482(2) | 50(1)  |
| C(27) | 2004(1) | 5206(4)  | 6224(2) | 56(1)  |
| C(28) | 2998(1) | 1751(4)  | 2077(2) | 62(1)  |
| C(29) | 3388(1) | 1975(4)  | 1947(2) | 60(1)  |
| C(30) | 3665(1) | 2972(5)  | 2246(2) | 73(1)  |
| C(31) | 3561(2) | 3762(4)  | 2689(2) | 82(1)  |
| C(32) | 3173(2) | 3573(5)  | 2834(2) | 87(2)  |
| C(33) | 2888(1) | 2581(5)  | 2532(2) | 77(1)  |
| C(34) | 2705(2) | 663(6)   | 1730(3) | 129(2) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles (deg) for pa646

|              |          |              |          |
|--------------|----------|--------------|----------|
| Ni(1)-O(1)   | 1.878(1) | Ni(1)-O(1)#2 | 1.878(1) |
| Ni(1)-N(1)#2 | 1.888(2) | Ni(1)-N(1)   | 1.888(2) |
| P(1)-N(1)    | 1.619(2) | P(1)-C(14)   | 1.772(2) |
| P(1)-C(2)    | 1.808(2) | P(1)-C(8)    | 1.811(2) |
| O(1)-C(15)   | 1.315(2) | N(1)-C(1)    | 1.479(3) |
| C(1)-C(1)#2  | 1.511(4) | C(1)-H(1A)   | 0.9900   |
| C(1)-H(1B)   | 0.9900   | C(2)-C(7)    | 1.393(3) |
| C(2)-C(3)    | 1.399(3) | C(3)-C(4)    | 1.389(3) |
| C(3)-H(3)    | 0.9500   | C(4)-C(5)    | 1.381(4) |
| C(4)-H(4)    | 0.9500   | C(5)-C(6)    | 1.381(4) |
| C(5)-H(5)    | 0.9500   | C(6)-C(7)    | 1.390(3) |
| C(6)-H(6)    | 0.9500   | C(7)-H(7)    | 0.9500   |
| C(8)-C(13)   | 1.387(3) | C(8)-C(9)    | 1.402(3) |
| C(9)-C(10)   | 1.386(3) | C(9)-H(9)    | 0.9500   |
| C(10)-C(11)  | 1.389(3) | C(10)-H(10)  | 0.9500   |
| C(11)-C(12)  | 1.380(3) | C(11)-H(11)  | 0.9500   |
| C(12)-C(13)  | 1.394(3) | C(12)-H(12)  | 0.9500   |
| C(13)-H(13)  | 0.9500   | C(14)-C(19)  | 1.400(3) |
| C(14)-C(15)  | 1.420(3) | C(15)-C(16)  | 1.431(3) |
| C(16)-C(17)  | 1.387(3) | C(16)-C(20)  | 1.537(3) |
| C(17)-C(18)  | 1.402(3) | C(17)-H(17)  | 0.9500   |
| C(18)-C(19)  | 1.382(3) | C(18)-C(24)  | 1.536(3) |
| C(19)-H(19)  | 0.9500   | C(20)-C(21)  | 1.538(3) |
| C(20)-C(22)  | 1.541(3) | C(20)-C(23)  | 1.542(3) |
| C(21)-H(21A) | 0.9800   | C(21)-H(21B) | 0.9800   |
| C(21)-H(21C) | 0.9800   | C(22)-H(22A) | 0.9800   |
| C(22)-H(22B) | 0.9800   | C(22)-H(22C) | 0.9800   |
| C(23)-H(23A) | 0.9800   | C(23)-H(23B) | 0.9800   |
| C(23)-H(23C) | 0.9800   | C(24)-C(25)  | 1.524(4) |
| C(24)-C(26)  | 1.529(4) | C(24)-C(27)  | 1.533(4) |
| C(25)-H(25A) | 0.9800   | C(25)-H(25B) | 0.9800   |
| C(25)-H(25C) | 0.9800   | C(26)-H(26A) | 0.9800   |
| C(26)-H(26B) | 0.9800   | C(26)-H(26C) | 0.9800   |
| C(27)-H(27A) | 0.9800   | C(27)-H(27B) | 0.9800   |
| C(27)-H(27C) | 0.9800   | C(28)-C(29)  | 1.360(5) |
| C(28)-C(33)  | 1.403(6) | C(28)-C(34)  | 1.481(6) |
| C(29)-C(30)  | 1.363(6) | C(29)-H(29)  | 0.9500   |
| C(30)-C(31)  | 1.349(6) | C(30)-H(30)  | 0.9500   |
| C(31)-C(32)  | 1.362(7) | C(31)-H(31)  | 0.9500   |
| C(32)-C(33)  | 1.370(7) | C(32)-H(32)  | 0.9500   |
| C(33)-H(33)  | 0.9500   | C(34)-H(34A) | 0.9800   |
| C(34)-H(34B) | 0.9800   | C(34)-H(34C) | 0.9800   |

|                     |           |                   |           |
|---------------------|-----------|-------------------|-----------|
| O(1)-Ni(1)-O(1)#2   | 85.2(1)   | O(1)-Ni(1)-N(1)#2 | 175.47(7) |
| O(1)#2-Ni(1)-N(1)#2 | 95.03(7)  | O(1)-Ni(1)-N(1)   | 95.03(7)  |
| O(1)#2-Ni(1)-N(1)   | 175.47(7) | N(1)#2-Ni(1)-N(1) | 85.1(1)   |
| N(1)-P(1)-C(14)     | 107.3(1)  | N(1)-P(1)-C(2)    | 109.4(1)  |
| C(14)-P(1)-C(2)     | 109.7(1)  | N(1)-P(1)-C(8)    | 114.2(1)  |
| C(14)-P(1)-C(8)     | 109.8(1)  | C(2)-P(1)-C(8)    | 106.6(1)  |
| C(15)-O(1)-Ni(1)    | 128.9(1)  | C(1)-N(1)-P(1)    | 118.9(1)  |
| C(1)-N(1)-Ni(1)     | 111.8(1)  | P(1)-N(1)-Ni(1)   | 116.2(1)  |
| N(1)-C(1)-C(1)#2    | 104.7(1)  | N(1)-C(1)-H(1A)   | 110.8     |
| C(1)#2-C(1)-H(1A)   | 110.8     | N(1)-C(1)-H(1B)   | 110.8     |
| C(1)#2-C(1)-H(1B)   | 110.8     | H(1A)-C(1)-H(1B)  | 108.9     |
| C(7)-C(2)-C(3)      | 119.4(2)  | C(7)-C(2)-P(1)    | 121.4(2)  |
| C(3)-C(2)-P(1)      | 118.9(2)  | C(4)-C(3)-C(2)    | 119.7(2)  |
| C(4)-C(3)-H(3)      | 120.1     | C(2)-C(3)-H(3)    | 120.1     |
| C(5)-C(4)-C(3)      | 120.5(2)  | C(5)-C(4)-H(4)    | 119.8     |
| C(3)-C(4)-H(4)      | 119.8     | C(4)-C(5)-C(6)    | 120.1(2)  |
| C(4)-C(5)-H(5)      | 120.0     | C(6)-C(5)-H(5)    | 120.0     |
| C(5)-C(6)-C(7)      | 120.1(2)  | C(5)-C(6)-H(6)    | 119.9     |
| C(7)-C(6)-H(6)      | 119.9     | C(6)-C(7)-C(2)    | 120.2(2)  |
| C(6)-C(7)-H(7)      | 119.9     | C(2)-C(7)-H(7)    | 119.9     |
| C(13)-C(8)-C(9)     | 119.5(2)  | C(13)-C(8)-P(1)   | 119.1(2)  |
| C(9)-C(8)-P(1)      | 121.4(2)  | C(10)-C(9)-C(8)   | 120.1(2)  |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(10)-C(9)-H(9)     | 119.9    | C(8)-C(9)-H(9)      | 119.9    |
| C(9)-C(10)-C(11)    | 119.7(2) | C(9)-C(10)-H(10)    | 120.1    |
| C(11)-C(10)-H(10)   | 120.1    | C(12)-C(11)-C(10)   | 120.6(2) |
| C(12)-C(11)-H(11)   | 119.7    | C(10)-C(11)-H(11)   | 119.7    |
| C(11)-C(12)-C(13)   | 119.8(2) | C(11)-C(12)-H(12)   | 120.1    |
| C(13)-C(12)-H(12)   | 120.1    | C(8)-C(13)-C(12)    | 120.2(2) |
| C(8)-C(13)-H(13)    | 119.9    | C(12)-C(13)-H(13)   | 119.9    |
| C(19)-C(14)-C(15)   | 121.9(2) | C(19)-C(14)-P(1)    | 122.3(2) |
| C(15)-C(14)-P(1)    | 115.8(2) | O(1)-C(15)-C(14)    | 121.2(2) |
| O(1)-C(15)-C(16)    | 121.6(2) | C(14)-C(15)-C(16)   | 117.2(2) |
| C(17)-C(16)-C(15)   | 118.1(2) | C(17)-C(16)-C(20)   | 121.6(2) |
| C(15)-C(16)-C(20)   | 120.4(2) | C(16)-C(17)-C(18)   | 124.8(2) |
| C(16)-C(17)-H(17)   | 117.6    | C(18)-C(17)-H(17)   | 117.6    |
| C(19)-C(18)-C(17)   | 116.8(2) | C(19)-C(18)-C(24)   | 120.5(2) |
| C(17)-C(18)-C(24)   | 122.8(2) | C(18)-C(19)-C(14)   | 121.0(2) |
| C(18)-C(19)-H(19)   | 119.5    | C(14)-C(19)-H(19)   | 119.5    |
| C(16)-C(20)-C(21)   | 112.0(2) | C(16)-C(20)-C(22)   | 110.7(2) |
| C(21)-C(20)-C(22)   | 107.4(2) | C(16)-C(20)-C(23)   | 109.0(2) |
| C(21)-C(20)-C(23)   | 107.9(2) | C(22)-C(20)-C(23)   | 109.8(2) |
| C(20)-C(21)-H(21A)  | 109.5    | C(20)-C(21)-H(21B)  | 109.5    |
| H(21A)-C(21)-H(21B) | 109.5    | C(20)-C(21)-H(21C)  | 109.5    |
| H(21A)-C(21)-H(21C) | 109.5    | H(21B)-C(21)-H(21C) | 109.5    |
| C(20)-C(22)-H(22A)  | 109.5    | C(20)-C(22)-H(22B)  | 109.5    |
| H(22A)-C(22)-H(22B) | 109.5    | C(20)-C(22)-H(22C)  | 109.5    |
| H(22A)-C(22)-H(22C) | 109.5    | H(22B)-C(22)-H(22C) | 109.5    |
| C(20)-C(23)-H(23A)  | 109.5    | C(20)-C(23)-H(23B)  | 109.5    |
| H(23A)-C(23)-H(23B) | 109.5    | C(20)-C(23)-H(23C)  | 109.5    |
| H(23A)-C(23)-H(23C) | 109.5    | H(23B)-C(23)-H(23C) | 109.5    |
| C(25)-C(24)-C(26)   | 108.4(2) | C(25)-C(24)-C(27)   | 108.2(3) |
| C(26)-C(24)-C(27)   | 108.7(2) | C(25)-C(24)-C(18)   | 112.5(2) |
| C(26)-C(24)-C(18)   | 109.3(2) | C(27)-C(24)-C(18)   | 109.6(2) |
| C(24)-C(25)-H(25A)  | 109.5    | C(24)-C(25)-H(25B)  | 109.5    |
| H(25A)-C(25)-H(25B) | 109.5    | C(24)-C(25)-H(25C)  | 109.5    |
| H(25A)-C(25)-H(25C) | 109.5    | H(25B)-C(25)-H(25C) | 109.5    |
| C(24)-C(26)-H(26A)  | 109.5    | C(24)-C(26)-H(26B)  | 109.5    |
| H(26A)-C(26)-H(26B) | 109.5    | C(24)-C(26)-H(26C)  | 109.5    |
| H(26A)-C(26)-H(26C) | 109.5    | H(26B)-C(26)-H(26C) | 109.5    |
| C(24)-C(27)-H(27A)  | 109.5    | C(24)-C(27)-H(27B)  | 109.5    |
| H(27A)-C(27)-H(27B) | 109.5    | C(24)-C(27)-H(27C)  | 109.5    |
| H(27A)-C(27)-H(27C) | 109.5    | H(27B)-C(27)-H(27C) | 109.5    |
| C(29)-C(28)-C(33)   | 117.9(4) | C(29)-C(28)-C(34)   | 119.3(4) |
| C(33)-C(28)-C(34)   | 122.9(4) | C(28)-C(29)-C(30)   | 121.4(4) |
| C(28)-C(29)-H(29)   | 119.3    | C(30)-C(29)-H(29)   | 119.3    |
| C(31)-C(30)-C(29)   | 120.5(4) | C(31)-C(30)-H(30)   | 119.8    |
| C(29)-C(30)-H(30)   | 119.8    | C(30)-C(31)-C(32)   | 120.0(5) |
| C(30)-C(31)-H(31)   | 120.0    | C(32)-C(31)-H(31)   | 120.0    |
| C(31)-C(32)-C(33)   | 120.3(4) | C(31)-C(32)-H(32)   | 119.9    |
| C(33)-C(32)-H(32)   | 119.9    | C(32)-C(33)-C(28)   | 119.9(4) |
| C(32)-C(33)-H(33)   | 120.0    | C(28)-C(33)-H(33)   | 120.0    |
| C(28)-C(34)-H(34A)  | 109.5    | C(28)-C(34)-H(34B)  | 109.5    |
| H(34A)-C(34)-H(34B) | 109.5    | C(28)-C(34)-H(34C)  | 109.5    |
| H(34A)-C(34)-H(34C) | 109.5    | H(34B)-C(34)-H(34C) | 109.5    |

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Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z                    2: -x, y, -z+1/2                    3: x+1/2, y+1/2, z  
4: -x+1/2, y+1/2, -z+1/2    5: -x, -y, -z                    6: x, -y, z-1/2  
7: -x+1/2, -y+1/2, -z       8: x+1/2, -y+1/2, z-1/2

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa646

| atom  | U11    | U22    | U33   | U23    | U13    | U12    |
|-------|--------|--------|-------|--------|--------|--------|
| Ni(1) | 17(1)  | 15(1)  | 17(1) | 0      | 5(1)   | 0      |
| P(1)  | 19(1)  | 17(1)  | 18(1) | -2(1)  | 6(1)   | 0(1)   |
| O(1)  | 20(1)  | 17(1)  | 22(1) | 2(1)   | 2(1)   | 1(1)   |
| N(1)  | 21(1)  | 15(1)  | 18(1) | 0(1)   | 6(1)   | 0(1)   |
| C(1)  | 29(1)  | 16(1)  | 24(1) | -1(1)  | 7(1)   | 1(1)   |
| C(2)  | 23(1)  | 19(1)  | 18(1) | -2(1)  | 3(1)   | -1(1)  |
| C(3)  | 28(1)  | 25(1)  | 29(1) | -1(1)  | 8(1)   | -3(1)  |
| C(4)  | 28(1)  | 29(1)  | 36(1) | -2(1)  | 5(1)   | -9(1)  |
| C(5)  | 41(1)  | 27(1)  | 37(1) | -8(1)  | 6(1)   | -8(1)  |
| C(6)  | 48(2)  | 30(1)  | 43(2) | -15(1) | 20(1)  | -3(1)  |
| C(7)  | 32(1)  | 25(1)  | 35(1) | -6(1)  | 14(1)  | -2(1)  |
| C(8)  | 22(1)  | 17(1)  | 24(1) | 0(1)   | 10(1)  | 2(1)   |
| C(9)  | 27(1)  | 24(1)  | 24(1) | 2(1)   | 10(1)  | 2(1)   |
| C(10) | 38(1)  | 26(1)  | 27(1) | 5(1)   | 18(1)  | 4(1)   |
| C(11) | 32(1)  | 21(1)  | 39(1) | 3(1)   | 22(1)  | 2(1)   |
| C(12) | 23(1)  | 25(1)  | 37(1) | -2(1)  | 13(1)  | -1(1)  |
| C(13) | 22(1)  | 22(1)  | 26(1) | 0(1)   | 10(1)  | 1(1)   |
| C(14) | 18(1)  | 19(1)  | 19(1) | 1(1)   | 8(1)   | 1(1)   |
| C(15) | 19(1)  | 18(1)  | 19(1) | 3(1)   | 6(1)   | -1(1)  |
| C(16) | 23(1)  | 20(1)  | 22(1) | 2(1)   | 8(1)   | 1(1)   |
| C(17) | 19(1)  | 24(1)  | 26(1) | 3(1)   | 8(1)   | 4(1)   |
| C(18) | 18(1)  | 25(1)  | 23(1) | 1(1)   | 5(1)   | -1(1)  |
| C(19) | 22(1)  | 23(1)  | 20(1) | -1(1)  | 6(1)   | -3(1)  |
| C(20) | 31(1)  | 22(1)  | 26(1) | -2(1)  | 7(1)   | 6(1)   |
| C(21) | 41(2)  | 36(1)  | 38(1) | -9(1)  | 8(1)   | 14(1)  |
| C(22) | 49(2)  | 36(1)  | 25(1) | -5(1)  | 12(1)  | 8(1)   |
| C(23) | 37(1)  | 24(1)  | 36(1) | -4(1)  | 4(1)   | -1(1)  |
| C(24) | 19(1)  | 33(1)  | 27(1) | 3(1)   | 1(1)   | 1(1)   |
| C(25) | 35(2)  | 48(2)  | 65(2) | -5(2)  | -16(1) | 14(1)  |
| C(26) | 32(1)  | 58(2)  | 48(2) | 0(1)   | 3(1)   | -14(1) |
| C(27) | 37(2)  | 92(3)  | 29(1) | 7(2)   | 1(1)   | 7(2)   |
| C(28) | 69(2)  | 71(2)  | 46(2) | 23(2)  | 20(2)  | 6(2)   |
| C(29) | 67(2)  | 75(2)  | 45(2) | 21(2)  | 32(2)  | 36(2)  |
| C(30) | 49(2)  | 118(4) | 47(2) | 33(2)  | 13(2)  | 14(2)  |
| C(31) | 87(3)  | 78(3)  | 54(2) | 9(2)   | -3(2)  | 10(2)  |
| C(32) | 103(4) | 99(3)  | 50(2) | 5(2)   | 19(2)  | 58(3)  |
| C(33) | 59(2)  | 133(4) | 53(2) | 37(3)  | 37(2)  | 41(3)  |
| C(34) | 156(6) | 126(5) | 88(4) | 27(3)  | 30(4)  | -51(4) |

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The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa646

| atom   | x     | y     | z    | U(eq) |
|--------|-------|-------|------|-------|
| H(1A)  | 289   | 9602  | 3137 | 29    |
| H(1B)  | -201  | 8986  | 3044 | 29    |
| H(3)   | 1363  | 8588  | 4248 | 34    |
| H(4)   | 1725  | 10403 | 4845 | 40    |
| H(5)   | 1380  | 11615 | 5467 | 45    |
| H(6)   | 674   | 11013 | 5511 | 48    |
| H(7)   | 315   | 9175  | 4944 | 36    |
| H(9)   | 486   | 6807  | 5442 | 30    |
| H(10)  | -97   | 6235  | 5848 | 34    |
| H(11)  | -863  | 6007  | 5005 | 34    |
| H(12)  | -1045 | 6292  | 3759 | 33    |
| H(13)  | -465  | 6894  | 3349 | 28    |
| H(17)  | 1723  | 3546  | 4345 | 28    |
| H(19)  | 1411  | 6725  | 5112 | 27    |
| H(21A) | 1321  | 1723  | 2825 | 61    |
| H(21B) | 1499  | 1923  | 3692 | 61    |
| H(21C) | 1662  | 2852  | 3207 | 61    |
| H(22A) | 541   | 4225  | 2224 | 56    |
| H(22B) | 773   | 3089  | 1970 | 56    |
| H(22C) | 1073  | 4305  | 2316 | 56    |
| H(23A) | 318   | 2860  | 3088 | 53    |
| H(23B) | 697   | 1928  | 3622 | 53    |
| H(23C) | 502   | 1726  | 2754 | 53    |
| H(25A) | 2644  | 3840  | 6021 | 90    |
| H(25B) | 2436  | 3741  | 5147 | 90    |
| H(25C) | 2160  | 3143  | 5600 | 90    |
| H(26A) | 2255  | 6911  | 5468 | 75    |
| H(26B) | 2475  | 6027  | 5037 | 75    |
| H(26C) | 2705  | 6093  | 5912 | 75    |
| H(27A) | 1841  | 5991  | 6204 | 84    |
| H(27B) | 2300  | 5209  | 6651 | 84    |
| H(27C) | 1811  | 4515  | 6266 | 84    |
| H(29)  | 3468  | 1424  | 1641 | 71    |
| H(30)  | 3934  | 3113  | 2142 | 87    |
| H(31)  | 3758  | 4449  | 2900 | 99    |
| H(32)  | 3100  | 4131  | 3145 | 104   |
| H(33)  | 2617  | 2456  | 2632 | 93    |
| H(34A) | 2680  | 585   | 1223 | 193   |
| H(34B) | 2394  | 774   | 1734 | 193   |
| H(34C) | 2847  | -89   | 2002 | 193   |

**Complex 37b**

Table 1. Crystal data for pa748

|  |  |
|--|--|
| Compound   | pa748  |
| Molecular formula                                    | $\text{C}_{58}\text{H}_{70}\text{N}_2\text{NiO}_2\text{P}_2 \cdot 2(\text{CH}_2\text{Cl}_2)$ |
| Molecular weight                                     | 1117.66  |
| Crystal habit  | Blue Needle  |
| Crystal dimensions(mm)                               | 0.40x0.12x0.12   |
| Crystal system                                       | monoclinic   |
| Space group  | $P2_1/c$   |
| $a(\text{\AA})$                                      | 15.723(1)  |
| $b(\text{\AA})$                                      | 20.228(1)  |
| $c(\text{\AA})$                                      | 18.106(1)  |
| $\alpha(^{\circ})$                                   | 90.00  |
| $\beta(^{\circ})$                                    | 94.940(1)  |
| $\gamma(^{\circ})$                                   | 90.00  |
| $V(\text{\AA}^3)$                                    | 5737.1(6)  |
| Z  | 4  |
| $d(\text{g}\cdot\text{cm}^{-3})$                     | 1.294  |
| $F(000)$   | 2360   |
| $\mu(\text{cm}^{-1})$                                | 0.623  |
| Absorption corrections                               | multi-scan ; 0.7886 min, 0.9289 max  |
| Diffractionmeter                                     | KappaCCD   |
| X-ray source   | MoK $\alpha$   |
| $\lambda(\text{\AA})$                                | 0.71069  |
| Monochromator  | graphite   |
| T (K)  | 150.0(1)   |
| Scan mode  | phi and omega scans  |
| Maximum $\theta$                                     | 25.03  |
| HKL ranges   | -18 18 ; -23 24 ; -17 21   |
| Reflections measured                                 | 25515  |
| Unique data  | 9844   |
| Rint   | 0.0780   |
| Reflections used                                     | 8140   |
| Criterion  | $I > 2\sigma(I)$   |
| Refinement type                                      | Fsqd   |
| Hydrogen atoms                                       | constr   |
| Parameters refined                                   | 598  |
| Reflections / parameter                              | 13   |
| wR2  | 0.2234   |
| R1   | 0.0901   |
| Weights a, b   | 0.1091 ; 12.643  |
| GoF  | 1.149  |
| difference peak / hole ( $\text{e}\text{\AA}^{-3}$ ) | 0.971(0.106) / -1.040(0.106)   |

# Appendix 1. Crystallographic data

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa748

| atom  | x        | y       | z       | U(eq) |
|-------|----------|---------|---------|-------|
| Ni(2) | 3011(1)  | 3615(1) | 4694(1) | 24(1) |
| P(1)  | 2114(1)  | 4304(1) | 5845(1) | 25(1) |
| P(2)  | 3826(1)  | 3809(1) | 3358(1) | 25(1) |
| O(1)  | 2228(2)  | 3029(2) | 5069(2) | 31(1) |
| O(2)  | 3585(2)  | 2830(2) | 4479(2) | 29(1) |
| N(1)  | 2590(2)  | 4419(2) | 5092(2) | 24(1) |
| N(2)  | 3694(3)  | 4176(2) | 4134(2) | 27(1) |
| C(1)  | 3247(3)  | 4934(2) | 5026(2) | 27(1) |
| C(2)  | 3477(3)  | 4880(2) | 4220(3) | 27(1) |
| C(3)  | 4183(3)  | 5358(3) | 4073(3) | 35(1) |
| C(4)  | 3965(4)  | 6063(3) | 4269(3) | 40(1) |
| C(5)  | 3742(4)  | 6107(3) | 5072(3) | 39(1) |
| C(6)  | 3029(4)  | 5633(3) | 5227(3) | 36(1) |
| C(7)  | 1281(3)  | 3711(2) | 5684(2) | 26(1) |
| C(8)  | 1467(3)  | 3142(2) | 5274(2) | 26(1) |
| C(9)  | 797(3)   | 2671(3) | 5134(3) | 34(1) |
| C(10) | 60(3)    | 2756(3) | 5479(3) | 36(1) |
| C(11) | -106(3)  | 3292(3) | 5940(3) | 34(1) |
| C(12) | 516(3)   | 3774(3) | 6023(2) | 30(1) |
| C(13) | 914(4)   | 2072(3) | 4621(3) | 43(1) |
| C(14) | 1592(5)  | 1611(3) | 4979(4) | 60(2) |
| C(15) | 1186(4)  | 2318(3) | 3866(3) | 55(2) |
| C(16) | 82(4)    | 1690(4) | 4458(5) | 68(2) |
| C(17) | -917(4)  | 3320(3) | 6348(3) | 42(1) |
| C(18) | -748(5)  | 2949(5) | 7088(4) | 87(3) |
| C(19) | -1163(4) | 4037(4) | 6505(4) | 57(2) |
| C(20) | -1671(4) | 3008(3) | 5892(4) | 52(2) |
| C(21) | 1592(3)  | 5045(2) | 6143(3) | 28(1) |
| C(22) | 1832(3)  | 5365(3) | 6820(3) | 37(1) |
| C(23) | 1424(4)  | 5954(3) | 6985(3) | 41(1) |
| C(24) | 794(4)   | 6224(3) | 6514(3) | 41(1) |
| C(25) | 546(4)   | 5896(3) | 5838(3) | 39(1) |
| C(26) | 955(3)   | 5320(3) | 5663(3) | 34(1) |
| C(27) | 2807(3)  | 3998(2) | 6622(2) | 27(1) |
| C(28) | 3640(3)  | 3821(2) | 6521(3) | 30(1) |
| C(29) | 4168(4)  | 3548(2) | 7092(3) | 37(1) |
| C(30) | 3853(4)  | 3451(3) | 7788(3) | 37(1) |
| C(31) | 3026(4)  | 3610(3) | 7886(3) | 40(1) |
| C(32) | 2494(4)  | 3881(3) | 7314(3) | 36(1) |
| C(33) | 4516(3)  | 3127(2) | 3571(2) | 28(1) |
| C(34) | 4311(3)  | 2747(2) | 4192(2) | 26(1) |
| C(35) | 4898(3)  | 2254(2) | 4463(2) | 27(1) |
| C(36) | 5634(3)  | 2159(2) | 4096(3) | 28(1) |
| C(37) | 5815(3)  | 2510(2) | 3457(2) | 27(1) |
| C(38) | 5245(3)  | 2992(2) | 3201(2) | 28(1) |
| C(39) | 4734(3)  | 1825(3) | 5137(3) | 34(1) |
| C(40) | 4574(4)  | 2273(3) | 5808(3) | 44(1) |
| C(41) | 3936(4)  | 1401(3) | 4945(3) | 38(1) |
| C(42) | 5482(4)  | 1369(3) | 5380(3) | 48(2) |
| C(43) | 6655(3)  | 2373(3) | 3099(3) | 34(1) |
| C(44) | 7413(3)  | 2533(3) | 3660(3) | 43(1) |
| C(45) | 6728(4)  | 2791(3) | 2410(3) | 51(2) |
| C(46) | 6701(4)  | 1644(3) | 2882(3) | 46(1) |
| C(47) | 2845(3)  | 3533(2) | 2859(3) | 31(1) |
| C(48) | 2873(4)  | 3056(3) | 2313(3) | 44(1) |
| C(49) | 2136(5)  | 2860(3) | 1891(4) | 60(2) |
| C(50) | 1367(5)  | 3153(4) | 2029(4) | 63(2) |
| C(51) | 1328(4)  | 3633(4) | 2574(4) | 57(2) |
| C(52) | 2067(3)  | 3812(3) | 2994(3) | 40(1) |
| C(53) | 4316(3)  | 4321(2) | 2687(2) | 27(1) |
| C(54) | 5174(3)  | 4499(2) | 2806(3) | 30(1) |
| C(55) | 5543(4)  | 4894(3) | 2295(3) | 35(1) |

# Appendix 1. Crystallographic data

|       |         |         |         |       |
|-------|---------|---------|---------|-------|
| C(56) | 5051(4) | 5125(3) | 1662(3) | 42(1) |
| C(57) | 4206(4) | 4958(3) | 1556(3) | 43(1) |
| C(58) | 3825(4) | 4551(2) | 2056(3) | 33(1) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa748

|              |          |              |          |
|--------------|----------|--------------|----------|
| Ni(2)-O(1)   | 1.877(3) | Ni(2)-O(2)   | 1.882(3) |
| Ni(2)-N(2)   | 1.912(4) | Ni(2)-N(1)   | 1.921(4) |
| P(1)-N(1)    | 1.627(4) | P(1)-C(7)    | 1.781(5) |
| P(1)-C(27)   | 1.813(5) | P(1)-C(21)   | 1.814(5) |
| P(2)-N(2)    | 1.618(4) | P(2)-C(33)   | 1.777(5) |
| P(2)-C(47)   | 1.808(5) | P(2)-C(53)   | 1.817(5) |
| O(1)-C(8)    | 1.303(6) | O(2)-C(34)   | 1.306(6) |
| N(1)-C(1)    | 1.478(6) | N(2)-C(2)    | 1.477(6) |
| C(1)-C(6)    | 1.507(7) | C(1)-C(2)    | 1.537(6) |
| C(1)-H(1)    | 1.0000   | C(2)-C(3)    | 1.513(7) |
| C(2)-H(2)    | 1.0000   | C(3)-C(4)    | 1.514(7) |
| C(3)-H(3A)   | 0.9900   | C(3)-H(3B)   | 0.9900   |
| C(4)-C(5)    | 1.527(7) | C(4)-H(4A)   | 0.9900   |
| C(4)-H(4B)   | 0.9900   | C(5)-C(6)    | 1.519(7) |
| C(5)-H(5A)   | 0.9900   | C(5)-H(5B)   | 0.9900   |
| C(6)-H(6A)   | 0.9900   | C(6)-H(6B)   | 0.9900   |
| C(7)-C(12)   | 1.403(7) | C(7)-C(8)    | 1.415(7) |
| C(8)-C(9)    | 1.427(7) | C(9)-C(10)   | 1.373(7) |
| C(9)-C(13)   | 1.546(7) | C(10)-C(11)  | 1.406(8) |
| C(10)-H(10)  | 0.9500   | C(11)-C(12)  | 1.381(7) |
| C(11)-C(17)  | 1.530(7) | C(12)-H(12)  | 0.9500   |
| C(13)-C(14)  | 1.52(1)  | C(13)-C(16)  | 1.527(8) |
| C(13)-C(15)  | 1.549(8) | C(14)-H(14A) | 0.9800   |
| C(14)-H(14B) | 0.9800   | C(14)-H(14C) | 0.9800   |
| C(15)-H(15A) | 0.9800   | C(15)-H(15B) | 0.9800   |
| C(15)-H(15C) | 0.9800   | C(16)-H(16A) | 0.9800   |
| C(16)-H(16B) | 0.9800   | C(16)-H(16C) | 0.9800   |
| C(17)-C(20)  | 1.52(1)  | C(17)-C(19)  | 1.53(1)  |
| C(17)-C(18)  | 1.538(8) | C(18)-H(18A) | 0.9800   |
| C(18)-H(18B) | 0.9800   | C(18)-H(18C) | 0.9800   |
| C(19)-H(19A) | 0.9800   | C(19)-H(19B) | 0.9800   |
| C(19)-H(19C) | 0.9800   | C(20)-H(20A) | 0.9800   |
| C(20)-H(20B) | 0.9800   | C(20)-H(20C) | 0.9800   |
| C(21)-C(26)  | 1.385(7) | C(21)-C(22)  | 1.408(7) |
| C(22)-C(23)  | 1.398(8) | C(22)-H(22)  | 0.9500   |
| C(23)-C(24)  | 1.364(8) | C(23)-H(23)  | 0.9500   |
| C(24)-C(25)  | 1.416(8) | C(24)-H(24)  | 0.9500   |
| C(25)-C(26)  | 1.381(7) | C(25)-H(25)  | 0.9500   |
| C(26)-H(26)  | 0.9500   | C(27)-C(28)  | 1.385(7) |
| C(27)-C(32)  | 1.404(7) | C(28)-C(29)  | 1.384(7) |
| C(28)-H(28)  | 0.9500   | C(29)-C(30)  | 1.407(8) |
| C(29)-H(29)  | 0.9500   | C(30)-C(31)  | 1.365(8) |
| C(30)-H(30)  | 0.9500   | C(31)-C(32)  | 1.387(7) |
| C(31)-H(31)  | 0.9500   | C(32)-H(32)  | 0.9500   |
| C(33)-C(38)  | 1.404(7) | C(33)-C(34)  | 1.421(6) |
| C(34)-C(35)  | 1.417(7) | C(35)-C(36)  | 1.397(7) |
| C(35)-C(39)  | 1.537(6) | C(36)-C(37)  | 1.408(6) |
| C(36)-H(36)  | 0.9500   | C(37)-C(38)  | 1.377(7) |
| C(37)-C(43)  | 1.544(7) | C(38)-H(38)  | 0.9500   |
| C(39)-C(42)  | 1.529(8) | C(39)-C(41)  | 1.535(7) |
| C(39)-C(40)  | 1.554(7) | C(40)-H(40A) | 0.9800   |
| C(40)-H(40B) | 0.9800   | C(40)-H(40C) | 0.9800   |
| C(41)-H(41A) | 0.9800   | C(41)-H(41B) | 0.9800   |
| C(41)-H(41C) | 0.9800   | C(42)-H(42A) | 0.9800   |
| C(42)-H(42B) | 0.9800   | C(42)-H(42C) | 0.9800   |
| C(43)-C(45)  | 1.520(8) | C(43)-C(46)  | 1.529(8) |
| C(43)-C(44)  | 1.532(7) | C(44)-H(44A) | 0.9800   |
| C(44)-H(44B) | 0.9800   | C(44)-H(44C) | 0.9800   |
| C(45)-H(45A) | 0.9800   | C(45)-H(45B) | 0.9800   |
| C(45)-H(45C) | 0.9800   | C(46)-H(46A) | 0.9800   |
| C(46)-H(46B) | 0.9800   | C(46)-H(46C) | 0.9800   |
| C(47)-C(48)  | 1.384(7) | C(47)-C(52)  | 1.386(8) |
| C(48)-C(49)  | 1.390(8) | C(48)-H(48)  | 0.9500   |
| C(49)-C(50)  | 1.39(1)  | C(49)-H(49)  | 0.9500   |
| C(50)-C(51)  | 1.39(1)  | C(50)-H(50)  | 0.9500   |
| C(51)-C(52)  | 1.381(8) | C(51)-H(51)  | 0.9500   |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(52)-H(52)         | 0.9500   | C(53)-C(54)         | 1.394(7) |
| C(53)-C(58)         | 1.403(7) | C(54)-C(55)         | 1.386(7) |
| C(54)-H(54)         | 0.9500   | C(55)-C(56)         | 1.405(8) |
| C(55)-H(55)         | 0.9500   | C(56)-C(57)         | 1.369(8) |
| C(56)-H(56)         | 0.9500   | C(57)-C(58)         | 1.397(7) |
| C(57)-H(57)         | 0.9500   | C(58)-H(58)         | 0.9500   |
| O(1)-Ni(2)-O(2)     | 83.3(1)  | O(1)-Ni(2)-N(2)     | 169.1(2) |
| O(2)-Ni(2)-N(2)     | 95.2(2)  | O(1)-Ni(2)-N(1)     | 98.1(2)  |
| O(2)-Ni(2)-N(1)     | 168.1(2) | N(2)-Ni(2)-N(1)     | 85.6(2)  |
| N(1)-P(1)-C(7)      | 110.1(2) | N(1)-P(1)-C(27)     | 114.2(2) |
| C(7)-P(1)-C(27)     | 106.4(2) | N(1)-P(1)-C(21)     | 112.6(2) |
| C(7)-P(1)-C(21)     | 105.0(2) | C(27)-P(1)-C(21)    | 107.9(2) |
| N(2)-P(2)-C(33)     | 106.8(2) | N(2)-P(2)-C(47)     | 114.1(2) |
| C(33)-P(2)-C(47)    | 110.4(2) | N(2)-P(2)-C(53)     | 114.3(2) |
| C(33)-P(2)-C(53)    | 107.6(2) | C(47)-P(2)-C(53)    | 103.6(2) |
| C(8)-O(1)-Ni(2)     | 129.8(3) | C(34)-O(2)-Ni(2)    | 129.9(3) |
| C(1)-N(1)-P(1)      | 122.9(3) | C(1)-N(1)-Ni(2)     | 107.5(3) |
| P(1)-N(1)-Ni(2)     | 113.0(2) | C(2)-N(2)-P(2)      | 125.6(3) |
| C(2)-N(2)-Ni(2)     | 111.8(3) | P(2)-N(2)-Ni(2)     | 107.9(2) |
| N(1)-C(1)-C(6)      | 117.8(4) | N(1)-C(1)-C(2)      | 104.5(4) |
| C(6)-C(1)-C(2)      | 111.9(4) | N(1)-C(1)-H(1)      | 107.4    |
| C(6)-C(1)-H(1)      | 107.4    | C(2)-C(1)-H(1)      | 107.4    |
| N(2)-C(2)-C(3)      | 114.7(4) | N(2)-C(2)-C(1)      | 104.1(4) |
| C(3)-C(2)-C(1)      | 111.0(4) | N(2)-C(2)-H(2)      | 108.9    |
| C(3)-C(2)-H(2)      | 108.9    | C(1)-C(2)-H(2)      | 108.9    |
| C(2)-C(3)-C(4)      | 112.1(4) | C(2)-C(3)-H(3A)     | 109.2    |
| C(4)-C(3)-H(3A)     | 109.2    | C(2)-C(3)-H(3B)     | 109.2    |
| C(4)-C(3)-H(3B)     | 109.2    | H(3A)-C(3)-H(3B)    | 107.9    |
| C(3)-C(4)-C(5)      | 110.7(4) | C(3)-C(4)-H(4A)     | 109.5    |
| C(5)-C(4)-H(4A)     | 109.5    | C(3)-C(4)-H(4B)     | 109.5    |
| C(5)-C(4)-H(4B)     | 109.5    | H(4A)-C(4)-H(4B)    | 108.1    |
| C(6)-C(5)-C(4)      | 111.9(4) | C(6)-C(5)-H(5A)     | 109.2    |
| C(4)-C(5)-H(5A)     | 109.2    | C(6)-C(5)-H(5B)     | 109.2    |
| C(4)-C(5)-H(5B)     | 109.2    | H(5A)-C(5)-H(5B)    | 107.9    |
| C(1)-C(6)-C(5)      | 111.1(4) | C(1)-C(6)-H(6A)     | 109.4    |
| C(5)-C(6)-H(6A)     | 109.4    | C(1)-C(6)-H(6B)     | 109.4    |
| C(5)-C(6)-H(6B)     | 109.4    | H(6A)-C(6)-H(6B)    | 108.0    |
| C(12)-C(7)-C(8)     | 121.8(5) | C(12)-C(7)-P(1)     | 120.9(4) |
| C(8)-C(7)-P(1)      | 116.9(4) | O(1)-C(8)-C(7)      | 121.8(4) |
| O(1)-C(8)-C(9)      | 121.0(4) | C(7)-C(8)-C(9)      | 117.0(4) |
| C(10)-C(9)-C(8)     | 118.3(5) | C(10)-C(9)-C(13)    | 121.4(5) |
| C(8)-C(9)-C(13)     | 120.3(4) | C(9)-C(10)-C(11)    | 125.0(5) |
| C(9)-C(10)-H(10)    | 117.5    | C(11)-C(10)-H(10)   | 117.5    |
| C(12)-C(11)-C(10)   | 116.4(5) | C(12)-C(11)-C(17)   | 122.1(5) |
| C(10)-C(11)-C(17)   | 121.4(5) | C(11)-C(12)-C(7)    | 120.9(5) |
| C(11)-C(12)-H(12)   | 119.6    | C(7)-C(12)-H(12)    | 119.6    |
| C(14)-C(13)-C(16)   | 109.3(5) | C(14)-C(13)-C(9)    | 109.9(5) |
| C(16)-C(13)-C(9)    | 111.6(5) | C(14)-C(13)-C(15)   | 109.7(5) |
| C(9)-C(13)-C(15)    | 106.8(5) | C(9)-C(13)-C(15)    | 109.6(5) |
| C(13)-C(14)-H(14A)  | 109.5    | C(13)-C(14)-H(14B)  | 109.5    |
| H(14A)-C(14)-H(14B) | 109.5    | C(13)-C(14)-H(14C)  | 109.5    |
| H(14A)-C(14)-H(14C) | 109.5    | H(14B)-C(14)-H(14C) | 109.5    |
| C(13)-C(15)-H(15A)  | 109.5    | C(13)-C(15)-H(15B)  | 109.5    |
| H(15A)-C(15)-H(15B) | 109.5    | C(13)-C(15)-H(15C)  | 109.5    |
| H(15A)-C(15)-H(15C) | 109.5    | H(15B)-C(15)-H(15C) | 109.5    |
| C(13)-C(16)-H(16A)  | 109.5    | C(13)-C(16)-H(16B)  | 109.5    |
| H(16A)-C(16)-H(16B) | 109.5    | C(13)-C(16)-H(16C)  | 109.5    |
| H(16A)-C(16)-H(16C) | 109.5    | H(16B)-C(16)-H(16C) | 109.5    |
| C(20)-C(17)-C(11)   | 111.4(5) | C(20)-C(17)-C(19)   | 107.2(5) |
| C(11)-C(17)-C(19)   | 111.0(5) | C(20)-C(17)-C(18)   | 109.7(6) |
| C(11)-C(17)-C(18)   | 108.2(5) | C(19)-C(17)-C(18)   | 109.2(6) |
| C(17)-C(18)-H(18A)  | 109.5    | C(17)-C(18)-H(18B)  | 109.5    |
| H(18A)-C(18)-H(18B) | 109.5    | C(17)-C(18)-H(18C)  | 109.5    |
| H(18A)-C(18)-H(18C) | 109.5    | H(18B)-C(18)-H(18C) | 109.5    |
| C(17)-C(19)-H(19A)  | 109.5    | C(17)-C(19)-H(19B)  | 109.5    |
| H(19A)-C(19)-H(19B) | 109.5    | C(17)-C(19)-H(19C)  | 109.5    |

## Appendix 1. Crystallographic data

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| H(19A)-C(19)-H(19C) | 109.5    | H(19B)-C(19)-H(19C) | 109.5    |
| C(17)-C(20)-H(20A)  | 109.5    | C(17)-C(20)-H(20B)  | 109.5    |
| H(20A)-C(20)-H(20B) | 109.5    | C(17)-C(20)-H(20C)  | 109.5    |
| H(20A)-C(20)-H(20C) | 109.5    | H(20B)-C(20)-H(20C) | 109.5    |
| C(26)-C(21)-C(22)   | 119.1(5) | C(26)-C(21)-P(1)    | 117.8(4) |
| C(22)-C(21)-P(1)    | 123.0(4) | C(23)-C(22)-C(21)   | 119.0(5) |
| C(23)-C(22)-H(22)   | 120.5    | C(21)-C(22)-H(22)   | 120.5    |
| C(24)-C(23)-C(22)   | 122.0(5) | C(24)-C(23)-H(23)   | 119.0    |
| C(22)-C(23)-H(23)   | 119.0    | C(23)-C(24)-C(25)   | 118.9(5) |
| C(23)-C(24)-H(24)   | 120.6    | C(25)-C(24)-H(24)   | 120.6    |
| C(26)-C(25)-C(24)   | 119.7(5) | C(26)-C(25)-H(25)   | 120.2    |
| C(24)-C(25)-H(25)   | 120.2    | C(25)-C(26)-C(21)   | 121.4(5) |
| C(25)-C(26)-H(26)   | 119.3    | C(21)-C(26)-H(26)   | 119.3    |
| C(28)-C(27)-C(32)   | 118.9(4) | C(28)-C(27)-P(1)    | 119.8(3) |
| C(32)-C(27)-P(1)    | 121.1(4) | C(29)-C(28)-C(27)   | 121.2(5) |
| C(29)-C(28)-H(28)   | 119.4    | C(27)-C(28)-H(28)   | 119.4    |
| C(28)-C(29)-C(30)   | 119.4(5) | C(28)-C(29)-H(29)   | 120.3    |
| C(30)-C(29)-H(29)   | 120.3    | C(31)-C(30)-C(29)   | 119.7(5) |
| C(31)-C(30)-H(30)   | 120.2    | C(29)-C(30)-H(30)   | 120.2    |
| C(30)-C(31)-C(32)   | 121.1(5) | C(30)-C(31)-H(31)   | 119.5    |
| C(32)-C(31)-H(31)   | 119.5    | C(31)-C(32)-C(27)   | 119.8(5) |
| C(31)-C(32)-H(32)   | 120.1    | C(27)-C(32)-H(32)   | 120.1    |
| C(38)-C(33)-C(34)   | 121.5(4) | C(38)-C(33)-P(2)    | 123.7(4) |
| C(34)-C(33)-P(2)    | 114.6(4) | O(2)-C(34)-C(35)    | 121.2(4) |
| O(2)-C(34)-C(33)    | 120.7(4) | C(35)-C(34)-C(33)   | 118.0(4) |
| C(36)-C(35)-C(34)   | 118.3(4) | C(36)-C(35)-C(39)   | 120.1(4) |
| C(34)-C(35)-C(39)   | 121.6(4) | C(35)-C(36)-C(37)   | 123.8(4) |
| C(35)-C(36)-H(36)   | 118.1    | C(37)-C(36)-H(36)   | 118.1    |
| C(38)-C(37)-C(36)   | 117.5(4) | C(38)-C(37)-C(43)   | 122.8(4) |
| C(36)-C(37)-C(43)   | 119.6(4) | C(37)-C(38)-C(33)   | 120.7(4) |
| C(37)-C(38)-H(38)   | 119.6    | C(33)-C(38)-H(38)   | 119.6    |
| C(42)-C(39)-C(41)   | 108.7(4) | C(42)-C(39)-C(35)   | 113.1(4) |
| C(41)-C(39)-C(35)   | 109.0(4) | C(42)-C(39)-C(40)   | 107.3(4) |
| C(41)-C(39)-C(40)   | 108.6(5) | C(35)-C(39)-C(40)   | 110.0(4) |
| C(39)-C(40)-H(40A)  | 109.5    | C(39)-C(40)-H(40B)  | 109.5    |
| H(40A)-C(40)-H(40B) | 109.5    | C(39)-C(40)-H(40C)  | 109.5    |
| H(40A)-C(40)-H(40C) | 109.5    | H(40B)-C(40)-H(40C) | 109.5    |
| C(39)-C(41)-H(41A)  | 109.5    | C(39)-C(41)-H(41B)  | 109.5    |
| H(41A)-C(41)-H(41B) | 109.5    | C(39)-C(41)-H(41C)  | 109.5    |
| H(41A)-C(41)-H(41C) | 109.5    | H(41B)-C(41)-H(41C) | 109.5    |
| C(39)-C(42)-H(42A)  | 109.5    | C(39)-C(42)-H(42B)  | 109.5    |
| H(42A)-C(42)-H(42B) | 109.5    | C(39)-C(42)-H(42C)  | 109.5    |
| H(42A)-C(42)-H(42C) | 109.5    | H(42B)-C(42)-H(42C) | 109.5    |
| C(45)-C(43)-C(46)   | 108.4(5) | C(45)-C(43)-C(44)   | 108.4(5) |
| C(46)-C(43)-C(44)   | 108.8(5) | C(45)-C(43)-C(37)   | 111.9(4) |
| C(46)-C(43)-C(37)   | 110.0(4) | C(44)-C(43)-C(37)   | 109.2(4) |
| C(43)-C(44)-H(44A)  | 109.5    | C(43)-C(44)-H(44B)  | 109.5    |
| H(44A)-C(44)-H(44B) | 109.5    | C(43)-C(44)-H(44C)  | 109.5    |
| H(44A)-C(44)-H(44C) | 109.5    | H(44B)-C(44)-H(44C) | 109.5    |
| C(43)-C(45)-H(45A)  | 109.5    | C(43)-C(45)-H(45B)  | 109.5    |
| H(45A)-C(45)-H(45B) | 109.5    | C(43)-C(45)-H(45C)  | 109.5    |
| H(45A)-C(45)-H(45C) | 109.5    | H(45B)-C(45)-H(45C) | 109.5    |
| C(43)-C(46)-H(46A)  | 109.5    | C(43)-C(46)-H(46B)  | 109.5    |
| H(46A)-C(46)-H(46B) | 109.5    | C(43)-C(46)-H(46C)  | 109.5    |
| H(46A)-C(46)-H(46C) | 109.5    | H(46B)-C(46)-H(46C) | 109.5    |
| C(48)-C(47)-C(52)   | 119.5(5) | C(48)-C(47)-P(2)    | 119.5(4) |
| C(52)-C(47)-P(2)    | 120.9(4) | C(47)-C(48)-C(49)   | 121.0(6) |
| C(47)-C(48)-H(48)   | 119.5    | C(49)-C(48)-H(48)   | 119.5    |
| C(50)-C(49)-C(48)   | 118.5(6) | C(50)-C(49)-H(49)   | 120.7    |
| C(48)-C(49)-H(49)   | 120.7    | C(51)-C(50)-C(49)   | 121.2(6) |
| C(51)-C(50)-H(50)   | 119.4    | C(49)-C(50)-H(50)   | 119.4    |
| C(52)-C(51)-C(50)   | 119.2(6) | C(52)-C(51)-H(51)   | 120.4    |
| C(50)-C(51)-H(51)   | 120.4    | C(51)-C(52)-C(47)   | 120.6(6) |
| C(51)-C(52)-H(52)   | 119.7    | C(47)-C(52)-H(52)   | 119.7    |
| C(54)-C(53)-C(58)   | 119.8(4) | C(54)-C(53)-P(2)    | 120.3(4) |
| C(58)-C(53)-P(2)    | 119.9(4) | C(55)-C(54)-C(53)   | 120.0(5) |
| C(55)-C(54)-H(54)   | 120.0    | C(53)-C(54)-H(54)   | 120.0    |
| C(54)-C(55)-C(56)   | 120.2(5) | C(54)-C(55)-H(55)   | 119.9    |

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|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(56)-C(55)-H(55) | 119.9    | C(57)-C(56)-C(55) | 119.4(5) |
| C(57)-C(56)-H(56) | 120.3    | C(55)-C(56)-H(56) | 120.3    |
| C(56)-C(57)-C(58) | 121.3(5) | C(56)-C(57)-H(57) | 119.3    |
| C(58)-C(57)-H(57) | 119.3    | C(57)-C(58)-C(53) | 119.1(5) |
| C(57)-C(58)-H(58) | 120.4    | C(53)-C(58)-H(58) | 120.4    |

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa748

| atom  | U11   | U22     | U33   | U23    | U13    | U12    |
|-------|-------|---------|-------|--------|--------|--------|
| N(1)  | 32(1) | 29(1)   | 10(1) | 0(1)   | 6(1)   | 0(1)   |
| P(1)  | 32(1) | 34(1)   | 11(1) | 1(1)   | 5(1)   | 1(1)   |
| P(2)  | 34(1) | 31(1)   | 10(1) | 0(1)   | 5(1)   | 0(1)   |
| O(1)  | 35(2) | 32(2)   | 26(2) | 2(1)   | 11(2)  | -1(1)  |
| O(2)  | 37(2) | 32(2)   | 21(2) | 1(1)   | 14(1)  | 4(1)   |
| N(1)  | 33(2) | 28(2)   | 14(2) | 1(2)   | 7(2)   | 0(2)   |
| N(2)  | 40(2) | 30(2)   | 13(2) | -1(2)  | 12(2)  | 4(2)   |
| C(1)  | 30(2) | 40(3)   | 11(2) | -2(2)  | 2(2)   | 0(2)   |
| C(2)  | 36(3) | 34(3)   | 13(2) | 0(2)   | 6(2)   | -3(2)  |
| C(3)  | 43(3) | 44(3)   | 19(3) | -6(2)  | 12(2)  | -1(2)  |
| C(4)  | 48(3) | 42(3)   | 32(3) | -4(2)  | 15(2)  | -7(3)  |
| C(5)  | 56(3) | 38(3)   | 23(3) | -8(2)  | 10(2)  | -6(3)  |
| C(6)  | 46(3) | 43(3)   | 19(3) | -7(2)  | 8(2)   | -4(2)  |
| C(7)  | 26(2) | 38(3)   | 15(2) | 4(2)   | 0(2)   | 1(2)   |
| C(8)  | 34(3) | 32(2)   | 14(2) | 7(2)   | 4(2)   | -1(2)  |
| C(9)  | 41(3) | 40(3)   | 23(3) | 4(2)   | 11(2)  | -3(2)  |
| C(10) | 40(3) | 40(3)   | 28(3) | 6(2)   | 7(2)   | -8(2)  |
| C(11) | 35(3) | 46(3)   | 21(2) | 12(2)  | 5(2)   | 1(2)   |
| C(12) | 36(3) | 45(3)   | 10(2) | 5(2)   | 2(2)   | 2(2)   |
| C(13) | 48(3) | 41(3)   | 41(3) | -10(3) | 15(3)  | -9(3)  |
| C(14) | 76(5) | 32(3)   | 74(5) | -4(3)  | 17(4)  | 3(3)   |
| C(15) | 68(4) | 63(4)   | 35(3) | -14(3) | 16(3)  | -6(3)  |
| C(16) | 56(4) | 69(5)   | 84(6) | -38(4) | 26(4)  | -22(4) |
| C(17) | 37(3) | 59(4)   | 33(3) | 14(3)  | 14(2)  | 4(3)   |
| C(18) | 51(4) | 160(10) | 53(5) | 61(5)  | 25(3)  | 21(5)  |
| C(19) | 43(3) | 81(5)   | 52(4) | -13(3) | 23(3)  | -8(3)  |
| C(20) | 35(3) | 63(4)   | 60(4) | -1(3)  | 17(3)  | 1(3)   |
| C(21) | 35(3) | 32(3)   | 18(2) | 0(2)   | 11(2)  | 0(2)   |
| C(22) | 40(3) | 53(3)   | 18(3) | -3(2)  | 7(2)   | 3(2)   |
| C(23) | 51(3) | 47(3)   | 28(3) | -10(2) | 13(2)  | 4(3)   |
| C(24) | 48(3) | 36(3)   | 40(3) | 0(2)   | 15(3)  | 7(2)   |
| C(25) | 43(3) | 41(3)   | 32(3) | 3(2)   | 4(2)   | 9(2)   |
| C(26) | 44(3) | 41(3)   | 17(2) | 5(2)   | 8(2)   | -3(2)  |
| C(27) | 40(3) | 30(2)   | 11(2) | 4(2)   | 1(2)   | -3(2)  |
| C(28) | 41(3) | 37(3)   | 14(2) | 1(2)   | 4(2)   | 4(2)   |
| C(29) | 48(3) | 33(3)   | 29(3) | 0(2)   | 0(2)   | 5(2)   |
| C(30) | 56(4) | 36(3)   | 17(2) | 4(2)   | -9(2)  | -7(2)  |
| C(31) | 50(3) | 51(3)   | 18(3) | 11(2)  | 3(2)   | -5(3)  |
| C(32) | 40(3) | 49(3)   | 19(3) | 2(2)   | 4(2)   | 0(2)   |
| C(33) | 37(3) | 35(3)   | 12(2) | -1(2)  | 5(2)   | -2(2)  |
| C(34) | 36(3) | 31(2)   | 12(2) | -5(2)  | 4(2)   | 0(2)   |
| C(35) | 40(3) | 31(2)   | 10(2) | -2(2)  | 6(2)   | -2(2)  |
| C(36) | 38(3) | 30(2)   | 16(2) | 2(2)   | 0(2)   | 3(2)   |
| C(37) | 40(3) | 28(2)   | 13(2) | -5(2)  | 5(2)   | -3(2)  |
| C(38) | 38(3) | 37(3)   | 11(2) | -3(2)  | 7(2)   | -2(2)  |
| C(39) | 49(3) | 37(3)   | 16(2) | 4(2)   | 6(2)   | 5(2)   |
| C(40) | 80(4) | 46(3)   | 8(2)  | -2(2)  | 10(2)  | 4(3)   |
| C(41) | 50(3) | 37(3)   | 28(3) | 3(2)   | 12(2)  | -5(2)  |
| C(42) | 62(4) | 54(4)   | 30(3) | 16(3)  | 13(3)  | 2(3)   |
| C(43) | 38(3) | 44(3)   | 21(3) | 0(2)   | 8(2)   | 4(2)   |
| C(44) | 32(3) | 62(4)   | 35(3) | -5(3)  | 7(2)   | 3(3)   |
| C(45) | 51(4) | 73(4)   | 33(3) | 5(3)   | 20(3)  | 11(3)  |
| C(46) | 52(3) | 48(3)   | 39(3) | -11(3) | 14(3)  | 5(3)   |
| C(47) | 41(3) | 36(3)   | 16(2) | 4(2)   | -2(2)  | -4(2)  |
| C(48) | 63(4) | 37(3)   | 29(3) | -6(2)  | -11(3) | 7(3)   |
| C(49) | 83(5) | 46(4)   | 45(4) | -8(3)  | -24(4) | -10(3) |
| C(50) | 56(4) | 82(5)   | 46(4) | 12(4)  | -26(3) | -28(4) |
| C(51) | 45(4) | 89(5)   | 37(4) | 14(3)  | 1(3)   | -4(3)  |
| C(52) | 37(3) | 62(4)   | 22(3) | 7(2)   | 4(2)   | -1(3)  |
| C(53) | 37(3) | 35(3)   | 11(2) | 1(2)   | 5(2)   | 0(2)   |
| C(54) | 45(3) | 29(2)   | 17(2) | -4(2)  | 10(2)  | 2(2)   |
| C(55) | 47(3) | 39(3)   | 22(3) | -5(2)  | 17(2)  | -11(2) |
| C(56) | 69(4) | 39(3)   | 23(3) | 1(2)   | 20(3)  | -9(3)  |

## Appendix 1. Crystallographic data

C(57) 73(4) 37(3) 18(3) 5(2) 4(3) -5(3)  
C(58) 51(3) 32(3) 16(2) 0(2) 6(2) 0(2)

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa748

| atom   | x          | y    | z    | U(eq) |
|--------|------------|------|------|-------|
| H(1)   | 3763       | 4801 | 5353 | 32    |
| H(2)   | 2960       | 4986 | 3880 | 33    |
| H(3A)  | 4287       | 5337 | 3542 | 42    |
| H(3B)  | 4715       | 5224 | 4367 | 42    |
| H(4A)  | 3475       | 6218 | 3934 | 48    |
| H(4B)  | 4458       | 6353 | 4199 | 48    |
| H(5A)  | 4255       | 6003 | 5407 | 47    |
| H(5B)  | 3564       | 6564 | 5176 | 47    |
| H(6A)  | 2931       | 5654 | 5759 | 43    |
| H(6B)  | 2495       | 5769 | 4937 | 43    |
| H(10)  | -370       | 2427 | 5400 | 43    |
| H(12)  | 424        | 4154 | 6315 | 36    |
| H(14A) | 1436       | 1478 | 5468 | 90    |
| H(14B) | 2144       | 1840 | 5030 | 90    |
| H(14C) | 1635       | 1218 | 4667 | 90    |
| H(15A) | 1248       | 1939 | 3538 | 82    |
| H(15B) | 1732       | 2552 | 3943 | 82    |
| H(15C) | 750        | 2619 | 3638 | 82    |
| H(16A) | 173        | 1326 | 4116 | 103   |
| H(16B) | -359       | 1987 | 4232 | 103   |
| H(16C) | -102       | 1511 | 4921 | 103   |
| H(18A) | -623       | 2484 | 6989 | 131   |
| H(18B) | -1253      | 2977 | 7367 | 131   |
| H(18C) | -259       | 3149 | 7377 | 131   |
| H(19A) | -732.9999  | 4232 | 6865 | 86    |
| H(19B) | -1720.9999 | 4046 | 6706 | 86    |
| H(19C) | -1190      | 4292 | 6043 | 86    |
| H(20A) | -1725      | 3203 | 5394 | 78    |
| H(20B) | -2196      | 3089 | 6134 | 78    |
| H(20C) | -1579      | 2531 | 5854 | 78    |
| H(22)  | 2264       | 5183 | 7159 | 44    |
| H(23)  | 1590       | 6172 | 7439 | 50    |
| H(24)  | 526        | 6626 | 6637 | 49    |
| H(25)  | 100        | 6072 | 5508 | 46    |
| H(26)  | 796        | 5108 | 5202 | 40    |
| H(28)  | 3853       | 3889 | 6052 | 36    |
| H(29)  | 4737       | 3428 | 7015 | 44    |
| H(30)  | 4214       | 3274 | 8187 | 44    |
| H(31)  | 2812       | 3533 | 8353 | 48    |
| H(32)  | 1920       | 3987 | 7390 | 43    |
| H(36)  | 6036       | 1839 | 4290 | 33    |
| H(38)  | 5347       | 3236 | 2768 | 34    |
| H(40A) | 5073       | 2556 | 5927 | 66    |
| H(40B) | 4480       | 1996 | 6238 | 66    |
| H(40C) | 4070       | 2548 | 5684 | 66    |
| H(41A) | 3446       | 1689 | 4812 | 57    |
| H(41B) | 3823       | 1131 | 5375 | 57    |
| H(41C) | 4031       | 1112 | 4525 | 57    |
| H(42A) | 5571       | 1056 | 4982 | 72    |
| H(42B) | 5355       | 1126 | 5826 | 72    |
| H(42C) | 6000       | 1634 | 5489 | 72    |
| H(44A) | 7395       | 2247 | 4095 | 64    |
| H(44B) | 7382       | 2997 | 3811 | 64    |
| H(44C) | 7947       | 2458 | 3431 | 64    |
| H(45A) | 7276       | 2701 | 2209 | 77    |
| H(45B) | 6696       | 3260 | 2539 | 77    |
| H(45C) | 6261       | 2681 | 2037 | 77    |
| H(46A) | 6696       | 1368 | 3327 | 69    |
| H(46B) | 7228       | 1564 | 2645 | 69    |
| H(46C) | 6208       | 1533 | 2536 | 69    |
| H(48)  | 3404       | 2861 | 2225 | 52    |
| H(49)  | 2158       | 2532 | 1518 | 71    |

# Appendix 1. Crystallographic data

|       |      |      |      |    |
|-------|------|------|------|----|
| H(50) | 858  | 3024 | 1745 | 76 |
| H(51) | 800  | 3835 | 2657 | 68 |
| H(52) | 2043 | 4128 | 3379 | 48 |
| H(54) | 5506 | 4350 | 3237 | 36 |
| H(55) | 6130 | 5008 | 2372 | 42 |
| H(56) | 5304 | 5395 | 1312 | 51 |
| H(57) | 3872 | 5123 | 1134 | 51 |
| H(58) | 3240 | 4430 | 1969 | 39 |



**Complex [37a][SbF<sub>6</sub>]**

Table 1. Crystal data for pa845

|   |   |
|---|---|
| Compound                                    | pa845   |
| Molecular formula                           | C <sub>54</sub> H <sub>64</sub> N <sub>2</sub> NiO <sub>2</sub> P <sub>2</sub> ,4(C <sub>7</sub> H <sub>8</sub> ),F <sub>6</sub> Sb |
| Molecular weight                            | 1498.01   |
| Crystal habit                               | Black Plate   |
| Crystal dimensions(mm)                      | 0.24x0.22x0.06  |
| Crystal system                              | triclinic   |
| Space group                                 | Pbar1   |
| a(Å)  | 9.993(1)  |
| b(Å)  | 19.417(2)   |
| c(Å)  | 20.297(2)   |
| α(°)  | 77.163(1)   |
| β(°)  | 88.532(1)   |
| γ(°)  | 78.116(1)   |
| V(Å <sup>3</sup> )                          | 3756.7(7)   |
| Z   | 2   |
| d(g·cm <sup>-3</sup> )                      | 1.324   |
| F(000)                                      | 1562  |
| μ(cm <sup>-1</sup> )                        | 0.715   |
| Absorption corrections                      | multi-scan ; 0.8472 min, 0.9584 max   |
| Diffractionmeter                            | KappaCCD  |
| X-ray source                                | MoKα  |
| λ(Å)  | 0.71069   |
| Monochromator                               | graphite  |
| T (K)                                       | 150.0(1)  |
| Scan mode                                   | phi and omega scans   |
| Maximum θ                                   | 25.02   |
| HKL ranges                                  | -11 11 ; -22 23 ; -23 24  |
| Reflections measured                        | 26224   |
| Unique data                                 | 12512   |
| Rint  | 0.0338  |
| Reflections used                            | 10755   |
| Criterion                                   | I > 2σ(I)   |
| Refinement type                             | Fsqd  |
| Hydrogen atoms                              | constr  |
| Parameters refined                          | 949   |
| Reflections / parameter                     | 11  |
| wR2   | 0.1398  |
| R1  | 0.0590  |
| Weights a, b                                | 0.0590 ; 9.1274   |
| GoF   | 1.077   |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.584(0.087) / -1.703(0.087)  |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa845

| atom   | x         | y        | z        | U(eq)   |
|--------|-----------|----------|----------|---------|
| Ni(1)  | 3901(1)   | 2429(1)  | 7345(1)  | 27(1)   |
| P(1)   | 3647(1)   | 3007(1)  | 8617(1)  | 29(1)   |
| P(2)   | 4387(1)   | 1002(1)  | 6924(1)  | 29(1)   |
| O(1)   | 3028(3)   | 3377(1)  | 7121(1)  | 33(1)   |
| O(2)   | 4373(3)   | 2581(1)  | 6447(1)  | 35(1)   |
| N(1)   | 3601(3)   | 2323(2)  | 8274(1)  | 29(1)   |
| N(2)   | 4498(3)   | 1442(2)  | 7522(2)  | 30(1)   |
| C(1)   | 4344(4)   | 1603(2)  | 8647(2)  | 35(1)   |
| C(2)   | 4203(4)   | 1084(2)  | 8221(2)  | 35(1)   |
| C(3)   | 2431(4)   | 3747(2)  | 8154(2)  | 31(1)   |
| C(4)   | 2177(4)   | 3779(2)  | 7466(2)  | 28(1)   |
| C(5)   | 1012(4)   | 4272(2)  | 7139(2)  | 29(1)   |
| C(6)   | 290(4)    | 4760(2)  | 7499(2)  | 32(1)   |
| C(7)   | 602(4)    | 4778(2)  | 8161(2)  | 31(1)   |
| C(8)   | 1671(4)   | 4246(2)  | 8492(2)  | 33(1)   |
| C(9)   | 593(4)    | 4310(2)  | 6405(2)  | 35(1)   |
| C(10)  | 707(6)    | 3558(3)  | 6261(2)  | 55(1)   |
| C(11)  | -893(4)   | 4706(3)  | 6255(2)  | 47(1)   |
| C(12)  | 1515(5)   | 4717(3)  | 5925(2)  | 50(1)   |
| C(13)  | -179(4)   | 5345(2)  | 8526(2)  | 41(1)   |
| C(14A) | -1312(8)  | 5874(4)  | 8082(3)  | 59(3)   |
| C(15A) | -868(8)   | 4945(4)  | 9160(4)  | 53(2)   |
| C(16A) | 800(10)   | 5741(4)  | 8759(5)  | 50(2)   |
| C(14B) | -110(50)  | 6150(10) | 8020(20) | 110(20) |
| C(15B) | -1600(40) | 5310(20) | 8580(30) | 130(20) |
| C(16B) | 620(50)   | 5430(30) | 9120(20) | 130(20) |
| C(17)  | 5327(4)   | 3201(2)  | 8626(2)  | 33(1)   |
| C(18)  | 5638(4)   | 3767(2)  | 8137(2)  | 40(1)   |
| C(19)  | 6949(5)   | 3889(3)  | 8095(2)  | 49(1)   |
| C(20)  | 7970(5)   | 3450(3)  | 8536(3)  | 49(1)   |
| C(21)  | 7670(5)   | 2888(2)  | 9024(2)  | 46(1)   |
| C(22)  | 6355(4)   | 2760(2)  | 9074(2)  | 36(1)   |
| C(23)  | 3029(4)   | 2820(2)  | 9466(2)  | 32(1)   |
| C(24)  | 1827(4)   | 2555(2)  | 9551(2)  | 42(1)   |
| C(25)  | 1221(5)   | 2449(3)  | 10176(2) | 50(1)   |
| C(26)  | 1815(5)   | 2611(3)  | 10713(2) | 50(1)   |
| C(27)  | 2993(5)   | 2868(3)  | 10633(2) | 52(1)   |
| C(28)  | 3616(5)   | 2982(2)  | 10007(2) | 42(1)   |
| C(29)  | 5201(4)   | 1419(2)  | 6205(2)  | 31(1)   |
| C(30)  | 5148(4)   | 2164(2)  | 6089(2)  | 31(1)   |
| C(31)  | 5932(4)   | 2483(2)  | 5549(2)  | 32(1)   |
| C(32)  | 6591(4)   | 2040(2)  | 5139(2)  | 35(1)   |
| C(33)  | 6578(4)   | 1302(2)  | 5222(2)  | 35(1)   |
| C(34)  | 5895(4)   | 998(2)   | 5769(2)  | 35(1)   |
| C(35)  | 6027(5)   | 3280(2)  | 5432(2)  | 42(1)   |
| C(36)  | 4613(6)   | 3759(2)  | 5235(3)  | 58(1)   |
| C(37)  | 6569(7)   | 3424(3)  | 6076(3)  | 70(2)   |
| C(38)  | 7006(5)   | 3485(3)  | 4864(3)  | 56(1)   |
| C(39)  | 7310(4)   | 890(2)   | 4708(2)  | 43(1)   |
| C(40)  | 6671(6)   | 1247(4)  | 4001(3)  | 70(2)   |
| C(41)  | 8824(5)   | 925(3)   | 4692(2)  | 50(1)   |
| C(42)  | 7219(6)   | 96(3)    | 4889(3)  | 71(2)   |
| C(43)  | 5366(4)   | 103(2)   | 7209(2)  | 33(1)   |
| C(44)  | 6715(5)   | 44(2)    | 7399(3)  | 50(1)   |
| C(45)  | 7548(6)   | -626(3)  | 7629(3)  | 61(1)   |
| C(46)  | 7024(6)   | -1235(3) | 7681(3)  | 64(2)   |
| C(47)  | 5697(7)   | -1186(3) | 7500(3)  | 66(2)   |
| C(48)  | 4847(5)   | -519(2)  | 7258(2)  | 48(1)   |
| C(49)  | 2642(4)   | 996(2)   | 6729(2)  | 35(1)   |
| C(50)  | 1865(4)   | 582(2)   | 7168(2)  | 42(1)   |
| C(51)  | 504(5)    | 629(3)   | 7011(3)  | 53(1)   |
| C(52)  | -95(5)    | 1091(3)  | 6427(3)  | 54(1)   |

|       |          |          |          |         |
|-------|----------|----------|----------|---------|
| C(53) | 667(5)   | 1510(3)  | 5998(3)  | 52(1)   |
| C(54) | 2034(4)  | 1462(2)  | 6147(2)  | 42(1)   |
| Sb(1) | 7959(1)  | 1665(1)  | 1406(1)  | 71(1)   |
| F(1)  | 8159(5)  | 1751(3)  | 492(2)   | 120(2)  |
| F(2)  | 7710(10) | 1521(5)  | 2324(2)  | 219(4)  |
| F(3)  | 8489(8)  | 2506(4)  | 1339(4)  | 190(3)  |
| F(4)  | 6130(4)  | 2064(3)  | 1246(3)  | 139(2)  |
| F(5)  | 7508(6)  | 755(2)   | 1457(2)  | 124(2)  |
| F(6)  | 9770(5)  | 1277(6)  | 1528(4)  | 268(6)  |
| C(55) | -210(10) | 2255(6)  | 3111(4)  | 143(4)  |
| C(56) | 643(6)   | 2409(4)  | 3635(3)  | 67(2)   |
| C(57) | 270(8)   | 3010(4)  | 3885(3)  | 84(2)   |
| C(58) | 970(10)  | 3167(4)  | 4335(4)  | 110(3)  |
| C(59) | 2140(10) | 2756(6)  | 4574(4)  | 103(3)  |
| C(60) | 2677(7)  | 2144(6)  | 4362(4)  | 115(4)  |
| C(61) | 1845(8)  | 1947(4)  | 3867(3)  | 90(2)   |
| C(62) | 4597(7)  | 2960(3)  | 2700(3)  | 77(2)   |
| C(63) | 4976(5)  | 3601(3)  | 2893(3)  | 52(1)   |
| C(64) | 4124(5)  | 4016(3)  | 3251(2)  | 52(1)   |
| C(65) | 4484(6)  | 4608(3)  | 3420(3)  | 59(1)   |
| C(66) | 5688(6)  | 4795(3)  | 3239(3)  | 62(1)   |
| C(67) | 6568(6)  | 4388(3)  | 2879(3)  | 70(2)   |
| C(68) | 6232(6)  | 3796(3)  | 2704(3)  | 70(2)   |
| C(69) | 230(10)  | 9498(6)  | 770(6)   | 141(4)  |
| C(70) | 563(7)   | 8882(4)  | 1351(3)  | 82(2)   |
| C(71) | -352(6)  | 8446(4)  | 1565(4)  | 82(2)   |
| C(72) | -78(7)   | 7896(5)  | 2102(4)  | 87(2)   |
| C(73) | 1125(7)  | 7757(4)  | 2442(4)  | 82(2)   |
| C(74) | 2076(6)  | 8172(4)  | 2267(4)  | 75(2)   |
| C(75) | 1788(6)  | 8749(4)  | 1716(4)  | 81(2)   |
| C(76) | 5520(20) | -850(10) | -620(10) | 74(7)   |
| C(77) | 5150(10) | -284(5)  | -225(4)  | 57(3)   |
| C(78) | 6158(8)  | 48(6)    | -58(5)   | 70(10)  |
| C(79) | 5840(10) | 574(5)   | 320(5)   | 84(4)   |
| C(80) | 4510(20) | 767(5)   | 531(5)   | 90(10)  |
| C(81) | 3500(10) | 435(6)   | 364(6)   | 75(4)   |
| C(82) | 3816(8)  | -91(5)   | -14(5)   | 64(8)   |
| C(83) | 4610(10) | 5246(5)  | 10447(6) | 87(6)   |
| C(84) | 5000(10) | 4696(6)  | 11017(4) | 87(5)   |
| C(85) | 5820(10) | 4045(5)  | 10953(4) | 107(6)  |
| C(86) | 6260(10) | 3944(5)  | 10320(5) | 84(4)   |
| C(87) | 5880(10) | 4494(6)  | 9750(4)  | 70(5)   |
| C(88) | 5050(10) | 5145(5)  | 9813(5)  | 93(5)   |
| C(89) | 4540(10) | 5761(7)  | 9187(6)  | 150(10) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa845

|               |          |               |          |
|---------------|----------|---------------|----------|
| Ni(1)-O(1)    | 1.828(2) | Ni(1)-N(2)    | 1.842(3) |
| Ni(1)-O(2)    | 1.844(2) | Ni(1)-N(1)    | 1.875(3) |
| P(1)-N(1)     | 1.639(3) | P(1)-C(3)     | 1.779(4) |
| P(1)-C(17)    | 1.796(4) | P(1)-C(23)    | 1.799(4) |
| P(2)-N(2)     | 1.650(3) | P(2)-C(29)    | 1.769(4) |
| P(2)-C(43)    | 1.794(4) | P(2)-C(49)    | 1.800(4) |
| O(1)-C(4)     | 1.327(4) | O(2)-C(30)    | 1.326(5) |
| N(1)-C(1)     | 1.486(5) | N(2)-C(2)     | 1.486(5) |
| C(1)-C(2)     | 1.494(5) | C(1)-H(1A)    | 0.9900   |
| C(1)-H(1B)    | 0.9900   | C(2)-H(2A)    | 0.9900   |
| C(2)-H(2B)    | 0.9900   | C(3)-C(8)     | 1.397(5) |
| C(3)-C(4)     | 1.412(5) | C(4)-C(5)     | 1.417(5) |
| C(5)-C(6)     | 1.397(5) | C(5)-C(9)     | 1.541(5) |
| C(6)-C(7)     | 1.397(5) | C(6)-H(6)     | 0.9500   |
| C(7)-C(8)     | 1.391(5) | C(7)-C(13)    | 1.533(5) |
| C(8)-H(8)     | 0.9500   | C(9)-C(12)    | 1.528(6) |
| C(9)-C(11)    | 1.529(6) | C(9)-C(10)    | 1.532(6) |
| C(10)-H(10A)  | 0.9800   | C(10)-H(10B)  | 0.9800   |
| C(10)-H(10C)  | 0.9800   | C(11)-H(11A)  | 0.9800   |
| C(11)-H(11B)  | 0.9800   | C(11)-H(11C)  | 0.9800   |
| C(12)-H(12A)  | 0.9800   | C(12)-H(12B)  | 0.9800   |
| C(12)-H(12C)  | 0.9800   | C(13)-C(15B)  | 1.43(3)  |
| C(13)-C(16A)  | 1.50(1)  | C(13)-C(16B)  | 1.52(3)  |
| C(13)-C(14A)  | 1.520(7) | C(13)-C(15A)  | 1.569(8) |
| C(13)-C(14B)  | 1.69(3)  | C(14A)-H(14A) | 0.9800   |
| C(14A)-H(14B) | 0.9800   | C(14A)-H(14C) | 0.9800   |
| C(15A)-H(15A) | 0.9800   | C(15A)-H(15B) | 0.9800   |
| C(15A)-H(15C) | 0.9800   | C(16A)-H(16A) | 0.9800   |
| C(16A)-H(16B) | 0.9800   | C(16A)-H(16C) | 0.9800   |
| C(14B)-H(14D) | 0.9800   | C(14B)-H(14E) | 0.9800   |
| C(14B)-H(14F) | 0.9800   | C(15B)-H(15D) | 0.9800   |
| C(15B)-H(15E) | 0.9800   | C(15B)-H(15F) | 0.9800   |
| C(16B)-H(16D) | 0.9800   | C(16B)-H(16E) | 0.9800   |
| C(16B)-H(16F) | 0.9800   | C(17)-C(18)   | 1.388(6) |
| C(17)-C(22)   | 1.399(5) | C(18)-C(19)   | 1.376(6) |
| C(18)-H(18)   | 0.9500   | C(19)-C(20)   | 1.385(7) |
| C(19)-H(19)   | 0.9500   | C(20)-C(21)   | 1.378(7) |
| C(20)-H(20)   | 0.9500   | C(21)-C(22)   | 1.384(6) |
| C(21)-H(21)   | 0.9500   | C(22)-H(22)   | 0.9500   |
| C(23)-C(28)   | 1.384(6) | C(23)-C(24)   | 1.393(6) |
| C(24)-C(25)   | 1.382(6) | C(24)-H(24)   | 0.9500   |
| C(25)-C(26)   | 1.379(7) | C(25)-H(25)   | 0.9500   |
| C(26)-C(27)   | 1.363(7) | C(26)-H(26)   | 0.9500   |
| C(27)-C(28)   | 1.393(6) | C(27)-H(27)   | 0.9500   |
| C(28)-H(28)   | 0.9500   | C(29)-C(30)   | 1.402(5) |
| C(29)-C(34)   | 1.410(5) | C(30)-C(31)   | 1.433(5) |
| C(31)-C(32)   | 1.386(5) | C(31)-C(35)   | 1.534(5) |
| C(32)-C(33)   | 1.408(6) | C(32)-H(32)   | 0.9500   |
| C(33)-C(34)   | 1.371(6) | C(33)-C(39)   | 1.534(5) |
| C(34)-H(34)   | 0.9500   | C(35)-C(37)   | 1.530(7) |
| C(35)-C(38)   | 1.530(6) | C(35)-C(36)   | 1.531(7) |
| C(36)-H(36A)  | 0.9800   | C(36)-H(36B)  | 0.9800   |
| C(36)-H(36C)  | 0.9800   | C(37)-H(37A)  | 0.9800   |
| C(37)-H(37B)  | 0.9800   | C(37)-H(37C)  | 0.9800   |
| C(38)-H(38A)  | 0.9800   | C(38)-H(38B)  | 0.9800   |
| C(38)-H(38C)  | 0.9800   | C(39)-C(42)   | 1.526(7) |
| C(39)-C(41)   | 1.528(6) | C(39)-C(40)   | 1.540(7) |
| C(40)-H(40A)  | 0.9800   | C(40)-H(40B)  | 0.9800   |
| C(40)-H(40C)  | 0.9800   | C(41)-H(41A)  | 0.9800   |
| C(41)-H(41B)  | 0.9800   | C(41)-H(41C)  | 0.9800   |
| C(42)-H(42A)  | 0.9800   | C(42)-H(42B)  | 0.9800   |
| C(42)-H(42C)  | 0.9800   | C(43)-C(44)   | 1.387(6) |
| C(43)-C(48)   | 1.392(6) | C(44)-C(45)   | 1.381(7) |
| C(44)-H(44)   | 0.9500   | C(45)-C(46)   | 1.372(8) |
| C(45)-H(45)   | 0.9500   | C(46)-C(47)   | 1.363(8) |
| C(46)-H(46)   | 0.9500   | C(47)-C(48)   | 1.387(7) |

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| C(47)-H(47)      | 0.9500   | C(48)-H(48)      | 0.9500   |
| C(49)-C(54)      | 1.385(6) | C(49)-C(50)      | 1.395(6) |
| C(50)-C(51)      | 1.385(6) | C(50)-H(50)      | 0.9500   |
| C(51)-C(52)      | 1.382(7) | C(51)-H(51)      | 0.9500   |
| C(52)-C(53)      | 1.381(7) | C(52)-H(52)      | 0.9500   |
| C(53)-C(54)      | 1.386(6) | C(53)-H(53)      | 0.9500   |
| C(54)-H(54)      | 0.9500   | Sb(1)-F(3)       | 1.795(5) |
| Sb(1)-F(6)       | 1.812(5) | Sb(1)-F(1)       | 1.835(4) |
| Sb(1)-F(4)       | 1.839(4) | Sb(1)-F(2)       | 1.840(5) |
| Sb(1)-F(5)       | 1.892(5) | C(55)-C(56)      | 1.50(1)  |
| C(55)-H(55A)     | 0.9800   | C(55)-H(55B)     | 0.9800   |
| C(55)-H(55C)     | 0.9800   | C(56)-C(57)      | 1.35(1)  |
| C(56)-C(61)      | 1.37(1)  | C(57)-C(58)      | 1.29(1)  |
| C(57)-H(57)      | 0.9500   | C(58)-C(59)      | 1.31(1)  |
| C(58)-H(58)      | 0.9500   | C(59)-C(60)      | 1.36(1)  |
| C(59)-H(59)      | 0.9500   | C(60)-C(61)      | 1.48(1)  |
| C(60)-H(60)      | 0.9500   | C(61)-H(61)      | 0.9500   |
| C(62)-C(63)      | 1.503(7) | C(62)-H(62A)     | 0.9800   |
| C(62)-H(62B)     | 0.9800   | C(62)-H(62C)     | 0.9800   |
| C(63)-C(64)      | 1.359(7) | C(63)-C(68)      | 1.405(8) |
| C(64)-C(65)      | 1.387(7) | C(64)-H(64)      | 0.9500   |
| C(65)-C(66)      | 1.346(8) | C(65)-H(65)      | 0.9500   |
| C(66)-C(67)      | 1.366(8) | C(66)-H(66)      | 0.9500   |
| C(67)-C(68)      | 1.381(8) | C(67)-H(67)      | 0.9500   |
| C(68)-H(68)      | 0.9500   | C(69)-C(70)      | 1.47(1)  |
| C(69)-H(69A)     | 0.9800   | C(69)-H(69B)     | 0.9800   |
| C(69)-H(69C)     | 0.9800   | C(70)-C(71)      | 1.37(1)  |
| C(70)-C(75)      | 1.39(1)  | C(71)-C(72)      | 1.34(1)  |
| C(71)-H(71)      | 0.9500   | C(72)-C(73)      | 1.35(1)  |
| C(72)-H(72)      | 0.9500   | C(73)-C(74)      | 1.36(1)  |
| C(73)-H(73)      | 0.9500   | C(74)-C(75)      | 1.38(1)  |
| C(74)-H(74)      | 0.9500   | C(75)-H(75)      | 0.9500   |
| C(76)-C(77)      | 1.49(2)  | C(76)-H(76A)     | 0.9800   |
| C(76)-H(76B)     | 0.9800   | C(76)-H(76C)     | 0.9800   |
| C(77)-C(78)      | 1.3900   | C(77)-C(82)      | 1.3900   |
| C(78)-C(79)      | 1.3900   | C(78)-H(78)      | 0.9500   |
| C(79)-C(80)      | 1.3900   | C(79)-H(79)      | 0.9500   |
| C(80)-C(81)      | 1.3900   | C(80)-H(80)      | 0.9500   |
| C(81)-C(82)      | 1.3900   | C(81)-H(81)      | 0.9500   |
| C(82)-H(82)      | 0.9500   | C(83)-C(84)      | 1.3900   |
| C(83)-C(88)      | 1.3900   | C(83)-H(83)      | 0.9500   |
| C(84)-C(85)      | 1.3900   | C(84)-H(84)      | 0.9500   |
| C(85)-C(86)      | 1.3900   | C(85)-H(85)      | 0.9500   |
| C(86)-C(87)      | 1.3900   | C(86)-H(86)      | 0.9500   |
| C(87)-C(88)      | 1.3900   | C(87)-H(87)      | 0.9500   |
| C(88)-C(89)      | 1.5518   | C(89)-H(89A)     | 0.9800   |
| C(89)-H(89B)     | 0.9800   | C(89)-H(89C)     | 0.9800   |
| O(1)-Ni(1)-N(2)  | 170.0(1) | O(1)-Ni(1)-O(2)  | 84.2(1)  |
| N(2)-Ni(1)-O(2)  | 95.3(1)  | O(1)-Ni(1)-N(1)  | 94.9(1)  |
| N(2)-Ni(1)-N(1)  | 86.8(1)  | O(2)-Ni(1)-N(1)  | 173.1(1) |
| N(1)-P(1)-C(3)   | 106.0(2) | N(1)-P(1)-C(17)  | 112.9(2) |
| C(3)-P(1)-C(17)  | 112.5(2) | N(1)-P(1)-C(23)  | 109.0(2) |
| C(3)-P(1)-C(23)  | 106.2(2) | C(17)-P(1)-C(23) | 109.9(2) |
| N(2)-P(2)-C(29)  | 107.2(2) | N(2)-P(2)-C(43)  | 107.2(2) |
| C(29)-P(2)-C(43) | 107.4(2) | N(2)-P(2)-C(49)  | 112.2(2) |
| C(29)-P(2)-C(49) | 111.3(2) | C(43)-P(2)-C(49) | 111.3(2) |
| C(4)-O(1)-Ni(1)  | 131.4(2) | C(30)-O(2)-Ni(1) | 132.6(2) |
| C(1)-N(1)-P(1)   | 116.4(2) | C(1)-N(1)-Ni(1)  | 110.1(2) |
| P(1)-N(1)-Ni(1)  | 118.4(2) | C(2)-N(2)-P(2)   | 116.8(2) |
| C(2)-N(2)-Ni(1)  | 112.7(2) | P(2)-N(2)-Ni(1)  | 119.6(2) |
| N(1)-C(1)-C(2)   | 106.1(3) | N(1)-C(1)-H(1A)  | 110.5    |
| C(2)-C(1)-H(1A)  | 110.5    | N(1)-C(1)-H(1B)  | 110.5    |
| C(2)-C(1)-H(1B)  | 110.5    | H(1A)-C(1)-H(1B) | 108.7    |
| N(2)-C(2)-C(1)   | 105.3(3) | N(2)-C(2)-H(2A)  | 110.7    |
| C(1)-C(2)-H(2A)  | 110.7    | N(2)-C(2)-H(2B)  | 110.7    |
| C(1)-C(2)-H(2B)  | 110.7    | H(2A)-C(2)-H(2B) | 108.8    |

|                      |          |                      |          |
|----------------------|----------|----------------------|----------|
| C(8)-C(3)-C(4)       | 121.6(3) | C(8)-C(3)-P(1)       | 119.3(3) |
| C(4)-C(3)-P(1)       | 118.8(3) | O(1)-C(4)-C(3)       | 121.2(3) |
| O(1)-C(4)-C(5)       | 120.3(3) | C(3)-C(4)-C(5)       | 118.5(3) |
| C(6)-C(5)-C(4)       | 117.1(3) | C(6)-C(5)-C(9)       | 120.4(3) |
| C(4)-C(5)-C(9)       | 122.4(3) | C(5)-C(6)-C(7)       | 124.8(3) |
| C(5)-C(6)-H(6)       | 117.6    | C(7)-C(6)-H(6)       | 117.6    |
| C(8)-C(7)-C(6)       | 116.9(3) | C(8)-C(7)-C(13)      | 119.9(3) |
| C(6)-C(7)-C(13)      | 123.2(3) | C(7)-C(8)-C(3)       | 120.4(3) |
| C(7)-C(8)-H(8)       | 119.8    | C(3)-C(8)-H(8)       | 119.8    |
| C(12)-C(9)-C(11)     | 108.8(3) | C(12)-C(9)-C(10)     | 109.2(4) |
| C(11)-C(9)-C(10)     | 106.9(4) | C(12)-C(9)-C(5)      | 109.0(3) |
| C(11)-C(9)-C(5)      | 110.9(3) | C(10)-C(9)-C(5)      | 112.0(3) |
| C(9)-C(10)-H(10A)    | 109.5    | C(9)-C(10)-H(10B)    | 109.5    |
| H(10A)-C(10)-H(10B)  | 109.5    | C(9)-C(10)-H(10C)    | 109.5    |
| H(10A)-C(10)-H(10C)  | 109.5    | H(10B)-C(10)-H(10C)  | 109.5    |
| C(9)-C(11)-H(11A)    | 109.5    | C(9)-C(11)-H(11B)    | 109.5    |
| H(11A)-C(11)-H(11B)  | 109.5    | C(9)-C(11)-H(11C)    | 109.5    |
| H(11A)-C(11)-H(11C)  | 109.5    | C(9)-C(12)-H(12A)    | 109.5    |
| C(9)-C(12)-H(12A)    | 109.5    | C(9)-C(12)-H(12B)    | 109.5    |
| H(12A)-C(12)-H(12B)  | 109.5    | H(12A)-C(12)-H(12C)  | 109.5    |
| H(12A)-C(12)-H(12C)  | 109.5    | C(15B)-C(13)-C(16A)  | 121(3)   |
| C(15B)-C(13)-C(16A)  | 139(1)   | C(15B)-C(13)-C(16B)  | 56(2)    |
| C(16A)-C(13)-C(16B)  | 34(3)    | C(15B)-C(13)-C(14A)  | 131(1)   |
| C(16A)-C(13)-C(14A)  | 110.4(5) | C(16A)-C(13)-C(14B)  | 109.9(4) |
| C(15B)-C(13)-C(7)    | 111(1)   | C(14A)-C(13)-C(7)    | 111.9(4) |
| C(16B)-C(13)-C(7)    | 113(1)   | C(16A)-C(13)-C(15A)  | 108.9(5) |
| C(15B)-C(13)-C(15A)  | 54(2)    | C(14A)-C(13)-C(15A)  | 107.4(5) |
| C(16B)-C(13)-C(15A)  | 76(3)    | C(15B)-C(13)-C(14B)  | 106(3)   |
| C(7)-C(13)-C(15A)    | 108.2(4) | C(16B)-C(13)-C(14B)  | 97(3)    |
| C(16A)-C(13)-C(14B)  | 65(2)    | C(7)-C(13)-C(14B)    | 106(1)   |
| C(14A)-C(13)-C(14B)  | 52(2)    | C(13)-C(14A)-H(14A)  | 109.5    |
| C(15A)-C(13)-C(14B)  | 145(1)   | C(13)-C(14A)-H(14C)  | 109.5    |
| C(13)-C(14A)-H(14B)  | 109.5    | C(13)-C(15A)-H(15B)  | 109.5    |
| C(13)-C(15A)-H(15A)  | 109.5    | C(13)-C(16A)-H(16A)  | 109.5    |
| C(13)-C(15A)-H(15C)  | 109.5    | C(13)-C(16A)-H(16C)  | 109.5    |
| C(13)-C(16A)-H(16B)  | 109.5    | C(13)-C(14B)-H(14E)  | 109.5    |
| C(13)-C(14B)-H(14D)  | 109.5    | C(13)-C(14B)-H(14F)  | 109.5    |
| H(14D)-C(14B)-H(14E) | 109.5    | H(14E)-C(14B)-H(14F) | 109.5    |
| C(13)-C(15B)-H(15D)  | 109.5    | C(13)-C(15B)-H(15E)  | 109.5    |
| H(15D)-C(15B)-H(15F) | 109.5    | C(13)-C(15B)-H(15F)  | 109.5    |
| H(15D)-C(15B)-H(15F) | 109.5    | H(15E)-C(15B)-H(15F) | 109.5    |
| C(13)-C(16B)-H(16D)  | 109.5    | C(13)-C(16B)-H(16E)  | 109.5    |
| H(16D)-C(16B)-H(16E) | 109.5    | C(13)-C(16B)-H(16F)  | 109.5    |
| H(16D)-C(16B)-H(16F) | 109.5    | H(16E)-C(16B)-H(16F) | 109.5    |
| C(18)-C(17)-C(22)    | 119.4(4) | C(18)-C(17)-P(1)     | 118.8(3) |
| C(22)-C(17)-P(1)     | 121.5(3) | C(19)-C(18)-C(17)    | 120.1(4) |
| C(19)-C(18)-H(18)    | 120.0    | C(17)-C(18)-H(18)    | 120.0    |
| C(18)-C(19)-C(20)    | 120.6(4) | C(18)-C(19)-H(19)    | 119.7    |
| C(20)-C(19)-H(19)    | 119.7    | C(21)-C(20)-C(19)    | 119.8(4) |
| C(21)-C(20)-H(20)    | 120.1    | C(19)-C(20)-H(20)    | 120.1    |
| C(20)-C(21)-C(22)    | 120.3(4) | C(20)-C(21)-H(21)    | 119.8    |
| C(22)-C(21)-H(21)    | 119.8    | C(21)-C(22)-C(17)    | 119.8(4) |
| C(21)-C(22)-H(22)    | 120.1    | C(17)-C(22)-H(22)    | 120.1    |
| C(28)-C(23)-C(24)    | 119.8(4) | C(28)-C(23)-P(1)     | 123.5(3) |
| C(24)-C(23)-P(1)     | 116.5(3) | C(25)-C(24)-C(23)    | 120.4(4) |
| C(25)-C(24)-H(24)    | 119.8    | C(23)-C(24)-H(24)    | 119.8    |
| C(26)-C(25)-C(24)    | 119.4(4) | C(26)-C(25)-H(25)    | 120.3    |
| C(24)-C(25)-H(25)    | 120.3    | C(27)-C(26)-C(25)    | 120.6(4) |
| C(27)-C(26)-H(26)    | 119.7    | C(25)-C(26)-H(26)    | 119.7    |
| C(26)-C(27)-C(28)    | 121.0(4) | C(26)-C(27)-H(27)    | 119.5    |
| C(28)-C(27)-H(27)    | 119.5    | C(23)-C(28)-C(27)    | 118.8(4) |
| C(23)-C(28)-H(28)    | 120.6    | C(27)-C(28)-H(28)    | 120.6    |
| C(30)-C(29)-C(34)    | 121.7(3) | C(30)-C(29)-P(2)     | 118.7(3) |
| C(34)-C(29)-P(2)     | 119.6(3) | O(2)-C(30)-C(29)     | 122.3(3) |
| O(2)-C(30)-C(31)     | 119.3(3) | C(29)-C(30)-C(31)    | 118.3(3) |
| C(32)-C(31)-C(30)    | 116.9(3) | C(32)-C(31)-C(35)    | 121.9(3) |
| C(30)-C(31)-C(35)    | 121.2(3) | C(31)-C(32)-C(33)    | 125.3(4) |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(31)-C(32)-H(32)   | 117.4    | C(33)-C(32)-H(32)   | 117.4    |
| C(34)-C(33)-C(32)   | 116.6(3) | C(34)-C(33)-C(39)   | 124.2(4) |
| C(32)-C(33)-C(39)   | 119.1(4) | C(33)-C(34)-C(29)   | 120.9(4) |
| C(33)-C(34)-H(34)   | 119.5    | C(29)-C(34)-H(34)   | 119.5    |
| C(37)-C(35)-C(38)   | 107.5(4) | C(37)-C(35)-C(36)   | 110.3(4) |
| C(38)-C(35)-C(36)   | 107.9(4) | C(37)-C(35)-C(31)   | 109.6(4) |
| C(38)-C(35)-C(31)   | 112.0(4) | C(36)-C(35)-C(31)   | 109.6(4) |
| C(35)-C(36)-H(36A)  | 109.5    | C(35)-C(36)-H(36B)  | 109.5    |
| H(36A)-C(36)-H(36B) | 109.5    | C(35)-C(36)-H(36C)  | 109.5    |
| H(36A)-C(36)-H(36C) | 109.5    | H(36B)-C(36)-H(36C) | 109.5    |
| C(35)-C(37)-H(37A)  | 109.5    | C(35)-C(37)-H(37B)  | 109.5    |
| H(37A)-C(37)-H(37B) | 109.5    | C(35)-C(37)-H(37C)  | 109.5    |
| H(37A)-C(37)-H(37C) | 109.5    | H(37B)-C(37)-H(37C) | 109.5    |
| C(35)-C(38)-H(38A)  | 109.5    | C(35)-C(38)-H(38B)  | 109.5    |
| H(38A)-C(38)-H(38B) | 109.5    | C(35)-C(38)-H(38C)  | 109.5    |
| H(38A)-C(38)-H(38C) | 109.5    | H(38B)-C(38)-H(38C) | 109.5    |
| C(42)-C(39)-C(41)   | 107.6(4) | C(42)-C(39)-C(33)   | 111.8(4) |
| C(41)-C(39)-C(33)   | 109.9(3) | C(42)-C(39)-C(40)   | 109.9(5) |
| C(41)-C(39)-C(40)   | 108.5(4) | C(33)-C(39)-C(40)   | 109.1(4) |
| C(39)-C(40)-H(40A)  | 109.5    | C(39)-C(40)-H(40B)  | 109.5    |
| H(40A)-C(40)-H(40B) | 109.5    | C(39)-C(40)-H(40C)  | 109.5    |
| H(40A)-C(40)-H(40C) | 109.5    | H(40B)-C(40)-H(40C) | 109.5    |
| C(39)-C(41)-H(41A)  | 109.5    | C(39)-C(41)-H(41B)  | 109.5    |
| H(41A)-C(41)-H(41B) | 109.5    | C(39)-C(41)-H(41C)  | 109.5    |
| H(41A)-C(41)-H(41C) | 109.5    | H(41B)-C(41)-H(41C) | 109.5    |
| C(39)-C(42)-H(42A)  | 109.5    | C(39)-C(42)-H(42B)  | 109.5    |
| H(42A)-C(42)-H(42B) | 109.5    | C(39)-C(42)-H(42C)  | 109.5    |
| H(42A)-C(42)-H(42C) | 109.5    | H(42B)-C(42)-H(42C) | 109.5    |
| C(44)-C(43)-C(48)   | 119.6(4) | C(44)-C(43)-P(2)    | 116.2(3) |
| C(48)-C(43)-P(2)    | 124.2(3) | C(45)-C(44)-C(43)   | 120.4(5) |
| C(45)-C(44)-H(44)   | 119.8    | C(43)-C(44)-H(44)   | 119.8    |
| C(46)-C(45)-C(44)   | 119.5(5) | C(46)-C(45)-H(45)   | 120.3    |
| C(44)-C(45)-H(45)   | 120.3    | C(47)-C(46)-C(45)   | 120.7(5) |
| C(47)-C(46)-H(46)   | 119.6    | C(45)-C(46)-H(46)   | 119.6    |
| C(46)-C(47)-C(48)   | 120.8(5) | C(46)-C(47)-H(47)   | 119.6    |
| C(48)-C(47)-H(47)   | 119.6    | C(47)-C(48)-C(43)   | 118.9(5) |
| C(47)-C(48)-H(48)   | 120.6    | C(43)-C(48)-H(48)   | 120.6    |
| C(54)-C(49)-C(50)   | 119.5(4) | C(54)-C(49)-P(2)    | 118.1(3) |
| C(50)-C(49)-P(2)    | 122.2(3) | C(51)-C(50)-C(49)   | 119.8(4) |
| C(51)-C(50)-H(50)   | 120.1    | C(49)-C(50)-H(50)   | 120.1    |
| C(52)-C(51)-C(50)   | 120.4(4) | C(52)-C(51)-H(51)   | 119.8    |
| C(50)-C(51)-H(51)   | 119.8    | C(53)-C(52)-C(51)   | 119.8(4) |
| C(53)-C(52)-H(52)   | 120.1    | C(51)-C(52)-H(52)   | 120.1    |
| C(52)-C(53)-C(54)   | 120.2(4) | C(52)-C(53)-H(53)   | 119.9    |
| C(54)-C(53)-H(53)   | 119.9    | C(49)-C(54)-C(53)   | 120.3(4) |
| C(49)-C(54)-H(54)   | 119.9    | C(53)-C(54)-H(54)   | 119.9    |
| F(3)-Sb(1)-F(6)     | 84.1(5)  | F(3)-Sb(1)-F(1)     | 89.7(3)  |
| F(6)-Sb(1)-F(1)     | 89.2(3)  | F(3)-Sb(1)-F(4)     | 95.7(3)  |
| F(6)-Sb(1)-F(4)     | 177.7(3) | F(1)-Sb(1)-F(4)     | 88.5(3)  |
| F(3)-Sb(1)-F(2)     | 94.2(3)  | F(6)-Sb(1)-F(2)     | 91.5(4)  |
| F(1)-Sb(1)-F(2)     | 176.0(3) | F(4)-Sb(1)-F(2)     | 90.9(4)  |
| F(3)-Sb(1)-F(5)     | 176.4(3) | F(6)-Sb(1)-F(5)     | 92.7(4)  |
| F(1)-Sb(1)-F(5)     | 88.5(2)  | F(4)-Sb(1)-F(5)     | 87.4(2)  |
| F(2)-Sb(1)-F(5)     | 87.5(3)  | C(56)-C(55)-H(55A)  | 109.5    |
| C(56)-C(55)-H(55B)  | 109.5    | H(55A)-C(55)-H(55B) | 109.5    |
| C(56)-C(55)-H(55C)  | 109.5    | H(55A)-C(55)-H(55C) | 109.5    |
| H(55B)-C(55)-H(55C) | 109.5    | C(57)-C(56)-C(61)   | 117.9(6) |
| C(57)-C(56)-C(55)   | 121.7(8) | C(61)-C(56)-C(55)   | 120.5(8) |
| C(58)-C(57)-C(56)   | 124.0(7) | C(58)-C(57)-H(57)   | 118.0    |
| C(56)-C(57)-H(57)   | 118.0    | C(57)-C(58)-C(59)   | 122(1)   |
| C(57)-C(58)-H(58)   | 119.2    | C(59)-C(58)-H(58)   | 119.2    |
| C(58)-C(59)-C(60)   | 121.6(8) | C(58)-C(59)-H(59)   | 119.2    |
| C(60)-C(59)-H(59)   | 119.2    | C(59)-C(60)-C(61)   | 116.7(6) |
| C(59)-C(60)-H(60)   | 121.6    | C(61)-C(60)-H(60)   | 121.6    |
| C(56)-C(61)-C(60)   | 118.1(7) | C(56)-C(61)-H(61)   | 120.9    |
| C(60)-C(61)-H(61)   | 120.9    | C(63)-C(62)-H(62A)  | 109.5    |
| C(63)-C(62)-H(62B)  | 109.5    | H(62A)-C(62)-H(62B) | 109.5    |
| C(63)-C(62)-H(62C)  | 109.5    | H(62A)-C(62)-H(62C) | 109.5    |

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| H(62B)-C(62)-H(62C) | 109.5    | C(64)-C(63)-C(68)   | 117.3(5) |
| C(64)-C(63)-C(62)   | 121.9(5) | C(68)-C(63)-C(62)   | 120.9(5) |
| C(63)-C(64)-C(65)   | 121.2(5) | C(63)-C(64)-H(64)   | 119.4    |
| C(65)-C(64)-H(64)   | 119.4    | C(66)-C(65)-C(64)   | 121.5(5) |
| C(66)-C(65)-H(65)   | 119.3    | C(64)-C(65)-H(65)   | 119.3    |
| C(65)-C(66)-C(67)   | 118.8(5) | C(65)-C(66)-H(66)   | 120.6    |
| C(67)-C(66)-H(66)   | 120.6    | C(66)-C(67)-C(68)   | 120.8(5) |
| C(66)-C(67)-H(67)   | 119.6    | C(68)-C(67)-H(67)   | 119.6    |
| C(67)-C(68)-C(63)   | 120.5(5) | C(67)-C(68)-H(68)   | 119.8    |
| C(63)-C(68)-H(68)   | 119.8    | C(70)-C(69)-H(69A)  | 109.5    |
| C(70)-C(69)-H(69B)  | 109.5    | H(69A)-C(69)-H(69B) | 109.5    |
| C(70)-C(69)-H(69C)  | 109.5    | H(69A)-C(69)-H(69C) | 109.5    |
| H(69B)-C(69)-H(69C) | 109.5    | C(71)-C(70)-C(75)   | 118.5(7) |
| C(71)-C(70)-C(69)   | 120.7(8) | C(75)-C(70)-C(69)   | 120.7(8) |
| C(72)-C(71)-C(70)   | 121.3(7) | C(72)-C(71)-H(71)   | 119.3    |
| C(70)-C(71)-H(71)   | 119.3    | C(71)-C(72)-C(73)   | 119.9(7) |
| C(71)-C(72)-H(72)   | 120.1    | C(73)-C(72)-H(72)   | 120.1    |
| C(72)-C(73)-C(74)   | 122.3(8) | C(72)-C(73)-H(73)   | 118.9    |
| C(74)-C(73)-H(73)   | 118.9    | C(73)-C(74)-C(75)   | 118.0(6) |
| C(73)-C(74)-H(74)   | 121.0    | C(75)-C(74)-H(74)   | 121.0    |
| C(74)-C(75)-C(70)   | 119.9(7) | C(74)-C(75)-H(75)   | 120.0    |
| C(70)-C(75)-H(75)   | 120.0    | C(78)-C(77)-C(82)   | 120.0    |
| C(78)-C(77)-C(76)   | 119(1)   | C(82)-C(77)-C(76)   | 121(1)   |
| C(79)-C(78)-C(77)   | 120.0    | C(79)-C(78)-H(78)   | 120.0    |
| C(77)-C(78)-H(78)   | 120.0    | C(78)-C(79)-C(80)   | 120.0    |
| C(78)-C(79)-H(79)   | 120.0    | C(80)-C(79)-H(79)   | 120.0    |
| C(79)-C(80)-C(81)   | 120.0    | C(79)-C(80)-H(80)   | 120.0    |
| C(81)-C(80)-H(80)   | 120.0    | C(82)-C(81)-C(80)   | 120.0    |
| C(82)-C(81)-H(81)   | 120.0    | C(80)-C(81)-H(81)   | 120.0    |
| C(81)-C(82)-C(77)   | 120.0    | C(81)-C(82)-H(82)   | 120.0    |
| C(77)-C(82)-H(82)   | 120.0    | C(84)-C(83)-C(88)   | 120.0    |
| C(84)-C(83)-H(83)   | 120.0    | C(88)-C(83)-H(83)   | 120.0    |
| C(85)-C(84)-C(83)   | 120.0    | C(85)-C(84)-H(84)   | 120.0    |
| C(83)-C(84)-H(84)   | 120.0    | C(84)-C(85)-C(86)   | 120.0    |
| C(84)-C(85)-H(85)   | 120.0    | C(86)-C(85)-H(85)   | 120.0    |
| C(87)-C(86)-C(85)   | 120.0    | C(87)-C(86)-H(86)   | 120.0    |
| C(85)-C(86)-H(86)   | 120.0    | C(86)-C(87)-C(88)   | 120.0    |
| C(86)-C(87)-H(87)   | 120.0    | C(88)-C(87)-H(87)   | 120.0    |
| C(87)-C(88)-C(83)   | 120.0    | C(87)-C(88)-C(89)   | 121.7    |
| C(83)-C(88)-C(89)   | 118.2    |                     |          |

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa845

| atom   | U11     | U22     | U33     | U23      | U13     | U12     |
|--------|---------|---------|---------|----------|---------|---------|
| N1(1)  | 30(1)   | 26(1)   | 24(1)   | -4(1)    | 2(1)    | -6(1)   |
| P(1)   | 29(1)   | 33(1)   | 24(1)   | -6(1)    | 0(1)    | -6(1)   |
| P(2)   | 32(1)   | 27(1)   | 31(1)   | -6(1)    | 2(1)    | -9(1)   |
| O(1)   | 37(2)   | 31(1)   | 26(1)   | -5(1)    | 4(1)    | 0(1)    |
| O(2)   | 49(2)   | 28(1)   | 26(1)   | -5(1)    | 10(1)   | -6(1)   |
| N(1)   | 33(2)   | 32(2)   | 21(1)   | -3(1)    | -3(1)   | -5(1)   |
| N(2)   | 36(2)   | 28(2)   | 25(2)   | -4(1)    | 2(1)    | -9(1)   |
| C(1)   | 43(2)   | 32(2)   | 26(2)   | -1(2)    | -1(2)   | -6(2)   |
| C(2)   | 43(2)   | 30(2)   | 29(2)   | 2(2)     | 1(2)    | -10(2)  |
| C(3)   | 30(2)   | 34(2)   | 29(2)   | -7(2)    | -1(2)   | -7(2)   |
| C(4)   | 30(2)   | 29(2)   | 26(2)   | -6(1)    | 1(1)    | -8(2)   |
| C(5)   | 32(2)   | 30(2)   | 27(2)   | -5(2)    | 2(2)    | -10(2)  |
| C(6)   | 29(2)   | 32(2)   | 32(2)   | -5(2)    | -1(2)   | -4(2)   |
| C(7)   | 27(2)   | 35(2)   | 33(2)   | -10(2)   | 2(2)    | -5(2)   |
| C(8)   | 35(2)   | 39(2)   | 29(2)   | -12(2)   | 3(2)    | -7(2)   |
| C(9)   | 37(2)   | 36(2)   | 28(2)   | -4(2)    | -2(2)   | -5(2)   |
| C(10)  | 69(3)   | 50(3)   | 48(3)   | -21(2)   | -21(2)  | -5(2)   |
| C(11)  | 39(2)   | 63(3)   | 35(2)   | -11(2)   | -4(2)   | -3(2)   |
| C(12)  | 50(3)   | 66(3)   | 30(2)   | -1(2)    | 6(2)    | -12(2)  |
| C(13)  | 42(2)   | 42(2)   | 39(2)   | -18(2)   | 1(2)    | 1(2)    |
| C(14A) | 55(5)   | 64(5)   | 51(4)   | -27(4)   | -7(3)   | 21(4)   |
| C(15A) | 54(4)   | 63(4)   | 48(4)   | -30(3)   | 18(3)   | -10(3)  |
| C(16A) | 48(4)   | 47(4)   | 62(5)   | -28(4)   | 2(4)    | -9(3)   |
| C(14B) | 170(40) | 40(10)  | 100(20) | -30(10)  | 80(20)  | -10(20) |
| C(15B) | 100(30) | 130(40) | 210(60) | -130(40) | 110(40) | -60(30) |
| C(16B) | 150(40) | 110(30) | 110(30) | -90(30)  | -80(30) | 80(30)  |
| C(17)  | 30(2)   | 38(2)   | 31(2)   | -10(2)   | 0(2)    | -8(2)   |
| C(18)  | 39(2)   | 43(2)   | 37(2)   | -6(2)    | 0(2)    | -9(2)   |
| C(19)  | 51(3)   | 49(3)   | 49(3)   | -6(2)    | 7(2)    | -19(2)  |
| C(20)  | 34(2)   | 53(3)   | 64(3)   | -19(2)   | 5(2)    | -17(2)  |
| C(21)  | 37(2)   | 51(3)   | 52(3)   | -14(2)   | -5(2)   | -8(2)   |
| C(22)  | 35(2)   | 40(2)   | 34(2)   | -8(2)    | -2(2)   | -8(2)   |
| C(23)  | 34(2)   | 34(2)   | 26(2)   | -4(2)    | 2(2)    | -4(2)   |
| C(24)  | 42(2)   | 53(3)   | 33(2)   | -10(2)   | 2(2)    | -12(2)  |
| C(25)  | 43(3)   | 60(3)   | 43(2)   | -2(2)    | 10(2)   | -11(2)  |
| C(26)  | 49(3)   | 58(3)   | 33(2)   | -5(2)    | 10(2)   | 2(2)    |
| C(27)  | 52(3)   | 68(3)   | 32(2)   | -16(2)   | 1(2)    | 0(2)    |
| C(28)  | 43(2)   | 50(2)   | 33(2)   | -12(2)   | 1(2)    | -9(2)   |
| C(29)  | 34(2)   | 31(2)   | 29(2)   | -6(2)    | 1(2)    | -8(2)   |
| C(30)  | 34(2)   | 33(2)   | 26(2)   | -5(2)    | -2(2)   | -7(2)   |
| C(31)  | 33(2)   | 36(2)   | 27(2)   | -6(2)    | 2(2)    | -9(2)   |
| C(32)  | 30(2)   | 44(2)   | 29(2)   | -5(2)    | 4(2)    | -8(2)   |
| C(33)  | 31(2)   | 41(2)   | 33(2)   | -14(2)   | 1(2)    | -4(2)   |
| C(34)  | 35(2)   | 32(2)   | 37(2)   | -9(2)    | -2(2)   | -5(2)   |
| C(35)  | 51(3)   | 39(2)   | 40(2)   | -8(2)    | 13(2)   | -17(2)  |
| C(36)  | 70(3)   | 34(2)   | 61(3)   | 1(2)     | 24(3)   | -5(2)   |
| C(37)  | 106(5)  | 67(3)   | 58(3)   | -21(3)   | 11(3)   | -55(3)  |
| C(38)  | 62(3)   | 49(3)   | 59(3)   | -5(2)    | 23(2)   | -26(2)  |
| C(39)  | 38(2)   | 52(3)   | 42(2)   | -23(2)   | 6(2)    | -3(2)   |
| C(40)  | 58(3)   | 109(5)  | 46(3)   | -43(3)   | -2(2)   | 6(3)    |
| C(41)  | 40(2)   | 58(3)   | 53(3)   | -22(2)   | 11(2)   | -2(2)   |
| C(42)  | 68(4)   | 69(3)   | 94(4)   | -53(3)   | 35(3)   | -23(3)  |
| C(43)  | 38(2)   | 28(2)   | 34(2)   | -6(2)    | 3(2)    | -7(2)   |
| C(44)  | 45(3)   | 39(2)   | 62(3)   | -10(2)   | -7(2)   | -3(2)   |
| C(45)  | 57(3)   | 54(3)   | 63(3)   | -8(2)    | -6(3)   | 6(2)    |
| C(46)  | 78(4)   | 40(3)   | 55(3)   | 3(2)     | -2(3)   | 13(3)   |
| C(47)  | 86(4)   | 32(2)   | 80(4)   | -11(2)   | 13(3)   | -12(3)  |
| C(48)  | 55(3)   | 34(2)   | 57(3)   | -12(2)   | 2(2)    | -12(2)  |
| C(49)  | 36(2)   | 34(2)   | 37(2)   | -11(2)   | 1(2)    | -11(2)  |
| C(50)  | 40(2)   | 47(2)   | 40(2)   | -7(2)    | 2(2)    | -14(2)  |
| C(51)  | 42(3)   | 68(3)   | 57(3)   | -21(2)   | 9(2)    | -26(2)  |
| C(52)  | 36(2)   | 74(3)   | 59(3)   | -25(3)   | -4(2)   | -13(2)  |
| C(53)  | 44(3)   | 63(3)   | 50(3)   | -14(2)   | -10(2)  | -8(2)   |

|       |         |         |         |         |         |          |
|-------|---------|---------|---------|---------|---------|----------|
| C(54) | 41(2)   | 45(2)   | 40(2)   | -7(2)   | -4(2)   | -10(2)   |
| Sb(1) | 50(1)   | 108(1)  | 51(1)   | 6(1)    | -1(1)   | -31(1)   |
| F(1)  | 138(4)  | 174(5)  | 53(2)   | 5(2)    | 11(2)   | -78(3)   |
| F(2)  | 270(8)  | 400(10) | 65(3)   | -55(5)  | 34(4)   | -240(10) |
| F(3)  | 229(7)  | 208(7)  | 205(7)  | -83(5)  | 59(6)   | -175(6)  |
| F(4)  | 62(3)   | 119(4)  | 233(6)  | -37(4)  | 13(3)   | -14(2)   |
| F(5)  | 151(4)  | 86(3)   | 115(4)  | 22(3)   | 15(3)   | -24(3)   |
| F(6)  | 44(3)   | 430(10) | 225(8)  | 110(8)  | -44(4)  | 4(5)     |
| C(55) | 170(10) | 200(10) | 85(6)   | -8(6)   | -16(6)  | -110(10) |
| C(56) | 61(3)   | 93(4)   | 46(3)   | -4(3)   | 4(2)    | -32(3)   |
| C(57) | 94(5)   | 82(4)   | 57(4)   | -4(3)   | 16(3)   | 9(4)     |
| C(58) | 200(10) | 70(4)   | 60(4)   | 4(3)    | -8(5)   | -36(6)   |
| C(59) | 111(7)  | 143(8)  | 69(5)   | 2(5)    | -1(5)   | -82(6)   |
| C(60) | 54(4)   | 180(10) | 55(4)   | 44(5)   | 11(3)   | 20(5)    |
| C(61) | 114(6)  | 79(4)   | 55(4)   | 1(3)    | 30(4)   | 13(4)    |
| C(62) | 96(5)   | 54(3)   | 85(4)   | -16(3)  | -5(4)   | -20(3)   |
| C(63) | 55(3)   | 47(3)   | 52(3)   | -5(2)   | -4(2)   | -11(2)   |
| C(64) | 44(3)   | 58(3)   | 52(3)   | -7(2)   | 1(2)    | -13(2)   |
| C(65) | 58(3)   | 51(3)   | 62(3)   | -10(2)  | -13(2)  | 1(2)     |
| C(66) | 74(4)   | 49(3)   | 60(3)   | 4(2)    | -17(3)  | -20(3)   |
| C(67) | 65(4)   | 84(4)   | 64(3)   | -1(3)   | 6(3)    | -39(3)   |
| C(68) | 59(3)   | 81(4)   | 71(4)   | -20(3)  | 18(3)   | -16(3)   |
| C(69) | 122(8)  | 140(10) | 140(10) | -19(7)  | 10(7)   | -10(7)   |
| C(70) | 73(4)   | 91(5)   | 75(4)   | -27(4)  | 11(3)   | 8(4)     |
| C(71) | 43(3)   | 119(6)  | 104(5)  | -68(5)  | 4(3)    | -18(4)   |
| C(72) | 60(4)   | 111(6)  | 102(5)  | -46(5)  | 10(4)   | -20(4)   |
| C(73) | 65(4)   | 104(5)  | 87(5)   | -36(4)  | 4(3)    | -22(4)   |
| C(74) | 45(3)   | 107(5)  | 83(4)   | -46(4)  | -2(3)   | -13(3)   |
| C(75) | 56(4)   | 109(5)  | 96(5)   | -56(4)  | 16(3)   | -21(4)   |
| C(76) | 80(10)  | 70(10)  | 70(10)  | -10(10) | 0(10)   | 0(10)    |
| C(77) | 78(8)   | 46(6)   | 36(5)   | 4(4)    | -13(5)  | 2(6)     |
| C(78) | 50(10)  | 80(20)  | 60(10)  | 20(10)  | -10(10) | -40(10)  |
| C(79) | 100(10) | 80(10)  | 69(8)   | 5(7)    | -21(8)  | -40(10)  |
| C(80) | 180(30) | 50(10)  | 40(10)  | 3(8)    | -10(10) | -10(10)  |
| C(81) | 100(10) | 49(7)   | 62(8)   | 1(6)    | 14(7)   | 4(7)     |
| C(82) | 80(20)  | 50(10)  | 60(10)  | -10(10) | 0(10)   | 0(10)    |
| C(83) | 60(10)  | 150(20) | 80(10)  | -70(10) | 30(10)  | -60(10)  |
| C(84) | 100(10) | 90(10)  | 100(10) | -50(10) | 10(10)  | -35(8)   |
| C(85) | 120(10) | 130(10) | 110(10) | -70(10) | 30(10)  | -60(10)  |
| C(86) | 80(10)  | 130(10) | 70(8)   | -40(10) | 12(7)   | -70(10)  |
| C(87) | 45(8)   | 90(10)  | 100(10) | -60(10) | 19(8)   | -29(7)   |
| C(88) | 100(10) | 120(10) | 90(10)  | -10(10) | 10(10)  | -90(10)  |
| C(89) | 150(20) | 220(30) | 100(20) | 20(20)  | -40(20) | -140(20) |

The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U(11) + \dots + 2hka^* b^* U(12)]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa845

| atom   | x          | y    | z     | U(eq) |
|--------|------------|------|-------|-------|
| H(1A)  | 3939       | 1467 | 9095  | 41    |
| H(1B)  | 5320       | 1608 | 8713  | 41    |
| H(2A)  | 4861       | 621  | 8373  | 42    |
| H(2B)  | 3265       | 989  | 8245  | 42    |
| H(6)   | -470.0000  | 5105 | 7276  | 38    |
| H(8)   | 1886       | 4222 | 8951  | 40    |
| H(10A) | 190        | 3277 | 6597  | 82    |
| H(10B) | 1670       | 3312 | 6286  | 82    |
| H(10C) | 332        | 3605 | 5808  | 82    |
| H(11A) | -1485      | 4481 | 6591  | 70    |
| H(11B) | -1166      | 4679 | 5802  | 70    |
| H(11C) | -980       | 5213 | 6276  | 70    |
| H(12A) | 1259       | 4740 | 5457  | 75    |
| H(12B) | 2471       | 4464 | 6013  | 75    |
| H(12C) | 1409       | 5207 | 5999  | 75    |
| H(14A) | -1964      | 5611 | 7952  | 88    |
| H(14B) | -916       | 6126 | 7676  | 88    |
| H(14C) | -1787      | 6226 | 8333  | 88    |
| H(15A) | -1348      | 5297 | 9409  | 79    |
| H(15B) | -164       | 4593 | 9454  | 79    |
| H(15C) | -1522      | 4694 | 9012  | 79    |
| H(16A) | 1220       | 5999 | 8365  | 75    |
| H(16B) | 1507       | 5395 | 9053  | 75    |
| H(16C) | 297        | 6087 | 9009  | 75    |
| H(14D) | -228       | 6135 | 7549  | 159   |
| H(14E) | 775        | 6274 | 8085  | 159   |
| H(14F) | -846       | 6524 | 8138  | 159   |
| H(15D) | -2090      | 5718 | 8764  | 194   |
| H(15E) | -1691      | 4857 | 8887  | 194   |
| H(15F) | -1976.0001 | 5338 | 8135  | 194   |
| H(16D) | 104        | 5823 | 9310  | 195   |
| H(16E) | 1507       | 5539 | 8965  | 195   |
| H(16F) | 769        | 4979 | 9467  | 195   |
| H(18)  | 4944       | 4070 | 7832  | 48    |
| H(19)  | 7155       | 4277 | 7760  | 59    |
| H(20)  | 8874       | 3536 | 8502  | 58    |
| H(21)  | 8369       | 2588 | 9327  | 56    |
| H(22)  | 6152       | 2373 | 9412  | 44    |
| H(24)  | 1421       | 2446 | 9179  | 51    |
| H(25)  | 403        | 2267 | 10233 | 60    |
| H(26)  | 1398       | 2543 | 11142 | 59    |
| H(27)  | 3395       | 2971 | 11010 | 62    |
| H(28)  | 4429       | 3169 | 9954  | 50    |
| H(32)  | 7091       | 2252 | 4773  | 41    |
| H(34)  | 5890       | 498  | 5855  | 42    |
| H(36A) | 3963       | 3630 | 5588  | 88    |
| H(36B) | 4306       | 3686 | 4806  | 88    |
| H(36C) | 4666       | 4266 | 5187  | 88    |
| H(37A) | 5933       | 3326 | 6443  | 106   |
| H(37B) | 6655       | 3930 | 5996  | 106   |
| H(37C) | 7468       | 3109 | 6200  | 106   |
| H(38A) | 7038       | 3996 | 4805  | 84    |
| H(38B) | 6682       | 3402 | 4443  | 84    |
| H(38C) | 7923       | 3190 | 4981  | 84    |
| H(40A) | 6688       | 1763 | 3898  | 105   |
| H(40B) | 5722       | 1186 | 3991  | 105   |
| H(40C) | 7195       | 1018 | 3662  | 105   |
| H(41A) | 9273       | 688  | 4343  | 75    |
| H(41B) | 9255       | 680  | 5133  | 75    |
| H(41C) | 8914       | 1430 | 4589  | 75    |
| H(42A) | 7751       | -157 | 4569  | 106   |
| H(42B) | 6261       | 55   | 4866  | 106   |

## Appendix 1. Crystallographic data

|        |        |            |           |     |
|--------|--------|------------|-----------|-----|
| H(42C) | 7588   | -122       | 5348      | 106 |
| H(44)  | 7069   | 468        | 7371      | 59  |
| H(45)  | 8477   | -665       | 7751      | 74  |
| H(46)  | 7591   | -1696      | 7845      | 76  |
| H(47)  | 5350   | -1613      | 7541      | 79  |
| H(48)  | 3926   | -487       | 7127      | 57  |
| H(50)  | 2268   | 268        | 7573      | 50  |
| H(51)  | -22    | 341        | 7306      | 63  |
| H(52)  | -1028  | 1119       | 6320      | 65  |
| H(53)  | 253    | 1833       | 5599      | 63  |
| H(54)  | 2555   | 1749       | 5849      | 50  |
| H(55A) | 6.0000 | 2515       | 2663      | 215 |
| H(55B) | -1180  | 2414       | 3199      | 215 |
| H(55C) | -11    | 1736       | 3129      | 215 |
| H(57)  | -557   | 3336       | 3718      | 100 |
| H(58)  | 626    | 3591       | 4498      | 133 |
| H(59)  | 2634   | 2891       | 4904      | 124 |
| H(60)  | 3542   | 1855       | 4524      | 139 |
| H(61)  | 2138   | 1513       | 3714      | 109 |
| H(62A) | 3837   | 2821       | 2976      | 116 |
| H(62B) | 5387   | 2556       | 2776      | 116 |
| H(62C) | 4320   | 3087       | 2221      | 116 |
| H(64)  | 3268   | 3898       | 3387      | 62  |
| H(65)  | 3867   | 4889       | 3670      | 70  |
| H(66)  | 5922   | 5202       | 3358      | 75  |
| H(67)  | 7421   | 4514       | 2748      | 84  |
| H(68)  | 6855   | 3518       | 2454      | 84  |
| H(69A) | 598    | 9350       | 359       | 211 |
| H(69B) | 644    | 9892       | 842       | 211 |
| H(69C) | -761   | 9662       | 721       | 211 |
| H(71)  | -1198  | 8537       | 1326      | 98  |
| H(72)  | -730   | 7602       | 2245      | 105 |
| H(73)  | 1314   | 7356       | 2816      | 99  |
| H(74)  | 2913   | 8069       | 2516      | 90  |
| H(75)  | 2425   | 9054       | 1587      | 98  |
| H(76A) | 5218   | -649.0001  | -1094     | 111 |
| H(76B) | 5072   | -1254.0001 | -433      | 111 |
| H(76C) | 6514   | -1026      | -602      | 111 |
| H(78)  | 7069   | -84        | -202.0000 | 82  |
| H(79)  | 6527   | 800        | 434       | 101 |
| H(80)  | 4285   | 1126       | 789       | 110 |
| H(81)  | 2584   | 567        | 508       | 90  |
| H(82)  | 3125   | -318.0000  | -128      | 77  |
| H(83)  | 4051   | 5691       | 10490     | 104 |
| H(84)  | 4699   | 4765       | 11450     | 105 |
| H(85)  | 6087   | 3669       | 11343     | 129 |
| H(86)  | 6826   | 3499       | 10276     | 101 |
| H(87)  | 6179   | 4425       | 9317      | 84  |
| H(89A) | 5281   | 6017       | 9032      | 226 |
| H(89B) | 3758   | 6098       | 9311      | 226 |
| H(89C) | 4273   | 5554       | 8825      | 226 |

## Chapter 5

### Complex 40

Table 1. Crystal data for pa582

|   |   |
|---|---|
| Compound                                    | pa582   |
| Molecular formula                           | C <sub>38</sub> H <sub>32</sub> AlClN <sub>2</sub> O <sub>2</sub> P <sub>2</sub> ,C <sub>4</sub> H <sub>8</sub> O |
| Molecular weight                            | 745.13  |
| Crystal habit                               | Colorless Block   |
| Crystal dimensions(mm)                      | 0.26x0.24x0.24  |
| Crystal system                              | monoclinic  |
| Space group                                 | P2 <sub>1</sub>   |
| a(Å)  | 12.236(1)   |
| b(Å)  | 12.934(1)   |
| c(Å)  | 12.697(1)   |
| α(°)  | 90.00   |
| β(°)  | 116.183(1)  |
| γ(°)  | 90.00   |
| V(Å <sup>3</sup> )                          | 1803.2(2)   |
| Z   | 2   |
| d(g·cm <sup>-3</sup> )                      | 1.372   |
| F(000)                                      | 780   |
| μ(cm <sup>-1</sup> )                        | 0.263   |
| Absorption corrections                      | multi-scan ; 0.9348 min, 0.9396 max   |
| Diffractometer                              | KappaCCD  |
| X-ray source                                | MoKα  |
| λ(Å)  | 0.71069   |
| Monochromator                               | graphite  |
| T (K)                                       | 150.0(1)  |
| Scan mode                                   | phi and omega scans   |
| Maximum θ                                   | 30.01   |
| HKL ranges                                  | -17 17 ; -18 9 ; -17 17   |
| Reflections measured                        | 16855   |
| Unique data                                 | 7237  |
| Rint  | 0.0280  |
| Reflections used                            | 6957  |
| Criterion                                   | I > 2σ(I)   |
| Refinement type                             | Fsqd  |
| Hydrogen atoms                              | constr  |
| Parameters refined                          | 460   |
| Reflections / parameter                     | 15  |
| wR2   | 0.1012  |
| R1  | 0.0383  |
| Flack's parameter                           | 0.04(6)   |
| Weights a, b                                | 0.0558 ; 0.8069   |
| GoF   | 1.052   |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.790(0.054) / -0.412(0.054)  |

## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa582

| atom  | x         | y        | z         | U(eq)  |
|-------|-----------|----------|-----------|--------|
| Cl(1) | -6857(1)  | 4538(1)  | -15734(1) | 29(1)  |
| P(1)  | -5412(1)  | 4537(1)  | -12193(1) | 20(1)  |
| P(2)  | -10364(1) | 4506(1)  | -15813(1) | 21(1)  |
| Al    | -7587(1)  | 3731(1)  | -14629(1) | 20(1)  |
| O(1)  | -6525(1)  | 2689(1)  | -13957(2) | 26(1)  |
| O(2)  | -8526(1)  | 2772(2)  | -15687(2) | 29(1)  |
| N(1)  | -6789(1)  | 4581(2)  | -13189(2) | 23(1)  |
| N(2)  | -9007(1)  | 4491(2)  | -14756(1) | 22(1)  |
| C(1)  | -7493(2)  | 5513(2)  | -13216(2) | 32(1)  |
| C(2)  | -8824(2)  | 5201(2)  | -13777(2) | 30(1)  |
| C(3)  | -4704(2)  | 3404(2)  | -12398(2) | 21(1)  |
| C(4)  | -5353(2)  | 2653(2)  | -13267(2) | 20(1)  |
| C(5)  | -4671(2)  | 1810(2)  | -13370(2) | 24(1)  |
| C(6)  | -3439(2)  | 1715(2)  | -12667(2) | 28(1)  |
| C(7)  | -2815(2)  | 2450(2)  | -11809(2) | 30(1)  |
| C(8)  | -3446(2)  | 3289(2)  | -11685(2) | 26(1)  |
| C(9)  | -4524(2)  | 5652(2)  | -12216(2) | 23(1)  |
| C(10) | -4839(2)  | 6155(2)  | -13278(2) | 27(1)  |
| C(11) | -4155(2)  | 6985(2)  | -13346(2) | 32(1)  |
| C(12) | -3129(2)  | 7296(2)  | -12366(3) | 33(1)  |
| C(13) | -2794(2)  | 6798(2)  | -11307(2) | 35(1)  |
| C(14) | -3492(2)  | 5976(2)  | -11216(2) | 30(1)  |
| C(15) | -5273(2)  | 4521(2)  | -10707(2) | 24(1)  |
| C(16) | -5383(2)  | 5438(2)  | -10179(2) | 31(1)  |
| C(17) | -5314(3)  | 5422(3)  | -9059(2)  | 39(1)  |
| C(18) | -5133(2)  | 4509(3)  | -8448(2)  | 40(1)  |
| C(19) | -5024(2)  | 3589(3)  | -8958(2)  | 35(1)  |
| C(20) | -5099(2)  | 3598(2)  | -10087(2) | 27(1)  |
| C(21) | -10530(2) | 3491(2)  | -16814(2) | 24(1)  |
| C(22) | -9594(2)  | 2769(2)  | -16613(2) | 24(1)  |
| C(23) | -9852(2)  | 1969(2)  | -17446(2) | 30(1)  |
| C(24) | -10970(2) | 1896(2)  | -18411(2) | 35(1)  |
| C(25) | -11887(2) | 2605(3)  | -18597(2) | 36(1)  |
| C(26) | -11665(2) | 3403(2)  | -17811(2) | 32(1)  |
| C(27) | -10712(2) | 5715(2)  | -16604(2) | 27(1)  |
| C(28) | -11912(2) | 6079(3)  | -17216(3) | 41(1)  |
| C(29) | -12132(3) | 6985(3)  | -17861(3) | 50(1)  |
| C(30) | -11183(3) | 7536(3)  | -17905(3) | 48(1)  |
| C(31) | -9996(3)  | 7169(3)  | -17306(3) | 45(1)  |
| C(32) | -9758(3)  | 6266(2)  | -16661(2) | 34(1)  |
| C(33) | -11528(2) | 4333(2)  | -15317(2) | 24(1)  |
| C(34) | -11964(2) | 3346(2)  | -15299(2) | 33(1)  |
| C(35) | -12825(3) | 3184(3)  | -14879(3) | 42(1)  |
| C(36) | -13233(2) | 3999(3)  | -14462(3) | 41(1)  |
| C(37) | -12783(2) | 4977(3)  | -14448(3) | 40(1)  |
| C(38) | -11943(2) | 5164(2)  | -14892(2) | 32(1)  |
| O(3)  | -9351(3)  | 4562(3)  | -10754(2) | 70(1)  |
| C(39) | -8490(3)  | 4579(5)  | -9542(4)  | 71(1)  |
| C(40) | -9214(3)  | 4620(10) | -8892(4)  | 137(3) |
| C(41) | -10423(4) | 4805(7)  | -9655(4)  | 102(3) |
| C(42) | -10531(4) | 4754(6)  | -10837(3) | 94(2)  |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths (A) and angles (deg) for pa582

|              |          |              |          |
|--------------|----------|--------------|----------|
| Cl(1)-Al     | 2.228(1) | P(1)-N(1)    | 1.600(2) |
| P(1)-C(3)    | 1.778(2) | P(1)-C(9)    | 1.813(3) |
| P(1)-C(15)   | 1.819(2) | P(2)-N(2)    | 1.609(2) |
| P(2)-C(21)   | 1.776(2) | P(2)-C(27)   | 1.805(3) |
| P(2)-C(33)   | 1.807(2) | Al-O(1)      | 1.804(2) |
| Al-O(2)      | 1.817(2) | Al-N(2)      | 1.940(2) |
| Al-N(1)      | 1.982(2) | O(1)-C(4)    | 1.311(2) |
| O(2)-C(22)   | 1.318(3) | N(1)-C(1)    | 1.474(3) |
| N(2)-C(2)    | 1.481(3) | C(1)-C(2)    | 1.517(3) |
| C(1)-H(1A)   | 0.9900   | C(1)-H(1B)   | 0.9900   |
| C(2)-H(2A)   | 0.9900   | C(2)-H(2B)   | 0.9900   |
| C(3)-C(8)    | 1.408(3) | C(3)-C(4)    | 1.421(3) |
| C(4)-C(5)    | 1.414(3) | C(5)-C(6)    | 1.378(3) |
| C(5)-H(5)    | 0.9500   | C(6)-C(7)    | 1.392(4) |
| C(6)-H(6)    | 0.9500   | C(7)-C(8)    | 1.381(3) |
| C(7)-H(7)    | 0.9500   | C(8)-H(8)    | 0.9500   |
| C(9)-C(10)   | 1.389(3) | C(9)-C(14)   | 1.403(3) |
| C(10)-C(11)  | 1.388(4) | C(10)-H(10)  | 0.9500   |
| C(11)-C(12)  | 1.381(4) | C(11)-H(11)  | 0.9500   |
| C(12)-C(13)  | 1.380(4) | C(12)-H(12)  | 0.9500   |
| C(13)-C(14)  | 1.401(4) | C(13)-H(13)  | 0.9500   |
| C(14)-H(14)  | 0.9500   | C(15)-C(20)  | 1.394(4) |
| C(15)-C(16)  | 1.397(4) | C(16)-C(17)  | 1.388(4) |
| C(16)-H(16)  | 0.9500   | C(17)-C(18)  | 1.376(5) |
| C(17)-H(17)  | 0.9500   | C(18)-C(19)  | 1.388(5) |
| C(18)-H(18)  | 0.9500   | C(19)-C(20)  | 1.396(3) |
| C(19)-H(19)  | 0.9500   | C(20)-H(20)  | 0.9500   |
| C(21)-C(22)  | 1.411(3) | C(21)-C(26)  | 1.411(3) |
| C(22)-C(23)  | 1.412(4) | C(23)-C(24)  | 1.380(3) |
| C(23)-H(23)  | 0.9500   | C(24)-C(25)  | 1.386(4) |
| C(24)-H(24)  | 0.9500   | C(25)-C(26)  | 1.378(4) |
| C(25)-H(25)  | 0.9500   | C(26)-H(26)  | 0.9500   |
| C(27)-C(32)  | 1.397(4) | C(27)-C(28)  | 1.405(3) |
| C(28)-C(29)  | 1.385(4) | C(28)-H(28)  | 0.9500   |
| C(29)-C(30)  | 1.385(5) | C(29)-H(29)  | 0.9500   |
| C(30)-C(31)  | 1.392(5) | C(30)-H(30)  | 0.9500   |
| C(31)-C(32)  | 1.381(4) | C(31)-H(31)  | 0.9500   |
| C(32)-H(32)  | 0.9500   | C(33)-C(34)  | 1.388(4) |
| C(33)-C(38)  | 1.395(3) | C(34)-C(35)  | 1.391(3) |
| C(34)-H(34)  | 0.9500   | C(35)-C(36)  | 1.369(5) |
| C(35)-H(35)  | 0.9500   | C(36)-C(37)  | 1.377(5) |
| C(36)-H(36)  | 0.9500   | C(37)-C(38)  | 1.393(4) |
| C(37)-H(37)  | 0.9500   | C(38)-H(38)  | 0.9500   |
| O(3)-C(42)   | 1.423(5) | O(3)-C(39)   | 1.431(5) |
| C(39)-C(40)  | 1.453(6) | C(39)-H(39A) | 0.9900   |
| C(39)-H(39B) | 0.9900   | C(40)-C(41)  | 1.386(5) |
| C(40)-H(40A) | 0.9900   | C(40)-H(40B) | 0.9900   |
| C(41)-C(42)  | 1.449(6) | C(41)-H(41A) | 0.9900   |
| C(41)-H(41B) | 0.9900   | C(42)-H(42A) | 0.9900   |
| C(42)-H(42B) | 0.9900   |              |          |

|                  |           |                  |          |
|------------------|-----------|------------------|----------|
| N(1)-P(1)-C(3)   | 109.0(1)  | N(1)-P(1)-C(9)   | 112.9(1) |
| C(3)-P(1)-C(9)   | 108.6(1)  | N(1)-P(1)-C(15)  | 113.8(1) |
| C(3)-P(1)-C(15)  | 108.3(1)  | C(9)-P(1)-C(15)  | 104.1(1) |
| N(2)-P(2)-C(21)  | 109.8(1)  | N(2)-P(2)-C(27)  | 112.2(1) |
| C(21)-P(2)-C(27) | 108.5(1)  | N(2)-P(2)-C(33)  | 112.9(1) |
| C(21)-P(2)-C(33) | 107.4(1)  | C(27)-P(2)-C(33) | 105.8(1) |
| O(1)-Al-O(2)     | 85.86(8)  | O(1)-Al-N(2)     | 148.2(1) |
| O(2)-Al-N(2)     | 91.94(8)  | O(1)-Al-N(1)     | 91.1(1)  |
| O(2)-Al-N(1)     | 162.6(1)  | N(2)-Al-N(1)     | 81.64(8) |
| O(1)-Al-Cl(1)    | 104.02(6) | O(2)-Al-Cl(1)    | 98.80(7) |
| N(2)-Al-Cl(1)    | 107.70(7) | N(1)-Al-Cl(1)    | 98.60(7) |
| C(4)-O(1)-Al     | 133.6(2)  | C(22)-O(2)-Al    | 135.8(2) |
| C(1)-N(1)-P(1)   | 116.7(2)  | C(1)-N(1)-Al     | 112.8(1) |
| P(1)-N(1)-Al     | 128.9(1)  | C(2)-N(2)-P(2)   | 114.2(2) |



## Appendix 1. Crystallographic data

|                     |          |                    |          |
|---------------------|----------|--------------------|----------|
| C(2)-N(2)-Al        | 116.5(1) | P(2)-N(2)-Al       | 129.2(1) |
| N(1)-C(1)-C(2)      | 106.8(2) | N(1)-C(1)-H(1A)    | 110.4    |
| C(2)-C(1)-H(1A)     | 110.4    | N(1)-C(1)-H(1B)    | 110.4    |
| C(2)-C(1)-H(1B)     | 110.4    | H(1A)-C(1)-H(1B)   | 108.6    |
| N(2)-C(2)-C(1)      | 107.0(2) | N(2)-C(2)-H(2A)    | 110.3    |
| C(1)-C(2)-H(2A)     | 110.3    | N(2)-C(2)-H(2B)    | 110.3    |
| C(1)-C(2)-H(2B)     | 110.3    | H(2A)-C(2)-H(2B)   | 108.6    |
| C(8)-C(3)-C(4)      | 120.3(2) | C(8)-C(3)-P(1)     | 117.2(2) |
| C(4)-C(3)-P(1)      | 122.4(2) | O(1)-C(4)-C(5)     | 118.8(2) |
| O(1)-C(4)-C(3)      | 124.5(2) | C(5)-C(4)-C(3)     | 116.7(2) |
| C(6)-C(5)-C(4)      | 122.0(2) | C(6)-C(5)-H(5)     | 119.0    |
| C(4)-C(5)-H(5)      | 119.0    | C(5)-C(6)-C(7)     | 120.7(2) |
| C(5)-C(6)-H(6)      | 119.6    | C(7)-C(6)-H(6)     | 119.6    |
| C(8)-C(7)-C(6)      | 119.1(2) | C(8)-C(7)-H(7)     | 120.5    |
| C(6)-C(7)-H(7)      | 120.5    | C(7)-C(8)-C(3)     | 121.1(2) |
| C(7)-C(8)-H(8)      | 119.4    | C(3)-C(8)-H(8)     | 119.4    |
| C(10)-C(9)-C(14)    | 119.5(2) | C(10)-C(9)-P(1)    | 118.4(2) |
| C(14)-C(9)-P(1)     | 121.9(2) | C(11)-C(10)-C(9)   | 120.4(2) |
| C(11)-C(10)-H(10)   | 119.8    | C(9)-C(10)-H(10)   | 119.8    |
| C(12)-C(11)-C(10)   | 120.2(2) | C(12)-C(11)-H(11)  | 119.9    |
| C(10)-C(11)-H(11)   | 119.9    | C(13)-C(12)-C(11)  | 120.2(2) |
| C(13)-C(12)-H(12)   | 119.9    | C(11)-C(12)-H(12)  | 119.9    |
| C(12)-C(13)-C(14)   | 120.3(2) | C(12)-C(13)-H(13)  | 119.8    |
| C(14)-C(13)-H(13)   | 119.8    | C(13)-C(14)-C(9)   | 119.4(2) |
| C(13)-C(14)-H(14)   | 120.3    | C(9)-C(14)-H(14)   | 120.3    |
| C(20)-C(15)-C(16)   | 118.6(2) | C(20)-C(15)-P(1)   | 121.1(2) |
| C(16)-C(15)-P(1)    | 120.2(2) | C(17)-C(16)-C(15)  | 120.3(3) |
| C(17)-C(16)-H(16)   | 119.9    | C(15)-C(16)-H(16)  | 119.9    |
| C(18)-C(17)-C(16)   | 120.8(3) | C(18)-C(17)-H(17)  | 119.6    |
| C(16)-C(17)-H(17)   | 119.6    | C(17)-C(18)-C(19)  | 119.8(2) |
| C(17)-C(18)-H(18)   | 120.1    | C(19)-C(18)-H(18)  | 120.1    |
| C(18)-C(19)-C(20)   | 119.7(3) | C(18)-C(19)-H(19)  | 120.2    |
| C(20)-C(19)-H(19)   | 120.2    | C(15)-C(20)-C(19)  | 120.8(3) |
| C(15)-C(20)-H(20)   | 119.6    | C(19)-C(20)-H(20)  | 119.6    |
| C(22)-C(21)-C(26)   | 120.5(2) | C(22)-C(21)-P(2)   | 122.1(2) |
| C(26)-C(21)-P(2)    | 117.3(2) | O(2)-C(22)-C(21)   | 124.5(2) |
| O(2)-C(22)-C(23)    | 118.4(2) | C(21)-C(22)-C(23)  | 117.0(2) |
| C(24)-C(23)-C(22)   | 121.5(3) | C(24)-C(23)-H(23)  | 119.3    |
| C(22)-C(23)-H(23)   | 119.3    | C(23)-C(24)-C(25)  | 121.1(3) |
| C(23)-C(24)-H(24)   | 119.4    | C(25)-C(24)-H(24)  | 119.4    |
| C(26)-C(25)-C(24)   | 119.1(2) | C(26)-C(25)-H(25)  | 120.4    |
| C(24)-C(25)-H(25)   | 120.4    | C(25)-C(26)-C(21)  | 120.8(2) |
| C(25)-C(26)-H(26)   | 119.6    | C(21)-C(26)-H(26)  | 119.6    |
| C(32)-C(27)-C(28)   | 119.5(3) | C(32)-C(27)-P(2)   | 118.2(2) |
| C(28)-C(27)-P(2)    | 122.1(2) | C(29)-C(28)-C(27)  | 119.6(3) |
| C(29)-C(28)-H(28)   | 120.2    | C(27)-C(28)-H(28)  | 120.2    |
| C(28)-C(29)-C(30)   | 120.7(3) | C(28)-C(29)-H(29)  | 119.6    |
| C(30)-C(29)-H(29)   | 119.6    | C(29)-C(30)-C(31)  | 119.6(3) |
| C(29)-C(30)-H(30)   | 120.2    | C(31)-C(30)-H(30)  | 120.2    |
| C(32)-C(31)-C(30)   | 120.6(3) | C(32)-C(31)-H(31)  | 119.7    |
| C(30)-C(31)-H(31)   | 119.7    | C(31)-C(32)-C(27)  | 120.0(3) |
| C(31)-C(32)-H(32)   | 120.0    | C(27)-C(32)-H(32)  | 120.0    |
| C(34)-C(33)-C(38)   | 119.6(2) | C(34)-C(33)-P(2)   | 119.1(2) |
| C(38)-C(33)-P(2)    | 121.2(2) | C(33)-C(34)-C(35)  | 120.5(3) |
| C(33)-C(34)-H(34)   | 119.8    | C(35)-C(34)-H(34)  | 119.8    |
| C(36)-C(35)-C(34)   | 119.9(3) | C(36)-C(35)-H(35)  | 120.0    |
| C(34)-C(35)-H(35)   | 120.0    | C(35)-C(36)-C(37)  | 120.0(2) |
| C(35)-C(36)-H(36)   | 120.0    | C(37)-C(36)-H(36)  | 120.0    |
| C(36)-C(37)-C(38)   | 121.0(3) | C(36)-C(37)-H(37)  | 119.5    |
| C(38)-C(37)-H(37)   | 119.5    | C(37)-C(38)-C(33)  | 118.9(3) |
| C(37)-C(38)-H(38)   | 120.6    | C(33)-C(38)-H(38)  | 120.6    |
| C(42)-O(3)-C(39)    | 108.5(3) | O(3)-C(39)-C(40)   | 105.5(3) |
| O(3)-C(39)-H(39A)   | 110.6    | C(40)-C(39)-H(39A) | 110.6    |
| O(3)-C(39)-H(39B)   | 110.6    | C(40)-C(39)-H(39B) | 110.6    |
| H(39A)-C(39)-H(39B) | 108.8    | C(41)-C(40)-C(39)  | 109.8(4) |
| C(41)-C(40)-H(40A)  | 109.7    | C(39)-C(40)-H(40A) | 109.7    |
| C(41)-C(40)-H(40B)  | 109.7    | C(39)-C(40)-H(40B) | 109.7    |
| H(40A)-C(40)-H(40B) | 108.2    | C(40)-C(41)-C(42)  | 107.3(4) |

## Appendix 1. Crystallographic data

|                     |       |                    |          |
|---------------------|-------|--------------------|----------|
| C(40)-C(41)-H(41A)  | 110.3 | C(42)-C(41)-H(41A) | 110.3    |
| C(40)-C(41)-H(41B)  | 110.3 | C(42)-C(41)-H(41B) | 110.3    |
| H(41A)-C(41)-H(41B) | 108.5 | O(3)-C(42)-C(41)   | 107.8(3) |
| O(3)-C(42)-H(42A)   | 110.2 | C(41)-C(42)-H(42A) | 110.2    |
| O(3)-C(42)-H(42B)   | 110.2 | C(41)-C(42)-H(42B) | 110.2    |
| H(42A)-C(42)-H(42B) | 108.5 |                    |          |

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa582

| atom  | U11   | U22     | U33   | U23    | U13   | U12    |
|-------|-------|---------|-------|--------|-------|--------|
| Cl(1) | 34(1) | 31(1)   | 26(1) | 1(1)   | 17(1) | -2(1)  |
| P(1)  | 19(1) | 19(1)   | 20(1) | -2(1)  | 8(1)  | 0(1)   |
| P(2)  | 18(1) | 22(1)   | 23(1) | -1(1)  | 8(1)  | 0(1)   |
| Al    | 20(1) | 18(1)   | 22(1) | -2(1)  | 8(1)  | 1(1)   |
| O(1)  | 24(1) | 19(1)   | 28(1) | -2(1)  | 5(1)  | 1(1)   |
| O(2)  | 23(1) | 24(1)   | 32(1) | -7(1)  | 3(1)  | 2(1)   |
| N(1)  | 20(1) | 22(1)   | 24(1) | -3(1)  | 7(1)  | 2(1)   |
| N(2)  | 19(1) | 23(1)   | 23(1) | -4(1)  | 8(1)  | 1(1)   |
| C(1)  | 25(1) | 27(1)   | 36(1) | -9(1)  | 7(1)  | 5(1)   |
| C(2)  | 26(1) | 30(1)   | 29(1) | -8(1)  | 9(1)  | 2(1)   |
| C(3)  | 23(1) | 20(1)   | 21(1) | 0(1)   | 11(1) | 2(1)   |
| C(4)  | 22(1) | 19(1)   | 19(1) | 3(1)   | 9(1)  | 3(1)   |
| C(5)  | 31(1) | 21(1)   | 20(1) | -1(1)  | 11(1) | 3(1)   |
| C(6)  | 34(1) | 25(1)   | 29(1) | 1(1)   | 17(1) | 8(1)   |
| C(7)  | 23(1) | 34(1)   | 32(1) | -1(1)  | 11(1) | 6(1)   |
| C(8)  | 22(1) | 26(1)   | 28(1) | -4(1)  | 8(1)  | 1(1)   |
| C(9)  | 23(1) | 19(1)   | 28(1) | -1(1)  | 11(1) | 1(1)   |
| C(10) | 31(1) | 24(1)   | 27(1) | -3(1)  | 12(1) | -3(1)  |
| C(11) | 39(1) | 26(1)   | 34(1) | 0(1)   | 20(1) | -4(1)  |
| C(12) | 36(1) | 25(1)   | 44(1) | -6(1)  | 23(1) | -10(1) |
| C(13) | 29(1) | 30(1)   | 39(1) | -2(1)  | 8(1)  | -8(1)  |
| C(14) | 27(1) | 25(1)   | 31(1) | -1(1)  | 7(1)  | -3(1)  |
| C(15) | 22(1) | 27(1)   | 23(1) | -5(1)  | 10(1) | -4(1)  |
| C(16) | 38(1) | 28(1)   | 30(1) | -6(1)  | 17(1) | -1(1)  |
| C(17) | 46(1) | 41(2)   | 36(1) | -14(1) | 26(1) | -6(1)  |
| C(18) | 45(1) | 51(2)   | 30(1) | -7(2)  | 23(1) | -10(2) |
| C(19) | 36(1) | 41(2)   | 29(1) | -1(1)  | 17(1) | -7(1)  |
| C(20) | 25(1) | 29(1)   | 26(1) | -2(1)  | 11(1) | -3(1)  |
| C(21) | 22(1) | 26(1)   | 21(1) | -2(1)  | 8(1)  | -1(1)  |
| C(22) | 22(1) | 21(1)   | 26(1) | -2(1)  | 10(1) | -3(1)  |
| C(23) | 30(1) | 27(1)   | 31(1) | -7(1)  | 12(1) | -2(1)  |
| C(24) | 37(1) | 36(2)   | 27(1) | -10(1) | 9(1)  | -5(1)  |
| C(25) | 30(1) | 42(2)   | 29(1) | -7(1)  | 5(1)  | -3(1)  |
| C(26) | 26(1) | 38(2)   | 26(1) | -3(1)  | 6(1)  | 5(1)   |
| C(27) | 25(1) | 27(1)   | 26(1) | 1(1)   | 9(1)  | 0(1)   |
| C(28) | 31(1) | 43(2)   | 43(1) | 15(1)  | 12(1) | 6(1)   |
| C(29) | 43(2) | 48(2)   | 50(2) | 21(2)  | 14(1) | 18(1)  |
| C(30) | 68(2) | 32(2)   | 38(2) | 10(1)  | 17(1) | 2(2)   |
| C(31) | 52(2) | 38(2)   | 43(2) | 9(1)   | 19(1) | -7(1)  |
| C(32) | 35(1) | 32(2)   | 35(1) | 4(1)   | 15(1) | -1(1)  |
| C(33) | 20(1) | 27(1)   | 25(1) | 1(1)   | 10(1) | 0(1)   |
| C(34) | 35(1) | 29(1)   | 40(1) | -2(1)  | 22(1) | -4(1)  |
| C(35) | 41(1) | 39(2)   | 54(2) | -3(1)  | 29(1) | -10(1) |
| C(36) | 30(1) | 56(2)   | 42(1) | 3(1)   | 22(1) | -1(1)  |
| C(37) | 34(1) | 49(2)   | 44(2) | -7(1)  | 24(1) | 7(1)   |
| C(38) | 30(1) | 31(1)   | 37(1) | -2(1)  | 16(1) | 3(1)   |
| O(3)  | 94(2) | 57(2)   | 69(2) | -13(2) | 44(2) | -4(2)  |
| C(39) | 52(2) | 78(3)   | 83(3) | 38(3)  | 29(2) | 27(2)  |
| C(40) | 40(2) | 320(10) | 46(2) | -2(5)  | 9(1)  | 20(4)  |
| C(41) | 49(2) | 192(8)  | 58(2) | 20(3)  | 18(2) | 16(3)  |
| C(42) | 56(2) | 162(7)  | 48(2) | 18(3)  | 7(2)  | -46(3) |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

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Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa582

| atom   | x           | y    | z           | U(eq) |
|--------|-------------|------|-------------|-------|
| H(1A)  | -7349       | 6065 | -13681.9990 | 38    |
| H(1B)  | -7249       | 5775 | -12411      | 38    |
| H(2A)  | -9032       | 4851 | -13196      | 36    |
| H(2B)  | -9350       | 5819 | -14076      | 36    |
| H(5)   | -5075       | 1293 | -13943      | 29    |
| H(6)   | -3010       | 1140 | -12767      | 34    |
| H(7)   | -1967.9999  | 2375 | -11317      | 36    |
| H(8)   | -3023       | 3798 | -11108      | 32    |
| H(10)  | -5528       | 5930 | -13961      | 33    |
| H(11)  | -4392       | 7340 | -14069      | 38    |
| H(12)  | -2653       | 7855 | -12421      | 40    |
| H(13)  | -2085       | 7014 | -10635.9990 | 42    |
| H(14)  | -3270       | 5641 | -10484      | 35    |
| H(16)  | -5505       | 6074 | -10589      | 38    |
| H(17)  | -5394       | 6049 | -8709       | 46    |
| H(18)  | -5082       | 4508 | -7680       | 48    |
| H(19)  | -4899       | 2957 | -8540       | 41    |
| H(20)  | -5030       | 2967 | -10437      | 32    |
| H(23)  | -9242       | 1471 | -17340      | 36    |
| H(24)  | -11115      | 1350 | -18957      | 42    |
| H(25)  | -12658      | 2541 | -19258      | 44    |
| H(26)  | -12283      | 3899 | -17941      | 38    |
| H(28)  | -12568.0010 | 5707 | -17189      | 49    |
| H(29)  | -12944      | 7231 | -18276      | 59    |
| H(30)  | -11341      | 8160 | -18342      | 58    |
| H(31)  | -9345       | 7542 | -17341      | 54    |
| H(32)  | -8946       | 6021 | -16256      | 41    |
| H(34)  | -11672      | 2778 | -15575      | 39    |
| H(35)  | -13128.9990 | 2508 | -14881.0010 | 50    |
| H(36)  | -13828      | 3890 | -14183      | 49    |
| H(37)  | -13048      | 5534 | -14130      | 48    |
| H(38)  | -11659      | 5845 | -14905      | 39    |
| H(39A) | -7957       | 5195 | -9367       | 85    |
| H(39B) | -7975.9995  | 3951 | -9335       | 85    |
| H(40A) | -9145       | 3951 | -8482       | 165   |
| H(40B) | -8905       | 5171 | -8294       | 165   |
| H(41A) | -10670      | 5497 | -9504       | 122   |
| H(41B) | -10954      | 4280 | -9548       | 122   |
| H(42A) | -11095.9990 | 4192 | -11280      | 113   |
| H(42B) | -10855      | 5414 | -11252      | 113   |

**Complex 4I**

Table 1. Crystal data for pa575

|   |  |
|---|--|
| Compound                                    | pa575  |
| Molecular formula                           | C <sub>42</sub> H <sub>41</sub> AlN <sub>2</sub> O <sub>3</sub> P <sub>2</sub> |
| Molecular weight                            | 710.69   |
| Crystal habit                               | Colorless Block  |
| Crystal dimensions(mm)                      | 0.22x0.14x0.08   |
| Crystal system                              | monoclinic   |
| Space group                                 | Pc   |
| a(Å)  | 14.115(1)  |
| b(Å)  | 9.151(1)   |
| c(Å)  | 16.812(1)  |
| α(°)  | 90.00  |
| β(°)  | 124.486(4)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 1789.9(3)  |
| Z   | 2  |
| d(g·cm <sup>-3</sup> )                      | 1.319  |
| F(000)                                      | 748  |
| μ(cm <sup>-1</sup> )                        | 0.189  |
| Absorption corrections                      | multi-scan ; 0.9595 min, 0.9850 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 25.35  |
| HKL ranges                                  | -13 16 ; -11 10 ; -20 17   |
| Reflections measured                        | 8740   |
| Unique data                                 | 4892   |
| Rint  | 0.0391   |
| Reflections used                            | 4480   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 485  |
| Reflections / parameter                     | 9  |
| wR2   | 0.1180   |
| R1  | 0.0516   |
| Flack's parameter                           | -0.05(12)  |
| Weights a, b                                | 0.0424 ; 2.1544  |
| GoF   | 1.063  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.856(0.051) / -0.238(0.051)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa575

| atom   | x         | y          | z         | U(eq) |
|--------|-----------|------------|-----------|-------|
| P(1)   | -895(1)   | -9855(1)   | -6027(1)  | 37(1) |
| P(2)   | -4666(1)  | -8518(1)   | -6190(1)  | 37(1) |
| Al(1)  | -3193(1)  | -11001(2)  | -6353(1)  | 40(1) |
| O(1)   | -1920(3)  | -12197(4)  | -5589(2)  | 46(1) |
| O(2)   | -3461(3)  | -11353(4)  | -5427(3)  | 51(1) |
| N(1)   | -2243(3)  | -9623(4)   | -6519(3)  | 40(1) |
| N(2)   | -4232(3)  | -9236(4)   | -6791(3)  | 38(1) |
| C(1)   | -2757(4)  | -8180(5)   | -6929(4)  | 45(1) |
| C(2)   | -4034(4)  | -8360(5)   | -7414(3)  | 42(1) |
| C(3)   | -596(4)   | -11753(5)  | -6004(3)  | 36(1) |
| C(4)   | -1177(4)  | -12695(5)  | -5759(3)  | 42(1) |
| C(5)   | -941(5)   | -14203(5)  | -5713(4)  | 48(1) |
| C(6)   | -168(5)   | -14698(5)  | -5895(4)  | 54(1) |
| C(7)   | 387(5)    | -13764(5)  | -6146(4)  | 49(1) |
| C(8)   | 176(4)    | -12275(5)  | -6206(4)  | 45(1) |
| C(9)   | -16(4)    | -9214(5)   | -4795(3)  | 38(1) |
| C(10)  | 1112(4)   | -9625(6)   | -4175(4)  | 52(1) |
| C(11)  | 1751(5)   | -9172(7)   | -3226(4)  | 62(2) |
| C(12)  | 1261(5)   | -8265(6)   | -2890(4)  | 51(1) |
| C(13)  | 143(5)    | -7857(6)   | -3499(4)  | 53(1) |
| C(14)  | -508(5)   | -8332(5)   | -4448(4)  | 45(1) |
| C(15)  | -417(4)   | -8976(5)   | -6697(3)  | 41(1) |
| C(16)  | 626(4)    | -8256(5)   | -6275(4)  | 47(1) |
| C(17)  | 964(5)    | -7674(6)   | -6838(5)  | 62(2) |
| C(18)  | 226(6)    | -7782(7)   | -7830(5)  | 65(2) |
| C(19)  | -801(6)   | -8458(6)   | -8262(4)  | 60(2) |
| C(20)  | -1127(5)  | -9081(5)   | -7702(4)  | 48(1) |
| C(21)  | -5079(4)  | -9972(5)   | -5740(3)  | 39(1) |
| C(22)  | -4375(4)  | -11226(5)  | -5397(3)  | 43(1) |
| C(23)  | -4672(5)  | -12366(6)  | -5015(4)  | 51(1) |
| C(24)  | -5632(5)  | -12261(6)  | -5000(4)  | 52(1) |
| C(25)  | -6329(5)  | -11057(7)  | -5358(4)  | 53(1) |
| C(26)  | -6054(4)  | -9909(6)   | -5725(3)  | 45(1) |
| C(27)  | -3669(4)  | -7368(5)   | -5184(3)  | 40(1) |
| C(28)  | -3300(5)  | -6060(5)   | -5354(4)  | 44(1) |
| C(29)  | -2562(4)  | -5117(6)   | -4603(4)  | 48(1) |
| C(30)  | -2144(5)  | -5498(6)   | -3664(4)  | 50(1) |
| C(31)  | -2489(5)  | -6809(6)   | -3484(4)  | 60(2) |
| C(32)  | -3238(4)  | -7737(6)   | -4234(3)  | 50(1) |
| C(33)  | -5894(4)  | -7352(5)   | -6936(3)  | 41(1) |
| C(34)  | -6617(4)  | -7602(6)   | -7919(4)  | 50(1) |
| C(35)  | -7568(5)  | -6703(6)   | -8487(4)  | 56(1) |
| C(36)  | -7810(5)  | -5569(7)   | -8088(4)  | 62(2) |
| C(37)  | -7109(5)  | -5341(7)   | -7106(4)  | 61(2) |
| C(38)  | -6149(5)  | -6216(6)   | -6530(4)  | 49(1) |
| O(3A)  | -3936(3)  | -12052(4)  | -7392(3)  | 67(1) |
| C(39A) | -4968(5)  | -12779(6)  | -7949(4)  | 52(1) |
| C(40A) | -5730(10) | -11860(20) | -8826(8)  | 83(4) |
| C(41A) | -5540(10) | -13000(10) | -7404(7)  | 65(3) |
| C(42A) | -4790(10) | -14270(10) | -8233(8)  | 75(4) |
| O(3B)  | -3936(3)  | -12052(4)  | -7392(3)  | 67(1) |
| C(39B) | -4968(5)  | -12779(6)  | -7949(4)  | 52(1) |
| C(40B) | -6020(20) | -12050(20) | -8160(10) | 77(6) |
| C(41B) | -4680(20) | -14120(20) | -7390(10) | 72(5) |
| C(42B) | -5320(20) | -13300(20) | -8980(10) | 76(6) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa575

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| P(1)-N(1)        | 1.602(4) | P(1)-C(3)        | 1.783(4) |
| P(1)-C(15)       | 1.798(5) | P(1)-C(9)        | 1.807(5) |
| P(2)-N(2)        | 1.591(4) | P(2)-C(21)       | 1.784(5) |
| P(2)-C(27)       | 1.803(5) | P(2)-C(33)       | 1.803(5) |
| Al(1)-O(3A)      | 1.733(4) | Al(1)-O(2)       | 1.827(4) |
| Al(1)-O(1)       | 1.861(4) | Al(1)-N(1)       | 1.973(4) |
| Al(1)-N(2)       | 2.019(4) | O(1)-C(4)        | 1.315(6) |
| O(2)-C(22)       | 1.324(6) | N(1)-C(1)        | 1.476(6) |
| N(2)-C(2)        | 1.466(6) | C(1)-C(2)        | 1.509(7) |
| C(1)-H(1A)       | 0.9900   | C(1)-H(1B)       | 0.9900   |
| C(2)-H(2A)       | 0.9900   | C(2)-H(2B)       | 0.9900   |
| C(3)-C(8)        | 1.398(6) | C(3)-C(4)        | 1.401(7) |
| C(4)-C(5)        | 1.411(7) | C(5)-C(6)        | 1.366(7) |
| C(5)-H(5)        | 0.9500   | C(6)-C(7)        | 1.378(7) |
| C(6)-H(6)        | 0.9500   | C(7)-C(8)        | 1.386(7) |
| C(7)-H(7)        | 0.9500   | C(8)-H(8)        | 0.9500   |
| C(9)-C(10)       | 1.371(6) | C(9)-C(14)       | 1.391(6) |
| C(10)-C(11)      | 1.379(7) | C(10)-H(10)      | 0.9500   |
| C(11)-C(12)      | 1.389(8) | C(11)-H(11)      | 0.9500   |
| C(12)-C(13)      | 1.360(7) | C(12)-H(12)      | 0.9500   |
| C(13)-C(14)      | 1.385(7) | C(13)-H(13)      | 0.9500   |
| C(14)-H(14)      | 0.9500   | C(15)-C(16)      | 1.387(7) |
| C(15)-C(20)      | 1.396(7) | C(16)-C(17)      | 1.385(7) |
| C(16)-H(16)      | 0.9500   | C(17)-C(18)      | 1.38(1)  |
| C(17)-H(17)      | 0.9500   | C(18)-C(19)      | 1.349(8) |
| C(18)-H(18)      | 0.9500   | C(19)-C(20)      | 1.384(7) |
| C(19)-H(19)      | 0.9500   | C(20)-H(20)      | 0.9500   |
| C(21)-C(26)      | 1.392(7) | C(21)-C(22)      | 1.410(7) |
| C(22)-C(23)      | 1.408(7) | C(23)-C(24)      | 1.374(7) |
| C(23)-H(23)      | 0.9500   | C(24)-C(25)      | 1.369(8) |
| C(24)-H(24)      | 0.9500   | C(25)-C(26)      | 1.382(7) |
| C(25)-H(25)      | 0.9500   | C(26)-H(26)      | 0.9500   |
| C(27)-C(32)      | 1.392(7) | C(27)-C(28)      | 1.397(7) |
| C(28)-C(29)      | 1.391(7) | C(28)-H(28)      | 0.9500   |
| C(29)-C(30)      | 1.381(7) | C(29)-H(29)      | 0.9500   |
| C(30)-C(31)      | 1.391(8) | C(30)-H(30)      | 0.9500   |
| C(31)-C(32)      | 1.386(7) | C(31)-H(31)      | 0.9500   |
| C(32)-H(32)      | 0.9500   | C(33)-C(34)      | 1.384(7) |
| C(33)-C(38)      | 1.398(7) | C(34)-C(35)      | 1.393(7) |
| C(34)-H(34)      | 0.9500   | C(35)-C(36)      | 1.379(8) |
| C(35)-H(35)      | 0.9500   | C(36)-C(37)      | 1.378(8) |
| C(36)-H(36)      | 0.9500   | C(37)-C(38)      | 1.389(7) |
| C(37)-H(37)      | 0.9500   | C(38)-H(38)      | 0.9500   |
| O(3A)-C(39A)     | 1.377(6) | C(39A)-C(40A)    | 1.50(1)  |
| C(39A)-C(42A)    | 1.52(1)  | C(39A)-C(41A)    | 1.54(1)  |
| C(40A)-H(40A)    | 0.9800   | C(40A)-H(40B)    | 0.9800   |
| C(40A)-H(40C)    | 0.9800   | C(41A)-H(41A)    | 0.9800   |
| C(41A)-H(41B)    | 0.9800   | C(41A)-H(41C)    | 0.9800   |
| C(42A)-H(42A)    | 0.9800   | C(42A)-H(42B)    | 0.9800   |
| C(42A)-H(42C)    | 0.9800   | C(40B)-H(40D)    | 0.9800   |
| C(40B)-H(40E)    | 0.9800   | C(40B)-H(40F)    | 0.9800   |
| C(41B)-H(41D)    | 0.9800   | C(41B)-H(41E)    | 0.9800   |
| C(41B)-H(41F)    | 0.9800   | C(42B)-H(42D)    | 0.9800   |
| C(42B)-H(42E)    | 0.9800   | C(42B)-H(42F)    | 0.9800   |
| N(1)-P(1)-C(3)   | 109.7(2) | N(1)-P(1)-C(15)  | 111.9(2) |
| C(3)-P(1)-C(15)  | 106.4(2) | N(1)-P(1)-C(9)   | 113.2(2) |
| C(3)-P(1)-C(9)   | 106.9(2) | C(15)-P(1)-C(9)  | 108.4(2) |
| N(2)-P(2)-C(21)  | 107.3(2) | N(2)-P(2)-C(27)  | 117.4(2) |
| C(21)-P(2)-C(27) | 107.9(2) | N(2)-P(2)-C(33)  | 111.5(2) |
| C(21)-P(2)-C(33) | 108.7(2) | C(27)-P(2)-C(33) | 103.8(2) |
| O(3A)-Al(1)-O(2) | 117.6(2) | O(3A)-Al(1)-O(1) | 99.5(2)  |
| O(2)-Al(1)-O(1)  | 83.9(2)  | O(3A)-Al(1)-N(1) | 106.4(2) |
| O(2)-Al(1)-N(1)  | 136.0(2) | O(1)-Al(1)-N(1)  | 90.3(2)  |
| O(3A)-Al(1)-N(2) | 100.2(2) | O(2)-Al(1)-N(2)  | 89.7(2)  |

|                     |          |                      |          |
|---------------------|----------|----------------------|----------|
| O(1)-Al(1)-N(2)     | 160.1(2) | N(1)-Al(1)-N(2)      | 81.3(2)  |
| C(4)-O(1)-Al(1)     | 129.2(3) | C(22)-O(2)-Al(1)     | 133.9(3) |
| C(1)-N(1)-P(1)      | 119.1(3) | C(1)-N(1)-Al(1)      | 116.4(3) |
| P(1)-N(1)-Al(1)     | 123.1(2) | C(2)-N(2)-P(2)       | 121.7(3) |
| C(2)-N(2)-Al(1)     | 107.8(3) | P(2)-N(2)-Al(1)      | 124.1(2) |
| N(1)-C(1)-C(2)      | 106.0(4) | N(1)-C(1)-H(1A)      | 110.5    |
| C(2)-C(1)-H(1A)     | 110.5    | N(1)-C(1)-H(1B)      | 110.5    |
| C(2)-C(1)-H(1B)     | 110.5    | H(1A)-C(1)-H(1B)     | 108.7    |
| N(2)-C(2)-C(1)      | 109.1(4) | N(2)-C(2)-H(2A)      | 109.9    |
| C(1)-C(2)-H(2A)     | 109.9    | N(2)-C(2)-H(2B)      | 109.9    |
| C(1)-C(2)-H(2B)     | 109.9    | H(2A)-C(2)-H(2B)     | 108.3    |
| C(8)-C(3)-C(4)      | 121.9(4) | C(8)-C(3)-P(1)       | 122.3(4) |
| C(4)-C(3)-P(1)      | 115.8(3) | O(1)-C(4)-C(3)       | 121.4(4) |
| O(1)-C(4)-C(5)      | 121.3(5) | C(3)-C(4)-C(5)       | 117.3(4) |
| C(6)-C(5)-C(4)      | 120.4(5) | C(6)-C(5)-H(5)       | 119.8    |
| C(4)-C(5)-H(5)      | 119.8    | C(5)-C(6)-C(7)       | 121.8(5) |
| C(5)-C(6)-H(6)      | 119.1    | C(7)-C(6)-H(6)       | 119.1    |
| C(6)-C(7)-C(8)      | 119.8(5) | C(6)-C(7)-H(7)       | 120.1    |
| C(8)-C(7)-H(7)      | 120.1    | C(7)-C(8)-C(3)       | 118.8(5) |
| C(7)-C(8)-H(8)      | 120.6    | C(3)-C(8)-H(8)       | 120.6    |
| C(10)-C(9)-C(14)    | 118.8(4) | C(10)-C(9)-P(1)      | 122.0(4) |
| C(14)-C(9)-P(1)     | 119.1(4) | C(9)-C(10)-C(11)     | 120.9(5) |
| C(9)-C(10)-H(10)    | 119.5    | C(11)-C(10)-H(10)    | 119.5    |
| C(10)-C(11)-C(12)   | 120.0(5) | C(10)-C(11)-H(11)    | 120.0    |
| C(12)-C(11)-H(11)   | 120.0    | C(13)-C(12)-C(11)    | 119.4(5) |
| C(13)-C(12)-H(12)   | 120.3    | C(11)-C(12)-H(12)    | 120.3    |
| C(12)-C(13)-C(14)   | 120.8(5) | C(12)-C(13)-H(13)    | 119.6    |
| C(14)-C(13)-H(13)   | 119.6    | C(13)-C(14)-C(9)     | 120.1(5) |
| C(13)-C(14)-H(14)   | 119.9    | C(9)-C(14)-H(14)     | 119.9    |
| C(16)-C(15)-C(20)   | 118.6(5) | C(16)-C(15)-P(1)     | 124.0(4) |
| C(20)-C(15)-P(1)    | 117.4(4) | C(17)-C(16)-C(15)    | 120.7(5) |
| C(17)-C(16)-H(16)   | 119.7    | C(15)-C(16)-H(16)    | 119.7    |
| C(18)-C(17)-C(16)   | 118.8(6) | C(18)-C(17)-H(17)    | 120.6    |
| C(16)-C(17)-H(17)   | 120.6    | C(19)-C(18)-C(17)    | 121.9(5) |
| C(19)-C(18)-H(18)   | 119.1    | C(17)-C(18)-H(18)    | 119.1    |
| C(18)-C(19)-C(20)   | 119.5(6) | C(18)-C(19)-H(19)    | 120.2    |
| C(20)-C(19)-H(19)   | 120.2    | C(19)-C(20)-C(15)    | 120.5(6) |
| C(19)-C(20)-H(20)   | 119.7    | C(15)-C(20)-H(20)    | 119.7    |
| C(26)-C(21)-C(22)   | 120.1(4) | C(26)-C(21)-P(2)     | 122.7(4) |
| C(22)-C(21)-P(2)    | 117.2(3) | O(2)-C(22)-C(23)     | 120.0(4) |
| O(2)-C(22)-C(21)    | 122.1(4) | C(23)-C(22)-C(21)    | 117.8(4) |
| C(24)-C(23)-C(22)   | 120.6(5) | C(24)-C(23)-H(23)    | 119.7    |
| C(22)-C(23)-H(23)   | 119.7    | C(25)-C(24)-C(23)    | 121.3(5) |
| C(25)-C(24)-H(24)   | 119.4    | C(23)-C(24)-H(24)    | 119.4    |
| C(24)-C(25)-C(26)   | 119.7(5) | C(24)-C(25)-H(25)    | 120.2    |
| C(26)-C(25)-H(25)   | 120.2    | C(25)-C(26)-C(21)    | 120.5(5) |
| C(25)-C(26)-H(26)   | 119.7    | C(21)-C(26)-H(26)    | 119.7    |
| C(32)-C(27)-C(28)   | 118.1(5) | C(32)-C(27)-P(2)     | 122.4(4) |
| C(28)-C(27)-P(2)    | 119.5(4) | C(29)-C(28)-C(27)    | 121.4(5) |
| C(29)-C(28)-H(28)   | 119.3    | C(27)-C(28)-H(28)    | 119.3    |
| C(30)-C(29)-C(28)   | 119.8(5) | C(30)-C(29)-H(29)    | 120.1    |
| C(28)-C(29)-H(29)   | 120.1    | C(29)-C(30)-C(31)    | 119.4(5) |
| C(29)-C(30)-H(30)   | 120.3    | C(31)-C(30)-H(30)    | 120.3    |
| C(32)-C(31)-C(30)   | 120.8(5) | C(32)-C(31)-H(31)    | 119.6    |
| C(30)-C(31)-H(31)   | 119.6    | C(31)-C(32)-C(27)    | 120.6(5) |
| C(31)-C(32)-H(32)   | 119.7    | C(27)-C(32)-H(32)    | 119.7    |
| C(34)-C(33)-C(38)   | 119.1(5) | C(34)-C(33)-P(2)     | 120.1(4) |
| C(38)-C(33)-P(2)    | 120.8(4) | C(33)-C(34)-C(35)    | 119.6(5) |
| C(33)-C(34)-H(34)   | 120.2    | C(35)-C(34)-H(34)    | 120.2    |
| C(36)-C(35)-C(34)   | 121.3(5) | C(36)-C(35)-H(35)    | 119.4    |
| C(34)-C(35)-H(35)   | 119.4    | C(37)-C(36)-C(35)    | 119.3(5) |
| C(37)-C(36)-H(36)   | 120.4    | C(35)-C(36)-H(36)    | 120.4    |
| C(36)-C(37)-C(38)   | 120.2(5) | C(36)-C(37)-H(37)    | 119.9    |
| C(38)-C(37)-H(37)   | 119.9    | C(37)-C(38)-C(33)    | 120.5(5) |
| C(37)-C(38)-H(38)   | 119.7    | C(33)-C(38)-H(38)    | 119.7    |
| C(39A)-O(3A)-Al(1)  | 139.1(3) | O(3A)-C(39A)-C(40A)  | 107.1(6) |
| O(3A)-C(39A)-C(42A) | 110.3(6) | C(40A)-C(39A)-C(42A) | 110.6(8) |
| O(3A)-C(39A)-C(41A) | 111.7(5) | C(40A)-C(39A)-C(41A) | 109.2(7) |

# Appendix 1. Crystallographic data

|                      |          |                      |       |
|----------------------|----------|----------------------|-------|
| C(42A)-C(39A)-C(41A) | 107.9(7) | H(40D)-C(40B)-H(40E) | 109.5 |
| H(40D)-C(40B)-H(40F) | 109.5    | H(40E)-C(40B)-H(40F) | 109.5 |
| H(41D)-C(41B)-H(41E) | 109.5    | H(41D)-C(41B)-H(41F) | 109.5 |
| H(41E)-C(41B)-H(41F) | 109.5    | H(42D)-C(42B)-H(42E) | 109.5 |
| H(42D)-C(42B)-H(42F) | 109.5    | H(42E)-C(42B)-H(42F) | 109.5 |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa575

| atom   | U11     | U22     | U33    | U23     | U13    | U12     |
|--------|---------|---------|--------|---------|--------|---------|
| P(1)   | 43(1)   | 27(1)   | 45(1)  | -1(1)   | 28(1)  | 0(1)    |
| P(2)   | 39(1)   | 33(1)   | 41(1)  | 3(1)    | 24(1)  | 2(1)    |
| Al(1)  | 46(1)   | 28(1)   | 50(1)  | -3(1)   | 31(1)  | -3(1)   |
| O(1)   | 58(2)   | 34(2)   | 63(2)  | 8(2)    | 45(2)  | 7(2)    |
| O(2)   | 60(2)   | 38(2)   | 70(2)  | 18(2)   | 47(2)  | 12(2)   |
| N(1)   | 44(2)   | 20(2)   | 54(2)  | 3(2)    | 27(2)  | 1(2)    |
| N(2)   | 41(2)   | 34(2)   | 42(2)  | 6(2)    | 26(2)  | 5(2)    |
| C(1)   | 49(3)   | 31(3)   | 58(3)  | 2(2)    | 33(3)  | 0(2)    |
| C(2)   | 49(3)   | 35(3)   | 41(2)  | 3(2)    | 25(2)  | 5(2)    |
| C(3)   | 43(3)   | 27(2)   | 38(2)  | -2(2)   | 22(2)  | 4(2)    |
| C(4)   | 50(3)   | 33(3)   | 44(2)  | 2(2)    | 27(2)  | 5(2)    |
| C(5)   | 63(4)   | 27(2)   | 60(3)  | 4(2)    | 38(3)  | 2(2)    |
| C(6)   | 65(4)   | 26(3)   | 73(4)  | -6(2)   | 41(3)  | 4(3)    |
| C(7)   | 55(3)   | 43(3)   | 56(3)  | -7(3)   | 36(3)  | 9(3)    |
| C(8)   | 45(3)   | 42(3)   | 49(3)  | -1(2)   | 28(2)  | 3(2)    |
| C(9)   | 44(3)   | 30(2)   | 47(3)  | -5(2)   | 29(2)  | -3(2)   |
| C(10)  | 46(3)   | 52(3)   | 49(3)  | -9(3)   | 22(3)  | 10(3)   |
| C(11)  | 52(3)   | 63(4)   | 64(4)  | -1(3)   | 29(3)  | 9(3)    |
| C(12)  | 61(4)   | 40(3)   | 47(3)  | -8(2)   | 27(3)  | -7(3)   |
| C(13)  | 66(4)   | 47(3)   | 55(3)  | -10(2)  | 40(3)  | 8(3)    |
| C(14)  | 48(3)   | 42(3)   | 48(3)  | 1(2)    | 30(2)  | 7(2)    |
| C(15)  | 51(3)   | 29(2)   | 53(3)  | 0(2)    | 35(3)  | 6(2)    |
| C(16)  | 46(3)   | 42(3)   | 63(3)  | 1(2)    | 37(3)  | 3(2)    |
| C(17)  | 65(4)   | 46(3)   | 96(5)  | 2(3)    | 58(4)  | 0(3)    |
| C(18)  | 91(5)   | 52(4)   | 96(5)  | 19(3)   | 79(5)  | 13(4)   |
| C(19)  | 94(5)   | 45(3)   | 62(3)  | 6(3)    | 56(4)  | 16(3)   |
| C(20)  | 63(3)   | 37(3)   | 58(3)  | 3(2)    | 42(3)  | 5(3)    |
| C(21)  | 40(3)   | 38(3)   | 39(2)  | -1(2)   | 23(2)  | -4(2)   |
| C(22)  | 58(3)   | 32(3)   | 48(3)  | 0(2)    | 36(3)  | -1(2)   |
| C(23)  | 67(4)   | 35(3)   | 66(3)  | 6(2)    | 48(3)  | 4(3)    |
| C(24)  | 69(4)   | 43(3)   | 52(3)  | -3(2)   | 40(3)  | -10(3)  |
| C(25)  | 46(3)   | 72(4)   | 50(3)  | -5(3)   | 32(3)  | -14(3)  |
| C(26)  | 47(3)   | 46(3)   | 46(3)  | 0(2)    | 28(2)  | 2(2)    |
| C(27)  | 40(3)   | 31(2)   | 50(3)  | 0(2)    | 26(2)  | 1(2)    |
| C(28)  | 57(3)   | 39(3)   | 46(3)  | 2(2)    | 35(2)  | 3(2)    |
| C(29)  | 52(3)   | 35(3)   | 60(3)  | -1(2)   | 34(3)  | -3(2)   |
| C(30)  | 47(3)   | 39(3)   | 51(3)  | -6(2)   | 20(2)  | -5(2)   |
| C(31)  | 66(4)   | 52(3)   | 43(3)  | 9(2)    | 20(3)  | -3(3)   |
| C(32)  | 52(3)   | 40(3)   | 49(3)  | 4(2)    | 24(3)  | -4(3)   |
| C(33)  | 43(3)   | 35(3)   | 46(3)  | 6(2)    | 27(2)  | 1(2)    |
| C(34)  | 40(3)   | 38(3)   | 63(3)  | -2(2)   | 23(3)  | -6(2)   |
| C(35)  | 44(3)   | 47(3)   | 57(3)  | 9(3)    | 16(3)  | -4(3)   |
| C(36)  | 52(4)   | 49(3)   | 75(4)  | 15(3)   | 30(3)  | 9(3)    |
| C(37)  | 58(4)   | 62(4)   | 68(4)  | 6(3)    | 38(3)  | 16(3)   |
| C(38)  | 47(3)   | 48(3)   | 51(3)  | 4(2)    | 28(3)  | 11(3)   |
| O(3A)  | 60(3)   | 62(3)   | 84(3)  | -40(2)  | 44(2)  | -20(2)  |
| C(39A) | 53(3)   | 49(3)   | 53(3)  | 1(3)    | 30(3)  | -9(3)   |
| C(40A) | 76(8)   | 100(10) | 76(7)  | 18(7)   | 46(7)  | 3(7)    |
| C(41A) | 60(7)   | 73(7)   | 68(6)  | -10(6)  | 40(6)  | -20(6)  |
| C(42A) | 120(10) | 36(5)   | 84(8)  | -20(5)  | 70(8)  | -35(6)  |
| O(3B)  | 60(3)   | 62(3)   | 84(3)  | -40(2)  | 44(2)  | -20(2)  |
| C(39B) | 53(3)   | 49(3)   | 53(3)  | 1(3)    | 30(3)  | -9(3)   |
| C(40B) | 90(10)  | 50(10)  | 90(10) | 0(10)   | 60(10) | 0(10)   |
| C(41B) | 80(10)  | 80(10)  | 50(10) | -8(8)   | 35(8)  | -20(10) |
| C(42B) | 90(10)  | 90(10)  | 60(10) | -30(10) | 50(10) | -20(10) |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa575

| atom   | x          | y           | z          | U(eq) |
|--------|------------|-------------|------------|-------|
| H(1A)  | -2591      | -7874       | -7404      | 54    |
| H(1B)  | -2445      | -7434       | -6414      | 54    |
| H(2A)  | -4401      | -7390       | -7530      | 50    |
| H(2B)  | -4378      | -8853       | -8045      | 50    |
| H(5)   | -1322      | -14878      | -5554.9995 | 58    |
| H(6)   | -9         | -15714.9990 | -5847      | 64    |
| H(7)   | 913        | -14139      | -6278      | 59    |
| H(8)   | 551        | -11619.9990 | -6382      | 53    |
| H(10)  | 1456       | -10230      | -4403      | 62    |
| H(11)  | 2527       | -9480       | -2802      | 75    |
| H(12)  | 1703       | -7932       | -2240      | 61    |
| H(13)  | -196       | -7240       | -3271      | 63    |
| H(14)  | -1293      | -8054.9995  | -4863      | 54    |
| H(16)  | 1114       | -8161       | -5593      | 57    |
| H(17)  | 1690       | -7209       | -6547      | 75    |
| H(18)  | 449        | -7368.9995  | -8219      | 78    |
| H(19)  | -1297      | -8506       | -8946      | 72    |
| H(20)  | -1839      | -9584       | -8003      | 58    |
| H(23)  | -4203      | -13214.9990 | -4765      | 61    |
| H(24)  | -5817.0005 | -13040      | -4736      | 62    |
| H(25)  | -6998.9995 | -11011      | -5353.9995 | 64    |
| H(26)  | -6534      | -9069       | -5970      | 55    |
| H(28)  | -3558      | -5809.9995  | -5995      | 53    |
| H(29)  | -2346      | -4214       | -4736      | 57    |
| H(30)  | -1625      | -4870       | -3145      | 60    |
| H(31)  | -2208      | -7070       | -2839      | 72    |
| H(32)  | -3459.9998 | -8633       | -4098      | 60    |
| H(34)  | -6465      | -8382       | -8204      | 60    |
| H(35)  | -8060      | -6874       | -9162      | 67    |
| H(36)  | -8454      | -4952       | -8486      | 74    |
| H(37)  | -7282      | -4582       | -6822      | 74    |
| H(38)  | -5662.9995 | -6042       | -5855      | 58    |
| H(40A) | -5913      | -10946      | -8635      | 124   |
| H(40B) | -6447      | -12394      | -9274      | 124   |
| H(40C) | -5342      | -11643      | -9142      | 124   |
| H(41A) | -5021      | -13549      | -6810      | 97    |
| H(41B) | -6258.9995 | -13542      | -7813      | 97    |
| H(41C) | -5704      | -12043.9990 | -7244      | 97    |
| H(42A) | -4466      | -14159      | -8615      | 112   |
| H(42B) | -5526.0005 | -14785      | -8617      | 112   |
| H(42C) | -4255      | -14840      | -7650      | 112   |
| H(40D) | -5924.9995 | -11789      | -7558      | 115   |
| H(40E) | -6672.0005 | -12718      | -8532      | 115   |
| H(40F) | -6154      | -11167.0010 | -8542      | 115   |
| H(41D) | -4008      | -14567      | -7318      | 108   |
| H(41E) | -5335.9995 | -14794      | -7735.0005 | 108   |
| H(41F) | -4521      | -13893      | -6758.0005 | 108   |
| H(42D) | -5195.9995 | -12501      | -9302      | 115   |
| H(42E) | -6131      | -13583      | -9372      | 115   |
| H(42F) | -4846      | -14141.0010 | -8911      | 115   |

**Complex 42**

Table 1. Crystal data for pa573\_a\_recollector

|   |   |
|---|---|
| Compound                                      | pa573_a_recollector   |
| Molecular formula                             | $\text{C}_{40}\text{H}_{37}\text{AlN}_2\text{O}_3\text{P}_2$ , 1.5 ( $\text{C}_7\text{H}_8$ ) |
| Molecular weight                              | 820.84  |
| Crystal habit                                 | Colorless Block   |
| Crystal dimensions(mm)                        | 0.10x0.08x0.02  |
| Crystal system                                | triclinic   |
| Space group                                   | P-1   |
| a( $\text{\AA}$ )                             | 9.510(1)  |
| b( $\text{\AA}$ )                             | 12.413(1)   |
| c( $\text{\AA}$ )                             | 19.634(1)   |
| $\alpha(^{\circ})$                            | 97.531(1)   |
| $\beta(^{\circ})$                             | 101.550(1)  |
| $\gamma(^{\circ})$                            | 105.694(1)  |
| V( $\text{\AA}^3$ )                           | 2143.6(3)   |
| Z   | 2   |
| d(g·cm <sup>-3</sup> )                        | 1.272   |
| F(000)  | 866   |
| $\mu(\text{cm}^{-1})$                         | 0.168   |
| Absorption corrections                        | multi-scan ; 0.9834 min, 0.9967 max   |
| Diffractionmeter                              | KappaCCD  |
| X-ray source                                  | MoK $\alpha$  |
| $\lambda(\text{\AA})$                         | 0.71069   |
| Monochromator                                 | graphite  |
| T (K)   | 150.0(1)  |
| Scan mode                                     | phi and omega scans   |
| Maximum $\theta$                              | 25.03   |
| HKL ranges                                    | -11 11 ; -14 14 ; -23 23  |
| Reflections measured                          | 24544   |
| Unique data                                   | 7522  |
| Rint  | 0.0544  |
| Reflections used                              | 5680  |
| Criterion                                     | I > 2 $\sigma$ (I)  |
| Refinement type                               | Fsqd  |
| Hydrogen atoms                                | mixed   |
| Parameters refined                            | 434   |
| Reflections / parameter                       | 13  |
| wR2   | 0.2374  |
| R1  | 0.0903  |
| Weights a, b                                  | 0.1045 ; 4.0645   |
| GoF   | 1.111   |
| difference peak / hole (e $\text{\AA}^{-3}$ ) | 0.402(0.100) / -0.402(0.100)  |

## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa573\_a\_recolleter

| atom  | x        | y        | z       | U(eq)  |
|-------|----------|----------|---------|--------|
| P(1)  | 7992(1)  | 8818(1)  | 2673(1) | 43(1)  |
| P(2)  | 3371(1)  | 4615(1)  | 1366(1) | 40(1)  |
| Al(1) | 4560(2)  | 7228(1)  | 2217(1) | 41(1)  |
| O(1)  | 4782(4)  | 8446(2)  | 2928(2) | 49(1)  |
| O(2)  | 3172(4)  | 6427(3)  | 2607(2) | 56(1)  |
| O(3)  | 3839(5)  | 7742(3)  | 1474(2) | 61(1)  |
| N(1)  | 6739(4)  | 7607(3)  | 2366(2) | 45(1)  |
| N(2)  | 4655(4)  | 5803(3)  | 1656(2) | 42(1)  |
| C(1)  | 7288(6)  | 6728(4)  | 2006(3) | 52(1)  |
| C(2)  | 6008(6)  | 6022(4)  | 1383(3) | 51(1)  |
| C(3)  | 7206(6)  | 9803(4)  | 3075(2) | 43(1)  |
| C(4)  | 5726(5)  | 9466(3)  | 3153(2) | 42(1)  |
| C(5)  | 5258(6)  | 10314(4) | 3530(3) | 52(1)  |
| C(6)  | 6219(6)  | 11409(4) | 3791(3) | 51(1)  |
| C(7)  | 7657(6)  | 11738(4) | 3685(2) | 51(1)  |
| C(8)  | 8150(6)  | 10936(4) | 3335(2) | 48(1)  |
| C(9)  | 8706(6)  | 9407(4)  | 1969(2) | 49(1)  |
| C(10) | 7650(6)  | 9220(4)  | 1328(3) | 53(1)  |
| C(11) | 8083(8)  | 9708(4)  | 778(3)  | 65(2)  |
| C(12) | 9545(8)  | 10367(4) | 862(3)  | 67(2)  |
| C(13) | 10599(7) | 10556(4) | 1490(3) | 64(2)  |
| C(14) | 10183(6) | 10080(4) | 2048(3) | 53(1)  |
| C(15) | 9566(5)  | 8718(4)  | 3324(2) | 45(1)  |
| C(16) | 10717(6) | 8354(4)  | 3129(3) | 53(1)  |
| C(17) | 11843(6) | 8192(4)  | 3633(3) | 58(1)  |
| C(18) | 11816(7) | 8393(5)  | 4345(3) | 65(2)  |
| C(19) | 10638(7) | 8721(5)  | 4536(3) | 62(1)  |
| C(20) | 9542(6)  | 8903(4)  | 4038(3) | 52(1)  |
| C(21) | 2057(5)  | 4504(4)  | 1906(2) | 43(1)  |
| C(22) | 2131(6)  | 5408(4)  | 2446(3) | 49(1)  |
| C(23) | 1018(7)  | 5219(5)  | 2829(3) | 67(2)  |
| C(24) | -110(7)  | 4191(5)  | 2674(3) | 76(2)  |
| C(25) | -183(7)  | 3325(5)  | 2153(3) | 65(2)  |
| C(26) | 883(6)   | 3483(4)  | 1766(3) | 51(1)  |
| C(27) | 2358(5)  | 4420(4)  | 458(2)  | 45(1)  |
| C(28) | 2337(6)  | 5403(5)  | 186(3)  | 55(1)  |
| C(29) | 1487(8)  | 5312(6)  | -483(3) | 71(2)  |
| C(30) | 656(7)   | 4266(7)  | -889(3) | 77(2)  |
| C(31) | 670(6)   | 3277(6)  | -627(3) | 67(2)  |
| C(32) | 1517(6)  | 3366(4)  | 44(3)   | 52(1)  |
| C(33) | 4135(5)  | 3425(4)  | 1392(3) | 49(1)  |
| C(34) | 4663(6)  | 3010(4)  | 841(3)  | 65(2)  |
| C(35) | 5379(7)  | 2161(5)  | 909(5)  | 91(2)  |
| C(36) | 5573(8)  | 1772(6)  | 1523(6) | 101(3) |
| C(37) | 5090(10) | 2171(6)  | 2073(5) | 94(2)  |
| C(38) | 4357(7)  | 3005(5)  | 2015(3) | 68(2)  |
| C(39) | 3310(7)  | 8671(4)  | 1465(3) | 65(2)  |
| C(40) | 3018(7)  | 8923(5)  | 732(3)  | 66(2)  |

U(eq) is defined as 1/3 the trace of the  $U_{ij}$  tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles (deg) for pa573\_a\_recolleter

|              |          |              |          |
|--------------|----------|--------------|----------|
| P(1)-N(1)    | 1.597(4) | P(1)-C(3)    | 1.775(5) |
| P(1)-C(15)   | 1.808(5) | P(1)-C(9)    | 1.809(5) |
| P(2)-N(2)    | 1.586(4) | P(2)-C(21)   | 1.783(5) |
| P(2)-C(27)   | 1.799(5) | P(2)-C(33)   | 1.816(5) |
| Al(1)-O(3)   | 1.756(4) | Al(1)-O(2)   | 1.792(4) |
| Al(1)-O(1)   | 1.853(3) | Al(1)-N(1)   | 1.948(4) |
| Al(1)-N(2)   | 1.991(4) | O(1)-C(4)    | 1.298(5) |
| O(2)-C(22)   | 1.331(5) | O(3)-C(39)   | 1.378(6) |
| N(1)-C(1)    | 1.488(6) | N(2)-C(2)    | 1.465(6) |
| C(1)-C(2)    | 1.515(7) | C(1)-H(1A)   | 0.9900   |
| C(1)-H(1B)   | 0.9900   | C(2)-H(2A)   | 0.9900   |
| C(2)-H(2B)   | 0.9900   | C(3)-C(4)    | 1.402(7) |
| C(3)-C(8)    | 1.411(6) | C(4)-C(5)    | 1.425(6) |
| C(5)-C(6)    | 1.380(7) | C(5)-H(5)    | 0.9500   |
| C(6)-C(7)    | 1.383(7) | C(6)-H(6)    | 0.9500   |
| C(7)-C(8)    | 1.374(7) | C(7)-H(7)    | 0.9500   |
| C(8)-H(8)    | 0.9500   | C(9)-C(10)   | 1.393(7) |
| C(9)-C(14)   | 1.393(7) | C(10)-C(11)  | 1.385(7) |
| C(10)-H(10)  | 0.9500   | C(11)-C(12)  | 1.374(8) |
| C(11)-H(11)  | 0.9500   | C(12)-C(13)  | 1.372(8) |
| C(12)-H(12)  | 0.9500   | C(13)-C(14)  | 1.386(7) |
| C(13)-H(13)  | 0.9500   | C(14)-H(14)  | 0.9500   |
| C(15)-C(16)  | 1.393(7) | C(15)-C(20)  | 1.397(7) |
| C(16)-C(17)  | 1.382(8) | C(16)-H(16)  | 0.9500   |
| C(17)-C(18)  | 1.393(8) | C(17)-H(17)  | 0.9500   |
| C(18)-C(19)  | 1.392(8) | C(18)-H(18)  | 0.9500   |
| C(19)-C(20)  | 1.368(7) | C(19)-H(19)  | 0.9500   |
| C(20)-H(20)  | 0.9500   | C(21)-C(26)  | 1.396(6) |
| C(21)-C(22)  | 1.415(7) | C(22)-C(23)  | 1.405(7) |
| C(23)-C(24)  | 1.378(8) | C(23)-H(23)  | 0.9500   |
| C(24)-C(25)  | 1.359(8) | C(24)-H(24)  | 0.9500   |
| C(25)-C(26)  | 1.372(7) | C(25)-H(25)  | 0.9500   |
| C(26)-H(26)  | 0.9500   | C(27)-C(32)  | 1.381(6) |
| C(27)-C(28)  | 1.399(7) | C(28)-C(29)  | 1.371(7) |
| C(28)-H(28)  | 0.9500   | C(29)-C(30)  | 1.37(1)  |
| C(29)-H(29)  | 0.9500   | C(30)-C(31)  | 1.39(1)  |
| C(30)-H(30)  | 0.9500   | C(31)-C(32)  | 1.373(7) |
| C(31)-H(31)  | 0.9500   | C(32)-H(32)  | 0.9500   |
| C(33)-C(34)  | 1.378(8) | C(33)-C(38)  | 1.391(7) |
| C(34)-C(35)  | 1.409(8) | C(34)-H(34)  | 0.9500   |
| C(35)-C(36)  | 1.35(1)  | C(35)-H(35)  | 0.9500   |
| C(36)-C(37)  | 1.34(1)  | C(36)-H(36)  | 0.9500   |
| C(37)-C(38)  | 1.40(1)  | C(37)-H(37)  | 0.9500   |
| C(38)-H(38)  | 0.9500   | C(39)-C(40)  | 1.500(7) |
| C(39)-H(39A) | 0.9900   | C(39)-H(39B) | 0.9900   |
| C(40)-H(40A) | 0.9800   | C(40)-H(40B) | 0.9800   |
| C(40)-H(40C) | 0.9800   |              |          |

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| N(1)-P(1)-C(3)   | 110.3(2) | N(1)-P(1)-C(15)  | 111.8(2) |
| C(3)-P(1)-C(15)  | 108.5(2) | N(1)-P(1)-C(9)   | 110.8(2) |
| C(3)-P(1)-C(9)   | 107.2(2) | C(15)-P(1)-C(9)  | 108.1(2) |
| N(2)-P(2)-C(21)  | 108.4(2) | N(2)-P(2)-C(27)  | 114.4(2) |
| C(21)-P(2)-C(27) | 108.3(2) | N(2)-P(2)-C(33)  | 111.6(2) |
| C(21)-P(2)-C(33) | 109.0(2) | C(27)-P(2)-C(33) | 105.0(2) |
| O(3)-Al(1)-O(2)  | 115.2(2) | O(3)-Al(1)-O(1)  | 99.7(2)  |
| O(2)-Al(1)-O(1)  | 85.7(2)  | O(3)-Al(1)-N(1)  | 108.8(2) |
| O(2)-Al(1)-N(1)  | 135.8(2) | O(1)-Al(1)-N(1)  | 90.8(2)  |
| O(3)-Al(1)-N(2)  | 94.9(2)  | O(2)-Al(1)-N(2)  | 91.3(2)  |
| O(1)-Al(1)-N(2)  | 165.0(2) | N(1)-Al(1)-N(2)  | 81.1(2)  |
| C(4)-O(1)-Al(1)  | 134.7(3) | C(22)-O(2)-Al(1) | 137.4(3) |
| C(39)-O(3)-Al(1) | 127.7(3) | C(1)-N(1)-P(1)   | 114.2(3) |
| C(1)-N(1)-Al(1)  | 115.7(3) | P(1)-N(1)-Al(1)  | 128.7(2) |
| C(2)-N(2)-P(2)   | 119.1(3) | C(2)-N(2)-Al(1)  | 111.0(3) |
| P(2)-N(2)-Al(1)  | 128.7(2) | N(1)-C(1)-C(2)   | 106.7(4) |
| N(1)-C(1)-H(1A)  | 110.4    | C(2)-C(1)-H(1A)  | 110.4    |

## Appendix 1. Crystallographic data

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| N(1)-C(1)-H(1B)     | 110.4    | C(2)-C(1)-H(1B)     | 110.4    |
| H(1A)-C(1)-H(1B)    | 108.6    | N(2)-C(2)-C(1)      | 105.3(4) |
| N(2)-C(2)-H(2A)     | 110.7    | C(1)-C(2)-H(2A)     | 110.7    |
| N(2)-C(2)-H(2B)     | 110.7    | C(1)-C(2)-H(2B)     | 110.7    |
| H(2A)-C(2)-H(2B)    | 108.8    | C(4)-C(3)-C(8)      | 121.0(4) |
| C(4)-C(3)-P(1)      | 121.7(3) | C(8)-C(3)-P(1)      | 117.2(4) |
| O(1)-C(4)-C(3)      | 125.0(4) | O(1)-C(4)-C(5)      | 118.4(4) |
| C(3)-C(4)-C(5)      | 116.5(4) | C(6)-C(5)-C(4)      | 121.0(5) |
| C(6)-C(5)-H(5)      | 119.5    | C(4)-C(5)-H(5)      | 119.5    |
| C(5)-C(6)-C(7)      | 121.7(4) | C(5)-C(6)-H(6)      | 119.2    |
| C(7)-C(6)-H(6)      | 119.2    | C(8)-C(7)-C(6)      | 118.7(4) |
| C(8)-C(7)-H(7)      | 120.7    | C(6)-C(7)-H(7)      | 120.7    |
| C(7)-C(8)-C(3)      | 121.0(5) | C(7)-C(8)-H(8)      | 119.5    |
| C(3)-C(8)-H(8)      | 119.5    | C(10)-C(9)-C(14)    | 119.5(4) |
| C(10)-C(9)-P(1)     | 115.9(4) | C(14)-C(9)-P(1)     | 124.4(4) |
| C(11)-C(10)-C(9)    | 119.5(5) | C(11)-C(10)-H(10)   | 120.3    |
| C(9)-C(10)-H(10)    | 120.3    | C(12)-C(11)-C(10)   | 120.4(6) |
| C(12)-C(11)-H(11)   | 119.8    | C(10)-C(11)-H(11)   | 119.8    |
| C(13)-C(12)-C(11)   | 120.8(5) | C(13)-C(12)-H(12)   | 119.6    |
| C(11)-C(12)-H(12)   | 119.6    | C(12)-C(13)-C(14)   | 119.7(5) |
| C(12)-C(13)-H(13)   | 120.2    | C(14)-C(13)-H(13)   | 120.2    |
| C(13)-C(14)-C(9)    | 120.2(5) | C(13)-C(14)-H(14)   | 119.9    |
| C(9)-C(14)-H(14)    | 119.9    | C(16)-C(15)-C(20)   | 119.3(5) |
| C(16)-C(15)-P(1)    | 121.9(4) | C(20)-C(15)-P(1)    | 118.5(4) |
| C(17)-C(16)-C(15)   | 120.8(5) | C(17)-C(16)-H(16)   | 119.6    |
| C(15)-C(16)-H(16)   | 119.6    | C(16)-C(17)-C(18)   | 119.4(5) |
| C(16)-C(17)-H(17)   | 120.3    | C(18)-C(17)-H(17)   | 120.3    |
| C(19)-C(18)-C(17)   | 119.7(5) | C(19)-C(18)-H(18)   | 120.1    |
| C(17)-C(18)-H(18)   | 120.1    | C(20)-C(19)-C(18)   | 120.8(5) |
| C(20)-C(19)-H(19)   | 119.6    | C(18)-C(19)-H(19)   | 119.6    |
| C(19)-C(20)-C(15)   | 119.9(5) | C(19)-C(20)-H(20)   | 120.0    |
| C(15)-C(20)-H(20)   | 120.0    | C(26)-C(21)-C(22)   | 119.4(4) |
| C(26)-C(21)-P(2)    | 117.5(4) | C(22)-C(21)-P(2)    | 123.0(3) |
| O(2)-C(22)-C(23)    | 118.0(4) | O(2)-C(22)-C(21)    | 124.4(4) |
| C(23)-C(22)-C(21)   | 117.6(4) | C(24)-C(23)-C(22)   | 120.6(5) |
| C(24)-C(23)-H(23)   | 119.7    | C(22)-C(23)-H(23)   | 119.7    |
| C(25)-C(24)-C(23)   | 121.7(6) | C(25)-C(24)-H(24)   | 119.2    |
| C(23)-C(24)-H(24)   | 119.2    | C(24)-C(25)-C(26)   | 119.2(5) |
| C(24)-C(25)-H(25)   | 120.4    | C(26)-C(25)-H(25)   | 120.4    |
| C(25)-C(26)-C(21)   | 121.4(5) | C(25)-C(26)-H(26)   | 119.3    |
| C(21)-C(26)-H(26)   | 119.3    | C(32)-C(27)-C(28)   | 119.1(5) |
| C(32)-C(27)-P(2)    | 123.5(4) | C(28)-C(27)-P(2)    | 117.2(4) |
| C(29)-C(28)-C(27)   | 120.0(5) | C(29)-C(28)-H(28)   | 120.0    |
| C(27)-C(28)-H(28)   | 120.0    | C(30)-C(29)-C(28)   | 120.5(6) |
| C(30)-C(29)-H(29)   | 119.7    | C(28)-C(29)-H(29)   | 119.7    |
| C(29)-C(30)-C(31)   | 120.2(5) | C(29)-C(30)-H(30)   | 119.9    |
| C(31)-C(30)-H(30)   | 119.9    | C(32)-C(31)-C(30)   | 119.3(5) |
| C(32)-C(31)-H(31)   | 120.3    | C(30)-C(31)-H(31)   | 120.3    |
| C(31)-C(32)-C(27)   | 120.9(5) | C(31)-C(32)-H(32)   | 119.6    |
| C(27)-C(32)-H(32)   | 119.6    | C(34)-C(33)-C(38)   | 118.6(5) |
| C(34)-C(33)-P(2)    | 121.8(4) | C(38)-C(33)-P(2)    | 119.2(4) |
| C(33)-C(34)-C(35)   | 120.1(7) | C(33)-C(34)-H(34)   | 120.0    |
| C(35)-C(34)-H(34)   | 120.0    | C(36)-C(35)-C(34)   | 119.7(8) |
| C(36)-C(35)-H(35)   | 120.2    | C(34)-C(35)-H(35)   | 120.2    |
| C(37)-C(36)-C(35)   | 121.6(7) | C(37)-C(36)-H(36)   | 119.2    |
| C(35)-C(36)-H(36)   | 119.2    | C(36)-C(37)-C(38)   | 119.8(7) |
| C(36)-C(37)-H(37)   | 120.1    | C(38)-C(37)-H(37)   | 120.1    |
| C(33)-C(38)-C(37)   | 120.3(7) | C(33)-C(38)-H(38)   | 119.9    |
| C(37)-C(38)-H(38)   | 119.9    | O(3)-C(39)-C(40)    | 110.6(5) |
| O(3)-C(39)-H(39A)   | 109.5    | C(40)-C(39)-H(39A)  | 109.5    |
| O(3)-C(39)-H(39B)   | 109.5    | C(40)-C(39)-H(39B)  | 109.5    |
| H(39A)-C(39)-H(39B) | 108.1    | C(39)-C(40)-H(40A)  | 109.5    |
| C(39)-C(40)-H(40B)  | 109.5    | H(40A)-C(40)-H(40B) | 109.5    |
| C(39)-C(40)-H(40C)  | 109.5    | H(40A)-C(40)-H(40C) | 109.5    |
| H(40B)-C(40)-H(40C) | 109.5    |                     |          |

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa573\_a\_recolleter

| atom  | U11   | U22    | U33     | U23    | U13    | U12   |
|-------|-------|--------|---------|--------|--------|-------|
| P(1)  | 51(1) | 31(1)  | 39(1)   | 0(1)   | 13(1)  | 4(1)  |
| P(2)  | 48(1) | 27(1)  | 40(1)   | 5(1)   | 5(1)   | 7(1)  |
| Al(1) | 51(1) | 29(1)  | 39(1)   | 4(1)   | 12(1)  | 7(1)  |
| O(1)  | 57(2) | 34(2)  | 48(2)   | -1(1)  | 18(2)  | 5(2)  |
| O(2)  | 65(2) | 37(2)  | 58(2)   | -2(1)  | 25(2)  | 2(2)  |
| O(3)  | 89(3) | 39(2)  | 52(2)   | 8(2)   | 8(2)   | 22(2) |
| N(1)  | 53(2) | 32(2)  | 44(2)   | -2(2)  | 16(2)  | 5(2)  |
| N(2)  | 52(2) | 30(2)  | 43(2)   | 4(2)   | 16(2)  | 7(2)  |
| C(1)  | 51(3) | 37(2)  | 60(3)   | -6(2)  | 24(2)  | 4(2)  |
| C(2)  | 61(3) | 32(2)  | 53(3)   | -2(2)  | 26(2)  | 2(2)  |
| C(3)  | 55(3) | 32(2)  | 40(2)   | 2(2)   | 12(2)  | 9(2)  |
| C(4)  | 57(3) | 26(2)  | 38(2)   | 1(2)   | 9(2)   | 5(2)  |
| C(5)  | 58(3) | 40(3)  | 58(3)   | 5(2)   | 17(2)  | 14(2) |
| C(6)  | 61(3) | 38(3)  | 52(3)   | -3(2)  | 11(2)  | 19(2) |
| C(7)  | 69(4) | 32(2)  | 46(3)   | -2(2)  | 9(2)   | 15(2) |
| C(8)  | 50(3) | 36(2)  | 48(3)   | 0(2)   | 9(2)   | 5(2)  |
| C(9)  | 68(3) | 32(2)  | 42(3)   | 1(2)   | 21(2)  | 5(2)  |
| C(10) | 59(3) | 47(3)  | 44(3)   | 3(2)   | 12(2)  | 3(2)  |
| C(11) | 92(5) | 47(3)  | 49(3)   | 8(2)   | 20(3)  | 8(3)  |
| C(12) | 99(5) | 44(3)  | 60(4)   | 10(2)  | 41(3)  | 10(3) |
| C(13) | 82(4) | 37(3)  | 70(4)   | 7(2)   | 33(3)  | 3(3)  |
| C(14) | 63(3) | 36(2)  | 54(3)   | 3(2)   | 21(3)  | 3(2)  |
| C(15) | 49(3) | 34(2)  | 47(3)   | 2(2)   | 12(2)  | 6(2)  |
| C(16) | 64(3) | 42(3)  | 53(3)   | 5(2)   | 22(3)  | 14(2) |
| C(17) | 56(3) | 47(3)  | 72(4)   | 8(2)   | 26(3)  | 13(2) |
| C(18) | 68(4) | 58(3)  | 65(4)   | 8(3)   | 5(3)   | 21(3) |
| C(19) | 74(4) | 60(3)  | 47(3)   | 0(2)   | 11(3)  | 22(3) |
| C(20) | 59(3) | 46(3)  | 46(3)   | 0(2)   | 10(2)  | 16(2) |
| C(21) | 48(3) | 36(2)  | 40(2)   | 12(2)  | 8(2)   | 6(2)  |
| C(22) | 50(3) | 40(3)  | 51(3)   | 10(2)  | 11(2)  | 3(2)  |
| C(23) | 76(4) | 51(3)  | 68(4)   | 4(3)   | 35(3)  | 0(3)  |
| C(24) | 79(4) | 62(4)  | 78(4)   | 7(3)   | 40(3)  | -3(3) |
| C(25) | 61(4) | 51(3)  | 71(4)   | 10(3)  | 16(3)  | -3(3) |
| C(26) | 54(3) | 41(3)  | 46(3)   | 8(2)   | 6(2)   | -1(2) |
| C(27) | 51(3) | 42(2)  | 39(2)   | 4(2)   | 7(2)   | 17(2) |
| C(28) | 74(4) | 60(3)  | 40(3)   | 11(2)  | 16(2)  | 31(3) |
| C(29) | 96(5) | 90(4)  | 45(3)   | 16(3)  | 19(3)  | 58(4) |
| C(30) | 70(4) | 135(6) | 38(3)   | 10(3)  | 11(3)  | 57(4) |
| C(31) | 54(3) | 88(4)  | 48(3)   | -15(3) | 6(3)   | 19(3) |
| C(32) | 54(3) | 50(3)  | 46(3)   | 0(2)   | 9(2)   | 11(2) |
| C(33) | 43(3) | 29(2)  | 64(3)   | 7(2)   | 0(2)   | 2(2)  |
| C(34) | 59(3) | 41(3)  | 88(4)   | -1(3)  | 7(3)   | 18(2) |
| C(35) | 60(4) | 48(4)  | 149(7)  | -9(4)  | 9(4)   | 17(3) |
| C(36) | 56(4) | 54(4)  | 180(10) | 28(5)  | -12(5) | 19(3) |
| C(37) | 82(5) | 67(4)  | 127(7)  | 43(4)  | -5(5)  | 24(4) |
| C(38) | 64(4) | 54(3)  | 79(4)   | 25(3)  | 0(3)   | 10(3) |
| C(39) | 70(4) | 43(3)  | 73(4)   | 9(2)   | 5(3)   | 13(3) |
| C(40) | 89(4) | 50(3)  | 60(3)   | 19(2)  | 7(3)   | 25(3) |

The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^*b^*U_{12}]$



Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa573\_a\_recollector

| atom   | x         | y     | z          | U(eq) |
|--------|-----------|-------|------------|-------|
| H(1A)  | 7567      | 6240  | 2337       | 62    |
| H(1B)  | 8184      | 7097  | 1841       | 62    |
| H(2A)  | 5910      | 6447  | 991        | 61    |
| H(2B)  | 6181      | 5297  | 1205       | 61    |
| H(5)   | 4269      | 10122 | 3602       | 63    |
| H(6)   | 5884      | 11950 | 4049       | 61    |
| H(7)   | 8290      | 12503 | 3852       | 61    |
| H(8)   | 9142      | 11148 | 3267       | 57    |
| H(10)  | 6639      | 8761  | 1268       | 64    |
| H(11)  | 7365      | 9587  | 341        | 79    |
| H(12)  | 9830      | 10696 | 480        | 80    |
| H(13)  | 11609     | 11009 | 1542       | 77    |
| H(14)  | 10908     | 10214 | 2485       | 64    |
| H(16)  | 10728     | 8214  | 2643       | 64    |
| H(17)  | 12625     | 7947  | 3495       | 69    |
| H(18)  | 12600     | 8307  | 4698       | 78    |
| H(19)  | 10595     | 8819  | 5019       | 75    |
| H(20)  | 8765      | 9155  | 4178       | 62    |
| H(23)  | 1043      | 5805  | 3199       | 80    |
| H(24)  | -856.0001 | 4084  | 2937       | 91    |
| H(25)  | -961.9999 | 2619  | 2059       | 78    |
| H(26)  | 820       | 2885  | 1395       | 61    |
| H(28)  | 2910      | 6134  | 465        | 66    |
| H(29)  | 1477      | 5982  | -666.9999  | 85    |
| H(30)  | 67        | 4212  | -1351.0001 | 92    |
| H(31)  | 99        | 2548  | -910       | 81    |
| H(32)  | 1524      | 2694  | 225        | 63    |
| H(34)  | 4543      | 3297  | 414        | 78    |
| H(35)  | 5723      | 1861  | 526        | 109   |
| H(36)  | 6065      | 1204  | 1566       | 121   |
| H(37)  | 5242      | 1888  | 2499       | 112   |
| H(38)  | 4010      | 3286  | 2403       | 82    |
| H(39A) | 4060      | 9345  | 1796       | 78    |
| H(39B) | 2365      | 8514  | 1626       | 78    |
| H(40A) | 3938      | 9033  | 562        | 99    |
| H(40B) | 2715      | 9618  | 743        | 99    |
| H(40C) | 2210      | 8283  | 413        | 99    |

**Complex 43**

Table 1. Crystal data for pa570

|   |  |
|---|--|
| Compound                                      | pa570  |
| Molecular formula                             | $\text{C}_{80}\text{H}_{74}\text{N}_4\text{O}_6\text{P}_4\text{Y}_2 \cdot 2(\text{C}_7\text{H}_8)$ |
| Molecular weight                              | 1673.40  |
| Crystal habit                                 | Colorless Block  |
| Crystal dimensions(mm)                        | 0.20x0.18x0.12   |
| Crystal system                                | triclinic  |
| Space group                                   | P-1  |
| a( $\text{\AA}$ )                             | 12.950(1)  |
| b( $\text{\AA}$ )                             | 13.948(1)  |
| c( $\text{\AA}$ )                             | 14.744(1)  |
| $\alpha(^{\circ})$                            | 102.175(1)   |
| $\beta(^{\circ})$                             | 108.382(1)   |
| $\gamma(^{\circ})$                            | 112.817(1)   |
| V( $\text{\AA}^3$ )                           | 2153.9(3)  |
| Z   | 1  |
| d(g·cm <sup>-3</sup> )                        | 1.290  |
| F(000)  | 868  |
| $\mu(\text{cm}^{-1})$                         | 1.469  |
| Absorption corrections                        | multi-scan ; 0.7576 min, 0.8434 max  |
| Diffractionmeter                              | KappaCCD   |
| X-ray source                                  | MoK $\alpha$   |
| $\lambda(\text{\AA})$                         | 0.71069  |
| Monochromator                                 | graphite   |
| T (K)   | 150.0(1)   |
| Scan mode                                     | phi and omega scans  |
| Maximum $\theta$                              | 25.03  |
| HKL ranges                                    | -15 15 ; -16 16 ; -17 17   |
| Reflections measured                          | 27959  |
| Unique data                                   | 7575   |
| Rint  | 0.0512   |
| Reflections used                              | 6201   |
| Criterion                                     | $I > 2\sigma(I)$   |
| Refinement type                               | Fsqd   |
| Hydrogen atoms                                | constr   |
| Parameters refined                            | 434  |
| Reflections / parameter                       | 14   |
| wR2   | 0.1368   |
| R1  | 0.0539   |
| Weights a, b                                  | 0.0731 ; 2.9994  |
| GoF   | 1.076  |
| difference peak / hole (e $\text{\AA}^{-3}$ ) | 1.108(0.086) / -0.503(0.086)   |

## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa570

| atom  | x        | y        | z        | U(eq)  |
|-------|----------|----------|----------|--------|
| Y(1)  | 772(1)   | 4466(1)  | 857(1)   | 26(1)  |
| P(1)  | 2105(1)  | 2661(1)  | 881(1)   | 26(1)  |
| P(2)  | -349(1)  | 3974(1)  | 2616(1)  | 26(1)  |
| O(1)  | 2301(3)  | 4714(2)  | 435(2)   | 33(1)  |
| O(2)  | 1929(3)  | 5382(2)  | 2545(2)  | 32(1)  |
| O(3)  | 774(3)   | 6049(2)  | 688(2)   | 33(1)  |
| N(1)  | 991(3)   | 2846(3)  | 967(3)   | 29(1)  |
| N(2)  | -700(3)  | 3385(3)  | 1430(2)  | 27(1)  |
| C(1)  | 96(4)    | 2032(3)  | 1206(3)  | 29(1)  |
| C(2)  | -1033(4) | 2211(3)  | 967(3)   | 30(1)  |
| C(3)  | 3498(4)  | 3925(3)  | 1206(3)  | 28(1)  |
| C(4)  | 3384(4)  | 4770(3)  | 877(3)   | 28(1)  |
| C(5)  | 4502(4)  | 5687(4)  | 1036(4)  | 39(1)  |
| C(6)  | 5628(4)  | 5740(4)  | 1485(4)  | 45(1)  |
| C(7)  | 5738(4)  | 4913(4)  | 1837(4)  | 45(1)  |
| C(8)  | 4672(4)  | 4014(4)  | 1696(4)  | 37(1)  |
| C(9)  | 1677(4)  | 1758(3)  | -414(3)  | 29(1)  |
| C(10) | 434(4)   | 1051(3)  | -1093(3) | 33(1)  |
| C(11) | 85(5)    | 330(4)   | -2078(3) | 41(1)  |
| C(12) | 1002(5)  | 358(4)   | -2382(3) | 43(1)  |
| C(13) | 2230(5)  | 1060(4)  | -1728(4) | 48(1)  |
| C(14) | 2590(4)  | 1763(4)  | -737(4)  | 45(1)  |
| C(15) | 2597(4)  | 1997(3)  | 1730(3)  | 29(1)  |
| C(16) | 2729(4)  | 1056(4)  | 1406(4)  | 38(1)  |
| C(17) | 3171(5)  | 628(4)   | 2112(5)  | 54(1)  |
| C(18) | 3512(5)  | 1156(5)  | 3150(5)  | 57(1)  |
| C(19) | 3377(4)  | 2081(4)  | 3476(4)  | 47(1)  |
| C(20) | 2932(4)  | 2512(4)  | 2778(3)  | 40(1)  |
| C(21) | 1198(4)  | 4407(3)  | 3553(3)  | 27(1)  |
| C(22) | 2181(4)  | 5100(3)  | 3352(3)  | 29(1)  |
| C(23) | 3411(4)  | 5461(4)  | 4057(3)  | 36(1)  |
| C(24) | 3648(4)  | 5160(4)  | 4903(3)  | 39(1)  |
| C(25) | 2687(4)  | 4493(4)  | 5089(3)  | 39(1)  |
| C(26) | 1461(4)  | 4117(4)  | 4407(3)  | 34(1)  |
| C(27) | -1421(4) | 3139(3)  | 3050(3)  | 28(1)  |
| C(28) | -1498(4) | 2122(3)  | 3091(3)  | 34(1)  |
| C(29) | -2338(4) | 1461(4)  | 3386(3)  | 40(1)  |
| C(30) | -3092(5) | 1813(4)  | 3659(4)  | 45(1)  |
| C(31) | -3030(4) | 2824(4)  | 3622(4)  | 44(1)  |
| C(32) | -2195(4) | 3481(4)  | 3319(3)  | 34(1)  |
| C(33) | -458(4)  | 5242(3)  | 2751(3)  | 29(1)  |
| C(34) | 131(4)   | 6102(3)  | 3715(3)  | 35(1)  |
| C(35) | 34(5)    | 7075(4)  | 3829(4)  | 44(1)  |
| C(36) | -645(5)  | 7178(4)  | 2960(4)  | 43(1)  |
| C(37) | -1233(4) | 6341(4)  | 1995(3)  | 36(1)  |
| C(38) | -1143(4) | 5371(4)  | 1890(3)  | 32(1)  |
| C(39) | 2080(10) | 7157(7)  | 1397(6)  | 146(5) |
| C(40) | 1860(10) | 7660(10) | 2140(10) | 163(5) |

U(eq) is defined as 1/3 the trace of the  $U_{ij}$  tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths ( $\text{\AA}$ ) and angles (deg) for pa570

|              |           |              |          |
|--------------|-----------|--------------|----------|
| Y(1)-O(1)    | 2.182(3)  | Y(1)-O(2)    | 2.213(3) |
| Y(1)-O(3)#2  | 2.243(3)  | Y(1)-O(3)    | 2.273(3) |
| Y(1)-N(1)    | 2.415(3)  | Y(1)-N(2)    | 2.438(3) |
| Y(1)-Y(1)#2  | 3.6492(7) | P(1)-N(1)    | 1.598(3) |
| P(1)-C(3)    | 1.796(4)  | P(1)-C(15)   | 1.810(4) |
| P(1)-C(9)    | 1.821(4)  | P(2)-N(2)    | 1.595(3) |
| P(2)-C(33)   | 1.803(4)  | P(2)-C(21)   | 1.803(4) |
| P(2)-C(27)   | 1.821(4)  | O(1)-C(4)    | 1.309(5) |
| O(2)-C(22)   | 1.315(5)  | O(3)-C(39)   | 1.58(1)  |
| O(3)-Y(1)#2  | 2.243(3)  | N(1)-C(1)    | 1.470(5) |
| N(2)-C(2)    | 1.458(5)  | C(1)-C(2)    | 1.523(5) |
| C(1)-H(1A)   | 0.9900    | C(1)-H(1B)   | 0.9900   |
| C(2)-H(2A)   | 0.9900    | C(2)-H(2B)   | 0.9900   |
| C(3)-C(8)    | 1.404(6)  | C(3)-C(4)    | 1.407(5) |
| C(4)-C(5)    | 1.418(6)  | C(5)-C(6)    | 1.363(6) |
| C(5)-H(5)    | 0.9500    | C(6)-C(7)    | 1.398(6) |
| C(6)-H(6)    | 0.9500    | C(7)-C(8)    | 1.374(6) |
| C(7)-H(7)    | 0.9500    | C(8)-H(8)    | 0.9500   |
| C(9)-C(10)   | 1.379(6)  | C(9)-C(14)   | 1.404(6) |
| C(10)-C(11)  | 1.393(6)  | C(10)-H(10)  | 0.9500   |
| C(11)-C(12)  | 1.386(7)  | C(11)-H(11)  | 0.9500   |
| C(12)-C(13)  | 1.359(7)  | C(12)-H(12)  | 0.9500   |
| C(13)-C(14)  | 1.388(6)  | C(13)-H(13)  | 0.9500   |
| C(14)-H(14)  | 0.9500    | C(15)-C(16)  | 1.394(6) |
| C(15)-C(20)  | 1.399(6)  | C(16)-C(17)  | 1.386(6) |
| C(16)-H(16)  | 0.9500    | C(17)-C(18)  | 1.388(8) |
| C(17)-H(17)  | 0.9500    | C(18)-C(19)  | 1.375(7) |
| C(18)-H(18)  | 0.9500    | C(19)-C(20)  | 1.382(6) |
| C(19)-H(19)  | 0.9500    | C(20)-H(20)  | 0.9500   |
| C(21)-C(26)  | 1.384(5)  | C(21)-C(22)  | 1.431(5) |
| C(22)-C(23)  | 1.408(6)  | C(23)-C(24)  | 1.380(6) |
| C(23)-H(23)  | 0.9500    | C(24)-C(25)  | 1.383(6) |
| C(24)-H(24)  | 0.9500    | C(25)-C(26)  | 1.390(6) |
| C(25)-H(25)  | 0.9500    | C(26)-H(26)  | 0.9500   |
| C(27)-C(32)  | 1.390(6)  | C(27)-C(28)  | 1.399(6) |
| C(28)-C(29)  | 1.382(6)  | C(28)-H(28)  | 0.9500   |
| C(29)-C(30)  | 1.377(6)  | C(29)-H(29)  | 0.9500   |
| C(30)-C(31)  | 1.395(7)  | C(30)-H(30)  | 0.9500   |
| C(31)-C(32)  | 1.385(6)  | C(31)-H(31)  | 0.9500   |
| C(32)-H(32)  | 0.9500    | C(33)-C(34)  | 1.389(6) |
| C(33)-C(38)  | 1.392(5)  | C(34)-C(35)  | 1.392(6) |
| C(34)-H(34)  | 0.9500    | C(35)-C(36)  | 1.379(6) |
| C(35)-H(35)  | 0.9500    | C(36)-C(37)  | 1.377(6) |
| C(36)-H(36)  | 0.9500    | C(37)-C(38)  | 1.384(6) |
| C(37)-H(37)  | 0.9500    | C(38)-H(38)  | 0.9500   |
| C(39)-C(40)  | 1.34(1)   | C(39)-H(39A) | 0.9900   |
| C(39)-H(39B) | 0.9900    | C(40)-H(40A) | 0.9800   |
| C(40)-H(40B) | 0.9800    | C(40)-H(40C) | 0.9800   |

|                  |           |                    |           |
|------------------|-----------|--------------------|-----------|
| O(1)-Y(1)-O(2)   | 97.1(1)   | O(1)-Y(1)-O(3)#2   | 100.3(1)  |
| O(2)-Y(1)-O(3)#2 | 156.1(1)  | O(1)-Y(1)-O(3)     | 93.6(1)   |
| O(2)-Y(1)-O(3)   | 90.6(1)   | O(3)#2-Y(1)-O(3)   | 72.2(1)   |
| O(1)-Y(1)-N(1)   | 78.8(1)   | O(2)-Y(1)-N(1)     | 90.5(1)   |
| O(3)#2-Y(1)-N(1) | 108.8(1)  | O(3)-Y(1)-N(1)     | 172.4(1)  |
| O(1)-Y(1)-N(2)   | 149.2(1)  | O(2)-Y(1)-N(2)     | 81.4(1)   |
| O(3)#2-Y(1)-N(2) | 91.6(1)   | O(3)-Y(1)-N(2)     | 117.2(1)  |
| N(1)-Y(1)-N(2)   | 70.4(1)   | O(1)-Y(1)-Y(1)#2   | 98.57(7)  |
| O(2)-Y(1)-Y(1)#2 | 124.66(7) | O(3)#2-Y(1)-Y(1)#2 | 36.37(7)  |
| O(3)-Y(1)-Y(1)#2 | 35.82(7)  | N(1)-Y(1)-Y(1)#2   | 144.61(8) |
| N(2)-Y(1)-Y(1)#2 | 107.59(7) | N(1)-P(1)-C(3)     | 115.0(2)  |
| N(1)-P(1)-C(15)  | 111.9(2)  | C(3)-P(1)-C(15)    | 105.2(2)  |
| N(1)-P(1)-C(9)   | 112.8(2)  | C(3)-P(1)-C(9)     | 105.4(2)  |
| C(15)-P(1)-C(9)  | 105.9(2)  | N(2)-P(2)-C(33)    | 106.9(2)  |
| N(2)-P(2)-C(21)  | 117.2(2)  | C(33)-P(2)-C(21)   | 105.8(2)  |
| N(2)-P(2)-C(27)  | 113.8(2)  | C(33)-P(2)-C(27)   | 106.3(2)  |

## Appendix 1. Crystallographic data

|                   |          |                    |          |
|-------------------|----------|--------------------|----------|
| C(21)-P(2)-C(27)  | 106.1(2) | C(4)-O(1)-Y(1)     | 133.9(2) |
| C(22)-O(2)-Y(1)   | 135.7(2) | C(39)-O(3)-Y(1)#2  | 133.1(3) |
| C(39)-O(3)-Y(1)   | 113.5(3) | Y(1)#2-O(3)-Y(1)   | 107.8(1) |
| C(1)-N(1)-P(1)    | 118.6(2) | C(1)-N(1)-Y(1)     | 117.5(2) |
| P(1)-N(1)-Y(1)    | 123.8(2) | C(2)-N(2)-P(2)     | 122.5(3) |
| C(2)-N(2)-Y(1)    | 106.9(2) | P(2)-N(2)-Y(1)     | 114.1(2) |
| N(1)-C(1)-C(2)    | 107.8(3) | N(1)-C(1)-H(1A)    | 110.1    |
| C(2)-C(1)-H(1A)   | 110.1    | N(1)-C(1)-H(1B)    | 110.1    |
| C(2)-C(1)-H(1B)   | 110.1    | H(1A)-C(1)-H(1B)   | 108.5    |
| N(2)-C(2)-C(1)    | 113.1(3) | N(2)-C(2)-H(2A)    | 109.0    |
| C(1)-C(2)-H(2A)   | 109.0    | N(2)-C(2)-H(2B)    | 109.0    |
| C(1)-C(2)-H(2B)   | 109.0    | H(2A)-C(2)-H(2B)   | 107.8    |
| C(8)-C(3)-C(4)    | 121.0(4) | C(8)-C(3)-P(1)     | 120.0(3) |
| C(4)-C(3)-P(1)    | 118.7(3) | O(1)-C(4)-C(3)     | 122.0(4) |
| O(1)-C(4)-C(5)    | 121.2(4) | C(3)-C(4)-C(5)     | 116.7(4) |
| C(6)-C(5)-C(4)    | 121.3(4) | C(6)-C(5)-H(5)     | 119.4    |
| C(4)-C(5)-H(5)    | 119.4    | C(5)-C(6)-C(7)     | 121.7(4) |
| C(5)-C(6)-H(6)    | 119.2    | C(7)-C(6)-H(6)     | 119.2    |
| C(8)-C(7)-C(6)    | 118.4(4) | C(8)-C(7)-H(7)     | 120.8    |
| C(6)-C(7)-H(7)    | 120.8    | C(7)-C(8)-C(3)     | 120.8(4) |
| C(7)-C(8)-H(8)    | 119.6    | C(3)-C(8)-H(8)     | 119.6    |
| C(10)-C(9)-C(14)  | 119.1(4) | C(10)-C(9)-P(1)    | 119.6(3) |
| C(14)-C(9)-P(1)   | 121.3(3) | C(9)-C(10)-C(11)   | 120.6(4) |
| C(9)-C(10)-H(10)  | 119.7    | C(11)-C(10)-H(10)  | 119.7    |
| C(12)-C(11)-C(10) | 119.2(4) | C(12)-C(11)-H(11)  | 120.4    |
| C(10)-C(11)-H(11) | 120.4    | C(13)-C(12)-C(11)  | 120.9(4) |
| C(13)-C(12)-H(12) | 119.5    | C(11)-C(12)-H(12)  | 119.5    |
| C(12)-C(13)-C(14) | 120.3(4) | C(12)-C(13)-H(13)  | 119.8    |
| C(14)-C(13)-H(13) | 119.8    | C(13)-C(14)-C(9)   | 119.8(4) |
| C(13)-C(14)-H(14) | 120.1    | C(9)-C(14)-H(14)   | 120.1    |
| C(16)-C(15)-C(20) | 119.2(4) | C(16)-C(15)-P(1)   | 123.5(3) |
| C(20)-C(15)-P(1)  | 117.1(3) | C(17)-C(16)-C(15)  | 120.2(4) |
| C(17)-C(16)-H(16) | 119.9    | C(15)-C(16)-H(16)  | 119.9    |
| C(16)-C(17)-C(18) | 119.8(5) | C(16)-C(17)-H(17)  | 120.1    |
| C(18)-C(17)-H(17) | 120.1    | C(19)-C(18)-C(17)  | 120.4(4) |
| C(19)-C(18)-H(18) | 119.8    | C(17)-C(18)-H(18)  | 119.8    |
| C(18)-C(19)-C(20) | 120.3(5) | C(18)-C(19)-H(19)  | 119.8    |
| C(20)-C(19)-H(19) | 119.8    | C(19)-C(20)-C(15)  | 120.1(4) |
| C(19)-C(20)-H(20) | 120.0    | C(15)-C(20)-H(20)  | 120.0    |
| C(26)-C(21)-C(22) | 120.8(4) | C(26)-C(21)-P(2)   | 124.8(3) |
| C(22)-C(21)-P(2)  | 114.4(3) | O(2)-C(22)-C(23)   | 122.4(4) |
| O(2)-C(22)-C(21)  | 120.6(4) | C(23)-C(22)-C(21)  | 116.9(3) |
| C(24)-C(23)-C(22) | 121.1(4) | C(24)-C(23)-H(23)  | 119.4    |
| C(22)-C(23)-H(23) | 119.4    | C(23)-C(24)-C(25)  | 121.3(4) |
| C(23)-C(24)-H(24) | 119.4    | C(25)-C(24)-H(24)  | 119.4    |
| C(24)-C(25)-C(26) | 119.2(4) | C(24)-C(25)-H(25)  | 120.4    |
| C(26)-C(25)-H(25) | 120.4    | C(21)-C(26)-C(25)  | 120.6(4) |
| C(21)-C(26)-H(26) | 119.7    | C(25)-C(26)-H(26)  | 119.7    |
| C(32)-C(27)-C(28) | 118.9(4) | C(32)-C(27)-P(2)   | 121.0(3) |
| C(28)-C(27)-P(2)  | 120.0(3) | C(29)-C(28)-C(27)  | 120.6(4) |
| C(29)-C(28)-H(28) | 119.7    | C(27)-C(28)-H(28)  | 119.7    |
| C(30)-C(29)-C(28) | 119.9(4) | C(30)-C(29)-H(29)  | 120.0    |
| C(28)-C(29)-H(29) | 120.0    | C(29)-C(30)-C(31)  | 120.3(4) |
| C(29)-C(30)-H(30) | 119.8    | C(31)-C(30)-H(30)  | 119.8    |
| C(32)-C(31)-C(30) | 119.7(4) | C(32)-C(31)-H(31)  | 120.2    |
| C(30)-C(31)-H(31) | 120.2    | C(31)-C(32)-C(27)  | 120.6(4) |
| C(31)-C(32)-H(32) | 119.7    | C(27)-C(32)-H(32)  | 119.7    |
| C(34)-C(33)-C(38) | 119.0(4) | C(34)-C(33)-P(2)   | 120.5(3) |
| C(38)-C(33)-P(2)  | 120.5(3) | C(33)-C(34)-C(35)  | 120.9(4) |
| C(33)-C(34)-H(34) | 119.5    | C(35)-C(34)-H(34)  | 119.5    |
| C(36)-C(35)-C(34) | 118.6(4) | C(36)-C(35)-H(35)  | 120.7    |
| C(34)-C(35)-H(35) | 120.7    | C(37)-C(36)-C(35)  | 121.6(4) |
| C(37)-C(36)-H(36) | 119.2    | C(35)-C(36)-H(36)  | 119.2    |
| C(36)-C(37)-C(38) | 119.4(4) | C(36)-C(37)-H(37)  | 120.3    |
| C(38)-C(37)-H(37) | 120.3    | C(37)-C(38)-C(33)  | 120.5(4) |
| C(37)-C(38)-H(38) | 119.8    | C(33)-C(38)-H(38)  | 119.8    |
| C(40)-C(39)-O(3)  | 103(1)   | C(40)-C(39)-H(39A) | 111.2    |
| O(3)-C(39)-H(39A) | 111.2    | C(40)-C(39)-H(39B) | 111.2    |

## Appendix 1. Crystallographic data

|                     |       |                     |       |
|---------------------|-------|---------------------|-------|
| O(3)-C(39)-H(39B)   | 111.2 | H(39A)-C(39)-H(39B) | 109.1 |
| C(39)-C(40)-H(40A)  | 109.5 | C(39)-C(40)-H(40B)  | 109.5 |
| H(40A)-C(40)-H(40B) | 109.5 | C(39)-C(40)-H(40C)  | 109.5 |
| H(40A)-C(40)-H(40C) | 109.5 | H(40B)-C(40)-H(40C) | 109.5 |

----- standard deviations are given in the parenthesis.  
Symmetry operators ::  
1: x, y, z                      2: -x, -y, -z

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa570

| atom  | U11     | U22     | U33     | U23     | U13     | U12     |
|-------|---------|---------|---------|---------|---------|---------|
| Y(1)  | 31(1)   | 31(1)   | 27(1)   | 16(1)   | 16(1)   | 20(1)   |
| P(1)  | 26(1)   | 26(1)   | 29(1)   | 12(1)   | 13(1)   | 15(1)   |
| P(2)  | 28(1)   | 31(1)   | 26(1)   | 14(1)   | 14(1)   | 18(1)   |
| O(1)  | 37(2)   | 44(2)   | 38(2)   | 26(1)   | 24(1)   | 28(1)   |
| O(2)  | 33(2)   | 34(2)   | 31(2)   | 15(1)   | 16(1)   | 15(1)   |
| O(3)  | 41(2)   | 28(2)   | 29(2)   | 12(1)   | 10(1)   | 19(1)   |
| N(1)  | 32(2)   | 31(2)   | 35(2)   | 16(2)   | 19(2)   | 18(2)   |
| N(2)  | 29(2)   | 32(2)   | 29(2)   | 17(2)   | 17(2)   | 19(2)   |
| C(1)  | 36(2)   | 26(2)   | 31(2)   | 14(2)   | 18(2)   | 17(2)   |
| C(2)  | 25(2)   | 34(2)   | 29(2)   | 10(2)   | 11(2)   | 15(2)   |
| C(3)  | 23(2)   | 26(2)   | 31(2)   | 11(2)   | 12(2)   | 10(2)   |
| C(4)  | 34(2)   | 32(2)   | 24(2)   | 11(2)   | 17(2)   | 19(2)   |
| C(5)  | 42(3)   | 33(2)   | 48(3)   | 21(2)   | 24(2)   | 18(2)   |
| C(6)  | 38(3)   | 39(2)   | 58(3)   | 22(2)   | 24(2)   | 13(2)   |
| C(7)  | 27(2)   | 47(3)   | 58(3)   | 24(2)   | 13(2)   | 17(2)   |
| C(8)  | 28(2)   | 37(2)   | 52(3)   | 23(2)   | 17(2)   | 17(2)   |
| C(9)  | 34(2)   | 29(2)   | 33(2)   | 14(2)   | 16(2)   | 21(2)   |
| C(10) | 32(2)   | 28(2)   | 37(2)   | 14(2)   | 14(2)   | 14(2)   |
| C(11) | 49(3)   | 30(2)   | 38(2)   | 13(2)   | 16(2)   | 17(2)   |
| C(12) | 63(3)   | 40(2)   | 34(2)   | 14(2)   | 20(2)   | 33(3)   |
| C(13) | 45(3)   | 59(3)   | 49(3)   | 14(2)   | 26(3)   | 34(3)   |
| C(14) | 37(3)   | 51(3)   | 43(3)   | 6(2)    | 17(2)   | 25(2)   |
| C(15) | 23(2)   | 30(2)   | 35(2)   | 17(2)   | 12(2)   | 12(2)   |
| C(16) | 39(3)   | 37(2)   | 51(3)   | 24(2)   | 27(2)   | 22(2)   |
| C(17) | 59(3)   | 56(3)   | 87(4)   | 50(3)   | 45(3)   | 42(3)   |
| C(18) | 49(3)   | 77(4)   | 81(4)   | 60(3)   | 36(3)   | 42(3)   |
| C(19) | 38(3)   | 58(3)   | 42(3)   | 28(2)   | 13(2)   | 18(2)   |
| C(20) | 40(3)   | 42(3)   | 39(2)   | 18(2)   | 16(2)   | 21(2)   |
| C(21) | 26(2)   | 31(2)   | 25(2)   | 9(2)    | 12(2)   | 15(2)   |
| C(22) | 35(2)   | 31(2)   | 26(2)   | 10(2)   | 16(2)   | 20(2)   |
| C(23) | 31(2)   | 40(2)   | 35(2)   | 10(2)   | 16(2)   | 17(2)   |
| C(24) | 35(3)   | 52(3)   | 27(2)   | 9(2)    | 5(2)    | 28(2)   |
| C(25) | 44(3)   | 49(3)   | 30(2)   | 18(2)   | 15(2)   | 29(2)   |
| C(26) | 33(2)   | 40(2)   | 31(2)   | 15(2)   | 15(2)   | 20(2)   |
| C(27) | 29(2)   | 35(2)   | 22(2)   | 13(2)   | 13(2)   | 16(2)   |
| C(28) | 37(2)   | 36(2)   | 38(2)   | 18(2)   | 20(2)   | 20(2)   |
| C(29) | 42(3)   | 36(2)   | 47(3)   | 21(2)   | 24(2)   | 17(2)   |
| C(30) | 47(3)   | 46(3)   | 44(3)   | 19(2)   | 30(2)   | 18(2)   |
| C(31) | 45(3)   | 51(3)   | 46(3)   | 19(2)   | 31(2)   | 24(2)   |
| C(32) | 37(2)   | 35(2)   | 32(2)   | 10(2)   | 16(2)   | 18(2)   |
| C(33) | 28(2)   | 36(2)   | 30(2)   | 17(2)   | 18(2)   | 18(2)   |
| C(34) | 43(3)   | 40(2)   | 28(2)   | 17(2)   | 15(2)   | 24(2)   |
| C(35) | 60(3)   | 37(2)   | 37(2)   | 13(2)   | 19(2)   | 29(2)   |
| C(36) | 58(3)   | 37(2)   | 47(3)   | 22(2)   | 26(2)   | 31(2)   |
| C(37) | 38(3)   | 47(3)   | 37(2)   | 27(2)   | 19(2)   | 27(2)   |
| C(38) | 32(2)   | 41(2)   | 32(2)   | 16(2)   | 18(2)   | 23(2)   |
| C(39) | 310(10) | 92(6)   | 65(5)   | 54(5)   | 59(7)   | 140(10) |
| C(40) | 150(10) | 170(10) | 290(20) | 150(10) | 140(10) | 110(10) |

The anisotropic displacement factor exponent takes the form  
 $\frac{1}{2} \pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^*b^*U_{12}]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa570

| atom   | x     | y    | z          | U(eq) |
|--------|-------|------|------------|-------|
| H(1A)  | 483   | 2150 | 1944       | 35    |
| H(1B)  | -161  | 1254 | 781        | 35    |
| H(2A)  | -1508 | 1940 | 208        | 36    |
| H(2B)  | -1586 | 1755 | 1224       | 36    |
| H(5)   | 4465  | 6276 | 826        | 46    |
| H(6)   | 6355  | 6355 | 1561       | 54    |
| H(7)   | 6531  | 4971 | 2165       | 54    |
| H(8)   | 4730  | 3446 | 1934       | 45    |
| H(10)  | -190  | 1055 | -888       | 39    |
| H(11)  | -771  | -174 | -2535.0002 | 49    |
| H(12)  | 768   | -121 | -3058      | 52    |
| H(13)  | 2847  | 1070 | -1949.9999 | 57    |
| H(14)  | 3450  | 2246 | -278       | 54    |
| H(16)  | 2515  | 706  | 697        | 45    |
| H(17)  | 3240  | -25  | 1887       | 65    |
| H(18)  | 3840  | 878  | 3638       | 68    |
| H(19)  | 3590  | 2424 | 4185       | 57    |
| H(20)  | 2854  | 3158 | 3010       | 48    |
| H(23)  | 4089  | 5920 | 3948       | 43    |
| H(24)  | 4487  | 5417 | 5367       | 47    |
| H(25)  | 2864  | 4294 | 5675       | 46    |
| H(26)  | 796   | 3657 | 4529       | 40    |
| H(28)  | -969  | 1883 | 2913       | 41    |
| H(29)  | -2394 | 765  | 3398       | 48    |
| H(30)  | -3658 | 1366 | 3875       | 53    |
| H(31)  | -3558 | 3062 | 3804       | 52    |
| H(32)  | -2151 | 4170 | 3295       | 41    |
| H(34)  | 607   | 6024 | 4306       | 42    |
| H(35)  | 425   | 7656 | 4492       | 53    |
| H(36)  | -708  | 7844 | 3028       | 51    |
| H(37)  | -1697 | 6427 | 1405       | 43    |
| H(38)  | -1551 | 4788 | 1227       | 38    |
| H(39A) | 2745  | 6976 | 1692       | 175   |
| H(39B) | 2313  | 7632 | 1005       | 175   |
| H(40A) | 1130  | 7753 | 1819       | 245   |
| H(40B) | 2588  | 8406 | 2587       | 245   |
| H(40C) | 1696  | 7206 | 2549       | 245   |

**Complex 44**

Table 1. Crystal data for pa574

|   |  |
|---|--|
| Compound                                    | pa574  |
| Molecular formula                           | C <sub>84</sub> H <sub>82</sub> N <sub>4</sub> O <sub>6</sub> P <sub>4</sub> Y <sub>2</sub> ·2(C <sub>7</sub> H <sub>8</sub> ) |
| Molecular weight                            | 1821.64  |
| Crystal habit                               | Colorless Block  |
| Crystal dimensions(mm)                      | 0.20x0.10x0.04   |
| Crystal system                              | triclinic  |
| Space group                                 | Pbar1  |
| a(Å)  | 10.5300(10)  |
| b(Å)  | 14.5750(10)  |
| c(Å)  | 16.4300(10)  |
| α(°)  | 65.4360(10)  |
| β(°)  | 87.9590(10)  |
| γ(°)  | 89.2980(10)  |
| V(Å <sup>3</sup> )                          | 2291.9(3)  |
| Z   | 1  |
| d(g·cm <sup>-3</sup> )                      | 1.320  |
| F(000)                                      | 950  |
| μ(cm <sup>-1</sup> )                        | 1.387  |
| Absorption corrections                      | multi-scan ; 0.7689 min, 0.9466 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 25.03  |
| HKL ranges                                  | -12 12 ; -17 17 ; -19 19   |
| Reflections measured                        | 27447  |
| Unique data                                 | 8058   |
| Rint  | 0.0582   |
| Reflections used                            | 6609   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | mixed  |
| Parameters refined                          | 518  |
| Reflections / parameter                     | 12   |
| wR2   | 0.1134   |
| R1  | 0.0562   |
| Weights a, b                                | 0.0275 ; 6.0762  |
| GoF   | 1.066  |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.193(0.079) / -0.506(0.079)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa574

| atom  | x        | y        | z       | U(eq) |
|-------|----------|----------|---------|-------|
| Y(1)  | 4452(1)  | 4295(1)  | 1229(1) | 23(1) |
| P(1)  | 5415(1)  | 2381(1)  | 3249(1) | 30(1) |
| P(2)  | 5154(1)  | 6610(1)  | 1269(1) | 28(1) |
| O(1)  | 4094(3)  | 2688(2)  | 1573(2) | 32(1) |
| O(2)  | 4244(2)  | 5760(2)  | -88(2)  | 25(1) |
| O(3)  | 2662(3)  | 4558(2)  | 1664(2) | 32(1) |
| N(1)  | 5691(3)  | 5528(2)  | 1430(2) | 32(1) |
| N(2)  | 5714(3)  | 3499(2)  | 2524(2) | 33(1) |
| C(1)  | 6387(6)  | 4208(4)  | 2798(4) | 68(2) |
| C(2)  | 6739(5)  | 5116(4)  | 2044(4) | 58(2) |
| C(3)  | 5253(4)  | 1500(3)  | 2761(3) | 30(1) |
| C(4)  | 4579(4)  | 1785(3)  | 1968(3) | 28(1) |
| C(5)  | 4427(4)  | 1056(3)  | 1622(3) | 36(1) |
| C(6)  | 4915(5)  | 99(3)    | 2060(3) | 44(1) |
| C(7)  | 5567(5)  | -185(3)  | 2845(3) | 44(1) |
| C(8)  | 5730(4)  | 517(3)   | 3189(3) | 40(1) |
| C(9)  | 4005(4)  | 2271(3)  | 3940(3) | 33(1) |
| C(10) | 3341(4)  | 1372(3)  | 4364(3) | 42(1) |
| C(11) | 2335(5)  | 1288(4)  | 4954(3) | 47(1) |
| C(12) | 1976(5)  | 2100(4)  | 5131(3) | 49(1) |
| C(13) | 2595(5)  | 3005(4)  | 4688(4) | 59(2) |
| C(14) | 3606(5)  | 3099(4)  | 4094(3) | 51(1) |
| C(15) | 6676(4)  | 1900(3)  | 4045(3) | 32(1) |
| C(16) | 6455(4)  | 1563(3)  | 4964(3) | 38(1) |
| C(17) | 7455(5)  | 1215(4)  | 5544(3) | 46(1) |
| C(18) | 8668(5)  | 1212(4)  | 5211(3) | 50(1) |
| C(19) | 8900(5)  | 1545(4)  | 4301(3) | 49(1) |
| C(20) | 7910(4)  | 1889(3)  | 3719(3) | 42(1) |
| C(21) | 3834(4)  | 6960(3)  | 542(3)  | 27(1) |
| C(22) | 3599(4)  | 6551(3)  | -81(2)  | 25(1) |
| C(23) | 2634(4)  | 6984(3)  | -698(3) | 34(1) |
| C(24) | 1906(4)  | 7765(3)  | -681(3) | 37(1) |
| C(25) | 2107(4)  | 8150(3)  | -53(3)  | 41(1) |
| C(26) | 3051(4)  | 7752(3)  | 543(3)  | 35(1) |
| C(27) | 6346(4)  | 7589(3)  | 785(3)  | 30(1) |
| C(28) | 6136(5)  | 8579(3)  | 692(3)  | 38(1) |
| C(29) | 7056(5)  | 9307(3)  | 297(3)  | 47(1) |
| C(30) | 8193(5)  | 9066(4)  | -8(3)   | 52(1) |
| C(31) | 8413(5)  | 8108(4)  | 63(3)   | 47(1) |
| C(32) | 7488(4)  | 7368(3)  | 456(3)  | 36(1) |
| C(33) | 4624(5)  | 6656(3)  | 2312(3) | 38(1) |
| C(34) | 3542(5)  | 6102(4)  | 2738(3) | 48(1) |
| C(35) | 3187(6)  | 5974(4)  | 3597(4) | 66(2) |
| C(36) | 3924(8)  | 6389(5)  | 4034(4) | 88(2) |
| C(37) | 5009(8)  | 6915(5)  | 3633(4) | 93(3) |
| C(38) | 5364(6)  | 7061(4)  | 2771(3) | 65(2) |
| C(39) | 1346(4)  | 4434(3)  | 1661(3) | 34(1) |
| C(40) | 899(5)   | 3624(4)  | 2561(4) | 68(2) |
| C(41) | 669(5)   | 5433(4)  | 1479(4) | 59(2) |
| C(42) | 1055(6)  | 4102(5)  | 919(4)  | 70(2) |
| C(43) | 969(7)   | 10867(5) | 2495(4) | 83(2) |
| C(44) | 498(6)   | 9970(4)  | 2391(3) | 58(2) |
| C(45) | -786(6)  | 9766(5)  | 2411(3) | 62(2) |
| C(46) | -1211(7) | 8957(6)  | 2307(4) | 80(2) |
| C(47) | -430(10) | 8296(6)  | 2173(4) | 86(2) |
| C(48) | 869(8)   | 8434(5)  | 2177(4) | 82(2) |
| C(49) | 1342(6)  | 9284(5)  | 2277(3) | 67(2) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa574

|                  |           |                  |          |
|------------------|-----------|------------------|----------|
| Y(1)-O(3)        | 2.079(3)  | Y(1)-O(1)        | 2.203(3) |
| Y(1)-O(2)#2      | 2.312(2)  | Y(1)-O(2)        | 2.338(2) |
| Y(1)-N(1)        | 2.372(3)  | Y(1)-N(2)        | 2.398(3) |
| Y(1)-Y(1)#2      | 3.8320(7) | P(1)-N(2)        | 1.596(3) |
| P(1)-C(3)        | 1.786(4)  | P(1)-C(9)        | 1.804(4) |
| P(1)-C(15)       | 1.818(4)  | P(2)-N(1)        | 1.586(3) |
| P(2)-C(21)       | 1.792(4)  | P(2)-C(27)       | 1.809(4) |
| P(2)-C(33)       | 1.811(4)  | O(1)-C(4)        | 1.308(5) |
| O(2)-C(22)       | 1.336(4)  | O(2)-Y(1)#2      | 2.312(2) |
| O(3)-C(39)       | 1.401(5)  | N(1)-C(2)        | 1.468(5) |
| N(2)-C(1)        | 1.484(6)  | C(1)-C(2)        | 1.429(7) |
| C(1)-H(1A)       | 0.9900    | C(1)-H(1B)       | 0.9900   |
| C(2)-H(2A)       | 0.9900    | C(2)-H(2B)       | 0.9900   |
| C(3)-C(8)        | 1.403(6)  | C(3)-C(4)        | 1.408(6) |
| C(4)-C(5)        | 1.409(6)  | C(5)-C(6)        | 1.380(6) |
| C(5)-H(5)        | 0.9500    | C(6)-C(7)        | 1.386(7) |
| C(6)-H(6)        | 0.9500    | C(7)-C(8)        | 1.373(6) |
| C(7)-H(7)        | 0.9500    | C(8)-H(8)        | 0.9500   |
| C(9)-C(10)       | 1.386(6)  | C(9)-C(14)       | 1.389(6) |
| C(10)-C(11)      | 1.381(6)  | C(10)-H(10)      | 0.9500   |
| C(11)-C(12)      | 1.377(7)  | C(11)-H(11)      | 0.9500   |
| C(12)-C(13)      | 1.373(7)  | C(12)-H(12)      | 0.9500   |
| C(13)-C(14)      | 1.386(7)  | C(13)-H(13)      | 0.9500   |
| C(14)-H(14)      | 0.9500    | C(15)-C(20)      | 1.390(6) |
| C(15)-C(16)      | 1.392(6)  | C(16)-C(17)      | 1.390(6) |
| C(16)-H(16)      | 0.9500    | C(17)-C(18)      | 1.373(7) |
| C(17)-H(17)      | 0.9500    | C(18)-C(19)      | 1.379(7) |
| C(18)-H(18)      | 0.9500    | C(19)-C(20)      | 1.383(6) |
| C(19)-H(19)      | 0.9500    | C(20)-H(20)      | 0.9500   |
| C(21)-C(26)      | 1.411(5)  | C(21)-C(22)      | 1.412(5) |
| C(22)-C(23)      | 1.408(6)  | C(23)-C(24)      | 1.374(6) |
| C(23)-H(23)      | 0.9500    | C(24)-C(25)      | 1.388(6) |
| C(24)-H(24)      | 0.9500    | C(25)-C(26)      | 1.367(6) |
| C(25)-H(25)      | 0.9500    | C(26)-H(26)      | 0.9500   |
| C(27)-C(32)      | 1.389(6)  | C(27)-C(28)      | 1.403(6) |
| C(28)-C(29)      | 1.376(6)  | C(28)-H(28)      | 0.9500   |
| C(29)-C(30)      | 1.379(7)  | C(29)-H(29)      | 0.9500   |
| C(30)-C(31)      | 1.370(7)  | C(30)-H(30)      | 0.9500   |
| C(31)-C(32)      | 1.391(6)  | C(31)-H(31)      | 0.9500   |
| C(32)-H(32)      | 0.9500    | C(33)-C(34)      | 1.392(6) |
| C(33)-C(38)      | 1.396(7)  | C(34)-C(35)      | 1.382(7) |
| C(34)-H(34)      | 0.9500    | C(35)-C(36)      | 1.38(1)  |
| C(35)-H(35)      | 0.9500    | C(36)-C(37)      | 1.37(1)  |
| C(36)-H(36)      | 0.9500    | C(37)-C(38)      | 1.378(7) |
| C(37)-H(37)      | 0.9500    | C(38)-H(38)      | 0.9500   |
| C(39)-C(40)      | 1.521(6)  | C(39)-C(42)      | 1.528(7) |
| C(39)-C(41)      | 1.531(6)  | C(40)-H(40A)     | 0.9800   |
| C(40)-H(40B)     | 0.9800    | C(40)-H(40C)     | 0.9800   |
| C(41)-H(41A)     | 0.9800    | C(41)-H(41B)     | 0.9800   |
| C(41)-H(41C)     | 0.9800    | C(42)-H(42A)     | 0.9800   |
| C(42)-H(42B)     | 0.9800    | C(42)-H(42C)     | 0.9800   |
| C(43)-C(44)      | 1.481(8)  | C(43)-H(43A)     | 0.9800   |
| C(43)-H(43B)     | 0.9800    | C(43)-H(43C)     | 0.9800   |
| C(44)-C(45)      | 1.384(8)  | C(44)-C(49)      | 1.395(8) |
| C(45)-C(46)      | 1.34(1)   | C(45)-H(45)      | 0.9500   |
| C(46)-C(47)      | 1.34(1)   | C(46)-H(46)      | 0.9500   |
| C(47)-C(48)      | 1.38(1)   | C(47)-H(47)      | 0.9500   |
| C(48)-C(49)      | 1.41(1)   | C(48)-H(48)      | 0.9500   |
| C(49)-H(49)      | 0.9500    |                  |          |
| O(3)-Y(1)-O(1)   | 94.8(1)   | O(3)-Y(1)-O(2)#2 | 148.8(1) |
| O(1)-Y(1)-O(2)#2 | 85.2(1)   | O(3)-Y(1)-O(2)   | 89.2(1)  |
| O(1)-Y(1)-O(2)   | 133.0(1)  | O(2)#2-Y(1)-O(2) | 69.0(1)  |
| O(3)-Y(1)-N(1)   | 101.3(1)  | O(1)-Y(1)-N(1)   | 148.1(1) |
| O(2)#2-Y(1)-N(1) | 94.4(1)   | O(2)-Y(1)-N(1)   | 74.9(1)  |

|                   |           |                    |           |
|-------------------|-----------|--------------------|-----------|
| O(3)-Y(1)-N(2)    | 107.6(1)  | O(1)-Y(1)-N(2)     | 78.6(1)   |
| O(2)#2-Y(1)-N(2)  | 102.9(1)  | O(2)-Y(1)-N(2)     | 143.7(1)  |
| N(1)-Y(1)-N(2)    | 70.4(1)   | O(3)-Y(1)-Y(1)#2   | 120.54(8) |
| O(1)-Y(1)-Y(1)#2  | 111.42(7) | O(2)#2-Y(1)-Y(1)#2 | 34.72(6)  |
| O(2)-Y(1)-Y(1)#2  | 34.28(6)  | N(1)-Y(1)-Y(1)#2   | 83.6(1)   |
| N(2)-Y(1)-Y(1)#2  | 128.8(1)  | N(2)-P(1)-C(3)     | 112.9(2)  |
| N(2)-P(1)-C(9)    | 114.3(2)  | C(3)-P(1)-C(9)     | 107.1(2)  |
| N(2)-P(1)-C(15)   | 111.6(2)  | C(3)-P(1)-C(15)    | 106.2(2)  |
| C(9)-P(1)-C(15)   | 104.1(2)  | N(1)-P(2)-C(21)    | 112.2(2)  |
| N(1)-P(2)-C(27)   | 112.3(2)  | C(21)-P(2)-C(27)   | 107.5(2)  |
| N(1)-P(2)-C(33)   | 111.3(2)  | C(21)-P(2)-C(33)   | 107.4(2)  |
| C(27)-P(2)-C(33)  | 105.7(2)  | C(4)-O(1)-Y(1)     | 143.3(2)  |
| C(22)-O(2)-Y(1)#2 | 127.5(2)  | C(22)-O(2)-Y(1)    | 120.6(2)  |
| Y(1)#2-O(2)-Y(1)  | 111.0(1)  | C(39)-O(3)-Y(1)    | 147.2(3)  |
| C(2)-N(1)-P(2)    | 118.6(3)  | C(2)-N(1)-Y(1)     | 114.4(3)  |
| P(2)-N(1)-Y(1)    | 122.5(2)  | C(1)-N(2)-P(1)     | 119.2(3)  |
| C(1)-N(2)-Y(1)    | 114.6(3)  | P(1)-N(2)-Y(1)     | 121.6(2)  |
| C(2)-C(1)-N(2)    | 111.5(4)  | C(2)-C(1)-H(1A)    | 109.3     |
| N(2)-C(1)-H(1A)   | 109.3     | C(2)-C(1)-H(1B)    | 109.3     |
| N(2)-C(1)-H(1B)   | 109.3     | H(1A)-C(1)-H(1B)   | 108.0     |
| C(1)-C(2)-N(1)    | 112.2(4)  | C(1)-C(2)-H(2A)    | 109.2     |
| N(1)-C(2)-H(2A)   | 109.2     | C(1)-C(2)-H(2B)    | 109.2     |
| N(1)-C(2)-H(2B)   | 109.2     | H(2A)-C(2)-H(2B)   | 107.9     |
| C(8)-C(3)-C(4)    | 120.2(4)  | C(8)-C(3)-P(1)     | 120.4(3)  |
| C(4)-C(3)-P(1)    | 119.3(3)  | O(1)-C(4)-C(3)     | 121.2(3)  |
| O(1)-C(4)-C(5)    | 121.2(4)  | C(3)-C(4)-C(5)     | 117.7(4)  |
| C(6)-C(5)-C(4)    | 120.5(4)  | C(6)-C(5)-H(5)     | 119.8     |
| C(4)-C(5)-H(5)    | 119.8     | C(5)-C(6)-C(7)     | 121.9(4)  |
| C(5)-C(6)-H(6)    | 119.0     | C(7)-C(6)-H(6)     | 119.0     |
| C(8)-C(7)-C(6)    | 118.4(4)  | C(8)-C(7)-H(7)     | 120.8     |
| C(6)-C(7)-H(7)    | 120.8     | C(7)-C(8)-C(3)     | 121.4(4)  |
| C(7)-C(8)-H(8)    | 119.3     | C(3)-C(8)-H(8)     | 119.3     |
| C(10)-C(9)-C(14)  | 118.5(4)  | C(10)-C(9)-P(1)    | 122.2(3)  |
| C(14)-C(9)-P(1)   | 119.2(3)  | C(11)-C(10)-C(9)   | 120.7(4)  |
| C(11)-C(10)-H(10) | 119.6     | C(9)-C(10)-H(10)   | 119.6     |
| C(12)-C(11)-C(10) | 120.4(5)  | C(12)-C(11)-H(11)  | 119.8     |
| C(10)-C(11)-H(11) | 119.8     | C(13)-C(12)-C(11)  | 119.2(5)  |
| C(13)-C(12)-H(12) | 120.4     | C(11)-C(12)-H(12)  | 120.4     |
| C(12)-C(13)-C(14) | 120.9(5)  | C(12)-C(13)-H(13)  | 119.6     |
| C(14)-C(13)-H(13) | 119.6     | C(13)-C(14)-C(9)   | 120.1(5)  |
| C(13)-C(14)-H(14) | 119.9     | C(9)-C(14)-H(14)   | 120.0     |
| C(20)-C(15)-C(16) | 119.0(4)  | C(20)-C(15)-P(1)   | 118.5(3)  |
| C(16)-C(15)-P(1)  | 122.4(3)  | C(17)-C(16)-C(15)  | 120.2(4)  |
| C(17)-C(16)-H(16) | 119.9     | C(15)-C(16)-H(16)  | 119.9     |
| C(18)-C(17)-C(16) | 119.9(4)  | C(18)-C(17)-H(17)  | 120.0     |
| C(16)-C(17)-H(17) | 120.0     | C(17)-C(18)-C(19)  | 120.3(5)  |
| C(17)-C(18)-H(18) | 119.8     | C(19)-C(18)-H(18)  | 119.8     |
| C(18)-C(19)-C(20) | 120.1(5)  | C(18)-C(19)-H(19)  | 120.0     |
| C(20)-C(19)-H(19) | 120.0     | C(19)-C(20)-C(15)  | 120.4(4)  |
| C(19)-C(20)-H(20) | 119.8     | C(15)-C(20)-H(20)  | 119.8     |
| C(26)-C(21)-C(22) | 118.3(4)  | C(26)-C(21)-P(2)   | 117.6(3)  |
| C(22)-C(21)-P(2)  | 123.9(3)  | O(2)-C(22)-C(23)   | 119.6(3)  |
| O(2)-C(22)-C(21)  | 122.0(3)  | C(23)-C(22)-C(21)  | 118.4(3)  |
| C(24)-C(23)-C(22) | 121.2(4)  | C(24)-C(23)-H(23)  | 119.4     |
| C(22)-C(23)-H(23) | 119.4     | C(23)-C(24)-C(25)  | 120.6(4)  |
| C(23)-C(24)-H(24) | 119.7     | C(25)-C(24)-H(24)  | 119.7     |
| C(26)-C(25)-C(24) | 119.2(4)  | C(26)-C(25)-H(25)  | 120.4     |
| C(24)-C(25)-H(25) | 120.4     | C(25)-C(26)-C(21)  | 122.2(4)  |
| C(25)-C(26)-H(26) | 118.9     | C(21)-C(26)-H(26)  | 118.9     |
| C(32)-C(27)-C(28) | 118.6(4)  | C(32)-C(27)-P(2)   | 119.1(3)  |
| C(28)-C(27)-P(2)  | 122.3(3)  | C(29)-C(28)-C(27)  | 120.3(4)  |
| C(29)-C(28)-H(28) | 119.8     | C(27)-C(28)-H(28)  | 119.8     |
| C(28)-C(29)-C(30) | 120.1(4)  | C(28)-C(29)-H(29)  | 119.9     |
| C(30)-C(29)-H(29) | 119.9     | C(31)-C(30)-C(29)  | 120.7(5)  |
| C(31)-C(30)-H(30) | 119.7     | C(29)-C(30)-H(30)  | 119.7     |
| C(30)-C(31)-C(32) | 119.7(5)  | C(30)-C(31)-H(31)  | 120.2     |
| C(32)-C(31)-H(31) | 120.2     | C(27)-C(32)-C(31)  | 120.6(4)  |
| C(27)-C(32)-H(32) | 119.7     | C(31)-C(32)-H(32)  | 119.7     |

## Appendix 1. Crystallographic data

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(34)-C(33)-C(38)   | 119.1(4) | C(34)-C(33)-P(2)    | 117.0(3) |
| C(38)-C(33)-P(2)    | 122.9(4) | C(35)-C(34)-C(33)   | 120.5(5) |
| C(35)-C(34)-H(34)   | 119.7    | C(33)-C(34)-H(34)   | 119.7    |
| C(36)-C(35)-C(34)   | 119.4(6) | C(36)-C(35)-H(35)   | 120.3    |
| C(34)-C(35)-H(35)   | 120.3    | C(37)-C(36)-C(35)   | 120.8(5) |
| C(37)-C(36)-H(36)   | 119.6    | C(35)-C(36)-H(36)   | 119.6    |
| C(36)-C(37)-C(38)   | 120.3(6) | C(36)-C(37)-H(37)   | 119.8    |
| C(38)-C(37)-H(37)   | 119.8    | C(37)-C(38)-C(33)   | 119.8(6) |
| C(37)-C(38)-H(38)   | 120.1    | C(33)-C(38)-H(38)   | 120.1    |
| O(3)-C(39)-C(40)    | 109.1(4) | O(3)-C(39)-C(42)    | 108.5(4) |
| C(40)-C(39)-C(42)   | 109.4(5) | O(3)-C(39)-C(41)    | 110.1(4) |
| C(40)-C(39)-C(41)   | 110.5(4) | C(42)-C(39)-C(41)   | 109.1(4) |
| C(39)-C(40)-H(40A)  | 109.5    | C(39)-C(40)-H(40B)  | 109.5    |
| H(40A)-C(40)-H(40B) | 109.5    | C(39)-C(40)-H(40C)  | 109.5    |
| H(40A)-C(40)-H(40C) | 109.5    | H(40B)-C(40)-H(40C) | 109.5    |
| C(39)-C(41)-H(41A)  | 109.5    | C(39)-C(41)-H(41B)  | 109.5    |
| H(41A)-C(41)-H(41B) | 109.5    | C(39)-C(41)-H(41C)  | 109.5    |
| H(41A)-C(41)-H(41C) | 109.5    | C(39)-C(42)-H(42A)  | 109.5    |
| C(39)-C(42)-H(42A)  | 109.5    | C(39)-C(42)-H(42B)  | 109.5    |
| H(42A)-C(42)-H(42B) | 109.5    | C(39)-C(42)-H(42C)  | 109.5    |
| H(42A)-C(42)-H(42C) | 109.5    | H(42B)-C(42)-H(42C) | 109.5    |
| C(44)-C(43)-H(43A)  | 109.5    | C(44)-C(43)-H(43B)  | 109.5    |
| H(43A)-C(43)-H(43B) | 109.5    | C(44)-C(43)-H(43C)  | 109.5    |
| H(43A)-C(43)-H(43C) | 109.5    | H(43B)-C(43)-H(43C) | 109.5    |
| C(45)-C(44)-C(49)   | 117.0(6) | C(45)-C(44)-C(43)   | 122.1(6) |
| C(49)-C(44)-C(43)   | 120.9(6) | C(46)-C(45)-C(44)   | 122.0(6) |
| C(46)-C(45)-H(45)   | 119.0    | C(44)-C(45)-H(45)   | 119.0    |
| C(45)-C(46)-C(47)   | 122.6(7) | C(45)-C(46)-H(46)   | 118.7    |
| C(47)-C(46)-H(46)   | 118.7    | C(46)-C(47)-C(48)   | 118.5(7) |
| C(46)-C(47)-H(47)   | 120.7    | C(48)-C(47)-H(47)   | 120.7    |
| C(47)-C(48)-C(49)   | 120.0(7) | C(47)-C(48)-H(48)   | 120.0    |
| C(49)-C(48)-H(48)   | 120.0    | C(44)-C(49)-C(48)   | 119.9(6) |
| C(44)-C(49)-H(49)   | 120.1    | C(48)-C(49)-H(49)   | 120.1    |

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Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z                      2: -x, -y, -z

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa574

| atom  | U11    | U22   | U33   | U23    | U13    | U12    |
|-------|--------|-------|-------|--------|--------|--------|
| Y(1)  | 24(1)  | 21(1) | 22(1) | -8(1)  | -1(1)  | -2(1)  |
| P(1)  | 35(1)  | 24(1) | 27(1) | -5(1)  | -7(1)  | -3(1)  |
| P(2)  | 32(1)  | 23(1) | 31(1) | -13(1) | -1(1)  | -3(1)  |
| O(1)  | 36(2)  | 23(2) | 34(2) | -10(1) | -9(1)  | -4(1)  |
| O(2)  | 28(2)  | 23(1) | 25(1) | -10(1) | -2(1)  | 4(1)   |
| O(3)  | 22(2)  | 35(2) | 36(2) | -13(1) | 2(1)   | -2(1)  |
| N(1)  | 27(2)  | 25(2) | 44(2) | -13(2) | -13(2) | 1(2)   |
| N(2)  | 39(2)  | 24(2) | 31(2) | -7(2)  | -10(2) | -5(2)  |
| C(1)  | 88(4)  | 34(3) | 67(4) | -1(3)  | -45(3) | -22(3) |
| C(2)  | 52(3)  | 32(3) | 83(4) | -15(3) | -39(3) | -1(2)  |
| C(3)  | 33(2)  | 26(2) | 28(2) | -6(2)  | 1(2)   | -5(2)  |
| C(4)  | 30(2)  | 24(2) | 27(2) | -8(2)  | -1(2)  | -7(2)  |
| C(5)  | 45(3)  | 30(2) | 34(2) | -15(2) | -4(2)  | -2(2)  |
| C(6)  | 57(3)  | 32(2) | 48(3) | -23(2) | 7(2)   | -3(2)  |
| C(7)  | 49(3)  | 30(2) | 48(3) | -11(2) | -7(2)  | 7(2)   |
| C(8)  | 45(3)  | 31(2) | 36(2) | -7(2)  | -11(2) | 3(2)   |
| C(9)  | 34(2)  | 30(2) | 29(2) | -6(2)  | -6(2)  | 2(2)   |
| C(10) | 40(3)  | 30(2) | 47(3) | -8(2)  | -3(2)  | 2(2)   |
| C(11) | 38(3)  | 41(3) | 50(3) | -6(2)  | -1(2)  | -4(2)  |
| C(12) | 40(3)  | 64(3) | 43(3) | -22(3) | -2(2)  | 3(3)   |
| C(13) | 65(4)  | 58(3) | 67(4) | -39(3) | 7(3)   | -3(3)  |
| C(14) | 56(3)  | 42(3) | 59(3) | -27(3) | 6(3)   | -9(2)  |
| C(15) | 37(3)  | 24(2) | 31(2) | -7(2)  | -8(2)  | -6(2)  |
| C(16) | 36(3)  | 42(3) | 31(2) | -10(2) | -7(2)  | 1(2)   |
| C(17) | 46(3)  | 55(3) | 28(2) | -7(2)  | -10(2) | -4(2)  |
| C(18) | 46(3)  | 49(3) | 41(3) | -5(2)  | -16(2) | -4(2)  |
| C(19) | 39(3)  | 54(3) | 37(3) | -2(2)  | -5(2)  | -6(2)  |
| C(20) | 41(3)  | 43(3) | 30(2) | -3(2)  | -3(2)  | -6(2)  |
| C(21) | 28(2)  | 23(2) | 31(2) | -10(2) | 3(2)   | -4(2)  |
| C(22) | 25(2)  | 21(2) | 26(2) | -8(2)  | 6(2)   | -2(2)  |
| C(23) | 31(2)  | 32(2) | 34(2) | -9(2)  | -4(2)  | 0(2)   |
| C(24) | 29(2)  | 28(2) | 46(3) | -7(2)  | -4(2)  | 5(2)   |
| C(25) | 29(2)  | 29(2) | 62(3) | -18(2) | 0(2)   | 5(2)   |
| C(26) | 37(3)  | 28(2) | 45(3) | -21(2) | 4(2)   | -3(2)  |
| C(27) | 37(2)  | 28(2) | 25(2) | -12(2) | -1(2)  | -7(2)  |
| C(28) | 50(3)  | 30(2) | 38(2) | -18(2) | 1(2)   | -5(2)  |
| C(29) | 66(4)  | 28(2) | 47(3) | -16(2) | -6(3)  | -11(2) |
| C(30) | 58(4)  | 48(3) | 44(3) | -14(2) | 1(2)   | -27(3) |
| C(31) | 33(3)  | 63(3) | 47(3) | -24(3) | 5(2)   | -11(2) |
| C(32) | 36(3)  | 34(2) | 41(3) | -17(2) | -3(2)  | 0(2)   |
| C(33) | 58(3)  | 30(2) | 31(2) | -16(2) | 3(2)   | -6(2)  |
| C(34) | 61(3)  | 40(3) | 40(3) | -15(2) | 11(2)  | -3(2)  |
| C(35) | 95(5)  | 54(3) | 50(3) | -24(3) | 26(3)  | -12(3) |
| C(36) | 155(7) | 72(4) | 47(3) | -36(3) | 38(4)  | -33(5) |
| C(37) | 163(8) | 84(5) | 42(3) | -38(3) | 13(4)  | -51(5) |
| C(38) | 101(5) | 59(3) | 39(3) | -26(3) | 7(3)   | -33(3) |
| C(39) | 21(2)  | 41(3) | 37(2) | -14(2) | 3(2)   | -6(2)  |
| C(40) | 43(3)  | 68(4) | 59(4) | 5(3)   | 9(3)   | -10(3) |
| C(41) | 28(3)  | 54(3) | 87(4) | -23(3) | 4(3)   | 5(2)   |
| C(42) | 51(4)  | 93(5) | 80(4) | -47(4) | -24(3) | 1(3)   |
| C(43) | 104(6) | 72(4) | 61(4) | -15(3) | -2(4)  | -7(4)  |
| C(44) | 66(4)  | 69(4) | 28(3) | -8(3)  | -2(2)  | -1(3)  |
| C(45) | 56(4)  | 69(4) | 45(3) | -6(3)  | -6(3)  | 2(3)   |
| C(46) | 75(5)  | 86(5) | 72(4) | -26(4) | -11(4) | 1(4)   |
| C(47) | 108(7) | 91(5) | 58(4) | -30(4) | -7(4)  | -13(5) |
| C(48) | 117(7) | 73(5) | 46(3) | -15(3) | 10(4)  | 26(4)  |
| C(49) | 67(4)  | 83(5) | 34(3) | -9(3)  | 3(3)   | 9(3)   |

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The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U(11) + \dots + 2hka^*b^*U(12)]$

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa574

| atom   | x     | y     | z     | U(eq) |
|--------|-------|-------|-------|-------|
| H(1A)  | 5829  | 4374  | 3216  | 82    |
| H(1B)  | 7159  | 3878  | 3119  | 82    |
| H(2A)  | 7471  | 4978  | 1717  | 69    |
| H(2B)  | 7009  | 5624  | 2257  | 69    |
| H(5)   | 3985  | 1226  | 1085  | 43    |
| H(6)   | 4801  | -380  | 1815  | 52    |
| H(7)   | 5893  | -849  | 3139  | 53    |
| H(8)   | 6175  | 334   | 3727  | 47    |
| H(10)  | 3580  | 806   | 4247  | 50    |
| H(11)  | 1889  | 666   | 5238  | 57    |
| H(12)  | 1306  | 2034  | 5554  | 59    |
| H(13)  | 2328  | 3574  | 4789  | 71    |
| H(14)  | 4026  | 3730  | 3792  | 61    |
| H(16)  | 5617  | 1570  | 5195  | 46    |
| H(17)  | 7299  | 981   | 6172  | 55    |
| H(18)  | 9351  | 978   | 5608  | 60    |
| H(19)  | 9741  | 1538  | 4074  | 59    |
| H(20)  | 8074  | 2119  | 3093  | 50    |
| H(23)  | 2484  | 6731  | -1134 | 40    |
| H(24)  | 1260  | 8044  | -1104 | 45    |
| H(25)  | 1594  | 8684  | -37   | 49    |
| H(26)  | 3185  | 8017  | 973   | 42    |
| H(28)  | 5355  | 8749  | 903   | 46    |
| H(29)  | 6907  | 9978  | 234   | 56    |
| H(30)  | 8830  | 9570  | -269  | 62    |
| H(31)  | 9195  | 7950  | -156  | 57    |
| H(32)  | 7637  | 6705  | 500   | 44    |
| H(34)  | 3044  | 5809  | 2437  | 57    |
| H(35)  | 2441  | 5603  | 3883  | 79    |
| H(36)  | 3677  | 6309  | 4622  | 106   |
| H(37)  | 5521  | 7180  | 3949  | 111   |
| H(38)  | 6109  | 7436  | 2492  | 77    |
| H(40A) | 1370  | 2999  | 2680  | 102   |
| H(40B) | -11   | 3500  | 2548  | 102   |
| H(40C) | 1051  | 3849  | 3034  | 102   |
| H(41A) | 856   | 5651  | 1952  | 89    |
| H(41B) | -250  | 5340  | 1471  | 89    |
| H(41C) | 968   | 5946  | 899   | 89    |
| H(42A) | 1362  | 4616  | 341   | 105   |
| H(42B) | 136   | 4016  | 906   | 105   |
| H(42C) | 1482  | 3461  | 1035  | 105   |
| H(43A) | 245   | 11274 | 2544  | 125   |
| H(43B) | 1509  | 11272 | 1973  | 125   |
| H(43C) | 1464  | 10650 | 3037  | 125   |
| H(45)  | -1384 | 10211 | 2500  | 75    |
| H(46)  | -2102 | 8849  | 2328  | 96    |
| H(47)  | -754  | 7745  | 2077  | 103   |
| H(48)  | 1442  | 7957  | 2112  | 99    |
| H(49)  | 2233  | 9388  | 2266  | 80    |

**Complex 45**

Table 1. Crystal data for pa653

|   |  |
|---|--|
| Compound                                      | pa653  |
| Molecular formula                             | $\text{C}_{58}\text{H}_{73}\text{N}_2\text{O}_3\text{P}_2\text{Y}$ |
| Molecular weight                              | 997.03   |
| Crystal habit                                 | Colorless Block  |
| Crystal dimensions(mm)                        | 0.30x0.12x0.06   |
| Crystal system                                | monoclinic   |
| Space group                                   | C2/c   |
| a( $\text{\AA}$ )                             | 20.514(1)  |
| b( $\text{\AA}$ )                             | 27.064(1)  |
| c( $\text{\AA}$ )                             | 22.120(1)  |
| $\alpha(^{\circ})$                            | 90.00  |
| $\beta(^{\circ})$                             | 117.231(1)   |
| $\gamma(^{\circ})$                            | 90.00  |
| V( $\text{\AA}^3$ )                           | 10919.7(8)   |
| Z   | 8  |
| d(g·cm <sup>-3</sup> )                        | 1.213  |
| F(000)  | 4224   |
| $\mu(\text{cm}^{-1})$                         | 1.170  |
| Absorption corrections                        | multi-scan ; 0.7204 min, 0.9331 max                                |
| Diffractionmeter                              | KappaCCD   |
| X-ray source                                  | MoK $\alpha$   |
| $\lambda(\text{\AA})$                         | 0.71069  |
| Monochromator                                 | graphite   |
| T (K)   | 150.0(1)   |
| Scan mode                                     | phi and omega scans  |
| Maximum $\theta$                              | 26.02  |
| HKL ranges                                    | -25 21 ; -32 33 ; -27 27   |
| Reflections measured                          | 41731  |
| Unique data                                   | 10687  |
| Rint  | 0.0514   |
| Reflections used                              | 8400   |
| Criterion                                     | I > 2 $\sigma$ (I)   |
| Refinement type                               | Fsqd   |
| Hydrogen atoms                                | constr   |
| Parameters refined                            | 610  |
| Reflections / parameter                       | 13   |
| wR2   | 0.0813   |
| R1  | 0.0458   |
| Weights a, b                                  | 0.0000 ; 33.731  |
| GoF   | 1.083  |
| difference peak / hole (e $\text{\AA}^{-3}$ ) | 0.416(0.063) / -0.305(0.063)                                       |



# Appendix 1. Crystallographic data

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa653

| atom  | x        | y       | z        | U(eq) |
|-------|----------|---------|----------|-------|
| Y(1)  | 366(1)   | 2359(1) | 670(1)   | 22(1) |
| P(1)  | 1732(1)  | 1423(1) | 1183(1)  | 22(1) |
| P(2)  | 1206(1)  | 3388(1) | 1646(1)  | 21(1) |
| O(1)  | 595(1)   | 1991(1) | -81(1)   | 28(1) |
| O(2)  | 109(1)   | 3104(1) | 265(1)   | 26(1) |
| O(3)  | -496(1)  | 2084(1) | 772(1)   | 37(1) |
| N(1)  | 1391(1)  | 1877(1) | 1404(1)  | 28(1) |
| N(2)  | 1049(1)  | 2815(1) | 1650(1)  | 25(1) |
| C(1)  | 1838(2)  | 2082(1) | 2094(1)  | 37(1) |
| C(2)  | 1429(2)  | 2483(1) | 2237(1)  | 36(1) |
| C(3)  | 1148(2)  | 1207(1) | 334(1)   | 23(1) |
| C(4)  | 645(2)   | 1516(1) | -188(1)  | 22(1) |
| C(5)  | 198(2)   | 1299(1) | -837(1)  | 23(1) |
| C(6)  | 302(2)   | 805(1)  | -930(1)  | 25(1) |
| C(7)  | 826(2)   | 501(1)  | -430(1)  | 25(1) |
| C(8)  | 1233(2)  | 709(1)  | 202(1)   | 26(1) |
| C(9)  | -378(2)  | 1610(1) | -1419(1) | 30(1) |
| C(10) | -930(2)  | 1839(1) | -1208(2) | 43(1) |
| C(11) | 7(2)     | 2020(1) | -1613(2) | 43(1) |
| C(12) | -823(2)  | 1297(1) | -2059(2) | 43(1) |
| C(13) | 922(2)   | -41(1)  | -582(2)  | 31(1) |
| C(14) | 404(3)   | -368(1) | -450(3)  | 73(1) |
| C(15) | 774(2)   | -102(1) | -1326(2) | 55(1) |
| C(16) | 1714(2)  | -210(1) | -152(2)  | 54(1) |
| C(17) | 2628(2)  | 1553(1) | 1249(1)  | 30(1) |
| C(18) | 2708(2)  | 1680(1) | 685(2)   | 48(1) |
| C(19) | 3392(2)  | 1792(2) | 739(2)   | 63(1) |
| C(20) | 3997(2)  | 1786(2) | 1356(2)  | 62(1) |
| C(21) | 3926(2)  | 1672(2) | 1926(2)  | 72(1) |
| C(22) | 3251(2)  | 1552(2) | 1877(2)  | 57(1) |
| C(23) | 1871(2)  | 898(1)  | 1740(1)  | 28(1) |
| C(24) | 1377(2)  | 841(1)  | 1999(2)  | 41(1) |
| C(25) | 1420(3)  | 436(2)  | 2396(2)  | 65(1) |
| C(26) | 1965(3)  | 87(2)   | 2543(2)  | 77(2) |
| C(27) | 2458(3)  | 141(1)  | 2294(2)  | 66(1) |
| C(28) | 2421(2)  | 545(1)  | 1894(2)  | 45(1) |
| C(29) | 410(2)   | 3737(1) | 1091(1)  | 23(1) |
| C(30) | -52(2)   | 3537(1) | 441(1)   | 23(1) |
| C(31) | -681(2)  | 3814(1) | -3(1)    | 25(1) |
| C(32) | -780(2)  | 4277(1) | 218(1)   | 27(1) |
| C(33) | -304(2)  | 4492(1) | 846(1)   | 26(1) |
| C(34) | 288(2)   | 4209(1) | 1277(1)  | 24(1) |
| C(35) | -1217(2) | 3609(1) | -703(1)  | 30(1) |
| C(36) | -820(2)  | 3495(1) | -1129(1) | 39(1) |
| C(37) | -1844(2) | 3972(1) | -1109(2) | 47(1) |
| C(38) | -1571(2) | 3129(1) | -612(2)  | 38(1) |
| C(39) | -449(2)  | 5019(1) | 1020(2)  | 30(1) |
| C(40) | -1133(2) | 5028(1) | 1130(2)  | 56(1) |
| C(41) | -561(2)  | 5372(1) | 441(2)   | 47(1) |
| C(42) | 195(2)   | 5213(1) | 1669(2)  | 45(1) |
| C(43) | 1905(2)  | 3528(1) | 1385(1)  | 26(1) |
| C(44) | 2014(2)  | 4008(1) | 1229(2)  | 38(1) |
| C(45) | 2559(2)  | 4108(1) | 1041(2)  | 49(1) |
| C(46) | 2993(2)  | 3734(2) | 1004(2)  | 45(1) |
| C(47) | 2872(2)  | 3255(1) | 1137(2)  | 44(1) |
| C(48) | 2331(2)  | 3151(1) | 1327(1)  | 33(1) |
| C(49) | 1523(2)  | 3635(1) | 2494(1)  | 21(1) |
| C(50) | 2220(2)  | 3824(1) | 2882(1)  | 31(1) |
| C(51) | 2434(2)  | 3959(1) | 3553(2)  | 40(1) |
| C(52) | 1963(2)  | 3903(1) | 3834(2)  | 38(1) |
| C(53) | 1270(2)  | 3714(1) | 3452(2)  | 35(1) |
| C(54) | 1054(2)  | 3581(1) | 2785(1)  | 31(1) |

# Appendix 1. Crystallographic data

|       |          |         |         |       |
|-------|----------|---------|---------|-------|
| C(55) | -1097(2) | 1963(1) | 882(2)  | 33(1) |
| C(56) | -1393(2) | 2429(1) | 1052(2) | 50(1) |
| C(57) | -1678(2) | 1727(1) | 236(2)  | 52(1) |
| C(58) | -846(2)  | 1601(1) | 1473(2) | 60(1) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa653

|              |          |              |          |
|--------------|----------|--------------|----------|
| Y(1)-O(3)    | 2.025(2) | Y(1)-O(1)    | 2.167(2) |
| Y(1)-O(2)    | 2.170(2) | Y(1)-N(2)    | 2.324(2) |
| Y(1)-N(1)    | 2.375(2) | P(1)-N(1)    | 1.595(2) |
| P(1)-C(3)    | 1.803(3) | P(1)-C(17)   | 1.812(3) |
| P(1)-C(23)   | 1.815(3) | P(2)-N(2)    | 1.584(2) |
| P(2)-C(29)   | 1.797(3) | P(2)-C(49)   | 1.809(3) |
| P(2)-C(43)   | 1.814(3) | O(1)-C(4)    | 1.319(3) |
| O(2)-C(30)   | 1.322(3) | O(3)-C(55)   | 1.399(3) |
| N(1)-C(1)    | 1.483(3) | N(2)-C(2)    | 1.476(3) |
| C(1)-C(2)    | 1.492(4) | C(1)-H(1A)   | 0.9900   |
| C(1)-H(1B)   | 0.9900   | C(2)-H(2A)   | 0.9900   |
| C(2)-H(2B)   | 0.9900   | C(3)-C(8)    | 1.405(4) |
| C(3)-C(4)    | 1.416(4) | C(4)-C(5)    | 1.429(4) |
| C(5)-C(6)    | 1.385(4) | C(5)-C(9)    | 1.541(4) |
| C(6)-C(7)    | 1.403(4) | C(6)-H(6)    | 0.9500   |
| C(7)-C(8)    | 1.378(4) | C(7)-C(13)   | 1.538(4) |
| C(8)-H(8)    | 0.9500   | C(9)-C(11)   | 1.531(4) |
| C(9)-C(10)   | 1.539(4) | C(9)-C(12)   | 1.541(4) |
| C(10)-H(10A) | 0.9800   | C(10)-H(10B) | 0.9800   |
| C(10)-H(10C) | 0.9800   | C(11)-H(11A) | 0.9800   |
| C(11)-H(11B) | 0.9800   | C(11)-H(11C) | 0.9800   |
| C(12)-H(12A) | 0.9800   | C(12)-H(12B) | 0.9800   |
| C(12)-H(12C) | 0.9800   | C(13)-C(14)  | 1.509(5) |
| C(13)-C(16)  | 1.529(5) | C(13)-C(15)  | 1.540(4) |
| C(14)-H(14A) | 0.9800   | C(14)-H(14B) | 0.9800   |
| C(14)-H(14C) | 0.9800   | C(15)-H(15A) | 0.9800   |
| C(15)-H(15B) | 0.9800   | C(15)-H(15C) | 0.9800   |
| C(16)-H(16A) | 0.9800   | C(16)-H(16B) | 0.9800   |
| C(16)-H(16C) | 0.9800   | C(17)-C(18)  | 1.374(4) |
| C(17)-C(22)  | 1.392(4) | C(18)-C(19)  | 1.387(5) |
| C(18)-H(18)  | 0.9500   | C(19)-C(20)  | 1.361(5) |
| C(19)-H(19)  | 0.9500   | C(20)-C(21)  | 1.369(5) |
| C(20)-H(20)  | 0.9500   | C(21)-C(22)  | 1.377(5) |
| C(21)-H(21)  | 0.9500   | C(22)-H(22)  | 0.9500   |
| C(23)-C(24)  | 1.381(4) | C(23)-C(28)  | 1.395(4) |
| C(24)-C(25)  | 1.381(5) | C(24)-H(24)  | 0.9500   |
| C(25)-C(26)  | 1.384(7) | C(25)-H(25)  | 0.9500   |
| C(26)-C(27)  | 1.363(7) | C(26)-H(26)  | 0.9500   |
| C(27)-C(28)  | 1.388(5) | C(27)-H(27)  | 0.9500   |
| C(28)-H(28)  | 0.9500   | C(29)-C(34)  | 1.400(4) |
| C(29)-C(30)  | 1.418(4) | C(30)-C(31)  | 1.426(4) |
| C(31)-C(32)  | 1.392(4) | C(31)-C(35)  | 1.536(4) |
| C(32)-C(33)  | 1.408(4) | C(32)-H(32)  | 0.9500   |
| C(33)-C(34)  | 1.382(4) | C(33)-C(39)  | 1.541(4) |
| C(34)-H(34)  | 0.9500   | C(35)-C(36)  | 1.533(4) |
| C(35)-C(37)  | 1.539(4) | C(35)-C(38)  | 1.545(4) |
| C(36)-H(36A) | 0.9800   | C(36)-H(36B) | 0.9800   |
| C(36)-H(36C) | 0.9800   | C(37)-H(37A) | 0.9800   |
| C(37)-H(37B) | 0.9800   | C(37)-H(37C) | 0.9800   |
| C(38)-H(38A) | 0.9800   | C(38)-H(38B) | 0.9800   |
| C(38)-H(38C) | 0.9800   | C(39)-C(41)  | 1.529(4) |
| C(39)-C(40)  | 1.531(4) | C(39)-C(42)  | 1.532(4) |
| C(40)-H(40A) | 0.9800   | C(40)-H(40B) | 0.9800   |
| C(40)-H(40C) | 0.9800   | C(41)-H(41A) | 0.9800   |
| C(41)-H(41B) | 0.9800   | C(41)-H(41C) | 0.9800   |
| C(42)-H(42A) | 0.9800   | C(42)-H(42B) | 0.9800   |
| C(42)-H(42C) | 0.9800   | C(43)-C(48)  | 1.388(4) |
| C(43)-C(44)  | 1.389(4) | C(44)-C(45)  | 1.386(4) |
| C(44)-H(44)  | 0.9500   | C(45)-C(46)  | 1.377(5) |
| C(45)-H(45)  | 0.9500   | C(46)-C(47)  | 1.377(5) |
| C(46)-H(46)  | 0.9500   | C(47)-C(48)  | 1.383(4) |
| C(47)-H(47)  | 0.9500   | C(48)-H(48)  | 0.9500   |
| C(49)-C(50)  | 1.383(4) | C(49)-C(54)  | 1.390(4) |
| C(50)-C(51)  | 1.390(4) | C(50)-H(50)  | 0.9500   |
| C(51)-C(52)  | 1.375(5) | C(51)-H(51)  | 0.9500   |
| C(52)-C(53)  | 1.377(4) | C(52)-H(52)  | 0.9500   |

|                     |           |                     |           |
|---------------------|-----------|---------------------|-----------|
| C(53)-C(54)         | 1.380(4)  | C(53)-H(53)         | 0.9500    |
| C(54)-H(54)         | 0.9500    | C(55)-C(56)         | 1.518(4)  |
| C(55)-C(58)         | 1.521(5)  | C(55)-C(57)         | 1.522(4)  |
| C(56)-H(56A)        | 0.9800    | C(56)-H(56B)        | 0.9800    |
| C(56)-H(56C)        | 0.9800    | C(57)-H(57A)        | 0.9800    |
| C(57)-H(57B)        | 0.9800    | C(57)-H(57C)        | 0.9800    |
| C(58)-H(58A)        | 0.9800    | C(58)-H(58B)        | 0.9800    |
| C(58)-H(58C)        | 0.9800    |                     |           |
| O(3)-Y(1)-O(1)      | 115.03(8) | O(3)-Y(1)-O(2)      | 109.16(8) |
| O(1)-Y(1)-O(2)      | 102.03(7) | O(3)-Y(1)-N(2)      | 106.04(8) |
| O(1)-Y(1)-N(2)      | 135.21(8) | O(2)-Y(1)-N(2)      | 79.68(7)  |
| O(3)-Y(1)-N(1)      | 105.5(1)  | O(1)-Y(1)-N(1)      | 80.51(7)  |
| O(2)-Y(1)-N(1)      | 139.87(8) | N(2)-Y(1)-N(1)      | 71.78(8)  |
| N(1)-P(1)-C(3)      | 113.2(1)  | N(1)-P(1)-C(17)     | 113.4(1)  |
| C(3)-P(1)-C(17)     | 108.2(1)  | N(1)-P(1)-C(23)     | 110.5(1)  |
| C(3)-P(1)-C(23)     | 106.0(1)  | C(17)-P(1)-C(23)    | 105.0(1)  |
| N(2)-P(2)-C(29)     | 113.2(1)  | N(2)-P(2)-C(49)     | 109.5(1)  |
| C(29)-P(2)-C(49)    | 107.3(1)  | N(2)-P(2)-C(43)     | 113.5(1)  |
| C(29)-P(2)-C(43)    | 106.0(1)  | C(49)-P(2)-C(43)    | 106.9(1)  |
| C(4)-O(1)-Y(1)      | 130.4(2)  | C(30)-O(2)-Y(1)     | 138.3(2)  |
| C(55)-O(3)-Y(1)     | 171.4(2)  | C(1)-N(1)-P(1)      | 116.9(2)  |
| C(1)-N(1)-Y(1)      | 115.7(2)  | P(1)-N(1)-Y(1)      | 126.1(1)  |
| C(2)-N(2)-P(2)      | 125.0(2)  | C(2)-N(2)-Y(1)      | 110.3(2)  |
| P(2)-N(2)-Y(1)      | 123.5(1)  | N(1)-C(1)-C(2)      | 110.4(2)  |
| N(1)-C(1)-H(1A)     | 109.6     | C(2)-C(1)-H(1A)     | 109.6     |
| N(1)-C(1)-H(1B)     | 109.6     | C(2)-C(1)-H(1B)     | 109.6     |
| H(1A)-C(1)-H(1B)    | 108.1     | N(2)-C(2)-C(1)      | 112.2(2)  |
| N(2)-C(2)-H(2A)     | 109.2     | C(1)-C(2)-H(2A)     | 109.2     |
| N(2)-C(2)-H(2B)     | 109.2     | C(1)-C(2)-H(2B)     | 109.2     |
| H(2A)-C(2)-H(2B)    | 107.9     | C(8)-C(3)-C(4)      | 120.7(2)  |
| C(8)-C(3)-P(1)      | 116.2(2)  | C(4)-C(3)-P(1)      | 123.1(2)  |
| O(1)-C(4)-C(3)      | 121.1(2)  | O(1)-C(4)-C(5)      | 120.9(2)  |
| C(3)-C(4)-C(5)      | 118.0(2)  | C(6)-C(5)-C(4)      | 118.3(2)  |
| C(6)-C(5)-C(9)      | 121.0(2)  | C(4)-C(5)-C(9)      | 120.6(2)  |
| C(5)-C(6)-C(7)      | 124.3(2)  | C(5)-C(6)-H(6)      | 117.9     |
| C(7)-C(6)-H(6)      | 117.9     | C(8)-C(7)-C(6)      | 116.8(2)  |
| C(8)-C(7)-C(13)     | 122.3(3)  | C(6)-C(7)-C(13)     | 121.0(2)  |
| C(7)-C(8)-C(3)      | 121.8(3)  | C(7)-C(8)-H(8)      | 119.1     |
| C(3)-C(8)-H(8)      | 119.1     | C(11)-C(9)-C(10)    | 109.8(3)  |
| C(11)-C(9)-C(12)    | 107.8(2)  | C(10)-C(9)-C(12)    | 107.0(3)  |
| C(11)-C(9)-C(5)     | 109.5(2)  | C(10)-C(9)-C(5)     | 110.7(2)  |
| C(12)-C(9)-C(5)     | 111.8(2)  | C(9)-C(10)-H(10A)   | 109.5     |
| C(9)-C(10)-H(10B)   | 109.5     | H(10A)-C(10)-H(10B) | 109.5     |
| C(9)-C(10)-H(10C)   | 109.5     | H(10A)-C(10)-H(10C) | 109.5     |
| H(10B)-C(10)-H(10C) | 109.5     | C(9)-C(11)-H(11A)   | 109.5     |
| C(9)-C(11)-H(11B)   | 109.5     | H(11A)-C(11)-H(11B) | 109.5     |
| C(9)-C(11)-H(11C)   | 109.5     | H(11A)-C(11)-H(11C) | 109.5     |
| H(11B)-C(11)-H(11C) | 109.5     | C(9)-C(12)-H(12A)   | 109.5     |
| C(9)-C(12)-H(12B)   | 109.5     | H(12A)-C(12)-H(12B) | 109.5     |
| C(9)-C(12)-H(12C)   | 109.5     | H(12A)-C(12)-H(12C) | 109.5     |
| H(12B)-C(12)-H(12C) | 109.5     | C(14)-C(13)-C(16)   | 110.3(3)  |
| C(14)-C(13)-C(7)    | 110.1(3)  | C(16)-C(13)-C(7)    | 110.8(2)  |
| C(14)-C(13)-C(15)   | 109.4(3)  | C(16)-C(13)-C(15)   | 105.5(3)  |
| C(7)-C(13)-C(15)    | 110.7(2)  | C(13)-C(14)-H(14A)  | 109.5     |
| C(13)-C(14)-H(14B)  | 109.5     | H(14A)-C(14)-H(14B) | 109.5     |
| C(13)-C(14)-H(14C)  | 109.5     | H(14A)-C(14)-H(14C) | 109.5     |
| H(14B)-C(14)-H(14C) | 109.5     | C(13)-C(15)-H(15A)  | 109.5     |
| C(13)-C(15)-H(15B)  | 109.5     | H(15A)-C(15)-H(15B) | 109.5     |
| C(13)-C(15)-H(15C)  | 109.5     | H(15A)-C(15)-H(15C) | 109.5     |
| H(15B)-C(15)-H(15C) | 109.5     | C(13)-C(16)-H(16A)  | 109.5     |
| C(13)-C(16)-H(16B)  | 109.5     | H(16A)-C(16)-H(16B) | 109.5     |
| C(13)-C(16)-H(16C)  | 109.5     | H(16A)-C(16)-H(16C) | 109.5     |
| H(16B)-C(16)-H(16C) | 109.5     | C(18)-C(17)-C(22)   | 118.1(3)  |
| C(18)-C(17)-P(1)    | 120.9(2)  | C(22)-C(17)-P(1)    | 121.0(2)  |
| C(17)-C(18)-C(19)   | 120.9(3)  | C(17)-C(18)-H(18)   | 119.6     |
| C(19)-C(18)-H(18)   | 119.6     | C(20)-C(19)-C(18)   | 120.4(4)  |

## Appendix 1. Crystallographic data

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(20)-C(19)-H(19)   | 119.8    | C(18)-C(19)-H(19)   | 119.8    |
| C(19)-C(20)-C(21)   | 119.6(4) | C(19)-C(20)-H(20)   | 120.2    |
| C(21)-C(20)-H(20)   | 120.2    | C(20)-C(21)-C(22)   | 120.5(4) |
| C(20)-C(21)-H(21)   | 119.7    | C(22)-C(21)-H(21)   | 119.7    |
| C(21)-C(22)-C(17)   | 120.5(3) | C(21)-C(22)-H(22)   | 119.7    |
| C(17)-C(22)-H(22)   | 119.7    | C(24)-C(23)-C(28)   | 119.1(3) |
| C(24)-C(23)-P(1)    | 116.8(2) | C(28)-C(23)-P(1)    | 124.0(3) |
| C(25)-C(24)-C(23)   | 120.4(4) | C(25)-C(24)-H(24)   | 119.8    |
| C(23)-C(24)-H(24)   | 119.8    | C(24)-C(25)-C(26)   | 120.0(4) |
| C(24)-C(25)-H(25)   | 120.0    | C(26)-C(25)-H(25)   | 120.0    |
| C(27)-C(26)-C(25)   | 120.1(4) | C(27)-C(26)-H(26)   | 120.0    |
| C(25)-C(26)-H(26)   | 120.0    | C(26)-C(27)-C(28)   | 120.5(4) |
| C(26)-C(27)-H(27)   | 119.8    | C(28)-C(27)-H(27)   | 119.8    |
| C(27)-C(28)-C(23)   | 119.8(4) | C(27)-C(28)-H(28)   | 120.1    |
| C(23)-C(28)-H(28)   | 120.1    | C(34)-C(29)-C(30)   | 121.3(2) |
| C(34)-C(29)-P(2)    | 120.5(2) | C(30)-C(29)-P(2)    | 118.0(2) |
| O(2)-C(30)-C(29)    | 119.6(2) | O(2)-C(30)-C(31)    | 122.2(2) |
| C(29)-C(30)-C(31)   | 118.2(2) | C(32)-C(31)-C(30)   | 117.6(2) |
| C(32)-C(31)-C(35)   | 121.8(2) | C(30)-C(31)-C(35)   | 120.6(2) |
| C(31)-C(32)-C(33)   | 124.9(3) | C(31)-C(32)-H(32)   | 117.6    |
| C(33)-C(32)-H(32)   | 117.6    | C(34)-C(33)-C(32)   | 116.4(2) |
| C(34)-C(33)-C(39)   | 123.4(3) | C(32)-C(33)-C(39)   | 120.2(2) |
| C(33)-C(34)-C(29)   | 121.5(3) | C(33)-C(34)-H(34)   | 119.2    |
| C(29)-C(34)-H(34)   | 119.2    | C(36)-C(35)-C(31)   | 110.7(2) |
| C(36)-C(35)-C(37)   | 107.9(3) | C(31)-C(35)-C(37)   | 112.2(2) |
| C(36)-C(35)-C(38)   | 109.0(2) | C(31)-C(35)-C(38)   | 109.6(2) |
| C(37)-C(35)-C(38)   | 107.3(3) | C(35)-C(36)-H(36A)  | 109.5    |
| C(35)-C(36)-H(36B)  | 109.5    | H(36A)-C(36)-H(36B) | 109.5    |
| C(35)-C(36)-H(36C)  | 109.5    | H(36A)-C(36)-H(36C) | 109.5    |
| H(36B)-C(36)-H(36C) | 109.5    | C(35)-C(37)-H(37A)  | 109.5    |
| C(35)-C(37)-H(37B)  | 109.5    | H(37A)-C(37)-H(37B) | 109.5    |
| C(35)-C(37)-H(37C)  | 109.5    | H(37A)-C(37)-H(37C) | 109.5    |
| H(37B)-C(37)-H(37C) | 109.5    | C(35)-C(38)-H(38A)  | 109.5    |
| C(35)-C(38)-H(38B)  | 109.5    | H(38A)-C(38)-H(38B) | 109.5    |
| C(35)-C(38)-H(38C)  | 109.5    | H(38A)-C(38)-H(38C) | 109.5    |
| H(38B)-C(38)-H(38C) | 109.5    | C(41)-C(39)-C(40)   | 109.1(3) |
| C(41)-C(39)-C(42)   | 107.8(3) | C(40)-C(39)-C(42)   | 107.7(3) |
| C(41)-C(39)-C(33)   | 110.0(2) | C(40)-C(39)-C(33)   | 110.5(2) |
| C(42)-C(39)-C(33)   | 111.6(2) | C(39)-C(40)-H(40A)  | 109.5    |
| C(39)-C(40)-H(40B)  | 109.5    | H(40A)-C(40)-H(40B) | 109.5    |
| C(39)-C(40)-H(40C)  | 109.5    | H(40A)-C(40)-H(40C) | 109.5    |
| H(40B)-C(40)-H(40C) | 109.5    | C(39)-C(41)-H(41A)  | 109.5    |
| C(39)-C(41)-H(41B)  | 109.5    | H(41A)-C(41)-H(41B) | 109.5    |
| C(39)-C(41)-H(41C)  | 109.5    | H(41A)-C(41)-H(41C) | 109.5    |
| H(41B)-C(41)-H(41C) | 109.5    | C(39)-C(42)-H(42A)  | 109.5    |
| C(39)-C(42)-H(42B)  | 109.5    | H(42A)-C(42)-H(42B) | 109.5    |
| C(39)-C(42)-H(42C)  | 109.5    | H(42A)-C(42)-H(42C) | 109.5    |
| H(42B)-C(42)-H(42C) | 109.5    | C(48)-C(43)-C(44)   | 119.1(3) |
| C(48)-C(43)-P(2)    | 119.9(2) | C(44)-C(43)-P(2)    | 121.0(2) |
| C(45)-C(44)-C(43)   | 120.0(3) | C(45)-C(44)-H(44)   | 120.0    |
| C(43)-C(44)-H(44)   | 120.0    | C(46)-C(45)-C(44)   | 120.5(3) |
| C(46)-C(45)-H(45)   | 119.7    | C(44)-C(45)-H(45)   | 119.7    |
| C(47)-C(46)-C(45)   | 119.7(3) | C(47)-C(46)-H(46)   | 120.2    |
| C(45)-C(46)-H(46)   | 120.2    | C(46)-C(47)-C(48)   | 120.3(3) |
| C(46)-C(47)-H(47)   | 119.8    | C(48)-C(47)-H(47)   | 119.8    |
| C(47)-C(48)-C(43)   | 120.4(3) | C(47)-C(48)-H(48)   | 119.8    |
| C(43)-C(48)-H(48)   | 119.8    | C(50)-C(49)-C(54)   | 119.3(2) |
| C(50)-C(49)-P(2)    | 124.0(2) | C(54)-C(49)-P(2)    | 116.4(2) |
| C(49)-C(50)-C(51)   | 119.4(3) | C(49)-C(50)-H(50)   | 120.3    |
| C(51)-C(50)-H(50)   | 120.3    | C(52)-C(51)-C(50)   | 120.6(3) |
| C(52)-C(51)-H(51)   | 119.7    | C(50)-C(51)-H(51)   | 119.7    |
| C(51)-C(52)-C(53)   | 120.3(3) | C(51)-C(52)-H(52)   | 119.9    |
| C(53)-C(52)-H(52)   | 119.9    | C(52)-C(53)-C(54)   | 119.4(3) |
| C(52)-C(53)-H(53)   | 120.3    | C(54)-C(53)-H(53)   | 120.3    |
| C(53)-C(54)-C(49)   | 121.0(3) | C(53)-C(54)-H(54)   | 119.5    |
| C(49)-C(54)-H(54)   | 119.5    | O(3)-C(55)-C(56)    | 109.5(3) |
| O(3)-C(55)-C(58)    | 108.8(3) | C(56)-C(55)-C(58)   | 109.8(3) |
| O(3)-C(55)-C(57)    | 107.9(2) | C(56)-C(55)-C(57)   | 110.5(3) |

## Appendix 1. Crystallographic data

|                     |          |                     |       |
|---------------------|----------|---------------------|-------|
| C(58)-C(55)-C(57)   | 110.3(3) | C(55)-C(56)-H(56A)  | 109.5 |
| C(55)-C(56)-H(56B)  | 109.5    | H(56A)-C(56)-H(56B) | 109.5 |
| C(55)-C(56)-H(56C)  | 109.5    | H(56A)-C(56)-H(56C) | 109.5 |
| H(56B)-C(56)-H(56C) | 109.5    | C(55)-C(57)-H(57A)  | 109.5 |
| C(55)-C(57)-H(57B)  | 109.5    | H(57A)-C(57)-H(57B) | 109.5 |
| C(55)-C(57)-H(57C)  | 109.5    | H(57A)-C(57)-H(57C) | 109.5 |
| H(57B)-C(57)-H(57C) | 109.5    | C(55)-C(58)-H(58A)  | 109.5 |
| C(55)-C(58)-H(58B)  | 109.5    | H(58A)-C(58)-H(58B) | 109.5 |
| C(55)-C(58)-H(58C)  | 109.5    | H(58A)-C(58)-H(58C) | 109.5 |
| H(58B)-C(58)-H(58C) | 109.5    |                     |       |

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa653

| atom  | U11    | U22    | U33    | U23    | U13   | U12    |
|-------|--------|--------|--------|--------|-------|--------|
| Y(1)  | 21(1)  | 23(1)  | 21(1)  | -3(1)  | 8(1)  | -2(1)  |
| P(1)  | 23(1)  | 23(1)  | 18(1)  | -1(1)  | 7(1)  | 0(1)   |
| P(2)  | 20(1)  | 22(1)  | 19(1)  | -2(1)  | 8(1)  | -1(1)  |
| O(1)  | 36(1)  | 23(1)  | 21(1)  | -1(1)  | 10(1) | 3(1)   |
| O(2)  | 29(1)  | 25(1)  | 21(1)  | -1(1)  | 10(1) | 2(1)   |
| O(3)  | 29(1)  | 44(1)  | 39(1)  | -6(1)  | 17(1) | -11(1) |
| N(1)  | 30(1)  | 27(1)  | 19(1)  | -3(1)  | 6(1)  | 6(1)   |
| N(2)  | 30(1)  | 23(1)  | 20(1)  | -2(1)  | 9(1)  | -1(1)  |
| C(1)  | 48(2)  | 30(2)  | 21(1)  | -1(1)  | 6(1)  | 6(2)   |
| C(2)  | 53(2)  | 28(2)  | 20(1)  | 0(1)   | 12(1) | 4(1)   |
| C(3)  | 21(2)  | 26(1)  | 20(1)  | -2(1)  | 9(1)  | -2(1)  |
| C(4)  | 22(2)  | 27(1)  | 20(1)  | 0(1)   | 11(1) | 0(1)   |
| C(5)  | 20(2)  | 29(2)  | 21(1)  | -1(1)  | 11(1) | -2(1)  |
| C(6)  | 22(2)  | 33(2)  | 21(1)  | -6(1)  | 10(1) | -5(1)  |
| C(7)  | 27(2)  | 24(1)  | 27(1)  | -4(1)  | 14(1) | -4(1)  |
| C(8)  | 24(2)  | 26(1)  | 24(1)  | 1(1)   | 8(1)  | 2(1)   |
| C(9)  | 29(2)  | 36(2)  | 21(1)  | -1(1)  | 7(1)  | 5(1)   |
| C(10) | 33(2)  | 56(2)  | 34(2)  | -1(2)  | 10(2) | 16(2)  |
| C(11) | 51(2)  | 46(2)  | 24(2)  | 8(1)   | 10(2) | 1(2)   |
| C(12) | 35(2)  | 51(2)  | 28(2)  | -4(2)  | 2(2)  | 8(2)   |
| C(13) | 38(2)  | 25(2)  | 33(2)  | -7(1)  | 17(1) | -2(1)  |
| C(14) | 102(4) | 30(2)  | 131(4) | -25(2) | 93(3) | -20(2) |
| C(15) | 77(3)  | 44(2)  | 45(2)  | -12(2) | 29(2) | 9(2)   |
| C(16) | 58(3)  | 32(2)  | 66(2)  | -3(2)  | 24(2) | 10(2)  |
| C(17) | 26(2)  | 36(2)  | 26(2)  | -6(1)  | 10(1) | -7(1)  |
| C(18) | 37(2)  | 75(3)  | 32(2)  | -3(2)  | 16(2) | -15(2) |
| C(19) | 48(3)  | 98(3)  | 51(2)  | -2(2)  | 29(2) | -20(2) |
| C(20) | 35(2)  | 84(3)  | 68(3)  | -15(2) | 24(2) | -19(2) |
| C(21) | 29(2)  | 131(4) | 47(2)  | -13(3) | 9(2)  | -20(2) |
| C(22) | 33(2)  | 101(3) | 32(2)  | -5(2)  | 10(2) | -14(2) |
| C(23) | 36(2)  | 24(1)  | 18(1)  | -2(1)  | 6(1)  | -3(1)  |
| C(24) | 48(2)  | 44(2)  | 28(2)  | 3(1)   | 15(2) | -11(2) |
| C(25) | 79(3)  | 72(3)  | 36(2)  | 6(2)   | 19(2) | -39(3) |
| C(26) | 121(5) | 41(2)  | 36(2)  | 12(2)  | 9(3)  | -24(3) |
| C(27) | 95(4)  | 33(2)  | 40(2)  | 4(2)   | 4(2)  | 15(2)  |
| C(28) | 60(2)  | 38(2)  | 29(2)  | 2(1)   | 12(2) | 12(2)  |
| C(29) | 21(2)  | 25(1)  | 23(1)  | 0(1)   | 11(1) | -1(1)  |
| C(30) | 25(2)  | 22(1)  | 23(1)  | 2(1)   | 13(1) | -2(1)  |
| C(31) | 21(2)  | 29(2)  | 24(1)  | 3(1)   | 9(1)  | -2(1)  |
| C(32) | 23(2)  | 28(2)  | 31(2)  | 9(1)   | 12(1) | 4(1)   |
| C(33) | 29(2)  | 23(1)  | 31(2)  | 4(1)   | 18(1) | 1(1)   |
| C(34) | 26(2)  | 24(1)  | 23(1)  | -1(1)  | 13(1) | -3(1)  |
| C(35) | 29(2)  | 30(2)  | 24(1)  | 3(1)   | 5(1)  | 1(1)   |
| C(36) | 49(2)  | 41(2)  | 23(2)  | 4(1)   | 13(2) | -1(2)  |
| C(37) | 41(2)  | 46(2)  | 31(2)  | 2(2)   | -4(2) | 6(2)   |
| C(38) | 28(2)  | 38(2)  | 38(2)  | 0(1)   | 8(1)  | -6(1)  |
| C(39) | 35(2)  | 22(1)  | 38(2)  | 4(1)   | 21(2) | 3(1)   |
| C(40) | 56(3)  | 35(2)  | 97(3)  | -10(2) | 54(2) | 0(2)   |
| C(41) | 70(3)  | 25(2)  | 44(2)  | 6(2)   | 23(2) | 2(2)   |
| C(42) | 58(2)  | 27(2)  | 46(2)  | -4(2)  | 21(2) | 3(2)   |
| C(43) | 23(2)  | 36(2)  | 18(1)  | -4(1)  | 8(1)  | -3(1)  |
| C(44) | 40(2)  | 39(2)  | 39(2)  | -2(2)  | 22(2) | -4(2)  |
| C(45) | 53(2)  | 56(2)  | 46(2)  | -4(2)  | 30(2) | -21(2) |
| C(46) | 32(2)  | 77(3)  | 33(2)  | -10(2) | 20(2) | -17(2) |
| C(47) | 33(2)  | 67(2)  | 36(2)  | -7(2)  | 20(2) | 2(2)   |
| C(48) | 27(2)  | 43(2)  | 28(2)  | -1(1)  | 13(1) | 3(1)   |
| C(49) | 22(2)  | 19(1)  | 19(1)  | -2(1)  | 7(1)  | 1(1)   |
| C(50) | 25(2)  | 37(2)  | 29(2)  | -4(1)  | 11(1) | -1(1)  |
| C(51) | 34(2)  | 48(2)  | 29(2)  | -11(2) | 6(2)  | -3(2)  |
| C(52) | 51(2)  | 36(2)  | 21(1)  | -3(1)  | 12(2) | 13(2)  |
| C(53) | 43(2)  | 36(2)  | 30(2)  | -3(1)  | 21(2) | 6(2)   |
| C(54) | 33(2)  | 31(2)  | 28(2)  | -4(1)  | 15(1) | -1(1)  |
| C(55) | 34(2)  | 32(2)  | 38(2)  | -7(1)  | 22(2) | -8(1)  |

## Appendix 1. Crystallographic data

|       |       |       |       |        |       |        |
|-------|-------|-------|-------|--------|-------|--------|
| C(56) | 64(3) | 45(2) | 53(2) | -6(2)  | 37(2) | 4(2)   |
| C(57) | 36(2) | 66(2) | 59(2) | -24(2) | 26(2) | -18(2) |
| C(58) | 86(3) | 45(2) | 62(2) | 4(2)   | 45(2) | -4(2)  |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

## Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa653

| atom   | x         | y         | z          | U(eq) |
|--------|-----------|-----------|------------|-------|
| H(1A)  | 2303      | 2215      | 2128       | 44    |
| H(1B)  | 1958      | 1816      | 2436       | 44    |
| H(2A)  | 1064      | 2333      | 2359       | 43    |
| H(2B)  | 1776      | 2678      | 2632       | 43    |
| H(6)   | 0         | 662       | -1362      | 30    |
| H(8)   | 1581      | 511       | 558        | 31    |
| H(10A) | -1329     | 1995      | -1603      | 65    |
| H(10B) | -681      | 2088      | -854       | 65    |
| H(10C) | -1129     | 1580      | -1031      | 65    |
| H(11A) | 333       | 1870      | -1776      | 64    |
| H(11B) | 294       | 2226      | -1214      | 64    |
| H(11C) | -361      | 2224      | -1974      | 64    |
| H(12A) | -1188     | 1506      | -2415      | 64    |
| H(12B) | -1072     | 1029      | -1948      | 64    |
| H(12C) | -492.0000 | 1156      | -2222      | 64    |
| H(14A) | 528       | -353      | 33         | 109   |
| H(14B) | 449       | -709      | -575       | 109   |
| H(14C) | -100      | -253      | -723       | 109   |
| H(15A) | 252       | -47       | -1629      | 82    |
| H(15B) | 908       | -437.0000 | -1395.0001 | 82    |
| H(15C) | 1066      | 139       | -1429      | 82    |
| H(16A) | 2046      | 19        | -215       | 81    |
| H(16B) | 1777      | -542      | -294       | 81    |
| H(16C) | 1825      | -216      | 329        | 81    |
| H(18)  | 2289      | 1691      | 253        | 57    |
| H(19)  | 3439      | 1874      | 343        | 75    |
| H(20)  | 4465      | 1861      | 1391       | 74    |
| H(21)  | 4345      | 1676      | 2358       | 87    |
| H(22)  | 3211      | 1468      | 2276       | 69    |
| H(24)  | 1005      | 1082      | 1903       | 49    |
| H(25)  | 1075      | 398       | 2568       | 78    |
| H(26)  | 1993      | -191.0000 | 2816       | 92    |
| H(27)  | 2830      | -100      | 2396       | 80    |
| H(28)  | 2769      | 582       | 1726       | 55    |
| H(32)  | -1200     | 4461      | -77        | 33    |
| H(34)  | 618       | 4337      | 1709       | 29    |
| H(36A) | -625      | 3802      | -1217      | 58    |
| H(36B) | -1164     | 3346      | -1562.0001 | 58    |
| H(36C) | -415.0000 | 3265      | -880       | 58    |
| H(37A) | -1639     | 4281      | -1179      | 71    |
| H(37B) | -2120     | 4040      | -855       | 71    |
| H(37C) | -2172     | 3827      | -1551      | 71    |
| H(38A) | -1918     | 3001      | -1059      | 56    |
| H(38B) | -1832     | 3199      | -345       | 56    |
| H(38C) | -1189     | 2882      | -374       | 56    |
| H(40A) | -1061     | 4806      | 1507       | 84    |
| H(40B) | -1558     | 4917      | 715        | 84    |
| H(40C) | -1217     | 5365      | 1240       | 84    |
| H(41A) | -990      | 5269      | 24         | 71    |
| H(41B) | -126      | 5366      | 365        | 71    |
| H(41C) | -637      | 5708      | 561        | 71    |
| H(42A) | 92        | 5552      | 1756       | 67    |
| H(42B) | 642       | 5209      | 1614       | 67    |
| H(42C) | 263       | 5001      | 2054       | 67    |
| H(44)  | 1715      | 4269      | 1252       | 46    |
| H(45)  | 2632      | 4438      | 936        | 58    |
| H(46)  | 3375      | 3806      | 886        | 54    |
| H(47)  | 3161      | 2994      | 1098       | 52    |
| H(48)  | 2251      | 2819      | 1418       | 39    |
| H(50)  | 2548      | 3861      | 2691       | 37    |
| H(51)  | 2911      | 4090      | 3820       | 48    |
| H(52)  | 2116      | 3996      | 4294       | 45    |

## Appendix 1. Crystallographic data

|        |           |      |      |    |
|--------|-----------|------|------|----|
| H(53)  | 945       | 3676 | 3646 | 41 |
| H(54)  | 576       | 3450 | 2521 | 37 |
| H(56A) | -1005     | 2585 | 1456 | 75 |
| H(56B) | -1805     | 2343 | 1141 | 75 |
| H(56C) | -1559     | 2658 | 668  | 75 |
| H(57A) | -1867     | 1973 | -129 | 78 |
| H(57B) | -2080     | 1604 | 317  | 78 |
| H(57C) | -1460     | 1452 | 103  | 78 |
| H(58A) | -636.0001 | 1307 | 1368 | 91 |
| H(58B) | -1267     | 1504 | 1543 | 91 |
| H(58C) | -475      | 1759 | 1886 | 91 |

**Complex 5I**

Table 1. Crystal data for pa652

|   |  |
|---|--|
| Compound                                    | pa652  |
| Molecular formula                           | C <sub>66</sub> H <sub>87</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Y |
| Molecular weight                            | 1123.23  |
| Crystal habit                               | Colourless Block   |
| Crystal dimensions(mm)                      | 0.28x0.26x0.22   |
| Crystal system                              | monoclinic   |
| Space group                                 | P2 <sub>1</sub>  |
| a(Å)  | 10.654(1)  |
| b(Å)  | 26.055(1)  |
| c(Å)  | 11.449(1)  |
| α(°)  | 90.00  |
| β(°)  | 107.091(1)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 3037.8(4)  |
| Z   | 2  |
| d(g·cm <sup>-3</sup> )                      | 1.228  |
| F(000)                                      | 1196   |
| μ(cm <sup>-1</sup> )                        | 1.060  |
| Absorption corrections                      | multi-scan ; 0.7556 min, 0.8002 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 27.48  |
| HKL ranges                                  | -12 13 ; -33 33 ; -14 11   |
| Reflections measured                        | 17115  |
| Unique data                                 | 12776  |
| Rint  | 0.0455   |
| Reflections used                            | 11429  |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 749  |
| Reflections / parameter                     | 15   |
| wR2   | 0.1178   |
| R1  | 0.0500   |
| Flack's parameter                           | 0.492(11)  |
| Weights a, b                                | 0.0478 ; 3.9788  |
| GoF   | 1.089  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.728(0.066) / -1.082(0.066)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa652

| atom  | x         | y        | z         | U(eq)  |
|-------|-----------|----------|-----------|--------|
| Y(1)  | 7748(1)   | 2129(1)  | 4826(1)   | 21(1)  |
| P(1)  | 9230(2)   | 1015(1)  | 4390(2)   | 22(1)  |
| P(2)  | 9243(2)   | 3241(1)  | 4397(2)   | 22(1)  |
| O(1)  | 7421(6)   | 2866(3)  | 5675(6)   | 27(1)  |
| O(2)  | 7425(6)   | 1381(3)  | 5659(6)   | 27(1)  |
| N(1)  | 9134(7)   | 2659(3)  | 4007(7)   | 27(2)  |
| N(2)  | 9112(7)   | 1607(3)  | 3999(7)   | 23(2)  |
| C(1A) | 9100(10)  | 2378(6)  | 2890(10)  | 19(2)  |
| C(2A) | 9630(10)  | 1855(6)  | 3080(10)  | 23(3)  |
| C(3A) | 9390(30)  | 1560(10) | 1970(30)  | 33(4)  |
| C(4A) | 10040(20) | 1847(8)  | 1040(20)  | 28(3)  |
| C(5A) | 9610(20)  | 2370(10) | 880(30)   | 32(4)  |
| C(6A) | 9780(10)  | 2682(7)  | 2040(20)  | 17(3)  |
| C(1B) | 9680(20)  | 2438(6)  | 3130(20)  | 19(2)  |
| C(2B) | 9130(20)  | 1856(8)  | 2820(20)  | 23(3)  |
| C(3B) | 9810(30)  | 1580(10) | 1970(30)  | 33(4)  |
| C(4B) | 9510(20)  | 1840(10) | 780(20)   | 28(3)  |
| C(5B) | 10030(30) | 2420(10) | 960(30)   | 32(4)  |
| C(6B) | 9390(20)  | 2680(10) | 1830(20)  | 17(3)  |
| C(7)  | 9374(8)   | 3331(3)  | 5957(8)   | 23(2)  |
| C(8)  | 8349(8)   | 3182(3)  | 6392(7)   | 25(2)  |
| C(9)  | 8189(7)   | 3367(3)  | 7489(7)   | 22(2)  |
| C(10) | 9340(10)  | 3599(3)  | 8277(7)   | 28(2)  |
| C(11) | 10520(10) | 3682(3)  | 7999(8)   | 25(2)  |
| C(12) | 10511(7)  | 3572(3)  | 6819(8)   | 23(2)  |
| C(13) | 6870(10)  | 3343(4)  | 7800(10)  | 39(2)  |
| C(14) | 5910(10)  | 3623(5)  | 6790(10)  | 47(3)  |
| C(15) | 6510(10)  | 2791(4)  | 7980(10)  | 55(3)  |
| C(16) | 7010(10)  | 3635(5)  | 9030(10)  | 54(3)  |
| C(17) | 11730(10) | 3878(3)  | 8990(10)  | 31(2)  |
| C(18) | 12930(10) | 3831(6)  | 8580(10)  | 81(4)  |
| C(19) | 11520(20) | 4462(6)  | 9150(20)  | 131(8) |
| C(20) | 12020(10) | 3548(6)  | 10130(10) | 75(4)  |
| C(21) | 10640(10) | 3574(3)  | 4125(8)   | 26(2)  |
| C(22) | 10490(10) | 4054(4)  | 3550(10)  | 38(2)  |
| C(23) | 11480(10) | 4295(4)  | 3300(10)  | 43(2)  |
| C(24) | 12790(10) | 4048(5)  | 3660(10)  | 54(3)  |
| C(25) | 12910(10) | 3582(4)  | 4170(10)  | 39(2)  |
| C(26) | 11820(10) | 3344(4)  | 4420(10)  | 35(2)  |
| C(27) | 7790(8)   | 3640(3)  | 3622(8)   | 26(2)  |
| C(28) | 6970(10)  | 3478(4)  | 2570(10)  | 40(2)  |
| C(29) | 5930(10)  | 3786(5)  | 1950(10)  | 46(3)  |
| C(30) | 5680(10)  | 4240(4)  | 2440(10)  | 42(3)  |
| C(31) | 6480(10)  | 4378(4)  | 3530(10)  | 43(3)  |
| C(32) | 7570(10)  | 4096(4)  | 4160(10)  | 40(2)  |
| C(33) | 9445(8)   | 923(3)   | 6026(7)   | 23(2)  |
| C(34) | 8271(8)   | 1084(3)  | 6345(7)   | 23(2)  |
| C(35) | 8256(8)   | 875(3)   | 7531(8)   | 30(2)  |
| C(36) | 9322(8)   | 655(3)   | 8297(8)   | 28(2)  |
| C(37) | 10513(8)  | 583(3)   | 7998(8)   | 26(2)  |
| C(38) | 10470(10) | 689(4)   | 6780(8)   | 28(2)  |
| C(39) | 6947(8)   | 907(3)   | 7823(7)   | 27(2)  |
| C(40) | 6480(10)  | 1461(4)  | 7910(10)  | 50(3)  |
| C(41) | 6970(10)  | 645(5)   | 9000(10)  | 47(3)  |
| C(42) | 5790(10)  | 658(5)   | 6780(10)  | 53(3)  |
| C(43) | 11739(8)  | 367(4)   | 8947(8)   | 33(2)  |
| C(44) | 11680(10) | -191(4)  | 9090(10)  | 84(4)  |
| C(45) | 11800(10) | 569(6)   | 10210(10) | 78(4)  |
| C(46) | 13020(10) | 489(5)   | 8630(10)  | 56(3)  |
| C(47) | 7834(8)   | 633(3)   | 3649(8)   | 28(2)  |
| C(48) | 6981(8)   | 779(4)   | 2486(8)   | 33(2)  |
| C(49) | 5890(10)  | 479(5)   | 1890(10)  | 43(3)  |

## Appendix 1. Crystallographic data

|        |           |          |          |       |
|--------|-----------|----------|----------|-------|
| C(50)  | 5640(10)  | 28(4)    | 2410(10) | 43(3) |
| C(51)  | 6470(10)  | -136(5)  | 3560(10) | 54(3) |
| C(52)  | 7520(10)  | 178(4)   | 4140(10) | 40(2) |
| C(53)  | 10601(8)  | 680(4)   | 4083(8)  | 27(2) |
| C(54)  | 10480(10) | 200(4)   | 3540(10) | 36(2) |
| C(55)  | 11620(10) | -28(4)   | 3330(10) | 50(3) |
| C(56)  | 12730(10) | 199(4)   | 3600(10) | 40(2) |
| C(57)  | 12910(10) | 677(5)   | 4190(10) | 47(3) |
| C(58)  | 11864(8)  | 925(4)   | 4420(8)  | 32(2) |
| O(3A)  | 9821(2)   | 2122(4)  | 6590(2)  | 27(1) |
| C(59A) | 11130(10) | 2190(10) | 6470(10) | 35(2) |
| C(60A) | 12070(10) | 2055(7)  | 7690(10) | 33(2) |
| C(61A) | 11270(10) | 1960(8)  | 8520(10) | 34(2) |
| C(62A) | 9910(10)  | 2150(10) | 7871(8)  | 32(1) |
| O(3B)  | 9821(2)   | 2122(4)  | 6590(2)  | 27(1) |
| C(59B) | 11125(8)  | 2070(10) | 6440(10) | 35(2) |
| C(60B) | 12020(10) | 2299(7)  | 7590(10) | 33(2) |
| C(61B) | 11380(10) | 2204(6)  | 8565(7)  | 34(2) |
| C(62B) | 9960(10)  | 2110(10) | 7885(7)  | 32(1) |
| O(4A)  | 6040(20)  | 2078(6)  | 3270(10) | 13(3) |
| C(63A) | 4847(7)   | 2136(7)  | 2487(7)  | 35(1) |
| C(64A) | 5000(10)  | 2210(6)  | 1216(8)  | 51(2) |
| C(65A) | 3950(20)  | 1675(8)  | 2440(30) | 67(4) |
| C(66A) | 4160(20)  | 2603(6)  | 2840(10) | 49(3) |
| O(4B)  | 6010(20)  | 2158(8)  | 3530(10) | 25(3) |
| C(63B) | 4634(6)   | 2128(7)  | 2990(6)  | 35(1) |
| C(64B) | 4031(7)   | 2130(10) | 4060(6)  | 51(2) |
| C(65B) | 4310(20)  | 1635(8)  | 2260(30) | 67(4) |
| C(66B) | 4110(20)  | 2606(6)  | 2220(20) | 49(3) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths (Å) and angles (deg) for pa652

|              |          |              |          |
|--------------|----------|--------------|----------|
| Y(1)-O(4B)   | 2.00(2)  | Y(1)-O(4A)   | 2.14(2)  |
| Y(1)-O(1)    | 2.227(7) | Y(1)-O(2)    | 2.240(7) |
| Y(1)-N(2)    | 2.380(7) | Y(1)-N(1)    | 2.404(7) |
| Y(1)-O(3A)   | 2.517(2) | Y(1)-C(1A)   | 3.05(1)  |
| P(1)-N(2)    | 1.602(7) | P(1)-C(47)   | 1.78(1)  |
| P(1)-C(53)   | 1.82(1)  | P(1)-C(33)   | 1.834(8) |
| P(2)-N(1)    | 1.576(8) | P(2)-C(7)    | 1.77(1)  |
| P(2)-C(21)   | 1.82(1)  | P(2)-C(27)   | 1.859(8) |
| O(1)-C(8)    | 1.36(1)  | O(2)-C(34)   | 1.27(1)  |
| N(1)-C(1B)   | 1.42(2)  | N(1)-C(1A)   | 1.47(2)  |
| N(2)-C(2A)   | 1.47(2)  | N(2)-C(2B)   | 1.50(2)  |
| C(1A)-C(2A)  | 1.46(2)  | C(1A)-C(6A)  | 1.59(2)  |
| C(1A)-H(1A)  | 1.0000   | C(2A)-C(3A)  | 1.44(3)  |
| C(2A)-H(2A)  | 1.0000   | C(3A)-C(4A)  | 1.61(3)  |
| C(3A)-H(3A1) | 0.9900   | C(3A)-H(3A2) | 0.9900   |
| C(4A)-C(5A)  | 1.44(4)  | C(4A)-H(4A1) | 0.9900   |
| C(4A)-H(4A2) | 0.9900   | C(5A)-C(6A)  | 1.51(4)  |
| C(5A)-H(5A1) | 0.9900   | C(5A)-H(5A2) | 0.9900   |
| C(6A)-H(6A1) | 0.9900   | C(6A)-H(6A2) | 0.9900   |
| C(1B)-C(6B)  | 1.57(3)  | C(1B)-C(2B)  | 1.63(2)  |
| C(1B)-H(1B)  | 1.0000   | C(2B)-C(3B)  | 1.56(3)  |
| C(2B)-H(2B)  | 1.0000   | C(3B)-C(4B)  | 1.48(4)  |
| C(3B)-H(3B1) | 0.9900   | C(3B)-H(3B2) | 0.9900   |
| C(4B)-C(5B)  | 1.60(4)  | C(4B)-H(4B1) | 0.9900   |
| C(4B)-H(4B2) | 0.9900   | C(5B)-C(6B)  | 1.52(4)  |
| C(5B)-H(5B1) | 0.9900   | C(5B)-H(5B2) | 0.9900   |
| C(6B)-H(6B1) | 0.9900   | C(6B)-H(6B2) | 0.9900   |
| C(7)-C(8)    | 1.38(1)  | C(7)-C(12)   | 1.46(1)  |
| C(8)-C(9)    | 1.40(1)  | C(9)-C(10)   | 1.43(1)  |
| C(9)-C(13)   | 1.55(1)  | C(10)-C(11)  | 1.40(1)  |
| C(10)-H(10)  | 0.9500   | C(11)-C(12)  | 1.38(1)  |
| C(11)-C(17)  | 1.53(1)  | C(12)-H(12)  | 0.9500   |
| C(13)-C(14)  | 1.50(1)  | C(13)-C(15)  | 1.52(1)  |
| C(13)-C(16)  | 1.56(1)  | C(14)-H(14A) | 0.9800   |
| C(14)-H(14B) | 0.9800   | C(14)-H(14C) | 0.9800   |
| C(15)-H(15A) | 0.9800   | C(15)-H(15B) | 0.9800   |
| C(15)-H(15C) | 0.9800   | C(16)-H(16A) | 0.9800   |
| C(16)-H(16B) | 0.9800   | C(16)-H(16C) | 0.9800   |
| C(17)-C(18)  | 1.49(1)  | C(17)-C(20)  | 1.52(1)  |
| C(17)-C(19)  | 1.56(2)  | C(18)-H(18A) | 0.9800   |
| C(18)-H(18B) | 0.9800   | C(18)-H(18C) | 0.9800   |
| C(19)-H(19A) | 0.9800   | C(19)-H(19B) | 0.9800   |
| C(19)-H(19C) | 0.9800   | C(20)-H(20A) | 0.9800   |
| C(20)-H(20B) | 0.9800   | C(20)-H(20C) | 0.9800   |
| C(21)-C(26)  | 1.35(1)  | C(21)-C(22)  | 1.40(1)  |
| C(22)-C(23)  | 1.33(1)  | C(22)-H(22)  | 0.9500   |
| C(23)-C(24)  | 1.48(2)  | C(23)-H(23)  | 0.9500   |
| C(24)-C(25)  | 1.34(2)  | C(24)-H(24)  | 0.9500   |
| C(25)-C(26)  | 1.42(1)  | C(25)-H(25)  | 0.9500   |
| C(26)-H(26)  | 0.9500   | C(27)-C(28)  | 1.34(1)  |
| C(27)-C(32)  | 1.39(1)  | C(28)-C(29)  | 1.38(1)  |
| C(28)-H(28)  | 0.9500   | C(29)-C(30)  | 1.37(2)  |
| C(29)-H(29)  | 0.9500   | C(30)-C(31)  | 1.34(1)  |
| C(30)-H(30)  | 0.9500   | C(31)-C(32)  | 1.39(1)  |
| C(31)-H(31)  | 0.9500   | C(32)-H(32)  | 0.9500   |
| C(33)-C(38)  | 1.33(1)  | C(33)-C(34)  | 1.46(1)  |
| C(34)-C(35)  | 1.47(1)  | C(35)-C(36)  | 1.34(1)  |
| C(35)-C(39)  | 1.53(1)  | C(36)-C(37)  | 1.42(1)  |
| C(36)-H(36)  | 0.9500   | C(37)-C(38)  | 1.41(1)  |
| C(37)-C(43)  | 1.54(1)  | C(38)-H(38)  | 0.9500   |
| C(39)-C(41)  | 1.51(1)  | C(39)-C(40)  | 1.54(1)  |
| C(39)-C(42)  | 1.58(1)  | C(40)-H(40A) | 0.9800   |
| C(40)-H(40B) | 0.9800   | C(40)-H(40C) | 0.9800   |
| C(41)-H(41A) | 0.9800   | C(41)-H(41B) | 0.9800   |
| C(41)-H(41C) | 0.9800   | C(42)-H(42A) | 0.9800   |
| C(42)-H(42B) | 0.9800   | C(42)-H(42C) | 0.9800   |

## Appendix 1. Crystallographic data

|                  |          |                  |           |
|------------------|----------|------------------|-----------|
| C(43)-C(44)      | 1.47(1)  | C(43)-C(45)      | 1.52(1)   |
| C(43)-C(46)      | 1.55(1)  | C(44)-H(44A)     | 0.9800    |
| C(44)-H(44B)     | 0.9800   | C(44)-H(44C)     | 0.9800    |
| C(45)-H(45A)     | 0.9800   | C(45)-H(45B)     | 0.9800    |
| C(45)-H(45C)     | 0.9800   | C(46)-H(46A)     | 0.9800    |
| C(46)-H(46B)     | 0.9800   | C(46)-H(46C)     | 0.9800    |
| C(47)-C(52)      | 1.39(1)  | C(47)-C(48)      | 1.42(1)   |
| C(48)-C(49)      | 1.40(1)  | C(48)-H(48)      | 0.9500    |
| C(49)-C(50)      | 1.37(2)  | C(49)-H(49)      | 0.9500    |
| C(50)-C(51)      | 1.42(2)  | C(50)-H(50)      | 0.9500    |
| C(51)-C(52)      | 1.39(1)  | C(51)-H(51)      | 0.9500    |
| C(52)-H(52)      | 0.9500   | C(53)-C(54)      | 1.38(1)   |
| C(53)-C(58)      | 1.44(1)  | C(54)-C(55)      | 1.44(1)   |
| C(54)-H(54)      | 0.9500   | C(55)-C(56)      | 1.28(2)   |
| C(55)-H(55)      | 0.9500   | C(56)-C(57)      | 1.41(2)   |
| C(56)-H(56)      | 0.9500   | C(57)-C(58)      | 1.38(1)   |
| C(57)-H(57)      | 0.9500   | C(58)-H(58)      | 0.9500    |
| O(3A)-C(62A)     | 1.443(8) | O(3A)-C(59A)     | 1.452(8)  |
| C(59A)-C(60A)    | 1.50(1)  | C(59A)-H(59A)    | 0.9900    |
| C(59A)-H(59B)    | 0.9900   | C(60A)-C(61A)    | 1.479(8)  |
| C(60A)-H(60A)    | 0.9900   | C(60A)-H(60B)    | 0.9900    |
| C(61A)-C(62A)    | 1.50(1)  | C(61A)-H(61A)    | 0.9900    |
| C(61A)-H(61B)    | 0.9900   | C(62A)-H(62A)    | 0.9900    |
| C(62A)-H(62B)    | 0.9900   | C(59B)-C(60B)    | 1.50(1)   |
| C(59B)-H(59C)    | 0.9900   | C(59B)-H(59D)    | 0.9900    |
| C(60B)-C(61B)    | 1.488(8) | C(60B)-H(60C)    | 0.9900    |
| C(60B)-H(60D)    | 0.9900   | C(61B)-C(62B)    | 1.51(1)   |
| C(61B)-H(61C)    | 0.9900   | C(61B)-H(61D)    | 0.9900    |
| C(62B)-H(62C)    | 0.9900   | C(62B)-H(62D)    | 0.9900    |
| O(4A)-C(63A)     | 1.33(2)  | C(63A)-C(64A)    | 1.525(8)  |
| C(63A)-C(65A)    | 1.53(1)  | C(63A)-C(66A)    | 1.54(1)   |
| C(64A)-H(64A)    | 0.9800   | C(64A)-H(64B)    | 0.9800    |
| C(64A)-H(64C)    | 0.9800   | C(65A)-H(65A)    | 0.9800    |
| C(65A)-H(65B)    | 0.9800   | C(65A)-H(65C)    | 0.9800    |
| C(66A)-H(66A)    | 0.9800   | C(66A)-H(66B)    | 0.9800    |
| C(66A)-H(66C)    | 0.9800   | O(4B)-C(63B)     | 1.42(2)   |
| C(63B)-C(65B)    | 1.52(1)  | C(63B)-C(66B)    | 1.53(1)   |
| C(63B)-C(64B)    | 1.541(7) | C(64B)-H(64D)    | 0.9800    |
| C(64B)-H(64E)    | 0.9800   | C(64B)-H(64F)    | 0.9800    |
| C(65B)-H(65D)    | 0.9800   | C(65B)-H(65E)    | 0.9800    |
| C(65B)-H(65F)    | 0.9800   | C(66B)-H(66D)    | 0.9800    |
| C(66B)-H(66E)    | 0.9800   | C(66B)-H(66F)    | 0.9800    |
| O(4B)-Y(1)-O(4A) | 9.6(7)   | O(4B)-Y(1)-O(1)  | 93.5(5)   |
| O(4A)-Y(1)-O(1)  | 102.3(4) | O(4B)-Y(1)-O(2)  | 97.2(7)   |
| O(4A)-Y(1)-O(2)  | 95.9(5)  | O(1)-Y(1)-O(2)   | 120.07(8) |
| O(4B)-Y(1)-N(2)  | 105.4(4) | O(4A)-Y(1)-N(2)  | 95.8(5)   |
| O(1)-Y(1)-N(2)   | 149.1(2) | O(2)-Y(1)-N(2)   | 82.0(2)   |
| O(4B)-Y(1)-N(1)  | 103.2(6) | O(4A)-Y(1)-N(1)  | 100.3(5)  |
| O(1)-Y(1)-N(1)   | 82.4(3)  | O(2)-Y(1)-N(1)   | 148.7(2)  |
| N(2)-Y(1)-N(1)   | 69.88(8) | O(4B)-Y(1)-O(3A) | 174.7(4)  |
| O(4A)-Y(1)-O(3A) | 175.3(5) | O(1)-Y(1)-O(3A)  | 82.4(3)   |
| O(2)-Y(1)-O(3A)  | 82.0(3)  | N(2)-Y(1)-O(3A)  | 79.7(2)   |
| N(1)-Y(1)-O(3A)  | 79.8(2)  | O(4B)-Y(1)-C(1A) | 89.0(5)   |
| O(4A)-Y(1)-C(1A) | 82.7(5)  | O(1)-Y(1)-C(1A)  | 107.6(3)  |
| O(2)-Y(1)-C(1A)  | 131.3(3) | N(2)-Y(1)-C(1A)  | 50.0(3)   |
| N(1)-Y(1)-C(1A)  | 28.2(3)  | O(3A)-Y(1)-C(1A) | 95.5(3)   |
| N(2)-P(1)-C(47)  | 114.8(4) | N(2)-P(1)-C(53)  | 114.1(4)  |
| C(47)-P(1)-C(53) | 104.1(4) | N(2)-P(1)-C(33)  | 112.8(4)  |
| C(47)-P(1)-C(33) | 104.4(4) | C(53)-P(1)-C(33) | 105.5(4)  |
| N(1)-P(2)-C(7)   | 113.0(4) | N(1)-P(2)-C(21)  | 113.9(4)  |
| C(7)-P(2)-C(21)  | 106.5(4) | N(1)-P(2)-C(27)  | 114.9(4)  |
| C(7)-P(2)-C(27)  | 102.5(4) | C(21)-P(2)-C(27) | 105.0(4)  |
| C(8)-O(1)-Y(1)   | 127.3(5) | C(34)-O(2)-Y(1)  | 128.6(5)  |
| C(1B)-N(1)-C(1A) | 24.9(7)  | C(1B)-N(1)-P(2)  | 125.2(8)  |
| C(1A)-N(1)-P(2)  | 135.1(7) | C(1B)-N(1)-Y(1)  | 118.0(7)  |
| C(1A)-N(1)-Y(1)  | 101.1(6) | P(2)-N(1)-Y(1)   | 116.5(4)  |

## Appendix 1. Crystallographic data

|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(2A)-N(2)-C(2B)    | 20.2(6)  | C(2A)-N(2)-P(1)     | 127.5(8) |
| C(2B)-N(2)-P(1)     | 130(1)   | C(2A)-N(2)-Y(1)     | 115.7(7) |
| C(2B)-N(2)-Y(1)     | 106(1)   | P(1)-N(2)-Y(1)      | 116.4(4) |
| C(2A)-C(1A)-N(1)    | 115(1)   | C(2A)-C(1A)-C(6A)   | 109(1)   |
| N(1)-C(1A)-C(6A)    | 113(1)   | C(2A)-C(1A)-Y(1)    | 86.4(8)  |
| N(1)-C(1A)-Y(1)     | 50.7(5)  | C(6A)-C(1A)-Y(1)    | 162(1)   |
| C(2A)-C(1A)-H(1A)   | 106.5    | N(1)-C(1A)-H(1A)    | 106.5    |
| C(6A)-C(1A)-H(1A)   | 106.5    | Y(1)-C(1A)-H(1A)    | 76.2     |
| C(3A)-C(2A)-C(1A)   | 114(2)   | C(3A)-C(2A)-N(2)    | 113(2)   |
| C(1A)-C(2A)-N(2)    | 108(1)   | C(3A)-C(2A)-H(2A)   | 107.3    |
| C(1A)-C(2A)-H(2A)   | 107.3    | N(2)-C(2A)-H(2A)    | 107.3    |
| C(2A)-C(3A)-C(4A)   | 110(2)   | C(2A)-C(3A)-H(3A1)  | 109.6    |
| C(4A)-C(3A)-H(3A1)  | 109.6    | C(2A)-C(3A)-H(3A2)  | 109.6    |
| C(4A)-C(3A)-H(3A2)  | 109.6    | H(3A1)-C(3A)-H(3A2) | 108.1    |
| C(5A)-C(4A)-C(3A)   | 110(2)   | C(5A)-C(4A)-H(4A1)  | 109.7    |
| C(3A)-C(4A)-H(4A1)  | 109.7    | C(5A)-C(4A)-H(4A2)  | 109.7    |
| C(3A)-C(4A)-H(4A2)  | 109.7    | H(4A1)-C(4A)-H(4A2) | 108.2    |
| C(4A)-C(5A)-C(6A)   | 116(2)   | C(4A)-C(5A)-H(5A1)  | 108.2    |
| C(6A)-C(5A)-H(5A1)  | 108.2    | C(4A)-C(5A)-H(5A2)  | 108.2    |
| C(6A)-C(5A)-H(5A2)  | 108.2    | H(5A1)-C(5A)-H(5A2) | 107.4    |
| C(5A)-C(6A)-C(1A)   | 108(2)   | C(5A)-C(6A)-H(6A1)  | 110.1    |
| C(1A)-C(6A)-H(6A1)  | 110.1    | C(5A)-C(6A)-H(6A2)  | 110.1    |
| C(1A)-C(6A)-H(6A2)  | 110.1    | H(6A1)-C(6A)-H(6A2) | 108.4    |
| N(1)-C(1B)-C(6B)    | 120(2)   | N(1)-C(1B)-C(2B)    | 109(1)   |
| C(6B)-C(1B)-C(2B)   | 102(2)   | N(1)-C(1B)-H(1B)    | 108.2    |
| C(6B)-C(1B)-H(1B)   | 108.2    | C(2B)-C(1B)-H(1B)   | 108.2    |
| N(2)-C(2B)-C(3B)    | 119(2)   | N(2)-C(2B)-C(1B)    | 108(1)   |
| C(3B)-C(2B)-C(1B)   | 112(2)   | N(2)-C(2B)-H(2B)    | 105.6    |
| C(3B)-C(2B)-H(2B)   | 105.6    | C(1B)-C(2B)-H(2B)   | 105.6    |
| C(4B)-C(3B)-C(2B)   | 110(2)   | C(4B)-C(3B)-H(3B1)  | 109.7    |
| C(2B)-C(3B)-H(3B1)  | 109.7    | C(4B)-C(3B)-H(3B2)  | 109.7    |
| C(2B)-C(3B)-H(3B2)  | 109.7    | H(3B1)-C(3B)-H(3B2) | 108.2    |
| C(3B)-C(4B)-C(5B)   | 111(2)   | C(3B)-C(4B)-H(4B1)  | 109.5    |
| C(5B)-C(4B)-H(4B1)  | 109.5    | C(3B)-C(4B)-H(4B2)  | 109.5    |
| C(5B)-C(4B)-H(4B2)  | 109.5    | H(4B1)-C(4B)-H(4B2) | 108.1    |
| C(6B)-C(5B)-C(4B)   | 107(2)   | C(6B)-C(5B)-H(5B1)  | 110.3    |
| C(4B)-C(5B)-H(5B1)  | 110.3    | C(6B)-C(5B)-H(5B2)  | 110.3    |
| C(4B)-C(5B)-H(5B2)  | 110.3    | H(5B1)-C(5B)-H(5B2) | 108.5    |
| C(5B)-C(6B)-C(1B)   | 116(2)   | C(5B)-C(6B)-H(6B1)  | 108.3    |
| C(1B)-C(6B)-H(6B1)  | 108.3    | C(5B)-C(6B)-H(6B2)  | 108.3    |
| C(1B)-C(6B)-H(6B2)  | 108.3    | H(6B1)-C(6B)-H(6B2) | 107.4    |
| C(8)-C(7)-C(12)     | 117.6(8) | C(8)-C(7)-P(2)      | 119.5(6) |
| C(12)-C(7)-P(2)     | 122.9(6) | O(1)-C(8)-C(7)      | 117.6(7) |
| O(1)-C(8)-C(9)      | 119.4(8) | C(7)-C(8)-C(9)      | 123.0(7) |
| C(8)-C(9)-C(10)     | 113.7(7) | C(8)-C(9)-C(13)     | 123.5(7) |
| C(10)-C(9)-C(13)    | 122.7(8) | C(11)-C(10)-C(9)    | 125.8(8) |
| C(11)-C(10)-H(10)   | 117.1    | C(9)-C(10)-H(10)    | 117.1    |
| C(12)-C(11)-C(10)   | 116.3(8) | C(12)-C(11)-C(17)   | 123.7(8) |
| C(10)-C(11)-C(17)   | 120.0(7) | C(11)-C(12)-C(7)    | 121.1(8) |
| C(11)-C(12)-H(12)   | 119.4    | C(7)-C(12)-H(12)    | 119.4    |
| C(14)-C(13)-C(15)   | 115(1)   | C(14)-C(13)-C(9)    | 105.0(7) |
| C(15)-C(13)-C(9)    | 110.6(8) | C(14)-C(13)-C(16)   | 109(1)   |
| C(15)-C(13)-C(16)   | 108(1)   | C(9)-C(13)-C(16)    | 109.7(8) |
| C(13)-C(14)-H(14A)  | 109.5    | C(13)-C(14)-H(14B)  | 109.5    |
| H(14A)-C(14)-H(14B) | 109.5    | C(13)-C(14)-H(14C)  | 109.5    |
| H(14A)-C(14)-H(14C) | 109.5    | C(13)-C(15)-H(15A)  | 109.5    |
| C(13)-C(15)-H(15A)  | 109.5    | C(13)-C(15)-H(15C)  | 109.5    |
| H(15A)-C(15)-H(15B) | 109.5    | H(15B)-C(15)-H(15C) | 109.5    |
| H(15A)-C(15)-H(15C) | 109.5    | C(13)-C(16)-H(16A)  | 109.5    |
| C(13)-C(16)-H(16A)  | 109.5    | C(13)-C(16)-H(16B)  | 109.5    |
| H(16A)-C(16)-H(16B) | 109.5    | H(16B)-C(16)-H(16C) | 109.5    |
| H(16A)-C(16)-H(16C) | 109.5    | C(18)-C(17)-C(11)   | 110.7(8) |
| C(18)-C(17)-C(20)   | 105(1)   | C(18)-C(17)-C(19)   | 107(1)   |
| C(20)-C(17)-C(11)   | 111.2(8) | C(11)-C(17)-C(19)   | 107.2(8) |
| C(20)-C(17)-C(19)   | 116(1)   | C(17)-C(18)-H(18B)  | 109.5    |
| C(17)-C(18)-H(18A)  | 109.5    | C(17)-C(18)-H(18C)  | 109.5    |
| H(18A)-C(18)-H(18B) | 109.5    | H(18B)-C(18)-H(18C) | 109.5    |
| H(18A)-C(18)-H(18C) | 109.5    |                     |          |



|                     |          |                     |          |
|---------------------|----------|---------------------|----------|
| C(17)-C(19)-H(19A)  | 109.5    | C(17)-C(19)-H(19B)  | 109.5    |
| H(19A)-C(19)-H(19B) | 109.5    | C(17)-C(19)-H(19C)  | 109.5    |
| H(19A)-C(19)-H(19C) | 109.5    | H(19B)-C(19)-H(19C) | 109.5    |
| C(17)-C(20)-H(20A)  | 109.5    | C(17)-C(20)-H(20B)  | 109.5    |
| H(20A)-C(20)-H(20B) | 109.5    | C(17)-C(20)-H(20C)  | 109.5    |
| H(20A)-C(20)-H(20C) | 109.5    | H(20B)-C(20)-H(20C) | 109.5    |
| C(26)-C(21)-C(22)   | 119(1)   | C(26)-C(21)-P(2)    | 119.6(7) |
| C(22)-C(21)-P(2)    | 121.3(8) | C(23)-C(22)-C(21)   | 122(1)   |
| C(23)-C(22)-H(22)   | 118.8    | C(21)-C(22)-H(22)   | 118.8    |
| C(22)-C(23)-C(24)   | 118(1)   | C(22)-C(23)-H(23)   | 120.8    |
| C(24)-C(23)-H(23)   | 120.8    | C(25)-C(24)-C(23)   | 119(1)   |
| C(25)-C(24)-H(24)   | 120.6    | C(23)-C(24)-H(24)   | 120.6    |
| C(24)-C(25)-C(26)   | 120(1)   | C(24)-C(25)-H(25)   | 119.9    |
| C(26)-C(25)-H(25)   | 119.9    | C(21)-C(26)-C(25)   | 121(1)   |
| C(21)-C(26)-H(26)   | 119.5    | C(25)-C(26)-H(26)   | 119.5    |
| C(28)-C(27)-C(32)   | 121.5(8) | C(28)-C(27)-P(2)    | 119.2(7) |
| C(32)-C(27)-P(2)    | 119.2(7) | C(27)-C(28)-C(29)   | 120(1)   |
| C(27)-C(28)-H(28)   | 120.2    | C(29)-C(28)-H(28)   | 120.2    |
| C(30)-C(29)-C(28)   | 121(1)   | C(30)-C(29)-H(29)   | 119.5    |
| C(28)-C(29)-H(29)   | 119.5    | C(31)-C(30)-C(29)   | 118(1)   |
| C(31)-C(30)-H(30)   | 121.1    | C(29)-C(30)-H(30)   | 121.1    |
| C(30)-C(31)-C(32)   | 124(1)   | C(30)-C(31)-H(31)   | 118.2    |
| C(32)-C(31)-H(31)   | 118.2    | C(31)-C(32)-C(27)   | 116(1)   |
| C(31)-C(32)-H(32)   | 121.8    | C(27)-C(32)-H(32)   | 121.8    |
| C(38)-C(33)-C(34)   | 124.8(7) | C(38)-C(33)-P(1)    | 123.8(6) |
| C(34)-C(33)-P(1)    | 111.0(6) | O(2)-C(34)-C(33)    | 121.6(7) |
| O(2)-C(34)-C(35)    | 126.9(7) | C(33)-C(34)-C(35)   | 111.5(7) |
| C(36)-C(35)-C(34)   | 121.7(7) | C(36)-C(35)-C(39)   | 122.2(7) |
| C(34)-C(35)-C(39)   | 116.1(7) | C(35)-C(36)-C(37)   | 122.9(7) |
| C(35)-C(36)-H(36)   | 118.5    | C(37)-C(36)-H(36)   | 118.5    |
| C(38)-C(37)-C(36)   | 116.3(8) | C(38)-C(37)-C(43)   | 122.9(8) |
| C(36)-C(37)-C(43)   | 120.7(8) | C(33)-C(38)-C(37)   | 120.9(8) |
| C(33)-C(38)-H(38)   | 119.5    | C(37)-C(38)-H(38)   | 119.5    |
| C(41)-C(39)-C(35)   | 113.4(7) | C(41)-C(39)-C(40)   | 106.6(8) |
| C(35)-C(39)-C(40)   | 113.5(7) | C(41)-C(39)-C(42)   | 106.9(8) |
| C(35)-C(39)-C(42)   | 111.8(8) | C(40)-C(39)-C(42)   | 104(1)   |
| C(39)-C(40)-H(40A)  | 109.5    | C(39)-C(40)-H(40B)  | 109.5    |
| H(40A)-C(40)-H(40B) | 109.5    | C(39)-C(40)-H(40C)  | 109.5    |
| H(40A)-C(40)-H(40C) | 109.5    | H(40B)-C(40)-H(40C) | 109.5    |
| C(39)-C(41)-H(41A)  | 109.5    | C(39)-C(41)-H(41B)  | 109.5    |
| H(41A)-C(41)-H(41B) | 109.5    | C(39)-C(41)-H(41C)  | 109.5    |
| H(41A)-C(41)-H(41C) | 109.5    | H(41B)-C(41)-H(41C) | 109.5    |
| C(39)-C(42)-H(42A)  | 109.5    | C(39)-C(42)-H(42B)  | 109.5    |
| H(42A)-C(42)-H(42B) | 109.5    | C(39)-C(42)-H(42C)  | 109.5    |
| H(42A)-C(42)-H(42C) | 109.5    | H(42B)-C(42)-H(42C) | 109.5    |
| C(44)-C(43)-C(45)   | 103(1)   | C(44)-C(43)-C(37)   | 112.8(8) |
| C(45)-C(43)-C(37)   | 109.5(8) | C(44)-C(43)-C(46)   | 107(1)   |
| C(45)-C(43)-C(46)   | 111(1)   | C(37)-C(43)-C(46)   | 112.6(8) |
| C(43)-C(44)-H(44A)  | 109.5    | C(43)-C(44)-H(44B)  | 109.5    |
| H(44A)-C(44)-H(44B) | 109.5    | C(43)-C(44)-H(44C)  | 109.5    |
| H(44A)-C(44)-H(44C) | 109.5    | H(44B)-C(44)-H(44C) | 109.5    |
| C(43)-C(45)-H(45A)  | 109.5    | C(43)-C(45)-H(45B)  | 109.5    |
| H(45A)-C(45)-H(45B) | 109.5    | C(43)-C(45)-H(45C)  | 109.5    |
| H(45A)-C(45)-H(45C) | 109.5    | H(45B)-C(45)-H(45C) | 109.5    |
| C(43)-C(46)-H(46A)  | 109.5    | C(43)-C(46)-H(46B)  | 109.5    |
| H(46A)-C(46)-H(46B) | 109.5    | C(43)-C(46)-H(46C)  | 109.5    |
| H(46A)-C(46)-H(46C) | 109.5    | H(46B)-C(46)-H(46C) | 109.5    |
| C(52)-C(47)-C(48)   | 116.0(8) | C(52)-C(47)-P(1)    | 123.4(7) |
| C(48)-C(47)-P(1)    | 120.6(7) | C(49)-C(48)-C(47)   | 121(1)   |
| C(49)-C(48)-H(48)   | 119.5    | C(47)-C(48)-H(48)   | 119.5    |
| C(50)-C(49)-C(48)   | 120(1)   | C(50)-C(49)-H(49)   | 119.8    |
| C(48)-C(49)-H(49)   | 119.8    | C(49)-C(50)-C(51)   | 121(1)   |
| C(49)-C(50)-H(50)   | 119.6    | C(51)-C(50)-H(50)   | 119.6    |
| C(52)-C(51)-C(50)   | 117(1)   | C(52)-C(51)-H(51)   | 121.4    |
| C(50)-C(51)-H(51)   | 121.4    | C(51)-C(52)-C(47)   | 125(1)   |
| C(51)-C(52)-H(52)   | 117.7    | C(47)-C(52)-H(52)   | 117.7    |
| C(54)-C(53)-C(58)   | 119(1)   | C(54)-C(53)-P(1)    | 122.9(7) |
| C(58)-C(53)-P(1)    | 118.4(8) | C(53)-C(54)-C(55)   | 119(1)   |

|                      |          |                      |          |
|----------------------|----------|----------------------|----------|
| C(53)-C(54)-H(54)    | 120.8    | C(55)-C(54)-H(54)    | 120.8    |
| C(56)-C(55)-C(54)    | 122(1)   | C(56)-C(55)-H(55)    | 118.8    |
| C(54)-C(55)-H(55)    | 118.8    | C(55)-C(56)-C(57)    | 121(1)   |
| C(55)-C(56)-H(56)    | 119.6    | C(57)-C(56)-H(56)    | 119.6    |
| C(58)-C(57)-C(56)    | 120(1)   | C(58)-C(57)-H(57)    | 119.8    |
| C(56)-C(57)-H(57)    | 119.8    | C(57)-C(58)-C(53)    | 119(1)   |
| C(57)-C(58)-H(58)    | 120.4    | C(53)-C(58)-H(58)    | 120.4    |
| C(62A)-O(3A)-C(59A)  | 107.9(8) | C(62A)-O(3A)-Y(1)    | 126.7(5) |
| C(59A)-O(3A)-Y(1)    | 124.3(5) | O(3A)-C(59A)-C(60A)  | 106.5(7) |
| O(3A)-C(59A)-H(59A)  | 110.4    | C(60A)-C(59A)-H(59A) | 110.4    |
| O(3A)-C(59A)-H(59B)  | 110.4    | C(60A)-C(59A)-H(59B) | 110.4    |
| H(59A)-C(59A)-H(59B) | 108.6    | C(61A)-C(60A)-C(59A) | 106.2(7) |
| C(61A)-C(60A)-H(60A) | 110.5    | C(59A)-C(60A)-H(60A) | 110.5    |
| C(61A)-C(60A)-H(60B) | 110.5    | C(59A)-C(60A)-H(60B) | 110.5    |
| H(60A)-C(60A)-H(60B) | 108.7    | C(60A)-C(61A)-C(62A) | 106.4(8) |
| C(60A)-C(61A)-H(61A) | 110.5    | C(62A)-C(61A)-H(61A) | 110.5    |
| C(60A)-C(61A)-H(61B) | 110.5    | C(62A)-C(61A)-H(61B) | 110.5    |
| H(61A)-C(61A)-H(61B) | 108.7    | O(3A)-C(62A)-C(61A)  | 104.6(8) |
| O(3A)-C(62A)-H(62A)  | 110.8    | C(61A)-C(62A)-H(62A) | 110.8    |
| O(3A)-C(62A)-H(62B)  | 110.8    | C(61A)-C(62A)-H(62B) | 110.8    |
| H(62A)-C(62A)-H(62B) | 108.9    | C(60B)-C(59B)-H(59C) | 110.9    |
| C(60B)-C(59B)-H(59D) | 110.9    | H(59C)-C(59B)-H(59D) | 108.9    |
| C(61B)-C(60B)-C(59B) | 106.0(8) | C(61B)-C(60B)-H(60C) | 110.5    |
| C(59B)-C(60B)-H(60C) | 110.5    | C(61B)-C(60B)-H(60D) | 110.5    |
| C(59B)-C(60B)-H(60D) | 110.5    | H(60C)-C(60B)-H(60D) | 108.7    |
| C(60B)-C(61B)-C(62B) | 104.8(6) | C(60B)-C(61B)-H(61C) | 110.8    |
| C(62B)-C(61B)-H(61C) | 110.8    | C(60B)-C(61B)-H(61D) | 110.8    |
| C(62B)-C(61B)-H(61D) | 110.8    | H(61C)-C(61B)-H(61D) | 108.9    |
| C(61B)-C(62B)-H(62C) | 110.1    | C(61B)-C(62B)-H(62D) | 110.1    |
| H(62C)-C(62B)-H(62D) | 108.4    | C(63A)-O(4A)-Y(1)    | 164(1)   |
| O(4A)-C(63A)-C(64A)  | 108(1)   | O(4A)-C(63A)-C(65A)  | 114(2)   |
| C(64A)-C(63A)-C(65A) | 108(1)   | O(4A)-C(63A)-C(66A)  | 110(1)   |
| C(64A)-C(63A)-C(66A) | 110(1)   | C(65A)-C(63A)-C(66A) | 107(1)   |
| C(63B)-O(4B)-Y(1)    | 159(1)   | O(4B)-C(63B)-C(65B)  | 109(1)   |
| O(4B)-C(63B)-C(66B)  | 111(2)   | C(65B)-C(63B)-C(66B) | 113(1)   |
| O(4B)-C(63B)-C(64B)  | 105.9(7) | C(65B)-C(63B)-C(64B) | 111(1)   |
| C(66B)-C(63B)-C(64B) | 107(1)   | C(63B)-C(64B)-H(64D) | 109.5    |
| C(63B)-C(64B)-H(64E) | 109.5    | H(64D)-C(64B)-H(64E) | 109.5    |
| C(63B)-C(64B)-H(64F) | 109.5    | H(64D)-C(64B)-H(64F) | 109.5    |
| H(64E)-C(64B)-H(64F) | 109.5    | C(63B)-C(65B)-H(65D) | 109.5    |
| C(63B)-C(65B)-H(65E) | 109.5    | H(65D)-C(65B)-H(65E) | 109.5    |
| C(63B)-C(65B)-H(65F) | 109.5    | H(65D)-C(65B)-H(65F) | 109.5    |
| H(65E)-C(65B)-H(65F) | 109.5    | C(63B)-C(66B)-H(66D) | 109.5    |
| C(63B)-C(66B)-H(66E) | 109.5    | H(66D)-C(66B)-H(66E) | 109.5    |
| C(63B)-C(66B)-H(66F) | 109.5    | H(66D)-C(66B)-H(66F) | 109.5    |
| H(66E)-C(66B)-H(66F) | 109.5    |                      |          |

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa652

| atom  | U11    | U22     | U33     | U23     | U13     | U12    |
|-------|--------|---------|---------|---------|---------|--------|
| Y(1)  | 15(1)  | 25(1)   | 22(1)   | -1(1)   | 4(1)    | 0(1)   |
| P(1)  | 19(1)  | 24(1)   | 22(1)   | 2(1)    | 3(1)    | 3(1)   |
| P(2)  | 16(1)  | 26(1)   | 22(1)   | 0(1)    | 5(1)    | -1(1)  |
| O(1)  | 19(3)  | 32(3)   | 28(3)   | -8(3)   | 5(2)    | -4(3)  |
| O(2)  | 17(3)  | 36(4)   | 28(3)   | 8(3)    | 6(2)    | 4(3)   |
| N(1)  | 22(3)  | 40(4)   | 20(3)   | 2(3)    | 6(3)    | -5(3)  |
| N(2)  | 27(4)  | 17(3)   | 27(4)   | 8(3)    | 12(3)   | 3(3)   |
| C(1A) | 22(7)  | 18(4)   | 21(5)   | 7(3)    | 10(5)   | -8(4)  |
| C(2A) | 8(8)   | 32(5)   | 23(7)   | 9(4)    | -6(5)   | -7(6)  |
| C(3A) | 50(10) | 29(5)   | 38(6)   | 12(4)   | 40(10)  | 11(8)  |
| C(4A) | 30(10) | 28(5)   | 21(6)   | 1(4)    | 5(5)    | 0(6)   |
| C(5A) | 40(10) | 36(7)   | 28(6)   | 8(5)    | 30(10)  | 0(8)   |
| C(6A) | 0(8)   | 28(4)   | 17(7)   | 6(5)    | -8(6)   | -2(7)  |
| C(1B) | 22(7)  | 18(4)   | 21(5)   | 7(3)    | 10(5)   | -8(4)  |
| C(2B) | 8(8)   | 32(5)   | 23(7)   | 9(4)    | -6(5)   | -7(6)  |
| C(3B) | 50(10) | 29(5)   | 38(6)   | 12(4)   | 40(10)  | 11(8)  |
| C(4B) | 30(10) | 28(5)   | 21(6)   | 1(4)    | 5(5)    | 0(6)   |
| C(5B) | 40(10) | 36(7)   | 28(6)   | 8(5)    | 30(10)  | 0(8)   |
| C(6B) | 0(8)   | 28(4)   | 17(7)   | 6(5)    | -8(6)   | -2(7)  |
| C(7)  | 19(3)  | 18(3)   | 28(4)   | -5(3)   | 0(3)    | -5(3)  |
| C(8)  | 20(3)  | 20(3)   | 25(4)   | -8(3)   | -8(3)   | -1(3)  |
| C(9)  | 15(3)  | 18(3)   | 24(3)   | -1(3)   | -10(2)  | -5(2)  |
| C(10) | 30(4)  | 24(4)   | 21(4)   | -8(3)   | -5(3)   | -5(3)  |
| C(11) | 28(4)  | 24(4)   | 24(4)   | -4(3)   | 11(3)   | -3(3)  |
| C(12) | 12(3)  | 22(4)   | 26(4)   | 0(3)    | -5(3)   | 0(3)   |
| C(13) | 21(4)  | 62(6)   | 43(5)   | -10(4)  | 24(3)   | -3(3)  |
| C(14) | 16(3)  | 66(6)   | 63(6)   | -4(5)   | 17(3)   | 8(3)   |
| C(15) | 58(7)  | 48(6)   | 72(7)   | -23(5)  | 37(6)   | -26(5) |
| C(16) | 39(5)  | 81(8)   | 55(6)   | -34(6)  | 32(5)   | -7(5)  |
| C(17) | 29(4)  | 21(3)   | 39(5)   | -4(3)   | 3(3)    | -4(3)  |
| C(18) | 31(5)  | 170(10) | 41(5)   | -26(6)  | 4(4)    | -41(6) |
| C(19) | 90(10) | 80(10)  | 170(10) | -90(10) | -40(10) | -5(7)  |
| C(20) | 42(5)  | 128(8)  | 43(4)   | 34(5)   | -6(3)   | -34(5) |
| C(21) | 30(4)  | 25(4)   | 30(4)   | -4(3)   | 16(3)   | -7(3)  |
| C(22) | 46(6)  | 37(5)   | 32(5)   | 3(4)    | 15(4)   | -8(4)  |
| C(23) | 40(4)  | 41(5)   | 49(5)   | 6(4)    | 14(3)   | 7(3)   |
| C(24) | 42(6)  | 73(8)   | 58(6)   | -18(5)  | 31(5)   | -40(5) |
| C(25) | 22(4)  | 50(6)   | 39(5)   | -5(4)   | -2(3)   | -5(4)  |
| C(26) | 36(5)  | 32(4)   | 40(5)   | -11(4)  | 17(4)   | -12(4) |
| C(27) | 18(3)  | 29(4)   | 24(4)   | 8(3)    | -4(3)   | 9(3)   |
| C(28) | 33(5)  | 31(4)   | 52(5)   | 7(4)    | 5(4)    | 15(4)  |
| C(29) | 25(5)  | 60(7)   | 43(6)   | 3(5)    | -5(4)   | 4(5)   |
| C(30) | 29(5)  | 53(6)   | 52(6)   | 10(5)   | 24(4)   | 11(4)  |
| C(31) | 37(5)  | 30(4)   | 62(7)   | 3(4)    | 18(5)   | 15(4)  |
| C(32) | 44(5)  | 41(5)   | 38(5)   | 0(4)    | 16(4)   | 18(4)  |
| C(33) | 18(3)  | 37(4)   | 16(3)   | 0(3)    | 7(2)    | -6(3)  |
| C(34) | 18(3)  | 30(4)   | 24(3)   | -2(3)   | 12(3)   | -4(3)  |
| C(35) | 27(4)  | 37(4)   | 36(4)   | 4(3)    | 25(3)   | -8(3)  |
| C(36) | 23(4)  | 35(5)   | 31(4)   | 0(4)    | 16(3)   | -6(3)  |
| C(37) | 19(4)  | 24(4)   | 28(4)   | 1(3)    | -6(3)   | -1(3)  |
| C(38) | 31(4)  | 31(4)   | 26(4)   | 1(3)    | 15(3)   | 0(4)   |
| C(39) | 26(4)  | 22(3)   | 28(4)   | 8(3)    | 0(3)    | -2(3)  |
| C(40) | 48(6)  | 57(7)   | 63(6)   | -3(5)   | 44(5)   | 3(5)   |
| C(41) | 29(5)  | 70(7)   | 43(5)   | 23(5)   | 10(4)   | 14(5)  |
| C(42) | 29(4)  | 82(8)   | 44(5)   | 3(5)    | 3(4)    | -17(4) |
| C(43) | 18(4)  | 62(5)   | 16(3)   | 6(3)    | 0(3)    | 5(4)   |
| C(44) | 37(4)  | 36(4)   | 140(10) | 30(5)   | -36(5)  | -9(3)  |
| C(45) | 33(4)  | 160(10) | 26(3)   | -13(4)  | -16(3)  | 28(5)  |
| C(46) | 18(3)  | 87(6)   | 57(6)   | 26(5)   | 4(3)    | -5(4)  |
| C(47) | 22(4)  | 32(4)   | 35(4)   | -1(3)   | 16(3)   | 7(3)   |
| C(48) | 22(4)  | 46(5)   | 25(3)   | 6(3)    | -6(3)   | 9(3)   |
| C(49) | 32(5)  | 52(7)   | 38(5)   | -8(5)   | -3(4)   | -7(5)  |
| C(50) | 25(4)  | 51(6)   | 47(6)   | -28(5)  | 2(4)    | -15(4) |

|        |       |        |        |        |       |        |
|--------|-------|--------|--------|--------|-------|--------|
| C(51)  | 60(7) | 65(7)  | 39(6)  | -4(5)  | 18(5) | -26(6) |
| C(52)  | 37(5) | 43(6)  | 32(5)  | 4(4)   | -2(4) | -4(4)  |
| C(53)  | 18(4) | 38(5)  | 24(4)  | 6(4)   | 2(3)  | 3(3)   |
| C(54)  | 23(4) | 37(5)  | 50(6)  | 3(4)   | 13(4) | 8(4)   |
| C(55)  | 51(5) | 55(6)  | 53(5)  | 7(4)   | 28(4) | 41(4)  |
| C(56)  | 36(5) | 45(5)  | 45(5)  | 6(4)   | 19(4) | 11(4)  |
| C(57)  | 25(4) | 69(7)  | 57(6)  | 29(5)  | 26(4) | 16(4)  |
| C(58)  | 12(3) | 46(5)  | 33(5)  | 1(4)   | 0(3)  | -4(3)  |
| O(3A)  | 19(1) | 39(1)  | 22(1)  | 5(4)   | 5(1)  | 3(4)   |
| C(59A) | 19(1) | 55(7)  | 30(2)  | -13(7) | 7(1)  | 2(7)   |
| C(60A) | 19(2) | 42(6)  | 35(2)  | 6(6)   | 1(2)  | -1(5)  |
| C(61A) | 27(2) | 46(7)  | 24(2)  | -2(6)  | -1(2) | -11(6) |
| C(62A) | 24(2) | 48(3)  | 23(1)  | 4(6)   | 5(1)  | 7(6)   |
| O(3B)  | 19(1) | 39(1)  | 22(1)  | 5(4)   | 5(1)  | 3(4)   |
| C(59B) | 19(1) | 55(7)  | 30(2)  | -13(7) | 7(1)  | 2(7)   |
| C(60B) | 19(2) | 42(6)  | 35(2)  | 6(6)   | 1(2)  | -1(5)  |
| C(61B) | 27(2) | 46(7)  | 24(2)  | -2(6)  | -1(2) | -11(6) |
| C(62B) | 24(2) | 48(3)  | 23(1)  | 4(6)   | 5(1)  | 7(6)   |
| O(4A)  | 23(3) | 5(8)   | 9(6)   | 1(4)   | 1(4)  | -1(3)  |
| C(63A) | 16(2) | 46(2)  | 39(4)  | 20(10) | 0(2)  | 12(6)  |
| C(64A) | 38(3) | 59(4)  | 54(3)  | -1(6)  | 10(2) | -2(6)  |
| C(65A) | 14(8) | 90(10) | 90(10) | -29(6) | 0(6)  | -22(7) |
| C(66A) | 32(6) | 40(5)  | 74(8)  | 19(7)  | 16(7) | 13(4)  |
| O(4B)  | 14(2) | 43(6)  | 14(5)  | -22(6) | -2(4) | 5(6)   |
| C(63B) | 16(2) | 46(2)  | 39(4)  | 20(10) | 0(2)  | 12(6)  |
| C(64B) | 38(3) | 59(4)  | 54(3)  | -1(6)  | 10(2) | -2(6)  |
| C(65B) | 14(8) | 90(10) | 90(10) | -29(6) | 0(6)  | -22(7) |
| C(66B) | 32(6) | 40(5)  | 74(8)  | 19(7)  | 16(7) | 13(4)  |

The anisotropic displacement factor exponent takes the form  
 $2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^*b^*U_{12}]$

Table 5. Hydrogen Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa652

| atom   | x     | y    | z     | U(eq) |
|--------|-------|------|-------|-------|
| H(1A)  | 8149  | 2344 | 2410  | 23    |
| H(2A)  | 10601 | 1886 | 3440  | 28    |
| H(3A1) | 8437  | 1526 | 1583  | 39    |
| H(3A2) | 9778  | 1217 | 2157  | 39    |
| H(4A1) | 11006 | 1835 | 1360  | 33    |
| H(4A2) | 9773  | 1669 | 237   | 33    |
| H(5A1) | 8662  | 2377 | 413   | 38    |
| H(5A2) | 10086 | 2549 | 375   | 38    |
| H(6A1) | 9376  | 3025 | 1839  | 21    |
| H(6A2) | 10728 | 2728 | 2465  | 21    |
| H(1B)  | 10659 | 2421 | 3497  | 23    |
| H(2B)  | 8192  | 1894 | 2334  | 28    |
| H(3B1) | 10773 | 1569 | 2362  | 39    |
| H(3B2) | 9496  | 1217 | 1847  | 39    |
| H(4B1) | 8550  | 1842 | 388   | 33    |
| H(4B2) | 9930  | 1659 | 240   | 33    |
| H(5B1) | 11000 | 2429 | 1307  | 38    |
| H(5B2) | 9794  | 2604 | 164   | 38    |
| H(6B1) | 8425  | 2680 | 1443  | 21    |
| H(6B2) | 9672  | 3045 | 1923  | 21    |
| H(10)  | 9308  | 3707 | 9060  | 33    |
| H(12)  | 11258 | 3653 | 6563  | 27    |
| H(14A) | 5036  | 3610 | 6908  | 70    |
| H(14B) | 5875  | 3461 | 6005  | 70    |
| H(14C) | 6184  | 3981 | 6779  | 70    |
| H(15A) | 7173  | 2644 | 8686  | 83    |
| H(15B) | 6478  | 2592 | 7248  | 83    |
| H(15C) | 5650  | 2782 | 8128  | 83    |
| H(16A) | 6135  | 3691 | 9126  | 82    |
| H(16B) | 7437  | 3966 | 9013  | 82    |
| H(16C) | 7537  | 3430 | 9715  | 82    |
| H(18A) | 12864 | 4068 | 7899  | 121   |
| H(18B) | 13000 | 3477 | 8305  | 121   |
| H(18C) | 13703 | 3914 | 9258  | 121   |
| H(19A) | 11537 | 4647 | 8415  | 197   |
| H(19B) | 12218 | 4592 | 9854  | 197   |
| H(19C) | 10664 | 4516 | 9300  | 197   |
| H(20A) | 12743 | 3700 | 10773 | 113   |
| H(20B) | 12258 | 3202 | 9947  | 113   |
| H(20C) | 11233 | 3532 | 10414 | 113   |
| H(22)  | 9650  | 4214 | 3338  | 45    |
| H(23)  | 11351 | 4618 | 2896  | 52    |
| H(24)  | 13523 | 4217 | 3531  | 65    |
| H(25)  | 13732 | 3409 | 4365  | 47    |
| H(26)  | 11924 | 3017 | 4809  | 42    |
| H(28)  | 7097  | 3153 | 2241  | 48    |
| H(29)  | 5380  | 3682 | 1169  | 55    |
| H(30)  | 4955  | 4450 | 2022  | 51    |
| H(31)  | 6293  | 4686 | 3888  | 51    |
| H(32)  | 8146  | 4209 | 4921  | 48    |
| H(36)  | 9279  | 543  | 9074  | 33    |
| H(38)  | 11190 | 591  | 6495  | 34    |
| H(40A) | 6214  | 1615 | 7095  | 75    |
| H(40B) | 7199  | 1662 | 8449  | 75    |
| H(40C) | 5732  | 1458 | 8244  | 75    |
| H(41A) | 6145  | 717  | 9194  | 71    |
| H(41B) | 7710  | 773  | 9666  | 71    |
| H(41C) | 7056  | 273  | 8918  | 71    |
| H(42A) | 5680  | 846  | 6019  | 80    |
| H(42B) | 4979  | 675  | 7016  | 80    |
| H(42C) | 6005  | 299  | 6674  | 80    |
| H(44A) | 11417 | -353 | 8277  | 126   |

|        |       |           |       |     |
|--------|-------|-----------|-------|-----|
| H(44B) | 11046 | -275      | 9522  | 126 |
| H(44C) | 12553 | -319      | 9551  | 126 |
| H(45A) | 12651 | 482       | 10789 | 117 |
| H(45B) | 11095 | 411       | 10481 | 117 |
| H(45C) | 11687 | 942       | 10177 | 117 |
| H(46A) | 13192 | 859       | 8709  | 83  |
| H(46B) | 12929 | 381       | 7788  | 83  |
| H(46C) | 13753 | 304       | 9190  | 83  |
| H(48)  | 7156  | 1084      | 2108  | 40  |
| H(49)  | 5312  | 589       | 1131  | 52  |
| H(50)  | 4910  | -176      | 1983  | 52  |
| H(51)  | 6309  | -448.0000 | 3923  | 65  |
| H(52)  | 8065  | 75        | 4915  | 48  |
| H(54)  | 9659  | 25        | 3324  | 43  |
| H(55)  | 11540 | -360.0000 | 2966  | 60  |
| H(56)  | 13446 | 42        | 3398  | 48  |
| H(57)  | 13753 | 831       | 4437  | 57  |
| H(58)  | 11976 | 1254      | 4794  | 38  |
| H(59A) | 11262 | 2548      | 6251  | 42  |
| H(59B) | 11262 | 1960      | 5827  | 42  |
| H(60A) | 12584 | 1744      | 7622  | 40  |
| H(60B) | 12694 | 2341      | 7997  | 40  |
| H(61A) | 11634 | 2145      | 9301  | 41  |
| H(61B) | 11239 | 1588      | 8694  | 41  |
| H(62A) | 9235  | 1940      | 8063  | 38  |
| H(62B) | 9805  | 2514      | 8108  | 38  |
| H(59C) | 11188 | 2267      | 5718  | 42  |
| H(59D) | 11343 | 1710      | 6355  | 42  |
| H(60C) | 12894 | 2131      | 7804  | 40  |
| H(60D) | 12140 | 2672      | 7494  | 40  |
| H(61C) | 11471 | 2506      | 9108  | 41  |
| H(61D) | 11770 | 1902      | 9064  | 41  |
| H(62C) | 9682  | 1769      | 8112  | 38  |
| H(62D) | 9399  | 2375      | 8094  | 38  |
| H(64A) | 5601  | 2497      | 1230  | 77  |
| H(64B) | 4143  | 2285      | 634   | 77  |
| H(64C) | 5359  | 1896      | 966   | 77  |
| H(65A) | 4466  | 1358      | 2558  | 100 |
| H(65B) | 3274  | 1665      | 1646  | 100 |
| H(65C) | 3523  | 1706      | 3091  | 100 |
| H(66A) | 4119  | 2561      | 3683  | 73  |
| H(66B) | 3265  | 2630      | 2286  | 73  |
| H(66C) | 4651  | 2915      | 2788  | 73  |
| H(64D) | 4383  | 1834      | 4599  | 77  |
| H(64E) | 3074  | 2092      | 3739  | 77  |
| H(64F) | 4251  | 2446      | 4521  | 77  |
| H(65D) | 4597  | 1661      | 1526  | 100 |
| H(65E) | 3359  | 1576      | 2025  | 100 |
| H(65F) | 4761  | 1347      | 2763  | 100 |
| H(66D) | 4336  | 2912      | 2741  | 73  |
| H(66E) | 3152  | 2581      | 1891  | 73  |
| H(66F) | 4502  | 2630      | 1553  | 73  |

**Complex 52**

Table 1. Crystal data for pa781

|                        |  |
|------------------------|--|
| Compound               | pa781  |
| Molecular formula      | C <sub>66</sub> H <sub>87</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Y |
| Molecular weight       | 1123.23  |
| Crystal habit          | Colorless Block  |
| Crystal dimensions(mm) | 0.24x0.22x0.08   |
| Crystal system         | monoclinic   |

## Appendix 1. Crystallographic data

|   |                                     |
|---|-------------------------------------|
| Space group                                 | P2 <sub>1</sub>                     |
| a(Å)  | 10.652(1)                           |
| b(Å)  | 26.078(1)                           |
| c(Å)  | 11.444(1)                           |
| α(°)  | 90.00                               |
| β(°)  | 107.043(1)                          |
| γ(°)  | 90.00                               |
| V(Å <sup>3</sup> )                          | 3039.3(4)                           |
| Z   | 2                                   |
| d(g·cm <sup>-3</sup> )                      | 1.227                               |
| F(000)                                      | 1196                                |
| μ(cm <sup>-1</sup> )                        | 1.060                               |
| Absorption corrections                      | multi-scan ; 0.7851 min, 0.9200 max |
| Diffractionmeter                            | KappaCCD                            |
| X-ray source                                | MoKα                                |
| λ(Å)  | 0.71069                             |
| Monochromator                               | graphite                            |
| T (K)                                       | 150.0(1)                            |
| Scan mode                                   | phi and omega scans                 |
| Maximum θ                                   | 27.47                               |
| HKL ranges                                  | -13 13 ; -33 26 ; -14 10            |
| Reflections measured                        | 13947                               |
| Unique data                                 | 10630                               |
| Rint  | 0.0321                              |
| Reflections used                            | 9073                                |
| Criterion                                   | I > 2σ(I)                           |
| Refinement type                             | Fsqd                                |
| Hydrogen atoms                              | constr                              |
| Parameters refined                          | 706                                 |
| Reflections / parameter                     | 12                                  |
| wR2   | 0.1190                              |
| R1  | 0.0603                              |
| Flack's parameter                           | 0.04(12)                            |
| Weights a, b                                | 0.0000 ; 8.1500                     |
| GoF   | 1.111                               |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.117(0.074) / -0.531(0.074)        |

## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa781

| atom  | x          | y        | z         | U(eq)   |
|-------|------------|----------|-----------|---------|
| Y(1)  | 2245(4)    | 2110(20) | 5176(3)   | 20(1)   |
| P(1)  | 770(20)    | 3230(20) | 5580(20)  | 20(4)   |
| P(2)  | 750(20)    | 1000(20) | 5630(20)  | 21(4)   |
| O(1)  | 2550(60)   | 2840(30) | 4300(50)  | 30(10)  |
| O(2)  | 2590(60)   | 1360(30) | 4350(50)  | 30(10)  |
| N(1)  | 930(70)    | 2640(30) | 6020(60)  | 20(10)  |
| N(2)  | 820(60)    | 1590(30) | 5980(60)  | 20(10)  |
| C(1)  | 340(60)    | 2400(30) | 6900(50)  | 20(10)  |
| C(2)  | 880(60)    | 1850(30) | 7150(50)  | 20(10)  |
| C(3)  | 230(70)    | 1560(30) | 7980(70)  | 30(10)  |
| C(4)  | 450(60)    | 1850(30) | 9190(60)  | 30(10)  |
| C(5)  | -60(60)    | 2390(30) | 8980(60)  | 30(10)  |
| C(6)  | 580(70)    | 2670(30) | 8120(70)  | 30(10)  |
| C(7)  | 590(80)    | 3310(30) | 3980(70)  | 20(20)  |
| C(8)  | 1650(80)   | 3150(30) | 3590(70)  | 20(20)  |
| C(9)  | 1770(80)   | 3340(30) | 2460(70)  | 20(10)  |
| C(10) | 660(80)    | 3570(30) | 1690(70)  | 20(20)  |
| C(11) | -520(80)   | 3650(30) | 1970(70)  | 20(20)  |
| C(12) | -490(80)   | 3550(30) | 3190(70)  | 20(20)  |
| C(13) | 3100(100)  | 3300(40) | 2120(80)  | 30(20)  |
| C(14) | 3400(100)  | 2740(40) | 2000(100) | 40(20)  |
| C(15) | 3000(100)  | 3590(50) | 900(100)  | 50(30)  |
| C(16) | 4200(100)  | 3540(40) | 3100(100) | 40(20)  |
| C(17) | -1700(100) | 3870(40) | 1020(80)  | 30(20)  |
| C(18) | -1900(100) | 3640(70) | -200(100) | 100(50) |
| C(19) | -1700(100) | 4450(50) | 1000(200) | 90(50)  |
| C(20) | -3000(100) | 3750(50) | 1400(100) | 60(30)  |
| C(21) | -610(80)   | 3550(30) | 5860(70)  | 30(20)  |
| C(22) | -1820(80)  | 3330(40) | 5550(80)  | 30(20)  |
| C(23) | -2900(100) | 3560(40) | 5800(100) | 40(20)  |
| C(24) | -2800(100) | 4040(50) | 6300(100) | 40(20)  |
| C(25) | -1500(100) | 4280(40) | 6600(100) | 40(20)  |
| C(26) | -500(100)  | 4040(40) | 6400(100) | 30(20)  |
| C(27) | 2200(80)   | 3620(40) | 6310(70)  | 20(20)  |
| C(28) | 2400(100)  | 4080(30) | 5800(100) | 30(20)  |
| C(29) | 3500(100)  | 4380(40) | 6400(100) | 40(20)  |
| C(30) | 4300(100)  | 4230(40) | 7500(100) | 40(20)  |
| C(31) | 4100(100)  | 3790(40) | 8000(100) | 40(20)  |
| C(32) | 3000(100)  | 3480(40) | 7420(80)  | 30(20)  |
| C(33) | 580(80)    | 910(30)  | 4040(70)  | 20(10)  |
| C(34) | 1710(80)   | 1050(30) | 3670(70)  | 20(20)  |
| C(35) | 1800(80)   | 850(30)  | 2540(80)  | 30(20)  |
| C(36) | 700(100)   | 620(30)  | 1750(80)  | 30(20)  |
| C(37) | -520(80)   | 560(30)  | 2040(70)  | 20(20)  |
| C(38) | -520(80)   | 670(30)  | 3220(70)  | 30(20)  |
| C(39) | 3100(100)  | 870(40)  | 2240(80)  | 30(20)  |
| C(40) | 3000(100)  | 590(50)  | 1000(100) | 60(30)  |
| C(41) | 3600(100)  | 1400(40) | 2100(100) | 40(20)  |
| C(42) | 4100(100)  | 580(40)  | 3300(100) | 40(20)  |
| C(43) | -1700(100) | 360(40)  | 1050(80)  | 30(20)  |
| C(44) | -1600(100) | -200(50) | 800(200)  | 110(70) |
| C(45) | -3000(100) | 420(60)  | 1400(100) | 60(30)  |
| C(46) | -2000(100) | 660(60)  | -100(100) | 70(40)  |
| C(47) | -630(80)   | 660(30)  | 5930(70)  | 30(20)  |
| C(48) | -500(100)  | 180(40)  | 6500(100) | 40(20)  |
| C(49) | -1600(100) | -60(40)  | 6800(100) | 50(30)  |
| C(50) | -2800(100) | 180(40)  | 6400(100) | 50(30)  |
| C(51) | -2900(100) | 650(50)  | 5900(100) | 50(30)  |
| C(52) | -1900(100) | 900(40)  | 5600(100) | 30(20)  |
| C(53) | 2160(80)   | 620(30)  | 6420(70)  | 20(20)  |
| C(54) | 2500(100)  | 170(40)  | 5910(80)  | 30(20)  |
| C(55) | 3600(100)  | -130(40) | 6500(100) | 50(30)  |

## Appendix 1. Crystallographic data

|        |            |           |           |        |
|--------|------------|-----------|-----------|--------|
| C(56)  | 4300(100)  | 30(40)    | 7600(100) | 40(20) |
| C(57)  | 4100(100)  | 480(40)   | 8100(100) | 40(20) |
| C(58)  | 3000(100)  | 780(40)   | 7540(80)  | 30(20) |
| O(3A)  | 160(70)    | 2120(50)  | 3410(80)  | 40(20) |
| C(59A) | -1200(100) | 2150(60)  | 3510(60)  | 40(20) |
| C(60A) | -2050(70)  | 2000(50)  | 2290(70)  | 40(20) |
| C(61A) | -1310(70)  | 2210(50)  | 1440(60)  | 40(20) |
| C(62A) | 90(70)     | 2080(70)  | 2100(100) | 40(20) |
| O(3B)  | 200(100)   | 2090(70)  | 3400(100) | 20(40) |
| C(59B) | -1100(200) | 2070(80)  | 3600(100) | 20(40) |
| C(60B) | -2100(100) | 2240(70)  | 2500(100) | 20(40) |
| C(61B) | -1500(100) | 1990(70)  | 1500(100) | 20(40) |
| C(62B) | 0(100)     | 2100(100) | 2100(200) | 20(40) |
| O(4A)  | 3940(20)   | 2080(20)  | 6580(30)  | 30(7)  |
| C(63A) | 5310(30)   | 2110(40)  | 7010(40)  | 40(20) |
| C(64A) | 5940(60)   | 2100(100) | 5950(70)  | 60(30) |
| C(65A) | 5800(100)  | 2600(50)  | 7800(100) | 40(40) |
| C(66A) | 5900(100)  | 1650(70)  | 7900(200) | 60(60) |
| O(4B)  | 3940(20)   | 2080(20)  | 6580(30)  | 30(7)  |
| C(63B) | 5200(80)   | 2140(30)  | 7480(60)  | 40(20) |
| C(64B) | 5000(100)  | 2160(80)  | 8750(40)  | 60(30) |
| C(65B) | 5900(100)  | 2640(60)  | 7200(100) | 40(40) |
| C(66B) | 6100(100)  | 1670(70)  | 7400(200) | 60(60) |

U(eq) is defined as 1/3 the trace of the Uij tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths (Å) and angles (deg) for pa781

|               |         |               |         |
|---------------|---------|---------------|---------|
| Y(1)-O(4A)    | 2.04(2) | Y(1)-O(1)     | 2.23(6) |
| Y(1)-O(2)     | 2.25(6) | Y(1)-N(1)     | 2.38(7) |
| Y(1)-N(2)     | 2.40(7) | Y(1)-O(3B)    | 2.5(1)  |
| Y(1)-O(3A)    | 2.53(6) | P(1)-N(1)     | 1.59(7) |
| P(1)-C(21)    | 1.8(1)  | P(1)-C(7)     | 1.81(8) |
| P(1)-C(27)    | 1.83(8) | P(2)-N(2)     | 1.59(7) |
| P(2)-C(33)    | 1.79(8) | P(2)-C(53)    | 1.81(8) |
| P(2)-C(47)    | 1.8(1)  | O(1)-C(8)     | 1.3(1)  |
| O(2)-C(34)    | 1.3(1)  | N(1)-C(1)     | 1.5(1)  |
| N(2)-C(2)     | 1.47(8) | C(1)-C(6)     | 1.5(1)  |
| C(1)-C(2)     | 1.54(7) | C(2)-C(3)     | 1.5(1)  |
| C(3)-C(4)     | 1.5(1)  | C(4)-C(5)     | 1.52(7) |
| C(5)-C(6)     | 1.5(1)  | C(7)-C(12)    | 1.4(1)  |
| C(7)-C(8)     | 1.4(1)  | C(8)-C(9)     | 1.4(1)  |
| C(9)-C(10)    | 1.4(1)  | C(9)-C(13)    | 1.5(1)  |
| C(10)-C(11)   | 1.4(1)  | C(11)-C(12)   | 1.4(1)  |
| C(11)-C(17)   | 1.5(1)  | C(13)-C(15)   | 1.5(1)  |
| C(13)-C(16)   | 1.5(1)  | C(13)-C(14)   | 1.5(1)  |
| C(17)-C(19)   | 1.5(2)  | C(17)-C(20)   | 1.5(1)  |
| C(17)-C(18)   | 1.5(2)  | C(21)-C(22)   | 1.4(1)  |
| C(21)-C(26)   | 1.4(1)  | C(22)-C(23)   | 1.4(1)  |
| C(23)-C(24)   | 1.4(2)  | C(24)-C(25)   | 1.4(2)  |
| C(25)-C(26)   | 1.4(1)  | C(27)-C(32)   | 1.4(1)  |
| C(27)-C(28)   | 1.4(1)  | C(28)-C(29)   | 1.4(1)  |
| C(29)-C(30)   | 1.4(1)  | C(30)-C(31)   | 1.4(1)  |
| C(31)-C(32)   | 1.4(1)  | C(33)-C(38)   | 1.4(1)  |
| C(33)-C(34)   | 1.4(1)  | C(34)-C(35)   | 1.4(1)  |
| C(35)-C(36)   | 1.4(1)  | C(35)-C(39)   | 1.5(1)  |
| C(36)-C(37)   | 1.4(1)  | C(37)-C(38)   | 1.4(1)  |
| C(37)-C(43)   | 1.5(1)  | C(39)-C(41)   | 1.5(1)  |
| C(39)-C(40)   | 1.5(1)  | C(39)-C(42)   | 1.5(1)  |
| C(43)-C(45)   | 1.5(1)  | C(43)-C(46)   | 1.5(1)  |
| C(43)-C(44)   | 1.5(1)  | C(47)-C(48)   | 1.4(1)  |
| C(47)-C(52)   | 1.4(1)  | C(48)-C(49)   | 1.4(1)  |
| C(49)-C(50)   | 1.4(2)  | C(50)-C(51)   | 1.4(2)  |
| C(51)-C(52)   | 1.4(1)  | C(53)-C(54)   | 1.4(1)  |
| C(53)-C(58)   | 1.4(1)  | C(54)-C(55)   | 1.4(1)  |
| C(55)-C(56)   | 1.4(2)  | C(56)-C(57)   | 1.4(1)  |
| C(57)-C(58)   | 1.4(1)  | O(3A)-C(62A)  | 1.43(1) |
| O(3A)-C(59A)  | 1.43(1) | C(59A)-C(60A) | 1.50(1) |
| C(60A)-C(61A) | 1.52(1) | C(61A)-C(62A) | 1.50(1) |
| O(3B)-C(62B)  | 1.44(1) | O(3B)-C(59B)  | 1.44(1) |
| C(59B)-C(60B) | 1.50(1) | C(60B)-C(61B) | 1.52(1) |
| C(61B)-C(62B) | 1.50(1) | O(4A)-C(63A)  | 1.40(1) |
| C(63A)-C(66A) | 1.55(1) | C(63A)-C(64A) | 1.55(1) |
| C(63A)-C(65A) | 1.55(1) | C(63B)-C(64B) | 1.55(1) |
| C(63B)-C(66B) | 1.55(1) | C(63B)-C(65B) | 1.55(1) |

|                  |        |                  |        |
|------------------|--------|------------------|--------|
| O(4A)-Y(1)-O(1)  | 100(2) | O(4A)-Y(1)-O(2)  | 95(2)  |
| O(1)-Y(1)-O(2)   | 120(1) | O(4A)-Y(1)-N(1)  | 101(2) |
| O(1)-Y(1)-N(1)   | 82(2)  | O(2)-Y(1)-N(1)   | 151(2) |
| O(4A)-Y(1)-N(2)  | 101(2) | O(1)-Y(1)-N(2)   | 148(2) |
| O(2)-Y(1)-N(2)   | 83(2)  | N(1)-Y(1)-N(2)   | 70(1)  |
| O(4A)-Y(1)-O(3B) | 177(4) | O(1)-Y(1)-O(3B)  | 82(4)  |
| O(2)-Y(1)-O(3B)  | 82(4)  | N(1)-Y(1)-O(3B)  | 82(5)  |
| N(2)-Y(1)-O(3B)  | 78(5)  | O(4A)-Y(1)-O(3A) | 179(3) |
| O(1)-Y(1)-O(3A)  | 81(3)  | O(2)-Y(1)-O(3A)  | 84(3)  |
| N(1)-Y(1)-O(3A)  | 80(3)  | N(2)-Y(1)-O(3A)  | 79(3)  |
| O(3B)-Y(1)-O(3A) | 2(5)   | N(1)-P(1)-C(21)  | 115(4) |
| N(1)-P(1)-C(7)   | 114(4) | C(21)-P(1)-C(7)  | 106(4) |
| N(1)-P(1)-C(27)  | 113(4) | C(21)-P(1)-C(27) | 105(4) |
| C(7)-P(1)-C(27)  | 102(4) | N(2)-P(2)-C(33)  | 112(4) |
| N(2)-P(2)-C(53)  | 116(4) | C(33)-P(2)-C(53) | 105(4) |
| N(2)-P(2)-C(47)  | 114(4) | C(33)-P(2)-C(47) | 106(4) |
| C(53)-P(2)-C(47) | 104(4) | C(8)-O(1)-Y(1)   | 128(5) |

|                      |         |                      |         |
|----------------------|---------|----------------------|---------|
| C(34)-O(2)-Y(1)      | 127(5)  | C(1)-N(1)-P(1)       | 127(5)  |
| C(1)-N(1)-Y(1)       | 116(4)  | P(1)-N(1)-Y(1)       | 117(3)  |
| C(2)-N(2)-P(2)       | 131(5)  | C(2)-N(2)-Y(1)       | 104(4)  |
| P(2)-N(2)-Y(1)       | 116(3)  | N(1)-C(1)-C(6)       | 115(6)  |
| N(1)-C(1)-C(2)       | 109(5)  | C(6)-C(1)-C(2)       | 108(5)  |
| N(2)-C(2)-C(3)       | 116(6)  | N(2)-C(2)-C(1)       | 110(5)  |
| C(3)-C(2)-C(1)       | 111(6)  | C(2)-C(3)-C(4)       | 111(6)  |
| C(5)-C(4)-C(3)       | 111(6)  | C(4)-C(5)-C(6)       | 110(6)  |
| C(1)-C(6)-C(5)       | 112(6)  | C(12)-C(7)-C(8)      | 122(7)  |
| C(12)-C(7)-P(1)      | 123(6)  | C(8)-C(7)-P(1)       | 116(6)  |
| O(1)-C(8)-C(7)       | 120(7)  | O(1)-C(8)-C(9)       | 122(7)  |
| C(7)-C(8)-C(9)       | 118(7)  | C(10)-C(9)-C(8)      | 116(7)  |
| C(10)-C(9)-C(13)     | 122(7)  | C(8)-C(9)-C(13)      | 122(7)  |
| C(9)-C(10)-C(11)     | 126(7)  | C(10)-C(11)-C(12)    | 115(7)  |
| C(10)-C(11)-C(17)    | 122(7)  | C(12)-C(11)-C(17)    | 123(8)  |
| C(7)-C(12)-C(11)     | 121(8)  | C(15)-C(13)-C(16)    | 108(8)  |
| C(15)-C(13)-C(9)     | 113(7)  | C(16)-C(13)-C(9)     | 110(7)  |
| C(15)-C(13)-C(14)    | 108(8)  | C(16)-C(13)-C(14)    | 108(8)  |
| C(9)-C(13)-C(14)     | 110(7)  | C(19)-C(17)-C(20)    | 106(10) |
| C(19)-C(17)-C(18)    | 110(10) | C(20)-C(17)-C(18)    | 109(10) |
| C(19)-C(17)-C(11)    | 110(8)  | C(20)-C(17)-C(11)    | 111(8)  |
| C(18)-C(17)-C(11)    | 109(8)  | C(22)-C(21)-C(26)    | 117(8)  |
| C(22)-C(21)-P(1)     | 120(7)  | C(26)-C(21)-P(1)     | 122(7)  |
| C(21)-C(22)-C(23)    | 122(9)  | C(24)-C(23)-C(22)    | 119(9)  |
| C(23)-C(24)-C(25)    | 120(9)  | C(26)-C(25)-C(24)    | 121(9)  |
| C(25)-C(26)-C(21)    | 121(9)  | C(32)-C(27)-C(28)    | 119(8)  |
| C(32)-C(27)-P(1)     | 120(7)  | C(28)-C(27)-P(1)     | 121(6)  |
| C(29)-C(28)-C(27)    | 119(9)  | C(30)-C(29)-C(28)    | 122(9)  |
| C(31)-C(30)-C(29)    | 120(9)  | C(30)-C(31)-C(32)    | 119(9)  |
| C(27)-C(32)-C(31)    | 121(9)  | C(38)-C(33)-C(34)    | 122(8)  |
| C(38)-C(33)-P(2)     | 123(6)  | C(34)-C(33)-P(2)     | 115(6)  |
| O(2)-C(34)-C(35)     | 123(7)  | O(2)-C(34)-C(33)     | 120(7)  |
| C(35)-C(34)-C(33)    | 117(7)  | C(36)-C(35)-C(34)    | 118(8)  |
| C(36)-C(35)-C(39)    | 122(8)  | C(34)-C(35)-C(39)    | 120(7)  |
| C(35)-C(36)-C(37)    | 124(8)  | C(38)-C(37)-C(36)    | 118(7)  |
| C(38)-C(37)-C(43)    | 124(8)  | C(36)-C(37)-C(43)    | 119(7)  |
| C(37)-C(38)-C(33)    | 120(8)  | C(41)-C(39)-C(35)    | 114(8)  |
| C(41)-C(39)-C(40)    | 108(8)  | C(35)-C(39)-C(40)    | 111(8)  |
| C(41)-C(39)-C(42)    | 110(8)  | C(35)-C(39)-C(42)    | 106(7)  |
| C(40)-C(39)-C(42)    | 108(8)  | C(45)-C(43)-C(46)    | 106(10) |
| C(45)-C(43)-C(44)    | 108(10) | C(46)-C(43)-C(44)    | 108(10) |
| C(45)-C(43)-C(37)    | 112(7)  | C(46)-C(43)-C(37)    | 112(8)  |
| C(44)-C(43)-C(37)    | 111(8)  | C(48)-C(47)-C(52)    | 119(8)  |
| C(48)-C(47)-P(2)     | 123(7)  | C(52)-C(47)-P(2)     | 118(7)  |
| C(47)-C(48)-C(49)    | 122(10) | C(50)-C(49)-C(48)    | 119(10) |
| C(49)-C(50)-C(51)    | 120(10) | C(50)-C(51)-C(52)    | 122(10) |
| C(51)-C(52)-C(47)    | 118(9)  | C(54)-C(53)-C(58)    | 118(8)  |
| C(54)-C(53)-P(2)     | 122(6)  | C(58)-C(53)-P(2)     | 120(6)  |
| C(53)-C(54)-C(55)    | 122(9)  | C(56)-C(55)-C(54)    | 118(10) |
| C(57)-C(56)-C(55)    | 120(8)  | C(58)-C(57)-C(56)    | 122(9)  |
| C(57)-C(58)-C(53)    | 120(9)  | C(62A)-O(3A)-C(59A)  | 109(3)  |
| C(62A)-O(3A)-Y(1)    | 126(5)  | C(59A)-O(3A)-Y(1)    | 125(5)  |
| O(3A)-C(59A)-C(60A)  | 107(4)  | C(59A)-C(60A)-C(61A) | 101(4)  |
| C(62A)-C(61A)-C(60A) | 102(4)  | O(3A)-C(62A)-C(61A)  | 106(4)  |
| C(62B)-O(3B)-C(59B)  | 109(4)  | C(62B)-O(3B)-Y(1)    | 131(10) |
| C(59B)-O(3B)-Y(1)    | 120(10) | O(3B)-C(59B)-C(60B)  | 105(5)  |
| C(59B)-C(60B)-C(61B) | 101(5)  | C(62B)-C(61B)-C(60B) | 101(5)  |
| O(3B)-C(62B)-C(61B)  | 106(5)  | C(63A)-O(4A)-Y(1)    | 150(3)  |
| O(4A)-C(63A)-C(66A)  | 112(2)  | O(4A)-C(63A)-C(64A)  | 112(2)  |
| C(66A)-C(63A)-C(64A) | 107(8)  | O(4A)-C(63A)-C(65A)  | 112(2)  |
| C(66A)-C(63A)-C(65A) | 106(7)  | C(64A)-C(63A)-C(65A) | 107(8)  |
| C(64B)-C(63B)-C(66B) | 109(9)  | C(64B)-C(63B)-C(65B) | 110(9)  |
| C(66B)-C(63B)-C(65B) | 110(9)  |                      |         |

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa781

| atom  | U11      | U22      | U33      | U23     | U13       | U12     |
|-------|----------|----------|----------|---------|-----------|---------|
| Y(1)  | 20(2)    | 22(2)    | 18(2)    | 0(4)    | 6(1)      | 0(4)    |
| P(1)  | 20(10)   | 20(10)   | 20(10)   | 1(7)    | 5(7)      | 1(7)    |
| P(2)  | 20(10)   | 20(10)   | 20(10)   | -1(7)   | 6(8)      | -2(7)   |
| O(1)  | 20(30)   | 30(30)   | 20(30)   | 10(20)  | 10(20)    | 0(20)   |
| O(2)  | 30(30)   | 30(30)   | 20(30)   | -10(20) | 10(20)    | 0(20)   |
| N(1)  | 30(30)   | 20(30)   | 20(30)   | 0(20)   | 10(20)    | 0(20)   |
| N(2)  | 20(30)   | 20(30)   | 20(30)   | -10(20) | 0(20)     | 0(20)   |
| C(1)  | 30(30)   | 20(30)   | 20(30)   | 0(20)   | 10(20)    | 0(20)   |
| C(2)  | 30(30)   | 30(30)   | 20(30)   | 0(20)   | 10(20)    | 0(30)   |
| C(3)  | 30(30)   | 20(30)   | 30(30)   | 0(20)   | 10(30)    | 0(20)   |
| C(4)  | 40(40)   | 30(30)   | 20(30)   | 0(20)   | 10(30)    | 0(30)   |
| C(5)  | 30(30)   | 30(30)   | 20(30)   | 0(20)   | 10(30)    | 0(30)   |
| C(6)  | 30(40)   | 20(30)   | 20(30)   | 0(20)   | 10(30)    | 0(30)   |
| C(7)  | 30(40)   | 20(40)   | 20(30)   | 0(30)   | 10(30)    | 0(30)   |
| C(8)  | 30(40)   | 10(40)   | 20(30)   | 0(20)   | 10(30)    | 0(30)   |
| C(9)  | 20(30)   | 20(40)   | 20(30)   | 0(30)   | 0(30)     | 0(30)   |
| C(10) | 20(40)   | 30(50)   | 10(30)   | 0(30)   | 0(30)     | 0(30)   |
| C(11) | 30(40)   | 20(40)   | 20(40)   | 0(30)   | 10(30)    | 0(30)   |
| C(12) | 20(40)   | 20(40)   | 20(40)   | 0(30)   | 10(30)    | 0(30)   |
| C(13) | 30(40)   | 30(40)   | 30(40)   | 10(30)  | 10(30)    | 0(30)   |
| C(14) | 40(50)   | 40(50)   | 60(60)   | 0(40)   | 40(40)    | 10(30)  |
| C(15) | 30(50)   | 60(70)   | 50(60)   | 20(50)  | 20(40)    | 10(40)  |
| C(16) | 30(40)   | 60(60)   | 40(50)   | 0(40)   | 20(40)    | -10(40) |
| C(17) | 30(50)   | 40(50)   | 30(50)   | 10(30)  | 10(40)    | 10(30)  |
| C(18) | 60(80)   | 200(200) | 20(50)   | -20(60) | -10(50)   | 40(80)  |
| C(19) | 60(80)   | 50(70)   | 100(100) | 30(70)  | -20(70)   | 0(50)   |
| C(20) | 30(50)   | 90(80)   | 60(70)   | 20(60)  | 0(50)     | 0(50)   |
| C(21) | 30(40)   | 30(40)   | 20(40)   | 10(30)  | 10(30)    | 0(30)   |
| C(22) | 20(40)   | 40(50)   | 30(40)   | 10(30)  | 10(30)    | 10(30)  |
| C(23) | 30(50)   | 40(50)   | 30(40)   | 10(40)  | 10(40)    | 10(40)  |
| C(24) | 40(50)   | 60(70)   | 40(50)   | 10(40)  | 20(40)    | 30(50)  |
| C(25) | 50(60)   | 30(50)   | 40(50)   | -10(40) | 20(40)    | 10(40)  |
| C(26) | 30(50)   | 30(50)   | 40(50)   | 0(40)   | 20(40)    | 0(40)   |
| C(27) | 20(40)   | 30(40)   | 20(30)   | 0(30)   | 10(30)    | 0(30)   |
| C(28) | 50(50)   | 20(40)   | 40(40)   | 10(30)  | 10(40)    | -10(30) |
| C(29) | 50(60)   | 30(50)   | 40(50)   | 0(30)   | 10(40)    | -10(40) |
| C(30) | 40(50)   | 40(50)   | 50(50)   | -10(40) | 20(40)    | -10(40) |
| C(31) | 20(40)   | 50(50)   | 50(50)   | 0(40)   | 10(30)    | 0(30)   |
| C(32) | 30(40)   | 40(50)   | 30(40)   | 0(30)   | 10(30)    | -10(30) |
| C(33) | 20(40)   | 20(40)   | 20(40)   | 0(30)   | 10(30)    | 0(30)   |
| C(34) | 20(30)   | 30(40)   | 20(30)   | 10(30)  | 0(30)     | 10(30)  |
| C(35) | 20(40)   | 30(40)   | 30(40)   | 0(30)   | 10(30)    | 0(30)   |
| C(36) | 40(50)   | 20(40)   | 30(40)   | 0(30)   | 20(40)    | 0(30)   |
| C(37) | 20(40)   | 20(40)   | 20(40)   | 0(30)   | 0(30)     | 0(30)   |
| C(38) | 20(40)   | 20(40)   | 20(40)   | 0(30)   | 0(30)     | 0(30)   |
| C(39) | 30(40)   | 40(50)   | 30(40)   | -10(30) | 20(30)    | 0(30)   |
| C(40) | 40(60)   | 90(80)   | 40(60)   | -40(50) | 30(50)    | -10(50) |
| C(41) | 40(50)   | 40(50)   | 40(50)   | 0(30)   | 20(40)    | 0(30)   |
| C(42) | 30(40)   | 50(50)   | 50(50)   | 10(40)  | 20(40)    | 10(30)  |
| C(43) | 30(50)   | 30(50)   | 20(40)   | 0(30)   | 0(30)     | 0(30)   |
| C(44) | 100(100) | 40(70)   | 200(100) | -60(80) | -100(100) | 10(60)  |
| C(45) | 40(60)   | 100(100) | 30(50)   | -20(50) | 10(40)    | -30(50) |
| C(46) | 50(60)   | 100(100) | 40(60)   | 30(60)  | 0(50)     | -40(60) |
| C(47) | 30(40)   | 30(40)   | 20(40)   | 0(30)   | 10(30)    | -10(30) |
| C(48) | 40(50)   | 40(50)   | 30(50)   | 0(40)   | 20(40)    | -10(40) |
| C(49) | 60(70)   | 50(60)   | 40(50)   | -10(40) | 30(50)    | -20(50) |
| C(50) | 50(70)   | 50(60)   | 60(70)   | -10(50) | 30(50)    | -20(50) |
| C(51) | 20(40)   | 70(70)   | 50(60)   | -20(50) | 20(40)    | 0(40)   |
| C(52) | 20(40)   | 40(50)   | 40(50)   | -10(30) | 10(30)    | 0(30)   |
| C(53) | 30(40)   | 20(40)   | 30(40)   | 0(30)   | 10(30)    | 0(30)   |
| C(54) | 30(50)   | 40(50)   | 20(40)   | 0(30)   | 0(30)     | 10(30)  |
| C(55) | 50(60)   | 40(60)   | 60(70)   | 10(40)  | 30(50)    | 20(40)  |
| C(56) | 20(40)   | 50(50)   | 40(50)   | 20(40)  | 10(30)    | 10(30)  |

# Appendix 1. Crystallographic data

|        |        |        |          |         |         |         |
|--------|--------|--------|----------|---------|---------|---------|
| C(57)  | 40(50) | 40(50) | 20(40)   | 0(30)   | 0(30)   | 10(40)  |
| C(58)  | 20(40) | 30(40) | 30(40)   | 0(30)   | 0(30)   | 0(30)   |
| O(3A)  | 20(30) | 60(40) | 20(30)   | 0(20)   | 10(20)  | 0(20)   |
| C(59A) | 20(30) | 60(40) | 20(30)   | 0(20)   | 10(20)  | 0(20)   |
| C(60A) | 20(30) | 60(40) | 20(30)   | 0(20)   | 10(20)  | 0(20)   |
| C(61A) | 20(30) | 60(40) | 20(30)   | 0(20)   | 10(20)  | 0(20)   |
| C(62A) | 20(30) | 60(40) | 20(30)   | 0(20)   | 10(20)  | 0(20)   |
| O(3B)  | 30(60) | 20(70) | 20(60)   | 0(30)   | 10(40)  | 0(30)   |
| C(59B) | 30(60) | 20(70) | 20(60)   | 0(30)   | 10(40)  | 0(30)   |
| C(60B) | 30(60) | 20(70) | 20(60)   | 0(30)   | 10(40)  | 0(30)   |
| C(61B) | 30(60) | 20(70) | 20(60)   | 0(30)   | 10(40)  | 0(30)   |
| C(62B) | 30(60) | 20(70) | 20(60)   | 0(30)   | 10(40)  | 0(30)   |
| O(4A)  | 30(20) | 30(20) | 30(20)   | 0(30)   | 0(10)   | 10(30)  |
| C(63A) | 30(30) | 40(30) | 40(60)   | -20(80) | -10(30) | 0(60)   |
| C(64A) | 50(50) | 60(70) | 60(50)   | -10(80) | 0(40)   | 20(80)  |
| C(65A) | 10(40) | 50(60) | 100(100) | 20(80)  | 10(60)  | -10(30) |
| C(66A) | 60(80) | 40(60) | 100(100) | 30(80)  | 10(80)  | 10(60)  |
| O(4B)  | 30(20) | 30(20) | 30(20)   | 0(30)   | 0(10)   | 10(30)  |
| C(63B) | 30(30) | 40(30) | 40(60)   | -20(80) | -10(30) | 0(60)   |
| C(64B) | 50(50) | 60(70) | 60(50)   | -10(80) | 0(40)   | 20(80)  |
| C(65B) | 10(40) | 50(60) | 100(100) | 20(80)  | 10(60)  | -10(30) |
| C(66B) | 60(80) | 40(60) | 100(100) | 30(80)  | 10(80)  | 10(60)  |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa781

| atom   | x          | y    | z         | U(eq) |
|--------|------------|------|-----------|-------|
| H(1)   | -633       | 2375 | 6506      | 28    |
| H(2)   | 1828       | 1879 | 7609      | 29    |
| H(3A)  | 593        | 1213 | 8136      | 30    |
| H(3B)  | -728       | 1534 | 7571      | 30    |
| H(4A)  | 1          | 1662 | 9709      | 34    |
| H(4B)  | 1404       | 1852 | 9630      | 34    |
| H(5A)  | 134        | 2577 | 9767      | 33    |
| H(5B)  | -1029      | 2388 | 8610      | 33    |
| H(6A)  | 220        | 3025 | 7973      | 31    |
| H(6B)  | 1535       | 2699 | 8519      | 31    |
| H(10)  | 700        | 3674 | 911       | 29    |
| H(12)  | -1217      | 3639 | 3464      | 27    |
| H(14A) | 4282       | 2718 | 1835      | 64    |
| H(14B) | 2757       | 2588 | 1250      | 64    |
| H(14C) | 3418       | 2540 | 2694      | 64    |
| H(15A) | 2787       | 3948 | 1022      | 71    |
| H(15B) | 2329       | 3431 | 261       | 71    |
| H(15C) | 3859       | 3563 | 787       | 71    |
| H(16A) | 4010       | 3902 | 3228      | 64    |
| H(16B) | 5010       | 3491 | 2966      | 64    |
| H(16C) | 4222       | 3362 | 3925      | 64    |
| H(18A) | -1169      | 3782 | -550      | 143   |
| H(18B) | -2720.0002 | 3717 | -804      | 143   |
| H(18C) | -1749      | 3265 | -159.0000 | 143   |
| H(19A) | -1648      | 4590 | 1766      | 129   |
| H(19B) | -2446      | 4579 | 344       | 129   |
| H(19C) | -877       | 4546 | 762       | 129   |
| H(20A) | -3154      | 3377 | 1316      | 94    |
| H(20B) | -3749.0002 | 3923 | 796       | 94    |
| H(20C) | -2901      | 3867 | 2198      | 94    |
| H(22)  | -1927      | 3000 | 5167      | 34    |
| H(23)  | -3737      | 3395 | 5571      | 42    |
| H(24)  | -3480      | 4200 | 6506      | 51    |
| H(25)  | -1445      | 4607 | 6998      | 47    |
| H(26)  | 352        | 4204 | 6674      | 39    |
| H(28)  | 1886       | 4184 | 5008      | 41    |
| H(29)  | 3652       | 4695 | 6053      | 50    |
| H(30)  | 5077       | 4436 | 7893      | 47    |
| H(31)  | 4665       | 3685 | 8803      | 48    |
| H(32)  | 2896       | 3163 | 7773      | 39    |
| H(36)  | 707        | 510  | 970       | 34    |
| H(38)  | -1265      | 586  | 3477      | 30    |
| H(40A) | 2405       | 771  | 361       | 84    |
| H(40B) | 2715       | 238  | 1080      | 84    |
| H(40C) | 3892       | 583  | 912       | 84    |
| H(41A) | 2897       | 1594 | 1538      | 62    |
| H(41B) | 4376       | 1389 | 1877      | 62    |
| H(41C) | 3777       | 1571 | 2936      | 62    |
| H(42A) | 4967       | 583  | 3146      | 62    |
| H(42B) | 3814       | 219  | 3295      | 62    |
| H(42C) | 4153       | 739  | 4066      | 62    |
| H(44A) | -1390      | -397 | 1543      | 159   |
| H(44B) | -833       | -237 | 440       | 159   |
| H(44C) | -2375      | -324 | 198       | 159   |
| H(45A) | -3074      | 775  | 1645      | 91    |
| H(45B) | -2906      | 198  | 2143      | 91    |
| H(45C) | -3725      | 312  | 754       | 91    |
| H(46A) | -2694      | 502  | -754      | 108   |
| H(46B) | -1167      | 646  | -391      | 108   |
| H(46C) | -2174      | 1015 | 2         | 108   |
| H(48)  | 318        | 11   | 6632      | 44    |
| H(49)  | -1428      | -378 | 7160      | 56    |

|        |            |      |      |    |
|--------|------------|------|------|----|
| H(50)  | -3479      | 13   | 6578 | 60 |
| H(51)  | -3748      | 807  | 5642 | 57 |
| H(52)  | -1995      | 1231 | 5236 | 39 |
| H(54)  | 1941       | 63   | 5132 | 42 |
| H(55)  | 3757       | -435 | 6151 | 58 |
| H(56)  | 5048       | -178 | 8098 | 44 |
| H(57)  | 4614       | 594  | 8902 | 44 |
| H(58)  | 2830       | 1092 | 7892 | 38 |
| H(59A) | -1345      | 2499 | 3728 | 43 |
| H(59B) | -1245      | 1908 | 4149 | 43 |
| H(60A) | -2922.9998 | 2163 | 2132 | 43 |
| H(60B) | -2164      | 1622 | 2209 | 43 |
| H(61A) | -1573      | 2031 | 638  | 43 |
| H(61B) | -1441      | 2579 | 1314 | 43 |
| H(62A) | 322        | 1734 | 1941 | 43 |
| H(62B) | 696        | 2332 | 1932 | 43 |
| H(59C) | -1110      | 2305 | 4306 | 28 |
| H(59D) | -1293      | 1718 | 3850 | 28 |
| H(60C) | -2082      | 2615 | 2371 | 28 |
| H(60D) | -2951      | 2108 | 2378 | 28 |
| H(61C) | -1661      | 1613 | 1467 | 28 |
| H(61D) | -1799      | 2146 | 721  | 28 |
| H(62C) | 499        | 1819 | 1877 | 28 |
| H(62D) | 208        | 2425 | 1842 | 28 |
| H(64A) | 5709       | 1784 | 5481 | 90 |
| H(64B) | 6899       | 2127 | 6280 | 90 |
| H(64C) | 5617       | 2396 | 5405 | 90 |
| H(65A) | 5606       | 2901 | 7208 | 66 |
| H(65B) | 6739       | 2581 | 8153 | 66 |
| H(65C) | 5333       | 2642 | 8378 | 66 |
| H(66A) | 5617       | 1672 | 8598 | 92 |
| H(66B) | 6870       | 1675 | 8096 | 92 |
| H(66C) | 5621       | 1331 | 7436 | 92 |
| H(64D) | 4391       | 2454 | 8781 | 90 |
| H(64E) | 5813       | 2210 | 9382 | 90 |
| H(64F) | 4560       | 1845 | 8906 | 90 |
| H(65D) | 6114       | 2604 | 6481 | 66 |
| H(65E) | 6653       | 2705 | 7921 | 66 |
| H(65F) | 5255       | 2929 | 7155 | 66 |
| H(66D) | 5710       | 1365 | 7694 | 92 |
| H(66E) | 6965       | 1734 | 7991 | 92 |
| H(66F) | 6132       | 1628 | 6603 | 92 |

**Complex 54a**

Table 1. Crystal data for pa666

|   |  |
|---|--|
| Compound                                    | pa666  |
| Molecular formula                           | C <sub>65</sub> H <sub>87</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Y |
| Molecular weight                            | 1111.22  |
| Crystal habit                               | Colorless Block  |
| Crystal dimensions(mm)                      | 0.40x0.26x0.22   |
| Crystal system                              | monoclinic   |
| Space group                                 | P2 <sub>1</sub> /c   |
| a(Å)  | 11.409(1)  |
| b(Å)  | 27.849(1)  |
| c(Å)  | 21.019(1)  |
| α(°)  | 90.00  |
| β(°)  | 113.905(5)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 6105.5(6)  |
| Z   | 4  |
| d(g·cm <sup>-3</sup> )                      | 1.209  |
| F(000)                                      | 2368   |
| μ(cm <sup>-1</sup> )                        | 1.054  |
| Absorption corrections                      | multi-scan ; 0.6778 min, 0.8012 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 25.02  |
| HKL ranges                                  | -13 13 ; -32 33 ; -25 25   |
| Reflections measured                        | 41671  |
| Unique data                                 | 10712  |
| Rint  | 0.0342   |
| Reflections used                            | 9775   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 684  |
| Reflections / parameter                     | 14   |
| wR2   | 0.1588   |
| R1  | 0.0783   |
| Weights a, b                                | 0.0000 ; 34.668  |
| GoF   | 1.159  |
| difference peak / hole (e Å <sup>-3</sup> ) | 3.735(0.088) / -2.505(0.088)   |



## Appendix 1. Crystallographic data

Table 2. Atomic Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa666

| atom  | x        | y       | z        | U(eq) |
|-------|----------|---------|----------|-------|
| Y(1)  | 2945(1)  | 2889(1) | 953(1)   | 26(1) |
| P(1)  | 4260(1)  | 3755(1) | 295(1)   | 20(1) |
| P(5)  | 3484(1)  | 1678(1) | 1107(1)  | 20(1) |
| O(1)  | 2724(3)  | 3665(1) | 1143(2)  | 25(1) |
| O(2)  | 2464(3)  | 2455(1) | 1683(2)  | 24(1) |
| O(3)  | 1177(3)  | 2814(1) | 125(2)   | 29(1) |
| O(4)  | 4919(3)  | 2956(1) | 2023(2)  | 30(1) |
| N(1)  | 4308(3)  | 3187(1) | 401(2)   | 19(1) |
| N(2)  | 3715(3)  | 2136(1) | 715(2)   | 20(1) |
| C(1)  | 4056(4)  | 2874(2) | -211(2)  | 21(1) |
| C(2)  | 4834(5)  | 2407(2) | -57(2)   | 23(1) |
| C(3)  | 4926(4)  | 2155(2) | 615(2)   | 21(1) |
| C(4)  | 6209(5)  | 2502(2) | 32(3)    | 34(1) |
| C(5)  | 4188(5)  | 2080(2) | -687(3)  | 32(1) |
| C(6)  | 4526(5)  | 4057(2) | 1094(2)  | 24(1) |
| C(7)  | 3615(4)  | 3995(2) | 1385(2)  | 24(1) |
| C(8)  | 3698(5)  | 4317(2) | 1936(3)  | 27(1) |
| C(9)  | 4797(5)  | 4592(2) | 2238(3)  | 30(1) |
| C(10) | 5801(5)  | 4598(2) | 2016(3)  | 30(1) |
| C(11) | 5616(5)  | 4347(2) | 1416(2)  | 27(1) |
| C(12) | 2577(5)  | 4352(2) | 2165(3)  | 31(1) |
| C(13) | 1327(5)  | 4442(2) | 1531(3)  | 44(1) |
| C(14) | 2472(6)  | 3893(2) | 2539(3)  | 39(1) |
| C(15) | 2759(6)  | 4775(2) | 2670(3)  | 46(2) |
| C(16) | 7037(5)  | 4876(2) | 2430(3)  | 36(1) |
| C(17) | 6752(6)  | 5416(2) | 2426(3)  | 44(2) |
| C(18) | 8043(6)  | 4803(2) | 2134(3)  | 47(2) |
| C(19) | 7595(6)  | 4699(2) | 3189(3)  | 49(2) |
| C(20) | 5505(4)  | 3986(2) | 42(2)    | 22(1) |
| C(21) | 6714(5)  | 3780(2) | 335(3)   | 30(1) |
| C(22) | 7730(5)  | 3974(2) | 223(3)   | 36(1) |
| C(23) | 7534(6)  | 4380(2) | -191(3)  | 41(1) |
| C(24) | 6331(6)  | 4585(2) | -493(3)  | 38(1) |
| C(25) | 5317(5)  | 4394(2) | -374(3)  | 30(1) |
| C(26) | 2777(4)  | 3981(2) | -382(2)  | 24(1) |
| C(27) | 2433(5)  | 3840(2) | -1073(2) | 29(1) |
| C(28) | 1294(5)  | 3985(2) | -1598(3) | 38(1) |
| C(29) | 477(5)   | 4281(2) | -1438(3) | 40(1) |
| C(30) | 801(5)   | 4430(2) | -763(3)  | 42(1) |
| C(31) | 1931(5)  | 4278(2) | -236(3)  | 34(1) |
| C(32) | 1956(4)  | 1687(2) | 1161(2)  | 22(1) |
| C(33) | 1665(4)  | 2087(2) | 1488(2)  | 21(1) |
| C(34) | 530(4)   | 2069(2) | 1621(2)  | 22(1) |
| C(35) | -275(4)  | 1681(2) | 1354(2)  | 26(1) |
| C(36) | -39(4)   | 1297(2) | 993(2)   | 24(1) |
| C(37) | 1109(4)  | 1303(2) | 916(2)   | 22(1) |
| C(38) | 223(5)   | 2473(2) | 2020(3)  | 28(1) |
| C(39) | -68(5)   | 2943(2) | 1604(3)  | 34(1) |
| C(40) | -967(5)  | 2352(2) | 2162(3)  | 42(1) |
| C(41) | 1357(5)  | 2543(2) | 2728(3)  | 34(1) |
| C(42) | -1024(4) | 890(2)  | 722(3)   | 27(1) |
| C(43) | -2337(5) | 1093(2) | 252(3)   | 44(1) |
| C(44) | -1123(6) | 633(2)  | 1349(3)  | 42(1) |
| C(45) | -643(5)  | 519(2)  | 305(3)   | 40(1) |
| C(46) | 4704(5)  | 1578(2) | 1979(2)  | 24(1) |
| C(47) | 5966(5)  | 1492(2) | 2074(3)  | 34(1) |
| C(48) | 6915(5)  | 1416(2) | 2728(3)  | 43(1) |
| C(49) | 6614(6)  | 1427(2) | 3300(3)  | 46(2) |
| C(50) | 5374(6)  | 1512(2) | 3216(3)  | 40(1) |
| C(51) | 4411(5)  | 1588(2) | 2560(3)  | 31(1) |
| C(52) | 3525(4)  | 1128(2) | 645(2)   | 22(1) |
| C(53) | 2882(5)  | 1133(2) | -71(3)   | 32(1) |

## Appendix 1. Crystallographic data

|       |          |         |          |       |
|-------|----------|---------|----------|-------|
| C(54) | 2890(5)  | 728(2)  | -456(3)  | 38(1) |
| C(55) | 3520(5)  | 321(2)  | -131(3)  | 38(1) |
| C(56) | 4141(6)  | 307(2)  | 582(3)   | 40(1) |
| C(57) | 4142(5)  | 708(2)  | 969(3)   | 32(1) |
| C(58) | 80(5)    | 2660(2) | -448(3)  | 37(1) |
| C(59) | -157(6)  | 3036(2) | -1013(3) | 50(2) |
| C(60) | -1064(6) | 2638(3) | -270(3)  | 56(2) |
| C(61) | 352(6)   | 2180(2) | -686(3)  | 49(2) |
| C(62) | 4944(6)  | 2934(2) | 2712(3)  | 45(2) |
| C(63) | 6020(6)  | 3272(3) | 3137(3)  | 56(2) |
| C(64) | 6822(7)  | 3301(3) | 2714(4)  | 60(2) |
| C(65) | 6226(5)  | 2979(2) | 2122(3)  | 44(2) |

U(eq) is defined as 1/3 the trace of the  $U_{ij}$  tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa666

|             |          |             |          |
|-------------|----------|-------------|----------|
| Y(1)-O(3)   | 2.072(3) | Y(1)-O(2)   | 2.191(3) |
| Y(1)-O(1)   | 2.232(3) | Y(1)-N(2)   | 2.402(4) |
| Y(1)-N(1)   | 2.432(4) | Y(1)-O(4)   | 2.462(3) |
| P(1)-N(1)   | 1.597(4) | P(1)-C(6)   | 1.791(5) |
| P(1)-C(20)  | 1.822(5) | P(1)-C(26)  | 1.825(5) |
| P(5)-N(2)   | 1.599(4) | P(5)-C(32)  | 1.793(5) |
| P(5)-C(46)  | 1.819(5) | P(5)-C(52)  | 1.823(5) |
| O(1)-C(7)   | 1.310(6) | O(2)-C(33)  | 1.322(5) |
| O(3)-C(58)  | 1.408(6) | O(4)-C(65)  | 1.421(6) |
| O(4)-C(62)  | 1.439(6) | N(1)-C(1)   | 1.481(5) |
| N(2)-C(1)   | 1.480(5) | C(1)-C(2)   | 1.534(6) |
| C(2)-C(4)   | 1.527(7) | C(2)-C(5)   | 1.527(7) |
| C(2)-C(3)   | 1.542(6) | C(6)-C(11)  | 1.404(7) |
| C(6)-C(7)   | 1.414(6) | C(7)-C(8)   | 1.436(7) |
| C(8)-C(9)   | 1.386(7) | C(8)-C(12)  | 1.542(7) |
| C(9)-C(10)  | 1.402(7) | C(10)-C(11) | 1.381(7) |
| C(10)-C(16) | 1.534(7) | C(12)-C(13) | 1.528(8) |
| C(12)-C(14) | 1.530(7) | C(12)-C(15) | 1.542(7) |
| C(16)-C(18) | 1.526(8) | C(16)-C(17) | 1.536(8) |
| C(16)-C(19) | 1.539(8) | C(20)-C(21) | 1.386(7) |
| C(20)-C(25) | 1.397(7) | C(21)-C(22) | 1.383(7) |
| C(22)-C(23) | 1.389(8) | C(23)-C(24) | 1.380(8) |
| C(24)-C(25) | 1.385(7) | C(26)-C(31) | 1.395(7) |
| C(26)-C(27) | 1.400(7) | C(27)-C(28) | 1.380(7) |
| C(28)-C(29) | 1.384(8) | C(29)-C(30) | 1.378(8) |
| C(30)-C(31) | 1.382(8) | C(32)-C(37) | 1.393(6) |
| C(32)-C(33) | 1.416(6) | C(33)-C(34) | 1.432(6) |
| C(34)-C(35) | 1.383(7) | C(34)-C(38) | 1.526(6) |
| C(35)-C(36) | 1.397(7) | C(36)-C(37) | 1.385(6) |
| C(36)-C(42) | 1.536(6) | C(38)-C(39) | 1.533(7) |
| C(38)-C(41) | 1.537(7) | C(38)-C(40) | 1.541(7) |
| C(42)-C(45) | 1.527(7) | C(42)-C(43) | 1.531(7) |
| C(42)-C(44) | 1.543(7) | C(46)-C(51) | 1.389(7) |
| C(46)-C(47) | 1.393(7) | C(47)-C(48) | 1.379(7) |
| C(48)-C(49) | 1.376(8) | C(49)-C(50) | 1.37(1)  |
| C(50)-C(51) | 1.388(7) | C(52)-C(53) | 1.383(7) |
| C(52)-C(57) | 1.390(7) | C(53)-C(54) | 1.391(7) |
| C(54)-C(55) | 1.366(8) | C(55)-C(56) | 1.373(8) |
| C(56)-C(57) | 1.383(7) | C(58)-C(60) | 1.499(8) |
| C(58)-C(61) | 1.504(8) | C(58)-C(59) | 1.522(8) |
| C(62)-C(63) | 1.516(8) | C(63)-C(64) | 1.51(1)  |
| C(64)-C(65) | 1.46(1)  |             |          |

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| O(3)-Y(1)-O(2)   | 95.6(1)  | O(3)-Y(1)-O(1)   | 96.1(1)  |
| O(2)-Y(1)-O(1)   | 109.3(1) | O(3)-Y(1)-N(2)   | 92.9(1)  |
| O(2)-Y(1)-N(2)   | 83.2(1)  | O(1)-Y(1)-N(2)   | 163.7(1) |
| O(3)-Y(1)-N(1)   | 103.1(1) | O(2)-Y(1)-N(1)   | 155.8(1) |
| O(1)-Y(1)-N(1)   | 84.0(1)  | N(2)-Y(1)-N(1)   | 80.8(1)  |
| O(3)-Y(1)-O(4)   | 173.5(1) | O(2)-Y(1)-O(4)   | 78.3(1)  |
| O(1)-Y(1)-O(4)   | 83.7(1)  | N(2)-Y(1)-O(4)   | 88.9(1)  |
| N(1)-Y(1)-O(4)   | 83.4(1)  | N(1)-P(1)-C(6)   | 110.6(2) |
| N(1)-P(1)-C(20)  | 113.8(2) | C(6)-P(1)-C(20)  | 104.6(2) |
| N(1)-P(1)-C(26)  | 114.8(2) | C(6)-P(1)-C(26)  | 108.7(2) |
| C(20)-P(1)-C(26) | 103.7(2) | N(2)-P(5)-C(32)  | 112.8(2) |
| N(2)-P(5)-C(46)  | 115.0(2) | C(32)-P(5)-C(46) | 107.7(2) |
| N(2)-P(5)-C(52)  | 110.7(2) | C(32)-P(5)-C(52) | 106.4(2) |
| C(46)-P(5)-C(52) | 103.6(2) | C(7)-O(1)-Y(1)   | 128.5(3) |
| C(33)-O(2)-Y(1)  | 123.1(3) | C(58)-O(3)-Y(1)  | 167.1(3) |
| C(65)-O(4)-C(62) | 105.3(4) | C(65)-O(4)-Y(1)  | 130.9(3) |
| C(62)-O(4)-Y(1)  | 123.6(3) | C(1)-N(1)-P(1)   | 118.6(3) |
| C(1)-N(1)-Y(1)   | 106.1(3) | P(1)-N(1)-Y(1)   | 114.3(2) |
| C(3)-N(2)-P(5)   | 117.3(3) | C(3)-N(2)-Y(1)   | 116.1(3) |
| P(5)-N(2)-Y(1)   | 116.1(2) | N(1)-C(1)-C(2)   | 115.1(4) |
| C(4)-C(2)-C(5)   | 108.7(4) | C(4)-C(2)-C(1)   | 110.9(4) |
| C(5)-C(2)-C(1)   | 106.8(4) | C(4)-C(2)-C(3)   | 106.4(4) |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(5)-C(2)-C(3)    | 110.7(4) | C(1)-C(2)-C(3)    | 113.3(4) |
| N(2)-C(3)-C(2)    | 115.2(4) | C(11)-C(6)-C(7)   | 121.6(4) |
| C(11)-C(6)-P(1)   | 120.1(4) | C(7)-C(6)-P(1)    | 118.2(3) |
| O(1)-C(7)-C(6)    | 120.6(4) | O(1)-C(7)-C(8)    | 122.5(4) |
| C(6)-C(7)-C(8)    | 116.9(4) | C(9)-C(8)-C(7)    | 117.8(4) |
| C(9)-C(8)-C(12)   | 122.2(4) | C(7)-C(8)-C(12)   | 120.0(4) |
| C(8)-C(9)-C(10)   | 124.3(5) | C(11)-C(10)-C(9)  | 117.1(5) |
| C(11)-C(10)-C(16) | 122.7(5) | C(9)-C(10)-C(16)  | 120.2(4) |
| C(10)-C(11)-C(6)  | 120.5(5) | C(13)-C(12)-C(14) | 110.2(5) |
| C(13)-C(12)-C(8)  | 109.7(4) | C(14)-C(12)-C(8)  | 110.8(4) |
| C(13)-C(12)-C(15) | 107.0(5) | C(14)-C(12)-C(15) | 107.5(4) |
| C(8)-C(12)-C(15)  | 111.5(4) | C(18)-C(16)-C(10) | 111.7(4) |
| C(18)-C(16)-C(17) | 108.7(5) | C(10)-C(16)-C(17) | 110.4(5) |
| C(18)-C(16)-C(19) | 108.4(5) | C(10)-C(16)-C(19) | 109.0(4) |
| C(17)-C(16)-C(19) | 108.6(5) | C(21)-C(20)-C(25) | 119.1(4) |
| C(21)-C(20)-P(1)  | 118.6(4) | C(25)-C(20)-P(1)  | 122.0(4) |
| C(22)-C(21)-C(20) | 121.0(5) | C(21)-C(22)-C(23) | 119.4(5) |
| C(24)-C(23)-C(22) | 120.1(5) | C(23)-C(24)-C(25) | 120.4(5) |
| C(24)-C(25)-C(20) | 119.9(5) | C(31)-C(26)-C(27) | 117.8(4) |
| C(31)-C(26)-P(1)  | 122.6(4) | C(27)-C(26)-P(1)  | 119.6(4) |
| C(28)-C(27)-C(26) | 121.6(5) | C(27)-C(28)-C(29) | 119.3(5) |
| C(30)-C(29)-C(28) | 120.2(5) | C(29)-C(30)-C(31) | 120.4(5) |
| C(30)-C(31)-C(26) | 120.7(5) | C(37)-C(32)-C(33) | 121.2(4) |
| C(37)-C(32)-P(5)  | 120.8(4) | C(33)-C(32)-P(5)  | 117.9(3) |
| O(2)-C(33)-C(32)  | 119.5(4) | O(2)-C(33)-C(34)  | 122.0(4) |
| C(32)-C(33)-C(34) | 118.5(4) | C(35)-C(34)-C(33) | 116.9(4) |
| C(35)-C(34)-C(38) | 122.5(4) | C(33)-C(34)-C(38) | 120.6(4) |
| C(34)-C(35)-C(36) | 125.2(4) | C(37)-C(36)-C(35) | 117.0(4) |
| C(37)-C(36)-C(42) | 123.4(4) | C(35)-C(36)-C(42) | 119.6(4) |
| C(36)-C(37)-C(32) | 120.9(4) | C(34)-C(38)-C(39) | 111.1(4) |
| C(34)-C(38)-C(41) | 109.6(4) | C(39)-C(38)-C(41) | 110.3(4) |
| C(39)-C(38)-C(40) | 111.2(4) | C(39)-C(38)-C(40) | 107.0(4) |
| C(41)-C(38)-C(40) | 107.6(4) | C(45)-C(42)-C(43) | 108.2(4) |
| C(45)-C(42)-C(36) | 112.1(4) | C(43)-C(42)-C(36) | 110.1(4) |
| C(45)-C(42)-C(44) | 108.4(5) | C(43)-C(42)-C(44) | 109.4(4) |
| C(36)-C(42)-C(44) | 108.7(4) | C(51)-C(46)-C(47) | 118.7(5) |
| C(51)-C(46)-P(5)  | 121.7(4) | C(47)-C(46)-P(5)  | 119.6(4) |
| C(48)-C(47)-C(46) | 121.1(5) | C(49)-C(48)-C(47) | 119.7(5) |
| C(50)-C(49)-C(48) | 120.0(5) | C(49)-C(50)-C(51) | 120.8(5) |
| C(50)-C(51)-C(46) | 119.7(5) | C(53)-C(52)-C(57) | 118.8(4) |
| C(53)-C(52)-P(5)  | 116.9(4) | C(57)-C(52)-P(5)  | 124.2(4) |
| C(52)-C(53)-C(54) | 119.8(5) | C(55)-C(54)-C(53) | 120.6(5) |
| C(54)-C(55)-C(56) | 120.3(5) | C(55)-C(56)-C(57) | 119.7(5) |
| C(56)-C(57)-C(52) | 120.8(5) | O(3)-C(58)-C(60)  | 111.1(5) |
| O(3)-C(58)-C(61)  | 108.9(5) | C(60)-C(58)-C(61) | 111.3(5) |
| O(3)-C(58)-C(59)  | 105.9(5) | C(60)-C(58)-C(59) | 109.1(5) |
| C(61)-C(58)-C(59) | 110.3(5) | O(4)-C(62)-C(63)  | 104.3(5) |
| C(64)-C(63)-C(62) | 103.0(5) | C(65)-C(64)-C(63) | 106.5(6) |
| O(4)-C(65)-C(64)  | 104.5(5) |                   |          |

# Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa666

| atom  | U11   | U22   | U33   | U23    | U13   | U12    |
|-------|-------|-------|-------|--------|-------|--------|
| Y(1)  | 34(1) | 24(1) | 31(1) | 6(1)   | 22(1) | 7(1)   |
| P(1)  | 18(1) | 22(1) | 21(1) | -2(1)  | 9(1)  | -2(1)  |
| P(5)  | 19(1) | 20(1) | 22(1) | -3(1)  | 11(1) | -2(1)  |
| O(1)  | 22(2) | 21(2) | 34(2) | -6(1)  | 15(2) | -3(1)  |
| O(2)  | 24(2) | 25(2) | 27(2) | -7(1)  | 16(1) | -8(1)  |
| O(3)  | 12(2) | 41(2) | 21(2) | -8(2)  | -6(1) | 2(1)   |
| O(4)  | 20(2) | 49(2) | 20(2) | 1(2)   | 8(1)  | -1(2)  |
| N(1)  | 18(2) | 22(2) | 16(2) | -2(2)  | 7(2)  | -1(2)  |
| N(2)  | 14(2) | 26(2) | 20(2) | 0(2)   | 9(2)  | -1(2)  |
| C(1)  | 22(2) | 24(2) | 17(2) | 1(2)   | 8(2)  | 3(2)   |
| C(2)  | 28(3) | 23(2) | 24(2) | 2(2)   | 16(2) | 2(2)   |
| C(3)  | 15(2) | 23(2) | 24(2) | -2(2)  | 9(2)  | -3(2)  |
| C(4)  | 32(3) | 35(3) | 47(3) | 10(2)  | 29(3) | 8(2)   |
| C(5)  | 43(3) | 28(3) | 31(3) | -1(2)  | 21(2) | 6(2)   |
| C(6)  | 25(2) | 20(2) | 27(2) | -5(2)  | 11(2) | -4(2)  |
| C(7)  | 23(2) | 22(2) | 28(3) | 1(2)   | 11(2) | 1(2)   |
| C(8)  | 29(3) | 22(2) | 30(3) | -3(2)  | 13(2) | -1(2)  |
| C(9)  | 38(3) | 25(3) | 28(3) | -8(2)  | 16(2) | -3(2)  |
| C(10) | 35(3) | 26(3) | 27(3) | -5(2)  | 12(2) | -9(2)  |
| C(11) | 30(3) | 28(3) | 25(2) | -3(2)  | 14(2) | -5(2)  |
| C(12) | 37(3) | 28(3) | 34(3) | -7(2)  | 21(2) | -1(2)  |
| C(13) | 35(3) | 52(4) | 50(4) | -8(3)  | 23(3) | 8(3)   |
| C(14) | 47(3) | 43(3) | 38(3) | -6(3)  | 28(3) | -4(3)  |
| C(15) | 55(4) | 42(3) | 57(4) | -23(3) | 38(3) | -9(3)  |
| C(16) | 40(3) | 39(3) | 29(3) | -12(2) | 14(2) | -17(3) |
| C(17) | 57(4) | 36(3) | 45(3) | -12(3) | 26(3) | -20(3) |
| C(18) | 36(3) | 52(4) | 52(4) | -20(3) | 17(3) | -18(3) |
| C(19) | 48(4) | 50(4) | 36(3) | -5(3)  | 4(3)  | -20(3) |
| C(20) | 22(2) | 26(2) | 20(2) | -6(2)  | 9(2)  | -7(2)  |
| C(21) | 28(3) | 30(3) | 32(3) | -2(2)  | 14(2) | -5(2)  |
| C(22) | 22(3) | 44(3) | 45(3) | -10(3) | 18(2) | -8(2)  |
| C(23) | 41(3) | 43(3) | 52(4) | -9(3)  | 31(3) | -19(3) |
| C(24) | 45(3) | 34(3) | 42(3) | 1(2)   | 24(3) | -14(3) |
| C(25) | 34(3) | 28(3) | 30(3) | -4(2)  | 15(2) | -6(2)  |
| C(26) | 17(2) | 24(2) | 28(3) | 4(2)   | 5(2)  | -3(2)  |
| C(27) | 30(3) | 28(3) | 23(2) | 3(2)   | 7(2)  | 0(2)   |
| C(28) | 41(3) | 36(3) | 30(3) | 10(2)  | 8(2)  | -1(3)  |
| C(29) | 25(3) | 46(3) | 42(3) | 21(3)  | 5(2)  | 3(2)   |
| C(30) | 32(3) | 42(3) | 53(4) | 12(3)  | 19(3) | 10(3)  |
| C(31) | 31(3) | 34(3) | 33(3) | 0(2)   | 12(2) | 2(2)   |
| C(32) | 20(2) | 26(2) | 20(2) | -1(2)  | 10(2) | -4(2)  |
| C(33) | 22(2) | 22(2) | 21(2) | -1(2)  | 11(2) | -2(2)  |
| C(34) | 13(2) | 26(2) | 27(2) | -1(2)  | 8(2)  | -2(2)  |
| C(35) | 20(2) | 33(3) | 27(2) | 4(2)   | 11(2) | -2(2)  |
| C(36) | 20(2) | 24(2) | 27(2) | 2(2)   | 8(2)  | -5(2)  |
| C(37) | 21(2) | 22(2) | 21(2) | -1(2)  | 5(2)  | -2(2)  |
| C(38) | 21(2) | 32(3) | 35(3) | -9(2)  | 17(2) | -4(2)  |
| C(39) | 30(3) | 34(3) | 40(3) | -7(2)  | 16(2) | 2(2)   |
| C(40) | 31(3) | 52(4) | 55(4) | -17(3) | 30(3) | -8(3)  |
| C(41) | 32(3) | 47(3) | 27(3) | -8(2)  | 16(2) | -6(2)  |
| C(42) | 19(2) | 27(3) | 31(3) | 0(2)   | 5(2)  | -7(2)  |
| C(43) | 29(3) | 36(3) | 52(4) | -1(3)  | 3(3)  | -5(2)  |
| C(44) | 44(3) | 39(3) | 41(3) | 4(3)   | 14(3) | -15(3) |
| C(45) | 35(3) | 31(3) | 53(4) | -14(3) | 17(3) | -13(2) |
| C(46) | 28(3) | 19(2) | 24(2) | -1(2)  | 9(2)  | -5(2)  |
| C(47) | 26(3) | 46(3) | 30(3) | 10(2)  | 12(2) | 4(2)   |
| C(48) | 28(3) | 56(4) | 38(3) | 13(3)  | 6(3)  | 2(3)   |
| C(49) | 48(4) | 51(4) | 29(3) | 11(3)  | 5(3)  | -3(3)  |
| C(50) | 48(4) | 47(3) | 23(3) | 4(2)   | 12(3) | -3(3)  |
| C(51) | 34(3) | 33(3) | 27(3) | -1(2)  | 15(2) | -2(2)  |
| C(52) | 20(2) | 22(2) | 26(2) | -5(2)  | 13(2) | -4(2)  |
| C(53) | 32(3) | 30(3) | 33(3) | -6(2)  | 13(2) | -4(2)  |
| C(54) | 36(3) | 43(3) | 35(3) | -17(3) | 13(3) | -12(3) |

# Appendix 1. Crystallographic data

|       |       |       |       |        |       |        |
|-------|-------|-------|-------|--------|-------|--------|
| C(55) | 37(3) | 28(3) | 58(4) | -18(3) | 27(3) | -6(2)  |
| C(56) | 46(3) | 26(3) | 54(4) | -1(3)  | 27(3) | 6(2)   |
| C(57) | 37(3) | 27(3) | 33(3) | -2(2)  | 17(2) | 0(2)   |
| C(58) | 33(3) | 47(3) | 30(3) | 1(2)   | 11(2) | -2(3)  |
| C(59) | 45(4) | 57(4) | 45(4) | 6(3)   | 16(3) | 4(3)   |
| C(60) | 37(3) | 93(6) | 38(3) | -10(3) | 16(3) | -8(3)  |
| C(61) | 45(4) | 55(4) | 38(3) | -4(3)  | 9(3)  | -3(3)  |
| C(62) | 47(4) | 59(4) | 30(3) | -4(3)  | 16(3) | -6(3)  |
| C(63) | 39(3) | 92(5) | 33(3) | -14(3) | 9(3)  | -12(4) |
| C(64) | 47(4) | 71(5) | 49(4) | -10(4) | 5(3)  | -6(4)  |
| C(65) | 21(3) | 66(4) | 38(3) | 2(3)   | 4(2)  | -4(3)  |

The anisotropic displacement factor exponent takes the form  

$$2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$$

Table 5. Hydrogen Coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa666

| atom   | x          | y    | z         | U(eq) |
|--------|------------|------|-----------|-------|
| H(1A)  | 4239       | 3058 | -562      | 25    |
| H(1B)  | 3133       | 2791 | -418      | 25    |
| H(3A)  | 5231       | 1822 | 614       | 25    |
| H(3B)  | 5578       | 2323 | 1018      | 25    |
| H(4A)  | 6203       | 2653 | -391      | 51    |
| H(4B)  | 6679       | 2198 | 113       | 51    |
| H(4C)  | 6630       | 2716 | 430       | 51    |
| H(5A)  | 3307       | 2011 | -745      | 48    |
| H(5B)  | 4667       | 1778 | -614      | 48    |
| H(5C)  | 4175       | 2239 | -1105     | 48    |
| H(9)   | 4876       | 4790 | 2622      | 35    |
| H(11)  | 6230       | 4371 | 1219      | 32    |
| H(13A) | 1167       | 4176 | 1202      | 66    |
| H(13B) | 1394       | 4742 | 1306      | 66    |
| H(13C) | 617        | 4465 | 1680      | 66    |
| H(14A) | 3274       | 3841 | 2949      | 59    |
| H(14B) | 2311       | 3619 | 2222      | 59    |
| H(14C) | 1762       | 3924 | 2685      | 59    |
| H(15A) | 2008       | 4800 | 2782      | 69    |
| H(15B) | 2858       | 5073 | 2451      | 69    |
| H(15C) | 3527       | 4720 | 3098      | 69    |
| H(17A) | 7532       | 5585 | 2728      | 66    |
| H(17B) | 6078       | 5467 | 2595      | 66    |
| H(17C) | 6466       | 5540 | 1949      | 66    |
| H(18A) | 8812       | 4989 | 2406      | 70    |
| H(18B) | 7699       | 4910 | 1648      | 70    |
| H(18C) | 8265       | 4461 | 2156      | 70    |
| H(19A) | 7799       | 4356 | 3201      | 73    |
| H(19B) | 6964       | 4748 | 3389      | 73    |
| H(19C) | 8376       | 4880 | 3459      | 73    |
| H(21)  | 6847       | 3502 | 616       | 36    |
| H(22)  | 8555       | 3831 | 427       | 43    |
| H(23)  | 8230       | 4518 | -266      | 50    |
| H(24)  | 6197       | 4858 | -785      | 46    |
| H(25)  | 4496       | 4541 | -575      | 36    |
| H(27)  | 2997       | 3640 | -1185     | 34    |
| H(28)  | 1073       | 3882 | -2063     | 45    |
| H(29)  | -309       | 4382 | -1796     | 48    |
| H(30)  | 243        | 4638 | -658.0001 | 50    |
| H(31)  | 2135       | 4376 | 229       | 40    |
| H(35)  | -1050      | 1674 | 1421      | 31    |
| H(37)  | 1323       | 1042 | 693       | 27    |
| H(39A) | 664        | 3030 | 1497      | 51    |
| H(39B) | -224.0000  | 3199 | 1879      | 51    |
| H(39C) | -832       | 2901 | 1170      | 51    |
| H(40A) | -1719      | 2327 | 1719      | 63    |
| H(40B) | -1106      | 2606 | 2446      | 63    |
| H(40C) | -831       | 2045 | 2410      | 63    |
| H(41A) | 1514       | 2244 | 2994      | 51    |
| H(41B) | 1154       | 2800 | 2986      | 51    |
| H(41C) | 2125       | 2630 | 2654      | 51    |
| H(43A) | -2638      | 1307 | 523       | 65    |
| H(43B) | -2949      | 829  | 65        | 65    |
| H(43C) | -2266      | 1272 | -132      | 65    |
| H(44A) | -288       | 495  | 1644      | 63    |
| H(44B) | -1764      | 377  | 1182      | 63    |
| H(44C) | -1377.9999 | 864  | 1620      | 63    |
| H(45A) | -602       | 674  | -105      | 60    |
| H(45B) | -1280      | 261  | 155       | 60    |
| H(45C) | 199        | 385  | 596       | 60    |
| H(47)  | 6178       | 1486 | 1681      | 40    |
| H(48)  | 7771       | 1357 | 2785      | 52    |

|        |       |      |            |    |
|--------|-------|------|------------|----|
| H(49)  | 7264  | 1375 | 3752       | 55 |
| H(50)  | 5173  | 1520 | 3613       | 48 |
| H(51)  | 3556  | 1646 | 2508       | 37 |
| H(53)  | 2436  | 1414 | -301       | 38 |
| H(54)  | 2454  | 732  | -948       | 46 |
| H(55)  | 3527  | 47   | -398       | 46 |
| H(56)  | 4568  | 22   | 807        | 48 |
| H(57)  | 4570  | 697  | 1461       | 38 |
| H(59A) | -312  | 3348 | -847.0001  | 75 |
| H(59B) | -907  | 2944 | -1430.0001 | 75 |
| H(59C) | 596   | 3057 | -1125      | 75 |
| H(60A) | -894  | 2412 | 116        | 84 |
| H(60B) | -1812 | 2529 | -675.9999  | 84 |
| H(60C) | -1234 | 2957 | -131       | 84 |
| H(61A) | 1110  | 2205 | -793       | 73 |
| H(61B) | -387  | 2079 | -1104      | 73 |
| H(61C) | 510   | 1942 | -317       | 73 |
| H(62A) | 5121  | 2603 | 2899       | 54 |
| H(62B) | 4116  | 3042 | 2712       | 54 |
| H(63A) | 5683  | 3591 | 3183       | 67 |
| H(63B) | 6523  | 3140 | 3607       | 67 |
| H(64A) | 6835  | 3633 | 2551       | 72 |
| H(64B) | 7713  | 3199 | 2998       | 72 |
| H(65A) | 6307  | 3107 | 1703       | 53 |
| H(65B) | 6627  | 2657 | 2225       | 53 |

**Complex 55**

Table 1. Crystal data for pa717

|   |  |
|---|--|
| Compound                                    | pa717  |
| Molecular formula                           | C <sub>66</sub> H <sub>81</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Y, 2(C <sub>6</sub> H <sub>12</sub> ) |
| Molecular weight                            | 1285.49  |
| Crystal habit                               | Colorless Block  |
| Crystal dimensions(mm)                      | 0.30x0.18x0.12   |
| Crystal system                              | monoclinic   |
| Space group                                 | C2/c   |
| a(Å)  | 35.816(1)  |
| b(Å)  | 19.399(1)  |
| c(Å)  | 25.180(1)  |
| α(°)  | 90.00  |
| β(°)  | 123.852(1)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 14529.2(10)  |
| Z   | 8  |
| d(g·cm <sup>-3</sup> )                      | 1.175  |
| F(000)                                      | 5504   |
| μ(cm <sup>-1</sup> )                        | 0.895  |
| Absorption corrections                      | multi-scan ; 0.7751 min, 0.9002 max  |
| Diffractometer                              | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 25.02  |
| HKL ranges                                  | -42 38 ; -23 23 ; -29 29   |
| Reflections measured                        | 38916  |
| Unique data                                 | 12685  |
| Rint  | 0.0564   |
| Reflections used                            | 9343   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 691  |
| Reflections / parameter                     | 13   |
| wR2   | 0.1679   |
| R1  | 0.0702   |
| Weights a, b                                | 0.0664 ; 81.241  |
| GoF   | 1.036  |
| difference peak / hole (e Å <sup>-3</sup> ) | 1.745(0.077) / -0.764(0.077)   |

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for pa717

| atom  | x       | y       | z       | U(eq) |
|-------|---------|---------|---------|-------|
| Y(1)  | 1954(1) | 4890(1) | 2493(1) | 32(1) |
| P(1)  | 1475(1) | 3891(1) | 3084(1) | 29(1) |
| P(2)  | 3070(1) | 4580(1) | 3088(1) | 37(1) |
| O(1)  | 1280(1) | 5130(1) | 2310(1) | 31(1) |
| O(2)  | 2351(1) | 5573(1) | 2279(1) | 32(1) |
| O(3)  | 1728(1) | 4258(2) | 1724(2) | 37(1) |
| O(4)  | 2088(1) | 5938(2) | 3131(2) | 57(1) |
| N(1)  | 1955(1) | 4080(2) | 3208(2) | 32(1) |
| N(2)  | 2687(1) | 4396(2) | 3210(2) | 33(1) |
| C(1)  | 2373(1) | 3868(2) | 3750(2) | 31(1) |
| C(2)  | 2763(1) | 4032(2) | 3752(2) | 33(1) |
| C(3)  | 3183(2) | 3833(2) | 4282(2) | 40(1) |
| C(4)  | 3233(2) | 3493(2) | 4796(2) | 41(1) |
| C(5)  | 2857(2) | 3336(2) | 4799(2) | 39(1) |
| C(6)  | 2437(2) | 3531(2) | 4285(2) | 34(1) |
| C(7)  | 1012(1) | 4008(2) | 2269(2) | 30(1) |
| C(8)  | 946(1)  | 4678(2) | 2009(2) | 30(1) |
| C(9)  | 519(1)  | 4835(2) | 1450(2) | 30(1) |
| C(10) | 210(2)  | 4301(2) | 1156(2) | 35(1) |
| C(11) | 282(1)  | 3624(2) | 1381(2) | 32(1) |
| C(12) | 687(1)  | 3493(2) | 1955(2) | 32(1) |
| C(13) | 407(2)  | 5580(2) | 1204(2) | 36(1) |
| C(14) | 732(2)  | 5826(2) | 1025(3) | 42(1) |
| C(15) | -75(2)  | 5661(2) | 616(2)  | 42(1) |
| C(16) | 454(2)  | 6041(2) | 1734(3) | 44(1) |
| C(17) | -56(2)  | 3049(2) | 1016(2) | 41(1) |
| C(18) | 56(2)   | 2703(3) | 567(3)  | 69(2) |
| C(19) | -542(2) | 3322(3) | 604(3)  | 54(2) |
| C(20) | -39(2)  | 2507(3) | 1470(3) | 78(2) |
| C(21) | 1333(2) | 4422(2) | 3538(2) | 34(1) |
| C(22) | 883(2)  | 4516(3) | 3337(3) | 45(1) |
| C(23) | 781(2)  | 4927(3) | 3680(3) | 61(2) |
| C(24) | 1123(2) | 5264(3) | 4230(3) | 60(2) |
| C(25) | 1561(2) | 5183(3) | 4428(3) | 54(1) |
| C(26) | 1669(2) | 4767(2) | 4080(2) | 43(1) |
| C(27) | 1430(1) | 2997(2) | 3257(2) | 32(1) |
| C(28) | 1617(2) | 2503(2) | 3070(2) | 39(1) |
| C(29) | 1554(2) | 1804(3) | 3132(3) | 51(1) |
| C(30) | 1302(2) | 1607(3) | 3358(3) | 54(1) |
| C(31) | 1117(2) | 2093(3) | 3541(3) | 51(1) |
| C(32) | 1180(2) | 2788(2) | 3491(2) | 42(1) |
| C(33) | 2859(2) | 4805(2) | 2270(2) | 39(1) |
| C(34) | 2542(2) | 5345(2) | 1993(2) | 34(1) |
| C(35) | 2445(1) | 5620(2) | 1399(2) | 33(1) |
| C(36) | 2648(2) | 5315(2) | 1121(2) | 38(1) |
| C(37) | 2946(2) | 4759(2) | 1390(3) | 43(1) |
| C(38) | 3053(2) | 4520(2) | 1976(3) | 41(1) |
| C(39) | 2116(2) | 6228(2) | 1078(2) | 37(1) |
| C(40) | 1641(2) | 6006(3) | 863(3)  | 47(1) |
| C(41) | 2268(2) | 6840(2) | 1536(3) | 47(1) |
| C(42) | 2090(2) | 6488(3) | 476(3)  | 53(1) |
| C(43) | 3149(2) | 4402(2) | 1057(3) | 50(1) |
| C(44) | 3033(3) | 4781(3) | 452(4)  | 75(2) |
| C(45) | 3662(2) | 4371(3) | 1511(4) | 73(2) |
| C(46) | 2964(2) | 3667(3) | 878(3)  | 66(2) |
| C(47) | 3421(2) | 5313(3) | 3560(3) | 46(1) |
| C(48) | 3619(2) | 5716(3) | 3329(3) | 62(2) |
| C(49) | 3886(2) | 6276(3) | 3686(4) | 84(2) |
| C(50) | 3951(2) | 6421(3) | 4266(4) | 84(2) |
| C(51) | 3747(2) | 6030(3) | 4488(3) | 81(2) |
| C(52) | 3479(2) | 5473(3) | 4131(3) | 60(2) |
| C(53) | 3457(2) | 3869(3) | 3282(3) | 47(1) |

## Appendix 1. Crystallographic data

|       |         |         |         |        |
|-------|---------|---------|---------|--------|
| C(54) | 3917(2) | 3969(3) | 3607(4) | 72(2)  |
| C(55) | 4191(2) | 3405(4) | 3720(5) | 109(3) |
| C(56) | 4010(3) | 2762(4) | 3517(5) | 104(3) |
| C(57) | 3560(3) | 2659(3) | 3212(4) | 82(2)  |
| C(58) | 3279(2) | 3216(3) | 3091(3) | 55(1)  |
| C(59) | 1608(2) | 3741(2) | 1269(2) | 41(1)  |
| C(60) | 1881(2) | 3805(3) | 980(3)  | 72(2)  |
| C(61) | 1121(2) | 3790(4) | 771(3)  | 80(2)  |
| C(62) | 1712(3) | 3045(3) | 1614(3) | 91(2)  |
| C(63) | 2453(2) | 6429(4) | 3352(4) | 94(3)  |
| C(64) | 2487(3) | 6833(5) | 3846(5) | 125(4) |
| C(65) | 2090(3) | 6656(4) | 3871(5) | 110(3) |
| C(66) | 1792(2) | 6242(4) | 3288(4) | 75(2)  |

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 $U(eq)$  is defined as 1/3 the trace of the  $U_{ij}$  tensor.

## Appendix 1. Crystallographic data

Table 3. Bond lengths (Å) and angles (deg) for pa717

|             |          |             |          |
|-------------|----------|-------------|----------|
| Y(1)-O(3)   | 2.040(3) | Y(1)-O(2)   | 2.220(3) |
| Y(1)-O(1)   | 2.243(3) | Y(1)-N(1)   | 2.389(4) |
| Y(1)-N(2)   | 2.406(3) | Y(1)-O(4)   | 2.467(3) |
| P(1)-N(1)   | 1.606(4) | P(1)-C(7)   | 1.795(4) |
| P(1)-C(21)  | 1.811(5) | P(1)-C(27)  | 1.818(4) |
| P(2)-N(2)   | 1.604(4) | P(2)-C(33)  | 1.806(5) |
| P(2)-C(53)  | 1.818(5) | P(2)-C(47)  | 1.831(5) |
| O(1)-C(8)   | 1.327(5) | O(2)-C(34)  | 1.313(5) |
| O(3)-C(59)  | 1.398(5) | O(4)-C(66)  | 1.449(7) |
| O(4)-C(63)  | 1.454(7) | N(1)-C(1)   | 1.413(5) |
| N(2)-C(2)   | 1.422(6) | C(1)-C(6)   | 1.398(6) |
| C(1)-C(2)   | 1.430(6) | C(2)-C(3)   | 1.397(6) |
| C(3)-C(4)   | 1.372(7) | C(4)-C(5)   | 1.383(7) |
| C(5)-C(6)   | 1.383(6) | C(7)-C(12)  | 1.397(6) |
| C(7)-C(8)   | 1.415(6) | C(8)-C(9)   | 1.420(6) |
| C(9)-C(10)  | 1.390(6) | C(9)-C(13)  | 1.535(6) |
| C(10)-C(11) | 1.395(6) | C(11)-C(12) | 1.385(6) |
| C(11)-C(17) | 1.522(6) | C(13)-C(15) | 1.533(7) |
| C(13)-C(16) | 1.537(7) | C(13)-C(14) | 1.539(6) |
| C(17)-C(20) | 1.530(7) | C(17)-C(19) | 1.539(7) |
| C(17)-C(18) | 1.550(8) | C(21)-C(26) | 1.389(7) |
| C(21)-C(22) | 1.406(6) | C(22)-C(23) | 1.368(7) |
| C(23)-C(24) | 1.397(8) | C(24)-C(25) | 1.363(8) |
| C(25)-C(26) | 1.395(7) | C(27)-C(32) | 1.380(6) |
| C(27)-C(28) | 1.390(6) | C(28)-C(29) | 1.398(7) |
| C(29)-C(30) | 1.364(8) | C(30)-C(31) | 1.369(8) |
| C(31)-C(32) | 1.385(7) | C(33)-C(38) | 1.384(6) |
| C(33)-C(34) | 1.411(6) | C(34)-C(35) | 1.436(6) |
| C(35)-C(36) | 1.393(6) | C(35)-C(39) | 1.539(6) |
| C(36)-C(37) | 1.397(7) | C(37)-C(38) | 1.382(7) |
| C(37)-C(43) | 1.546(7) | C(39)-C(41) | 1.530(7) |
| C(39)-C(40) | 1.534(7) | C(39)-C(42) | 1.549(7) |
| C(43)-C(44) | 1.527(8) | C(43)-C(46) | 1.529(7) |
| C(43)-C(45) | 1.532(8) | C(47)-C(52) | 1.370(8) |
| C(47)-C(48) | 1.383(7) | C(48)-C(49) | 1.39(1)  |
| C(49)-C(50) | 1.38(1)  | C(50)-C(51) | 1.37(1)  |
| C(51)-C(52) | 1.391(8) | C(53)-C(58) | 1.379(8) |
| C(53)-C(54) | 1.386(8) | C(54)-C(55) | 1.39(1)  |
| C(55)-C(56) | 1.37(1)  | C(56)-C(57) | 1.36(1)  |
| C(57)-C(58) | 1.390(8) | C(59)-C(61) | 1.477(8) |
| C(59)-C(60) | 1.515(7) | C(59)-C(62) | 1.535(8) |
| C(63)-C(64) | 1.42(1)  | C(64)-C(65) | 1.50(1)  |
| C(65)-C(66) | 1.48(1)  |             |          |

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| O(3)-Y(1)-O(2)   | 95.5(1)  | O(3)-Y(1)-O(1)   | 96.8(1)  |
| O(2)-Y(1)-O(1)   | 126.1(1) | O(3)-Y(1)-N(1)   | 98.9(1)  |
| O(2)-Y(1)-N(1)   | 147.6(1) | O(1)-Y(1)-N(1)   | 80.8(1)  |
| O(3)-Y(1)-N(2)   | 99.4(1)  | O(2)-Y(1)-N(2)   | 80.9(1)  |
| O(1)-Y(1)-N(2)   | 146.9(1) | N(1)-Y(1)-N(2)   | 68.3(1)  |
| O(3)-Y(1)-O(4)   | 160.6(1) | O(2)-Y(1)-O(4)   | 75.4(1)  |
| O(1)-Y(1)-O(4)   | 76.0(1)  | N(1)-Y(1)-O(4)   | 97.6(1)  |
| N(2)-Y(1)-O(4)   | 96.0(1)  | N(1)-P(1)-C(7)   | 113.7(2) |
| N(1)-P(1)-C(21)  | 113.2(2) | C(7)-P(1)-C(21)  | 104.1(2) |
| N(1)-P(1)-C(27)  | 113.5(2) | C(7)-P(1)-C(27)  | 104.2(2) |
| C(21)-P(1)-C(27) | 107.3(2) | N(2)-P(2)-C(33)  | 114.4(2) |
| N(2)-P(2)-C(53)  | 112.6(2) | C(33)-P(2)-C(53) | 105.3(2) |
| N(2)-P(2)-C(47)  | 113.5(2) | C(33)-P(2)-C(47) | 104.7(2) |
| C(53)-P(2)-C(47) | 105.6(2) | C(8)-O(1)-Y(1)   | 120.2(2) |
| C(34)-O(2)-Y(1)  | 122.1(3) | C(59)-O(3)-Y(1)  | 170.8(3) |
| C(66)-O(4)-C(63) | 105.5(4) | C(66)-O(4)-Y(1)  | 127.4(3) |
| C(63)-O(4)-Y(1)  | 126.6(4) | C(1)-N(1)-P(1)   | 124.5(3) |
| C(1)-N(1)-Y(1)   | 118.2(3) | P(1)-N(1)-Y(1)   | 116.8(2) |
| C(2)-N(2)-P(2)   | 124.6(3) | C(2)-N(2)-Y(1)   | 117.6(3) |
| P(2)-N(2)-Y(1)   | 117.3(2) | C(6)-C(1)-N(1)   | 125.6(4) |
| C(6)-C(1)-C(2)   | 117.7(4) | N(1)-C(1)-C(2)   | 116.7(4) |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(3)-C(2)-N(2)    | 125.6(4) | C(3)-C(2)-C(1)    | 118.1(4) |
| N(2)-C(2)-C(1)    | 116.2(4) | C(4)-C(3)-C(2)    | 122.6(4) |
| C(3)-C(4)-C(5)    | 119.7(4) | C(4)-C(5)-C(6)    | 119.3(4) |
| C(5)-C(6)-C(1)    | 122.6(4) | C(12)-C(7)-C(8)   | 121.6(4) |
| C(12)-C(7)-P(1)   | 120.4(3) | C(8)-C(7)-P(1)    | 117.0(3) |
| O(1)-C(8)-C(7)    | 118.6(4) | O(1)-C(8)-C(9)    | 123.7(4) |
| C(7)-C(8)-C(9)    | 117.7(4) | C(10)-C(9)-C(8)   | 117.8(4) |
| C(10)-C(9)-C(13)  | 122.4(4) | C(8)-C(9)-C(13)   | 119.8(4) |
| C(9)-C(10)-C(11)  | 124.9(4) | C(12)-C(11)-C(10) | 116.5(4) |
| C(12)-C(11)-C(17) | 120.9(4) | C(10)-C(11)-C(17) | 122.6(4) |
| C(11)-C(12)-C(7)  | 121.1(4) | C(15)-C(13)-C(9)  | 112.7(4) |
| C(15)-C(13)-C(16) | 107.4(4) | C(9)-C(13)-C(16)  | 108.6(4) |
| C(15)-C(13)-C(14) | 108.3(4) | C(9)-C(13)-C(14)  | 109.9(4) |
| C(16)-C(13)-C(14) | 109.8(4) | C(11)-C(17)-C(20) | 111.5(4) |
| C(11)-C(17)-C(19) | 112.1(4) | C(20)-C(17)-C(19) | 107.4(4) |
| C(11)-C(17)-C(18) | 108.3(4) | C(20)-C(17)-C(18) | 109.3(5) |
| C(19)-C(17)-C(18) | 108.1(5) | C(26)-C(21)-C(22) | 118.9(4) |
| C(26)-C(21)-P(1)  | 120.0(3) | C(22)-C(21)-P(1)  | 121.0(4) |
| C(23)-C(22)-C(21) | 120.2(5) | C(22)-C(23)-C(24) | 120.2(5) |
| C(25)-C(24)-C(23) | 120.4(5) | C(24)-C(25)-C(26) | 120.0(5) |
| C(21)-C(26)-C(25) | 120.3(5) | C(32)-C(27)-C(28) | 119.4(4) |
| C(32)-C(27)-P(1)  | 123.2(4) | C(28)-C(27)-P(1)  | 116.9(3) |
| C(27)-C(28)-C(29) | 119.6(5) | C(30)-C(29)-C(28) | 120.2(5) |
| C(29)-C(30)-C(31) | 120.3(5) | C(30)-C(31)-C(32) | 120.3(5) |
| C(27)-C(32)-C(31) | 120.2(5) | C(38)-C(33)-C(34) | 122.5(4) |
| C(38)-C(33)-P(2)  | 119.8(4) | C(34)-C(33)-P(2)  | 117.1(4) |
| O(2)-C(34)-C(33)  | 119.9(4) | O(2)-C(34)-C(35)  | 123.2(4) |
| C(33)-C(34)-C(35) | 116.9(4) | C(36)-C(35)-C(34) | 118.3(4) |
| C(36)-C(35)-C(39) | 121.6(4) | C(34)-C(35)-C(39) | 120.1(4) |
| C(35)-C(36)-C(37) | 123.8(5) | C(38)-C(37)-C(36) | 117.3(4) |
| C(38)-C(37)-C(43) | 119.6(4) | C(36)-C(37)-C(43) | 123.1(5) |
| C(37)-C(38)-C(33) | 121.0(4) | C(41)-C(39)-C(40) | 110.0(4) |
| C(41)-C(39)-C(35) | 110.6(4) | C(40)-C(39)-C(35) | 110.1(4) |
| C(41)-C(39)-C(42) | 106.7(4) | C(40)-C(39)-C(42) | 107.3(4) |
| C(35)-C(39)-C(42) | 112.0(4) | C(44)-C(43)-C(46) | 108.8(5) |
| C(44)-C(43)-C(45) | 108.1(5) | C(46)-C(43)-C(45) | 109.0(5) |
| C(44)-C(43)-C(37) | 112.1(4) | C(46)-C(43)-C(37) | 108.8(4) |
| C(45)-C(43)-C(37) | 110.0(5) | C(52)-C(47)-C(48) | 120.0(5) |
| C(52)-C(47)-P(2)  | 120.4(4) | C(48)-C(47)-P(2)  | 119.6(5) |
| C(47)-C(48)-C(49) | 119.9(7) | C(50)-C(49)-C(48) | 119.5(6) |
| C(51)-C(50)-C(49) | 120.5(6) | C(50)-C(51)-C(52) | 120.1(7) |
| C(47)-C(52)-C(51) | 120.0(6) | C(58)-C(53)-C(54) | 120.0(5) |
| C(58)-C(53)-P(2)  | 117.9(4) | C(54)-C(53)-P(2)  | 122.0(4) |
| C(53)-C(54)-C(55) | 118.9(7) | C(56)-C(55)-C(54) | 120.5(7) |
| C(57)-C(56)-C(55) | 120.8(6) | C(56)-C(57)-C(58) | 119.6(7) |
| C(53)-C(58)-C(57) | 120.1(6) | O(3)-C(59)-C(61)  | 109.2(4) |
| O(3)-C(59)-C(60)  | 110.3(4) | C(61)-C(59)-C(60) | 111.0(5) |
| O(3)-C(59)-C(62)  | 107.5(4) | C(61)-C(59)-C(62) | 109.7(5) |
| C(60)-C(59)-C(62) | 109.0(5) | C(64)-C(63)-O(4)  | 108.4(6) |
| C(63)-C(64)-C(65) | 107.0(7) | C(66)-C(65)-C(64) | 105.1(6) |
| O(4)-C(66)-C(65)  | 105.0(6) |                   |          |

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa717

| atom  | U11    | U22   | U33    | U23    | U13   | U12    |
|-------|--------|-------|--------|--------|-------|--------|
| Y(1)  | 30(1)  | 31(1) | 40(1)  | 5(1)   | 22(1) | 2(1)   |
| P(1)  | 31(1)  | 29(1) | 33(1)  | 3(1)   | 20(1) | 2(1)   |
| P(2)  | 30(1)  | 35(1) | 50(1)  | 10(1)  | 25(1) | 5(1)   |
| O(1)  | 26(2)  | 28(2) | 42(2)  | -2(1)  | 21(1) | -1(1)  |
| O(2)  | 37(2)  | 28(2) | 43(2)  | 2(1)   | 29(2) | 1(1)   |
| O(3)  | 39(2)  | 32(2) | 42(2)  | -7(1)  | 25(2) | -3(1)  |
| O(4)  | 59(2)  | 55(2) | 71(3)  | -24(2) | 44(2) | -14(2) |
| N(1)  | 31(2)  | 34(2) | 34(2)  | 1(2)   | 20(2) | 2(2)   |
| N(2)  | 30(2)  | 39(2) | 34(2)  | 7(2)   | 20(2) | 3(2)   |
| C(1)  | 29(2)  | 31(2) | 35(2)  | -3(2)  | 20(2) | 2(2)   |
| C(2)  | 30(2)  | 33(2) | 37(3)  | 1(2)   | 19(2) | 2(2)   |
| C(3)  | 30(2)  | 44(3) | 49(3)  | 5(2)   | 23(2) | 1(2)   |
| C(4)  | 36(3)  | 41(3) | 32(3)  | 5(2)   | 12(2) | 4(2)   |
| C(5)  | 39(3)  | 37(3) | 37(3)  | 5(2)   | 19(2) | 2(2)   |
| C(6)  | 34(2)  | 36(2) | 34(3)  | 1(2)   | 21(2) | -1(2)  |
| C(7)  | 27(2)  | 33(2) | 37(3)  | 2(2)   | 20(2) | 2(2)   |
| C(8)  | 32(2)  | 30(2) | 36(2)  | 2(2)   | 25(2) | 4(2)   |
| C(9)  | 31(2)  | 27(2) | 40(3)  | 8(2)   | 25(2) | 5(2)   |
| C(10) | 30(2)  | 36(2) | 39(3)  | 5(2)   | 19(2) | 4(2)   |
| C(11) | 32(2)  | 32(2) | 38(3)  | 2(2)   | 23(2) | -1(2)  |
| C(12) | 32(2)  | 29(2) | 38(3)  | 4(2)   | 22(2) | 2(2)   |
| C(13) | 34(2)  | 33(2) | 48(3)  | 4(2)   | 26(2) | 2(2)   |
| C(14) | 42(3)  | 37(3) | 57(3)  | 12(2)  | 33(3) | 4(2)   |
| C(15) | 41(3)  | 34(3) | 53(3)  | 8(2)   | 27(3) | 2(2)   |
| C(16) | 44(3)  | 34(3) | 59(3)  | 7(2)   | 33(3) | 8(2)   |
| C(17) | 35(3)  | 32(2) | 52(3)  | 4(2)   | 21(2) | -4(2)  |
| C(18) | 62(4)  | 55(4) | 93(5)  | -30(3) | 46(4) | -15(3) |
| C(19) | 34(3)  | 47(3) | 68(4)  | -1(3)  | 19(3) | -8(2)  |
| C(20) | 63(4)  | 67(4) | 62(4)  | 20(3)  | 8(3)  | -35(3) |
| C(21) | 38(3)  | 34(2) | 38(3)  | 3(2)   | 26(2) | 0(2)   |
| C(22) | 40(3)  | 48(3) | 51(3)  | -5(2)  | 28(3) | 2(2)   |
| C(23) | 50(3)  | 68(4) | 81(4)  | -8(3)  | 47(3) | 3(3)   |
| C(24) | 65(4)  | 64(4) | 73(4)  | -12(3) | 53(4) | 5(3)   |
| C(25) | 55(3)  | 64(4) | 48(3)  | -13(3) | 32(3) | -1(3)  |
| C(26) | 41(3)  | 47(3) | 43(3)  | -1(2)  | 25(2) | 4(2)   |
| C(27) | 29(2)  | 34(2) | 31(2)  | 8(2)   | 15(2) | 3(2)   |
| C(28) | 39(3)  | 38(3) | 40(3)  | 6(2)   | 22(2) | 4(2)   |
| C(29) | 54(3)  | 34(3) | 58(3)  | 4(2)   | 28(3) | 6(2)   |
| C(30) | 55(3)  | 35(3) | 65(4)  | 15(3)  | 30(3) | -2(2)  |
| C(31) | 53(3)  | 49(3) | 54(3)  | 18(3)  | 31(3) | -1(2)  |
| C(32) | 44(3)  | 43(3) | 45(3)  | 11(2)  | 28(2) | 2(2)   |
| C(33) | 38(3)  | 34(2) | 53(3)  | 5(2)   | 31(2) | 5(2)   |
| C(34) | 34(2)  | 30(2) | 45(3)  | 3(2)   | 27(2) | -3(2)  |
| C(35) | 35(2)  | 24(2) | 47(3)  | 0(2)   | 29(2) | -4(2)  |
| C(36) | 44(3)  | 34(2) | 51(3)  | 1(2)   | 35(2) | -2(2)  |
| C(37) | 52(3)  | 30(2) | 70(4)  | 1(2)   | 48(3) | 1(2)   |
| C(38) | 43(3)  | 33(3) | 62(3)  | 9(2)   | 38(3) | 6(2)   |
| C(39) | 44(3)  | 31(2) | 48(3)  | 6(2)   | 34(2) | 4(2)   |
| C(40) | 40(3)  | 54(3) | 48(3)  | 17(2)  | 25(3) | 10(2)  |
| C(41) | 51(3)  | 32(3) | 72(4)  | 4(2)   | 43(3) | 7(2)   |
| C(42) | 73(4)  | 45(3) | 59(3)  | 16(3)  | 48(3) | 15(3)  |
| C(43) | 65(4)  | 35(3) | 77(4)  | 0(3)   | 57(3) | 5(2)   |
| C(44) | 119(6) | 56(4) | 108(6) | 20(4)  | 99(5) | 29(4)  |
| C(45) | 72(4)  | 69(4) | 113(6) | -10(4) | 73(4) | 7(3)   |
| C(46) | 92(5)  | 45(3) | 96(5)  | -7(3)  | 74(4) | -1(3)  |
| C(47) | 26(2)  | 43(3) | 57(3)  | 17(2)  | 16(2) | 5(2)   |
| C(48) | 50(3)  | 51(3) | 86(5)  | 13(3)  | 39(3) | -8(3)  |
| C(49) | 60(4)  | 65(4) | 112(7) | 16(4)  | 39(4) | -20(3) |
| C(50) | 65(4)  | 59(4) | 83(5)  | 12(4)  | 14(4) | -22(3) |
| C(51) | 83(5)  | 62(4) | 61(4)  | 5(3)   | 17(4) | -21(3) |
| C(52) | 58(4)  | 52(3) | 53(4)  | 8(3)   | 22(3) | -13(3) |
| C(53) | 46(3)  | 43(3) | 70(4)  | 24(3)  | 43(3) | 14(2)  |
| C(54) | 43(3)  | 62(4) | 118(6) | 36(4)  | 49(4) | 21(3)  |

# Appendix 1. Crystallographic data

|       |        |        |         |        |        |        |
|-------|--------|--------|---------|--------|--------|--------|
| C(55) | 65(5)  | 89(6)  | 190(10) | 67(6)  | 85(6)  | 41(4)  |
| C(56) | 104(6) | 69(5)  | 190(10) | 65(5)  | 111(7) | 55(5)  |
| C(57) | 112(6) | 45(4)  | 135(7)  | 27(4)  | 99(6)  | 24(4)  |
| C(58) | 64(4)  | 50(3)  | 72(4)   | 19(3)  | 52(3)  | 15(3)  |
| C(59) | 45(3)  | 40(3)  | 48(3)   | -4(2)  | 31(3)  | -3(2)  |
| C(60) | 88(5)  | 71(4)  | 84(5)   | -31(4) | 64(4)  | -25(3) |
| C(61) | 61(4)  | 113(6) | 65(4)   | -44(4) | 34(4)  | -7(4)  |
| C(62) | 141(7) | 47(4)  | 74(5)   | -4(3)  | 53(5)  | -7(4)  |
| C(63) | 61(4)  | 99(6)  | 116(6)  | -54(5) | 46(4)  | -30(4) |
| C(64) | 139(8) | 122(7) | 150(10) | -81(7) | 105(8) | -66(6) |
| C(65) | 143(8) | 91(6)  | 141(8)  | -55(5) | 107(7) | -46(5) |
| C(66) | 92(5)  | 73(4)  | 94(5)   | -25(4) | 72(5)  | -21(4) |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa717

| atom   | x         | y    | z    | U(eq) |
|--------|-----------|------|------|-------|
| H(3)   | 3444      | 3938 | 4287 | 48    |
| H(4)   | 3524      | 3366 | 5147 | 49    |
| H(5)   | 2888      | 3096 | 5150 | 46    |
| H(6)   | 2182      | 3433 | 4297 | 40    |
| H(10)  | -72       | 4405 | 774  | 42    |
| H(12)  | 744       | 3046 | 2138 | 38    |
| H(14A) | 639       | 6283 | 826  | 64    |
| H(14B) | 726       | 5500 | 723  | 64    |
| H(14C) | 1037      | 5852 | 1411 | 64    |
| H(15A) | -287      | 5493 | 717  | 64    |
| H(15B) | -112.0000 | 5391 | 260  | 64    |
| H(15C) | -135      | 6148 | 494  | 64    |
| H(16A) | 378       | 6517 | 1580 | 66    |
| H(16B) | 763       | 6021 | 2110 | 66    |
| H(16C) | 249       | 5878 | 1850 | 66    |
| H(18A) | 49        | 3050 | 278  | 103   |
| H(18B) | -166      | 2343 | 315  | 103   |
| H(18C) | 357       | 2497 | 823  | 103   |
| H(19A) | -614      | 3565 | 876  | 82    |
| H(19B) | -749      | 2934 | 392  | 82    |
| H(19C) | -571      | 3639 | 279  | 82    |
| H(20A) | 261       | 2299 | 1719 | 118   |
| H(20B) | -264      | 2149 | 1222 | 118   |
| H(20C) | -105      | 2726 | 1761 | 118   |
| H(22)  | 649       | 4292 | 2961 | 54    |
| H(23)  | 477       | 4985 | 3545 | 73    |
| H(24)  | 1051      | 5550 | 4466 | 72    |
| H(25)  | 1793      | 5411 | 4803 | 65    |
| H(26)  | 1974      | 4719 | 4215 | 52    |
| H(28)  | 1786      | 2640 | 2902 | 46    |
| H(29)  | 1687      | 1465 | 3015 | 61    |
| H(30)  | 1254      | 1131 | 3389 | 64    |
| H(31)  | 945       | 1951 | 3704 | 61    |
| H(32)  | 1051      | 3122 | 3617 | 50    |
| H(36)  | 2581      | 5493 | 726  | 45    |
| H(38)  | 3263      | 4154 | 2179 | 49    |
| H(40A) | 1536      | 5640 | 542  | 70    |
| H(40B) | 1437      | 6402 | 678  | 70    |
| H(40C) | 1645      | 5833 | 1233 | 70    |
| H(41A) | 2258      | 6712 | 1905 | 71    |
| H(41B) | 2067      | 7232 | 1315 | 71    |
| H(41C) | 2576      | 6968 | 1683 | 71    |
| H(42A) | 2391      | 6618 | 593  | 79    |
| H(42B) | 1891      | 6889 | 300  | 79    |
| H(42C) | 1972      | 6120 | 155  | 79    |
| H(44A) | 2705      | 4803 | 152  | 113   |
| H(44B) | 3163      | 4534 | 252  | 113   |
| H(44C) | 3155      | 5249 | 562  | 113   |
| H(45A) | 3788      | 4165 | 1289 | 109   |
| H(45B) | 3744      | 4090 | 1885 | 109   |
| H(45C) | 3781      | 4839 | 1650 | 109   |
| H(46A) | 2637      | 3683 | 577  | 99    |
| H(46B) | 3041      | 3416 | 1264 | 99    |
| H(46C) | 3098      | 3431 | 677  | 99    |
| H(48)  | 3573      | 5612 | 2928 | 74    |
| H(49)  | 4023      | 6555 | 3529 | 101   |
| H(50)  | 4139      | 6796 | 4515 | 100   |
| H(51)  | 3789      | 6139 | 4885 | 97    |
| H(52)  | 3336      | 5204 | 4284 | 71    |
| H(54)  | 4043      | 4416 | 3750 | 87    |
| H(55)  | 4507      | 3467 | 3940 | 130   |
| H(56)  | 4201      | 2383 | 3590 | 125   |



Appendix 1. Crystallographic data

|        |      |      |      |     |
|--------|------|------|------|-----|
| H(57)  | 3438 | 2208 | 3084 | 98  |
| H(58)  | 2964 | 3147 | 2875 | 66  |
| H(60A) | 1823 | 4254 | 770  | 108 |
| H(60B) | 1796 | 3437 | 666  | 108 |
| H(60C) | 2202 | 3765 | 1319 | 108 |
| H(61A) | 952  | 3728 | 966  | 120 |
| H(61B) | 1036 | 3430 | 449  | 120 |
| H(61C) | 1054 | 4243 | 566  | 120 |
| H(62A) | 2024 | 3043 | 1986 | 137 |
| H(62B) | 1669 | 2674 | 1321 | 137 |
| H(62C) | 1509 | 2974 | 1755 | 137 |
| H(63A) | 2739 | 6181 | 3514 | 112 |
| H(63B) | 2392 | 6729 | 2994 | 112 |
| H(64A) | 2484 | 7329 | 3755 | 151 |
| H(64B) | 2770 | 6727 | 4261 | 151 |
| H(65A) | 2184 | 6386 | 4260 | 132 |
| H(65B) | 1935 | 7079 | 3870 | 132 |
| H(66A) | 1636 | 5880 | 3371 | 90  |
| H(66B) | 1564 | 6539 | 2935 | 90  |

Appendix 1. Crystallographic data

**Complex 56'**

Table 1. Crystal data for pa679bis

|   |  |
|---|--|
| Compound                                    | pa679bis   |
| Molecular formula                           | C <sub>114</sub> H <sub>144</sub> N <sub>6</sub> O <sub>6</sub> P <sub>4</sub> Y <sub>2</sub> , 2(C <sub>6</sub> H <sub>12</sub> ) |
| Molecular weight                            | 2164.36  |
| Crystal habit                               | Colorless Block  |
| Crystal dimensions(mm)                      | 0.22x0.20x0.20   |
| Crystal system                              | monoclinic   |
| Space group                                 | C2/c   |
| a(Å)  | 27.529(1)  |
| b(Å)  | 28.356(1)  |
| c(Å)  | 18.325(1)  |
| α(°)  | 90.00  |
| β(°)  | 124.463(1)   |
| γ(°)  | 90.00  |
| V(Å <sup>3</sup> )                          | 11794.1(9)   |
| Z   | 4  |
| d(g·cm <sup>-3</sup> )                      | 1.219  |
| F(000)                                      | 4608   |
| μ(cm <sup>-1</sup> )                        | 1.089  |
| Absorption corrections                      | multi-scan ; 0.7956 min, 0.8116 max  |
| Diffractionmeter                            | KappaCCD   |
| X-ray source                                | MoKα   |
| λ(Å)  | 0.71069  |
| Monochromator                               | graphite   |
| T (K)                                       | 150.0(1)   |
| Scan mode                                   | phi and omega scans  |
| Maximum θ                                   | 26.02  |
| HKL ranges                                  | -33 33 ; -32 34 ; -16 22   |
| Reflections measured                        | 28082  |
| Unique data                                 | 11468  |
| Rint  | 0.0465   |
| Reflections used                            | 8593   |
| Criterion                                   | I > 2σ(I)  |
| Refinement type                             | Fsqd   |
| Hydrogen atoms                              | constr   |
| Parameters refined                          | 635  |
| Reflections / parameter                     | 13   |
| wR2   | 0.1136   |
| R1  | 0.0565   |
| Weights a, b                                | 0.0259 ; 50.837  |
| GoF   | 1.050  |
| difference peak / hole (e Å <sup>-3</sup> ) | 0.584(0.072) / -0.391(0.072)   |

# Appendix 1. Crystallographic data

Table 2. Atomic Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa679bis

| atom   | x       | y       | z        | U(eq) |
|--------|---------|---------|----------|-------|
| Y(1)   | 5043(1) | 3027(1) | 3605(1)  | 24(1) |
| P(1)   | 5190(1) | 3610(1) | 5491(1)  | 27(1) |
| P(2)   | 4297(1) | 1907(1) | 3541(1)  | 28(1) |
| O(1)   | 5856(1) | 3447(1) | 4610(2)  | 28(1) |
| O(2)   | 5507(1) | 2403(1) | 4469(2)  | 26(1) |
| O(3)   | 5000    | 3521(1) | 2500     | 30(1) |
| O(4)   | 5000    | 2639(1) | 2500     | 31(1) |
| N(1)   | 4774(1) | 3410(1) | 4517(2)  | 31(1) |
| N(2)   | 4019(1) | 3361(1) | 2691(2)  | 32(1) |
| N(3)   | 4246(1) | 2438(1) | 3217(2)  | 29(1) |
| C(1)   | 4134(2) | 3364(2) | 4122(3)  | 38(1) |
| C(2)   | 3808(2) | 3570(1) | 3200(3)  | 37(1) |
| C(3)   | 3635(2) | 3000(1) | 2038(2)  | 34(1) |
| C(4)   | 3632(2) | 2566(1) | 2505(2)  | 34(1) |
| C(5)   | 5850(2) | 3882(1) | 5718(2)  | 28(1) |
| C(6)   | 6108(2) | 3752(1) | 5263(2)  | 26(1) |
| C(7)   | 6665(1) | 3975(1) | 5564(2)  | 26(1) |
| C(8)   | 6896(2) | 4300(1) | 6245(2)  | 31(1) |
| C(9)   | 6637(2) | 4432(1) | 6688(2)  | 34(1) |
| C(10)  | 6112(2) | 4216(1) | 6410(2)  | 31(1) |
| C(11)  | 6999(2) | 3854(1) | 5143(2)  | 30(1) |
| C(12)  | 6609(2) | 3990(1) | 4161(2)  | 34(1) |
| C(13)  | 7143(2) | 3325(1) | 5258(2)  | 32(1) |
| C(14)  | 7579(2) | 4126(2) | 5557(3)  | 41(1) |
| C(15)  | 6928(2) | 4805(2) | 7425(3)  | 47(1) |
| C(16A) | 7555(3) | 4664(3) | 8170(5)  | 68(3) |
| C(17A) | 7002(4) | 5265(2) | 7034(5)  | 63(2) |
| C(18A) | 6533(4) | 4967(3) | 7720(7)  | 84(3) |
| C(16B) | 7592(3) | 4854(7) | 7850(10) | 68(3) |
| C(17B) | 6549(6) | 5250(3) | 7130(10) | 63(2) |
| C(18B) | 6896(8) | 4608(5) | 8187(8)  | 84(3) |
| C(19)  | 4815(2) | 4057(1) | 5712(2)  | 29(1) |
| C(20)  | 4662(2) | 4478(1) | 5242(3)  | 35(1) |
| C(21)  | 4355(2) | 4824(1) | 5354(3)  | 41(1) |
| C(22)  | 4199(2) | 4749(2) | 5941(3)  | 59(1) |
| C(23)  | 4340(3) | 4330(2) | 6400(4)  | 73(2) |
| C(24)  | 4647(2) | 3985(2) | 6288(3)  | 50(1) |
| C(25)  | 5413(2) | 3166(1) | 6341(2)  | 32(1) |
| C(26)  | 5807(2) | 3252(2) | 7247(3)  | 43(1) |
| C(27)  | 5949(2) | 2897(2) | 7851(3)  | 50(1) |
| C(28)  | 5711(2) | 2454(2) | 7569(3)  | 52(1) |
| C(29)  | 5331(2) | 2358(2) | 6677(3)  | 47(1) |
| C(30)  | 5181(2) | 2716(1) | 6068(3)  | 36(1) |
| C(31)  | 4973(2) | 1778(1) | 4570(2)  | 29(1) |
| C(32)  | 5497(2) | 2029(1) | 4873(2)  | 27(1) |
| C(33)  | 6025(2) | 1854(1) | 5666(2)  | 29(1) |
| C(34)  | 5987(2) | 1453(1) | 6064(2)  | 36(1) |
| C(35)  | 5464(2) | 1200(1) | 5755(3)  | 39(1) |
| C(36)  | 4962(2) | 1373(1) | 5006(2)  | 35(1) |
| C(37)  | 6618(2) | 2103(1) | 6063(2)  | 33(1) |
| C(38)  | 6779(2) | 2108(1) | 5382(3)  | 38(1) |
| C(39)  | 7119(2) | 1853(2) | 6897(3)  | 54(1) |
| C(40)  | 6581(2) | 2612(1) | 6325(2)  | 35(1) |
| C(41)  | 5469(2) | 760(2)  | 6246(3)  | 48(1) |
| C(42)  | 5583(3) | 913(2)  | 7124(4)  | 85(2) |
| C(43)  | 5955(3) | 432(2)  | 6414(4)  | 81(2) |
| C(44)  | 4880(3) | 506(2)  | 5728(4)  | 98(2) |
| C(45)  | 4214(2) | 1468(1) | 2749(2)  | 32(1) |
| C(46)  | 4212(2) | 984(1)  | 2884(3)  | 42(1) |
| C(47)  | 4202(2) | 666(2)  | 2300(3)  | 50(1) |
| C(48)  | 4199(2) | 821(2)  | 1585(3)  | 44(1) |
| C(49)  | 4196(2) | 1298(2) | 1441(3)  | 42(1) |

# Appendix 1. Crystallographic data

|       |         |         |         |       |
|-------|---------|---------|---------|-------|
| C(50) | 4200(2) | 1619(1) | 2014(2) | 36(1) |
| C(51) | 3699(2) | 1787(1) | 3671(3) | 34(1) |
| C(52) | 3724(2) | 2001(2) | 4378(3) | 46(1) |
| C(53) | 3238(2) | 2003(2) | 4413(3) | 60(1) |
| C(54) | 2720(2) | 1796(2) | 3751(3) | 58(1) |
| C(55) | 2684(2) | 1581(2) | 3048(3) | 45(1) |
| C(56) | 3177(2) | 1575(1) | 3010(3) | 37(1) |
| C(57) | 4986(8) | 4008(2) | 2330(7) | 32(3) |
| C(58) | 4892(4) | 4296(2) | 2928(5) | 44(2) |

U(eq) is defined as 1/3 the trace of the U<sub>ij</sub> tensor.

Table 3. Bond lengths (Å) and angles (deg) for pa679bis

|               |          |               |           |
|---------------|----------|---------------|-----------|
| Y(1)-O(2)     | 2.230(2) | Y(1)-O(4)     | 2.248(2)  |
| Y(1)-O(1)     | 2.271(2) | Y(1)-O(3)     | 2.411(2)  |
| Y(1)-N(1)     | 2.433(3) | Y(1)-N(2)     | 2.511(3)  |
| Y(1)-N(3)     | 2.517(3) | Y(1)-Y(1)#2   | 3.9225(7) |
| P(1)-N(1)     | 1.583(3) | P(1)-C(5)     | 1.794(3)  |
| P(1)-C(25)    | 1.819(4) | P(1)-C(19)    | 1.820(4)  |
| P(2)-N(3)     | 1.596(3) | P(2)-C(31)    | 1.784(4)  |
| P(2)-C(51)    | 1.824(4) | P(2)-C(45)    | 1.825(4)  |
| O(1)-C(6)     | 1.311(4) | O(2)-C(32)    | 1.303(4)  |
| O(3)-C(57)#2  | 1.411(4) | O(3)-C(57)    | 1.411(4)  |
| O(3)-Y(1)#2   | 2.411(2) | O(4)-Y(1)#2   | 2.248(2)  |
| O(4)-H(40)    | 0.76(6)  | N(1)-C(1)     | 1.483(4)  |
| N(2)-C(3)     | 1.469(5) | N(2)-C(2)     | 1.474(5)  |
| N(2)-H(2N)    | 0.93(4)  | N(3)-C(4)     | 1.482(4)  |
| C(1)-C(2)     | 1.512(5) | C(1)-H(1A)    | 0.9900    |
| C(1)-H(1B)    | 0.9900   | C(2)-H(2A)    | 0.9900    |
| C(2)-H(2B)    | 0.9900   | C(3)-C(4)     | 1.502(5)  |
| C(3)-H(3A)    | 0.9900   | C(3)-H(3B)    | 0.9900    |
| C(4)-H(4A)    | 0.9900   | C(4)-H(4B)    | 0.9900    |
| C(5)-C(10)    | 1.409(5) | C(5)-C(6)     | 1.417(5)  |
| C(6)-C(7)     | 1.448(5) | C(7)-C(8)     | 1.382(5)  |
| C(7)-C(11)    | 1.537(5) | C(8)-C(9)     | 1.400(5)  |
| C(8)-H(8)     | 0.9500   | C(9)-C(10)    | 1.375(5)  |
| C(9)-C(15)    | 1.536(5) | C(10)-H(10)   | 0.9500    |
| C(11)-C(14)   | 1.533(5) | C(11)-C(12)   | 1.533(5)  |
| C(11)-C(13)   | 1.534(5) | C(12)-H(12A)  | 0.9800    |
| C(12)-H(12B)  | 0.9800   | C(12)-H(12C)  | 0.9800    |
| C(13)-H(13A)  | 0.9800   | C(13)-H(13B)  | 0.9800    |
| C(13)-H(13C)  | 0.9800   | C(14)-H(14A)  | 0.9800    |
| C(14)-H(14B)  | 0.9800   | C(14)-H(14C)  | 0.9800    |
| C(15)-C(17B)  | 1.527(5) | C(15)-C(16A)  | 1.529(5)  |
| C(15)-C(18A)  | 1.533(4) | C(15)-C(16B)  | 1.534(5)  |
| C(15)-C(18B)  | 1.551(5) | C(15)-C(17A)  | 1.557(4)  |
| C(16A)-H(16A) | 0.9800   | C(16A)-H(16B) | 0.9800    |
| C(16A)-H(16C) | 0.9800   | C(17A)-H(17A) | 0.9800    |
| C(17A)-H(17B) | 0.9800   | C(17A)-H(17C) | 0.9800    |
| C(18A)-H(18A) | 0.9800   | C(18A)-H(18B) | 0.9800    |
| C(18A)-H(18C) | 0.9800   | C(16B)-H(16D) | 0.9800    |
| C(16B)-H(16E) | 0.9800   | C(16B)-H(16F) | 0.9800    |
| C(17B)-H(17D) | 0.9800   | C(17B)-H(17E) | 0.9800    |
| C(17B)-H(17F) | 0.9800   | C(18B)-H(18D) | 0.9800    |
| C(18B)-H(18E) | 0.9800   | C(18B)-H(18F) | 0.9800    |
| C(19)-C(24)   | 1.386(5) | C(19)-C(20)   | 1.392(5)  |
| C(20)-C(21)   | 1.385(5) | C(20)-H(20)   | 0.9500    |
| C(21)-C(22)   | 1.381(6) | C(21)-H(21)   | 0.9500    |
| C(22)-C(23)   | 1.378(6) | C(22)-H(22)   | 0.9500    |
| C(23)-C(24)   | 1.382(6) | C(23)-H(23)   | 0.9500    |
| C(24)-H(24)   | 0.9500   | C(25)-C(30)   | 1.389(5)  |
| C(25)-C(26)   | 1.398(5) | C(26)-C(27)   | 1.377(6)  |
| C(26)-H(26)   | 0.9500   | C(27)-C(28)   | 1.377(6)  |
| C(27)-H(27)   | 0.9500   | C(28)-C(29)   | 1.380(6)  |
| C(28)-H(28)   | 0.9500   | C(29)-C(30)   | 1.386(6)  |
| C(29)-H(29)   | 0.9500   | C(30)-H(30)   | 0.9500    |
| C(31)-C(36)   | 1.409(5) | C(31)-C(32)   | 1.411(5)  |
| C(32)-C(33)   | 1.443(5) | C(33)-C(34)   | 1.385(5)  |
| C(33)-C(37)   | 1.534(5) | C(34)-C(35)   | 1.410(5)  |
| C(34)-H(34)   | 0.9500   | C(35)-C(36)   | 1.374(5)  |
| C(35)-C(41)   | 1.533(5) | C(36)-H(36)   | 0.9500    |
| C(37)-C(39)   | 1.534(5) | C(37)-C(38)   | 1.541(5)  |
| C(37)-C(40)   | 1.543(5) | C(38)-H(38A)  | 0.9800    |
| C(38)-H(38B)  | 0.9800   | C(38)-H(38C)  | 0.9800    |
| C(39)-H(39A)  | 0.9800   | C(39)-H(39B)  | 0.9800    |
| C(39)-H(39C)  | 0.9800   | C(40)-H(40A)  | 0.9800    |
| C(40)-H(40B)  | 0.9800   | C(40)-H(40C)  | 0.9800    |
| C(41)-C(43)   | 1.511(7) | C(41)-C(42)   | 1.517(7)  |
| C(41)-C(44)   | 1.519(7) | C(42)-H(42A)  | 0.9800    |

|                    |           |                     |           |
|--------------------|-----------|---------------------|-----------|
| C(42)-H(42B)       | 0.9800    | C(42)-H(42C)        | 0.9800    |
| C(43)-H(43A)       | 0.9800    | C(43)-H(43B)        | 0.9800    |
| C(43)-H(43C)       | 0.9800    | C(44)-H(44A)        | 0.9800    |
| C(44)-H(44B)       | 0.9800    | C(44)-H(44C)        | 0.9800    |
| C(45)-C(50)        | 1.393(5)  | C(45)-C(46)         | 1.395(5)  |
| C(46)-C(47)        | 1.389(6)  | C(46)-H(46)         | 0.9500    |
| C(47)-C(48)        | 1.379(6)  | C(47)-H(47)         | 0.9500    |
| C(48)-C(49)        | 1.377(6)  | C(48)-H(48)         | 0.9500    |
| C(49)-C(50)        | 1.384(5)  | C(49)-H(49)         | 0.9500    |
| C(50)-H(50)        | 0.9500    | C(51)-C(56)         | 1.387(5)  |
| C(51)-C(52)        | 1.398(5)  | C(52)-C(53)         | 1.375(6)  |
| C(52)-H(52)        | 0.9500    | C(53)-C(54)         | 1.376(6)  |
| C(53)-H(53)        | 0.9500    | C(54)-C(55)         | 1.378(6)  |
| C(54)-H(54)        | 0.9500    | C(55)-C(56)         | 1.396(5)  |
| C(55)-H(55)        | 0.9500    | C(56)-H(56)         | 0.9500    |
| C(57)-C(58)        | 1.500(2)  | C(57)-H(57A)        | 0.9900    |
| C(57)-H(57B)       | 0.9900    | C(58)-H(58A)        | 0.9800    |
| C(58)-H(58B)       | 0.9800    | C(58)-H(58C)        | 0.9800    |
| O(2)-Y(1)-O(4)     | 88.2(1)   | O(2)-Y(1)-O(1)      | 86.26(8)  |
| O(4)-Y(1)-O(1)     | 120.81(6) | O(2)-Y(1)-O(3)      | 142.48(7) |
| O(4)-Y(1)-O(3)     | 64.8(1)   | O(1)-Y(1)-O(3)      | 86.17(7)  |
| O(2)-Y(1)-N(1)     | 98.2(1)   | O(4)-Y(1)-N(1)      | 162.89(7) |
| O(1)-Y(1)-N(1)     | 75.7(1)   | O(3)-Y(1)-N(1)      | 115.3(1)  |
| O(2)-Y(1)-N(2)     | 138.4(1)  | O(4)-Y(1)-N(2)      | 96.66(8)  |
| O(1)-Y(1)-N(2)     | 124.3(1)  | O(3)-Y(1)-N(2)      | 73.59(7)  |
| N(1)-Y(1)-N(2)     | 68.1(1)   | O(2)-Y(1)-N(3)      | 74.5(1)   |
| O(4)-Y(1)-N(3)     | 80.1(1)   | O(1)-Y(1)-N(3)      | 151.5(1)  |
| O(3)-Y(1)-N(3)     | 121.84(7) | N(1)-Y(1)-N(3)      | 86.3(1)   |
| N(2)-Y(1)-N(3)     | 65.9(1)   | O(2)-Y(1)-Y(1)#2    | 114.10(6) |
| O(4)-Y(1)-Y(1)#2   | 29.25(8)  | O(1)-Y(1)-Y(1)#2    | 107.04(6) |
| O(3)-Y(1)-Y(1)#2   | 35.55(6)  | N(1)-Y(1)-Y(1)#2    | 147.69(7) |
| N(2)-Y(1)-Y(1)#2   | 85.53(7)  | N(3)-Y(1)-Y(1)#2    | 100.05(7) |
| N(1)-P(1)-C(5)     | 114.1(2)  | N(1)-P(1)-C(25)     | 113.3(2)  |
| C(5)-P(1)-C(25)    | 107.0(2)  | N(1)-P(1)-C(19)     | 111.2(2)  |
| C(5)-P(1)-C(19)    | 106.1(2)  | C(25)-P(1)-C(19)    | 104.5(2)  |
| N(3)-P(2)-C(31)    | 114.0(2)  | N(3)-P(2)-C(51)     | 109.3(2)  |
| C(31)-P(2)-C(51)   | 107.6(2)  | N(3)-P(2)-C(45)     | 113.7(2)  |
| C(31)-P(2)-C(45)   | 106.7(2)  | C(51)-P(2)-C(45)    | 105.1(2)  |
| C(6)-O(1)-Y(1)     | 148.8(2)  | C(32)-O(2)-Y(1)     | 149.4(2)  |
| C(57)#2-O(3)-C(57) | 23.8(5)   | C(57)#2-O(3)-Y(1)   | 113.7(2)  |
| C(57)-O(3)-Y(1)    | 137.4(2)  | C(57)#2-O(3)-Y(1)#2 | 137.4(2)  |
| C(57)-O(3)-Y(1)#2  | 113.7(2)  | Y(1)-O(3)-Y(1)#2    | 108.9(1)  |
| Y(1)-O(4)-Y(1)#2   | 121.5(2)  | Y(1)-O(4)-H(40)     | 119.25(8) |
| Y(1)#2-O(4)-H(40)  | 119.25(8) | C(1)-N(1)-P(1)      | 118.9(2)  |
| C(1)-N(1)-Y(1)     | 111.4(2)  | P(1)-N(1)-Y(1)      | 128.8(2)  |
| C(3)-N(2)-C(2)     | 115.8(3)  | C(3)-N(2)-Y(1)      | 107.4(2)  |
| C(2)-N(2)-Y(1)     | 115.1(2)  | C(3)-N(2)-H(2N)     | 107(2)    |
| C(2)-N(2)-H(2N)    | 106(2)    | Y(1)-N(2)-H(2N)     | 104(2)    |
| C(4)-N(3)-P(2)     | 112.0(2)  | C(4)-N(3)-Y(1)      | 117.7(2)  |
| P(2)-N(3)-Y(1)     | 129.9(2)  | N(1)-C(1)-C(2)      | 107.5(3)  |
| N(1)-C(1)-H(1A)    | 110.2     | C(2)-C(1)-H(1A)     | 110.2     |
| N(1)-C(1)-H(1B)    | 110.2     | C(2)-C(1)-H(1B)     | 110.2     |
| H(1A)-C(1)-H(1B)   | 108.5     | N(2)-C(2)-C(1)      | 110.7(3)  |
| N(2)-C(2)-H(2A)    | 109.5     | C(1)-C(2)-H(2A)     | 109.5     |
| N(2)-C(2)-H(2B)    | 109.5     | C(1)-C(2)-H(2B)     | 109.5     |
| H(2A)-C(2)-H(2B)   | 108.1     | N(2)-C(3)-C(4)      | 109.9(3)  |
| N(2)-C(3)-H(3A)    | 109.7     | C(4)-C(3)-H(3A)     | 109.7     |
| N(2)-C(3)-H(3B)    | 109.7     | C(4)-C(3)-H(3B)     | 109.7     |
| H(3A)-C(3)-H(3B)   | 108.2     | N(3)-C(4)-C(3)      | 109.3(3)  |
| N(3)-C(4)-H(4A)    | 109.8     | C(3)-C(4)-H(4A)     | 109.8     |
| N(3)-C(4)-H(4B)    | 109.8     | C(3)-C(4)-H(4B)     | 109.8     |
| H(4A)-C(4)-H(4B)   | 108.3     | C(10)-C(5)-C(6)     | 122.2(3)  |
| C(10)-C(5)-P(1)    | 115.7(2)  | C(6)-C(5)-P(1)      | 122.0(3)  |
| O(1)-C(6)-C(5)     | 121.8(3)  | O(1)-C(6)-C(7)      | 122.4(3)  |
| C(5)-C(6)-C(7)     | 115.8(3)  | C(8)-C(7)-C(6)      | 128.9(3)  |
| C(8)-C(7)-C(11)    | 120.1(3)  | C(6)-C(7)-C(11)     | 121.0(3)  |

|                      |          |                      |       |
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| C(7)-C(8)-C(9)       | 125.2(3) | C(7)-C(8)-H(8)       | 117.7 |
| C(9)-C(8)-H(8)       | 117.4    | C(10)-C(9)-C(8)      | 116.6 |
| C(10)-C(9)-C(15)     | 123.3(3) | C(8)-C(9)-C(15)      | 120.1 |
| C(9)-C(10)-C(5)      | 121.9(3) | C(9)-C(10)-H(10)     | 119.9 |
| C(5)-C(10)-H(10)     | 119.1    | C(14)-C(11)-C(12)    | 107.9 |
| C(14)-C(11)-C(13)    | 107.9(3) | C(12)-C(11)-C(13)    | 111.1 |
| C(14)-C(11)-C(7)     | 113.0(3) | C(12)-C(11)-C(7)     | 108.8 |
| C(13)-C(11)-C(7)     | 109.3(3) | C(11)-C(12)-H(12A)   | 109.9 |
| C(11)-C(12)-H(12B)   | 109.5    | H(12A)-C(12)-H(12B)  | 109.9 |
| C(11)-C(12)-H(12C)   | 109.5    | H(12A)-C(12)-H(12C)  | 109.9 |
| H(12B)-C(12)-H(12C)  | 109.5    | C(11)-C(13)-H(13A)   | 109.9 |
| C(11)-C(13)-H(13B)   | 109.5    | H(13A)-C(13)-H(13B)  | 109.9 |
| C(11)-C(13)-H(13C)   | 109.5    | H(13A)-C(13)-H(13C)  | 109.9 |
| H(13B)-C(13)-H(13C)  | 109.5    | C(11)-C(14)-H(14A)   | 109.9 |
| C(11)-C(14)-H(14B)   | 109.5    | H(14A)-C(14)-H(14B)  | 109.9 |
| C(11)-C(14)-H(14C)   | 109.5    | H(14A)-C(14)-H(14C)  | 109.9 |
| H(14B)-C(14)-H(14C)  | 109.5    | C(17B)-C(15)-C(16A)  | 137.1 |
| C(17B)-C(15)-C(18A)  | 53.2(7)  | C(16A)-C(15)-C(18A)  | 115.1 |
| C(17B)-C(15)-C(16B)  | 119(1)   | C(16A)-C(15)-C(16B)  | 31.1  |
| C(18A)-C(15)-C(16B)  | 132.1(8) | C(17B)-C(15)-C(9)    | 110.1 |
| C(16A)-C(15)-C(9)    | 111.5(4) | C(18A)-C(15)-C(9)    | 113.1 |
| C(16B)-C(15)-C(9)    | 112.9(7) | C(17B)-C(15)-C(18B)  | 104.1 |
| C(16A)-C(15)-C(18B)  | 73.3(8)  | C(18A)-C(15)-C(18B)  | 51.1  |
| C(16B)-C(15)-C(18B)  | 103(1)   | C(9)-C(15)-C(18B)    | 106.1 |
| C(17B)-C(15)-C(17A)  | 52.1(7)  | C(16A)-C(15)-C(17A)  | 104.1 |
| C(18A)-C(15)-C(17A)  | 102.5(5) | C(16B)-C(15)-C(17A)  | 74.1  |
| C(9)-C(15)-C(17A)    | 108.1(4) | C(18B)-C(15)-C(17A)  | 143.1 |
| C(15)-C(16A)-H(16A)  | 109.5    | C(15)-C(16A)-H(16B)  | 109.9 |
| C(15)-C(16A)-H(16C)  | 109.5    | C(15)-C(17A)-H(17A)  | 109.9 |
| C(15)-C(17A)-H(17B)  | 109.5    | C(15)-C(17A)-H(17C)  | 109.9 |
| C(15)-C(18A)-H(18A)  | 109.5    | C(15)-C(18A)-H(18B)  | 109.9 |
| C(15)-C(18A)-H(18C)  | 109.5    | C(15)-C(16B)-H(16D)  | 109.9 |
| C(15)-C(16B)-H(16E)  | 109.5    | H(16D)-C(16B)-H(16E) | 109.9 |
| C(15)-C(16B)-H(16F)  | 109.5    | H(16D)-C(16B)-H(16F) | 109.9 |
| H(16E)-C(16B)-H(16F) | 109.5    | C(15)-C(17B)-H(17D)  | 109.9 |
| C(15)-C(17B)-H(17E)  | 109.5    | H(17D)-C(17B)-H(17E) | 109.9 |
| C(15)-C(17B)-H(17F)  | 109.5    | H(17D)-C(17B)-H(17F) | 109.9 |
| H(17E)-C(17B)-H(17F) | 109.5    | C(15)-C(18B)-H(18D)  | 109.9 |
| C(15)-C(18B)-H(18E)  | 109.5    | H(18D)-C(18B)-H(18E) | 109.9 |
| C(15)-C(18B)-H(18F)  | 109.5    | H(18D)-C(18B)-H(18F) | 109.9 |
| H(18E)-C(18B)-H(18F) | 109.5    | C(24)-C(19)-C(20)    | 119.9 |
| C(24)-C(19)-P(1)     | 122.9(3) | C(20)-C(19)-P(1)     | 118.9 |
| C(21)-C(20)-C(19)    | 120.7(4) | C(21)-C(20)-H(20)    | 119.9 |
| C(19)-C(20)-H(20)    | 119.7    | C(22)-C(21)-C(20)    | 119.9 |
| C(22)-C(21)-H(21)    | 120.3    | C(20)-C(21)-H(21)    | 120.1 |
| C(23)-C(22)-C(21)    | 120.3(4) | C(23)-C(22)-H(22)    | 119.9 |
| C(21)-C(22)-H(22)    | 119.8    | C(22)-C(23)-C(24)    | 120.1 |
| C(22)-C(23)-H(23)    | 119.9    | C(24)-C(23)-H(23)    | 119.9 |
| C(23)-C(24)-C(19)    | 120.3(4) | C(23)-C(24)-H(24)    | 119.9 |
| C(19)-C(24)-H(24)    | 119.9    | C(30)-C(25)-C(26)    | 118.9 |
| C(30)-C(25)-P(1)     | 117.7(3) | C(26)-C(25)-P(1)     | 123.1 |
| C(27)-C(26)-C(25)    | 120.3(4) | C(27)-C(26)-H(26)    | 119.9 |
| C(25)-C(26)-H(26)    | 119.9    | C(28)-C(27)-C(26)    | 120.1 |
| C(28)-C(27)-H(27)    | 119.8    | C(26)-C(27)-H(27)    | 119.9 |
| C(27)-C(28)-C(29)    | 120.2(4) | C(27)-C(28)-H(28)    | 119.9 |
| C(29)-C(28)-H(28)    | 119.9    | C(28)-C(29)-C(30)    | 119.9 |
| C(28)-C(29)-H(29)    | 120.3    | C(30)-C(29)-H(29)    | 120.1 |
| C(29)-C(30)-C(25)    | 121.0(4) | C(29)-C(30)-H(30)    | 119.9 |
| C(25)-C(30)-H(30)    | 119.5    | C(36)-C(31)-C(32)    | 122.1 |
| C(36)-C(31)-P(2)     | 115.0(3) | C(32)-C(31)-P(2)     | 122.1 |
| O(2)-C(32)-C(31)     | 122.2(3) | O(2)-C(32)-C(33)     | 121.1 |
| C(31)-C(32)-C(33)    | 116.5(3) | C(34)-C(33)-C(32)    | 118.9 |
| C(34)-C(33)-C(37)    | 120.4(3) | C(32)-C(33)-C(37)    | 121.1 |
| C(33)-C(34)-C(35)    | 124.8(3) | C(33)-C(34)-H(34)    | 117.1 |
| C(35)-C(34)-H(34)    | 117.6    | C(36)-C(35)-C(3      |       |

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| C(33)-C(37)-C(38)   | 109.6(3) | C(39)-C(37)-C(38)   | 107.8(3) |
| C(33)-C(37)-C(40)   | 109.8(3) | C(39)-C(37)-C(40)   | 107.8(3) |
| C(38)-C(37)-C(40)   | 110.1(3) | C(37)-C(38)-H(38A)  | 109.5    |
| C(37)-C(38)-H(38B)  | 109.5    | H(38A)-C(38)-H(38B) | 109.5    |
| C(37)-C(38)-H(38C)  | 109.5    | H(38A)-C(38)-H(38C) | 109.5    |
| H(38B)-C(38)-H(38C) | 109.5    | C(37)-C(39)-H(39A)  | 109.5    |
| C(37)-C(39)-H(39B)  | 109.5    | H(39A)-C(39)-H(39B) | 109.5    |
| C(37)-C(39)-H(39C)  | 109.5    | H(39A)-C(39)-H(39C) | 109.5    |
| H(39B)-C(39)-H(39C) | 109.5    | C(37)-C(40)-H(40A)  | 109.5    |
| C(37)-C(40)-H(40B)  | 109.5    | H(40A)-C(40)-H(40B) | 109.5    |
| C(37)-C(40)-H(40C)  | 109.5    | H(40A)-C(40)-H(40C) | 109.5    |
| H(40B)-C(40)-H(40C) | 109.5    | C(43)-C(41)-C(42)   | 109.5    |
| C(43)-C(41)-C(44)   | 110.1(5) | C(42)-C(41)-C(44)   | 107.8(3) |
| C(43)-C(41)-C(35)   | 109.5(4) | C(42)-C(41)-C(35)   | 108.0(4) |
| C(44)-C(41)-C(35)   | 111.5(4) | C(41)-C(42)-H(42A)  | 109.5    |
| C(41)-C(42)-H(42B)  | 109.5    | H(42A)-C(42)-H(42B) | 109.5    |
| C(41)-C(42)-H(42C)  | 109.5    | H(42A)-C(42)-H(42C) | 109.5    |
| H(42B)-C(42)-H(42C) | 109.5    | C(41)-C(43)-H(43A)  | 109.5    |
| C(41)-C(43)-H(43B)  | 109.5    | H(43A)-C(43)-H(43B) | 109.5    |
| C(41)-C(43)-H(43C)  | 109.5    | H(43A)-C(43)-H(43C) | 109.5    |
| H(43B)-C(43)-H(43C) | 109.5    | C(41)-C(44)-H(44A)  | 109.5    |
| C(41)-C(44)-H(44B)  | 109.5    | H(44A)-C(44)-H(44B) | 109.5    |
| C(41)-C(44)-H(44C)  | 109.5    | H(44A)-C(44)-H(44C) | 109.5    |
| H(44B)-C(44)-H(44C) | 109.5    | C(50)-C(45)-C(46)   | 118.8(3) |
| C(50)-C(45)-P(2)    | 118.8(3) | C(46)-C(45)-P(2)    | 122.2(3) |
| C(47)-C(46)-C(45)   | 120.2(4) | C(47)-C(46)-H(46)   | 119.9    |
| C(45)-C(46)-H(46)   | 119.9    | C(48)-C(47)-C(46)   | 119.6    |
| C(48)-C(47)-H(47)   | 119.6    | C(46)-C(47)-H(47)   | 119.6    |
| C(49)-C(48)-C(47)   | 119.5(4) | C(49)-C(48)-H(48)   | 120.3    |
| C(47)-C(48)-H(48)   | 120.3    | C(48)-C(49)-C(50)   | 119.9    |
| C(48)-C(49)-H(49)   | 119.9    | C(50)-C(49)-H(49)   | 119.9    |
| C(49)-C(50)-C(45)   | 121.0(4) | C(49)-C(50)-H(50)   | 119.5    |
| C(45)-C(50)-H(50)   | 119.5    | C(56)-C(51)-C(52)   | 122.2(3) |
| C(56)-C(51)-P(2)    | 122.2(3) | C(52)-C(51)-P(2)    | 120.4(4) |
| C(53)-C(52)-C(51)   | 120.4(4) | C(53)-C(52)-H(52)   | 119.8    |
| C(51)-C(52)-H(52)   | 119.8    | C(52)-C(53)-C(54)   | 119.8    |
| C(52)-C(53)-H(53)   | 119.8    | C(54)-C(53)-H(53)   | 120.3(4) |
| C(53)-C(54)-C(55)   | 120.3(4) | C(53)-C(54)-H(54)   | 119.9    |
| C(55)-C(54)-H(54)   | 119.9    | C(54)-C(55)-C(56)   | 120.2    |
| C(54)-C(55)-H(55)   | 120.2    | C(56)-C(55)-H(55)   | 120.5(4) |
| C(51)-C(56)-C(55)   | 120.5(4) | C(51)-C(56)-H(56)   | 119.8    |
| C(55)-C(56)-H(56)   | 119.8    | O(3)-C(57)-C(58)    | 109.3    |
| O(3)-C(57)-H(57A)   | 109.3    | C(58)-C(57)-H(57A)  | 109.3    |
| O(3)-C(57)-H(57B)   | 109.3    | C(58)-C(57)-H(57B)  | 108.0    |
| H(57A)-C(57)-H(57B) | 108.0    | C(57)-C(58)-H(58A)  | 109.5    |
| C(57)-C(58)-H(58B)  | 109.5    | H(58A)-C(58)-H(58B) | 109.5    |
| C(57)-C(58)-H(58C)  | 109.5    | H(58A)-C(58)-H(58C) | 109.5    |
| H(58B)-C(58)-H(58C) | 109.5    |                     |          |

-----  
Estimated standard deviations are given in the parenthesis.  
Symmetry operators ::  
1: x, y, z  
4: -x+1/2, y+1/2, -z+1/2  
7: -x+1/2, -y+1/2, -z  
2: -x, y, -z+1/2  
5: -x, -y, -z  
8: x+1/2, -y+1/2, z-1/2  
3: x+1/2, y+1/2, z  
6: x, -y, z-1/2

## Appendix 1. Crystallographic data

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for pa679bis

| atom   | U11    | U22   | U33    | U23    | U13   | U12    |
|--------|--------|-------|--------|--------|-------|--------|
| Y(1)   | 22(1)  | 26(1) | 23(1)  | -1(1)  | 13(1) | -1(1)  |
| P(1)   | 27(1)  | 32(1) | 28(1)  | -4(1)  | 18(1) | 0(1)   |
| P(2)   | 24(1)  | 31(1) | 25(1)  | 3(1)   | 11(1) | -4(1)  |
| O(1)   | 24(1)  | 32(1) | 28(1)  | -5(1)  | 15(1) | -3(1)  |
| O(2)   | 25(1)  | 27(1) | 27(1)  | 3(1)   | 15(1) | -1(1)  |
| O(3)   | 33(2)  | 24(2) | 37(2)  | 0      | 22(2) | 0      |
| O(4)   | 38(2)  | 30(2) | 29(2)  | 0      | 22(2) | 0      |
| N(1)   | 23(2)  | 37(2) | 34(2)  | -7(1)  | 18(1) | -3(1)  |
| N(2)   | 27(2)  | 31(2) | 31(2)  | 2(1)   | 13(1) | -3(1)  |
| N(3)   | 22(1)  | 32(2) | 25(2)  | 8(1)   | 8(1)  | -1(1)  |
| C(1)   | 27(2)  | 50(2) | 42(2)  | -12(2) | 21(2) | -3(2)  |
| C(2)   | 23(2)  | 38(2) | 45(2)  | -4(2)  | 16(2) | 5(2)   |
| C(3)   | 26(2)  | 39(2) | 27(2)  | 4(2)   | 9(2)  | 2(2)   |
| C(4)   | 24(2)  | 36(2) | 29(2)  | 1(2)   | 8(2)  | -4(2)  |
| C(5)   | 26(2)  | 33(2) | 27(2)  | -2(2)  | 15(2) | 0(2)   |
| C(6)   | 25(2)  | 27(2) | 20(2)  | -4(1)  | 10(2) | -1(1)  |
| C(7)   | 21(2)  | 31(2) | 24(2)  | 0(2)   | 12(2) | 1(1)   |
| C(8)   | 25(2)  | 35(2) | 28(2)  | -4(2)  | 13(2) | -5(2)  |
| C(9)   | 34(2)  | 35(2) | 31(2)  | -7(2)  | 17(2) | -3(2)  |
| C(10)  | 33(2)  | 36(2) | 26(2)  | -3(2)  | 19(2) | 3(2)   |
| C(11)  | 26(2)  | 35(2) | 31(2)  | -3(2)  | 17(2) | -2(2)  |
| C(12)  | 39(2)  | 38(2) | 32(2)  | -1(2)  | 24(2) | 4(2)   |
| C(13)  | 29(2)  | 39(2) | 30(2)  | -3(2)  | 18(2) | 3(2)   |
| C(14)  | 31(2)  | 55(3) | 41(2)  | -10(2) | 23(2) | -9(2)  |
| C(15)  | 47(2)  | 56(3) | 40(2)  | -24(2) | 25(2) | -11(2) |
| C(16A) | 73(4)  | 62(7) | 36(5)  | -20(4) | 10(4) | -4(4)  |
| C(17A) | 75(5)  | 44(4) | 60(4)  | -27(3) | 32(4) | -8(4)  |
| C(18A) | 97(7)  | 92(7) | 101(7) | -72(6) | 79(7) | -51(5) |
| C(16B) | 73(4)  | 62(7) | 36(5)  | -20(4) | 10(4) | -4(4)  |
| C(17B) | 75(5)  | 44(4) | 60(4)  | -27(3) | 32(4) | -8(4)  |
| C(18B) | 97(7)  | 92(7) | 101(7) | -72(6) | 79(7) | -51(5) |
| C(19)  | 26(2)  | 36(2) | 27(2)  | -7(2)  | 15(2) | -2(2)  |
| C(20)  | 37(2)  | 35(2) | 37(2)  | -2(2)  | 23(2) | -1(2)  |
| C(21)  | 42(2)  | 35(2) | 46(2)  | 3(2)   | 24(2) | 8(2)   |
| C(22)  | 69(3)  | 64(3) | 66(3)  | 16(3)  | 51(3) | 34(3)  |
| C(23)  | 103(4) | 79(4) | 83(4)  | 35(3)  | 80(4) | 50(3)  |
| C(24)  | 71(3)  | 47(3) | 58(3)  | 18(2)  | 52(3) | 26(2)  |
| C(25)  | 34(2)  | 36(2) | 35(2)  | 0(2)   | 24(2) | 5(2)   |
| C(26)  | 52(3)  | 34(2) | 40(2)  | 0(2)   | 26(2) | 6(2)   |
| C(27)  | 51(3)  | 57(3) | 35(2)  | 2(2)   | 21(2) | 8(2)   |
| C(28)  | 63(3)  | 47(3) | 58(3)  | 19(2)  | 43(3) | 11(2)  |
| C(29)  | 49(3)  | 41(2) | 57(3)  | 4(2)   | 35(2) | -1(2)  |
| C(30)  | 35(2)  | 38(2) | 43(2)  | -1(2)  | 26(2) | -1(2)  |
| C(31)  | 25(2)  | 32(2) | 23(2)  | 4(2)   | 10(2) | 1(2)   |
| C(32)  | 27(2)  | 30(2) | 25(2)  | -1(2)  | 15(2) | 0(2)   |
| C(33)  | 28(2)  | 31(2) | 30(2)  | 1(2)   | 17(2) | 3(2)   |
| C(34)  | 29(2)  | 42(2) | 26(2)  | 7(2)   | 8(2)  | 4(2)   |
| C(35)  | 40(2)  | 36(2) | 36(2)  | 11(2)  | 19(2) | 3(2)   |
| C(36)  | 33(2)  | 34(2) | 32(2)  | 4(2)   | 14(2) | -6(2)  |
| C(37)  | 21(2)  | 39(2) | 33(2)  | 5(2)   | 11(2) | 2(2)   |
| C(38)  | 33(2)  | 40(2) | 49(2)  | -3(2)  | 28(2) | 1(2)   |
| C(39)  | 28(2)  | 61(3) | 55(3)  | 14(2)  | 13(2) | 1(2)   |
| C(40)  | 29(2)  | 43(2) | 31(2)  | -9(2)  | 16(2) | -10(2) |
| C(41)  | 44(2)  | 44(2) | 45(3)  | 22(2)  | 19(2) | -1(2)  |
| C(42)  | 123(5) | 75(4) | 72(4)  | 26(3)  | 64(4) | -5(4)  |
| C(43)  | 90(4)  | 46(3) | 115(5) | 46(3)  | 62(4) | 15(3)  |
| C(44)  | 79(4)  | 79(4) | 87(4)  | 48(4)  | 18(4) | -28(3) |
| C(45)  | 28(2)  | 33(2) | 30(2)  | 2(2)   | 14(2) | -4(2)  |
| C(46)  | 50(2)  | 35(2) | 40(2)  | 5(2)   | 25(2) | 2(2)   |
| C(47)  | 69(3)  | 32(2) | 54(3)  | 7(2)   | 38(3) | 6(2)   |
| C(48)  | 43(2)  | 48(3) | 40(2)  | -3(2)  | 23(2) | 3(2)   |
| C(49)  | 39(2)  | 50(3) | 36(2)  | 2(2)   | 21(2) | -8(2)  |
| C(50)  | 32(2)  | 36(2) | 34(2)  | 0(2)   | 15(2) | -9(2)  |

## Appendix 1. Crystallographic data

|       |       |       |        |        |       |        |
|-------|-------|-------|--------|--------|-------|--------|
| C(51) | 28(2) | 34(2) | 37(2)  | 6(2)   | 17(2) | -4(2)  |
| C(52) | 39(2) | 58(3) | 40(2)  | -7(2)  | 22(2) | -15(2) |
| C(53) | 52(3) | 87(4) | 56(3)  | -19(3) | 40(3) | -20(3) |
| C(54) | 42(3) | 76(3) | 66(3)  | -5(3)  | 38(3) | -13(2) |
| C(55) | 31(2) | 50(3) | 46(3)  | 4(2)   | 16(2) | -9(2)  |
| C(56) | 31(2) | 41(2) | 36(2)  | 3(2)   | 16(2) | -7(2)  |
| C(57) | 29(4) | 28(3) | 30(10) | 9(3)   | 12(7) | 0(4)   |
| C(58) | 52(5) | 29(4) | 52(5)  | -7(4)  | 30(5) | 0(4)   |

The anisotropic displacement factor exponent takes the form  
 $2 \pi^2 [h^2 a^{*2} U(11) + \dots + 2 h k a^* b^* U(12)]$

# Appendix 1. Crystallographic data

Table 5. Hydrogen Coordinates (A x 10<sup>4</sup>) and equivalent isotropic displacement parameters (A<sup>2</sup> x 10<sup>3</sup>) for pa679bis

| atom   | x        | y        | z        | U(eq) |
|--------|----------|----------|----------|-------|
| H(4O)  | 5000     | 2370(20) | 2500     | 37    |
| H(2N)  | 4050(20) | 3610(10) | 2380(30) | 38    |
| H(1A)  | 4030     | 3536     | 4485     | 46    |
| H(1B)  | 4028     | 3028     | 4096     | 46    |
| H(2A)  | 3380     | 3509     | 2891     | 45    |
| H(2B)  | 3868     | 3916     | 3238     | 45    |
| H(3A)  | 3779     | 2920     | 1666     | 40    |
| H(3B)  | 3229     | 3125     | 1648     | 40    |
| H(4A)  | 3403     | 2626     | 2761     | 40    |
| H(4B)  | 3441     | 2303     | 2078     | 40    |
| H(8)   | 7259     | 4445     | 6427     | 37    |
| H(10)  | 5920     | 4294     | 6691     | 37    |
| H(12A) | 6236     | 3816     | 3872     | 51    |
| H(12B) | 6811     | 3910     | 3878     | 51    |
| H(12C) | 6529     | 4329     | 4107     | 51    |
| H(13A) | 6777     | 3143     | 4986     | 48    |
| H(13B) | 7400     | 3250     | 5890     | 48    |
| H(13C) | 7343     | 3245     | 4972     | 48    |
| H(14A) | 7774     | 4032     | 5270     | 61    |
| H(14B) | 7835     | 4054     | 6190     | 61    |
| H(14C) | 7497     | 4465     | 5475     | 61    |
| H(16A) | 7751     | 4930     | 8575     | 103   |
| H(16B) | 7774     | 4575     | 7917     | 103   |
| H(16C) | 7542     | 4395     | 8494     | 103   |
| H(17A) | 6614     | 5378     | 6547     | 94    |
| H(17B) | 7246     | 5200     | 6812     | 94    |
| H(17C) | 7192     | 5507     | 7496     | 94    |
| H(18A) | 6705     | 5246     | 8097     | 126   |
| H(18B) | 6500     | 4713     | 8053     | 126   |
| H(18C) | 6140     | 5044     | 7199     | 126   |
| H(16D) | 7658     | 4998     | 7431     | 103   |
| H(16E) | 7776     | 4542     | 8025     | 103   |
| H(16F) | 7766     | 5054     | 8381     | 103   |
| H(17D) | 6755     | 5495     | 7583     | 94    |
| H(17E) | 6172     | 5177     | 7045     | 94    |
| H(17F) | 6478     | 5363     | 6571     | 94    |
| H(18D) | 7048     | 4844     | 8658     | 126   |
| H(18E) | 7134     | 4320     | 8423     | 126   |
| H(18F) | 6486     | 4534     | 7960     | 126   |
| H(20)  | 4771     | 4529     | 4839     | 42    |
| H(21)  | 4251     | 5110     | 5030     | 49    |
| H(22)  | 3995     | 4987     | 6030     | 71    |
| H(23)  | 4225     | 4278     | 6794     | 88    |
| H(24)  | 4743     | 3697     | 6608     | 60    |
| H(26)  | 5978     | 3555     | 7447     | 51    |
| H(27)  | 6212     | 2960     | 8466     | 59    |
| H(28)  | 5808     | 2212     | 7991     | 62    |
| H(29)  | 5175     | 2050     | 6481     | 56    |
| H(30)  | 4915     | 2651     | 5454     | 43    |
| H(34)  | 6340     | 1341     | 6582     | 43    |
| H(36)  | 4598     | 1215     | 4776     | 42    |
| H(38A) | 6814     | 1782     | 5235     | 58    |
| H(38B) | 7155     | 2272     | 5633     | 58    |
| H(38C) | 6469     | 2271     | 4845     | 58    |
| H(39A) | 7034     | 1852     | 7349     | 81    |
| H(39B) | 7490     | 2020     | 7124     | 81    |
| H(39C) | 7152     | 1527     | 6752     | 81    |
| H(40A) | 6269     | 2784     | 5801     | 52    |
| H(40B) | 6959     | 2772     | 6570     | 52    |
| H(40C) | 6491     | 2605     | 6771     | 52    |
| H(42A) | 5960     | 1079     | 7473     | 127   |
| H(42B) | 5594     | 634      | 7450     | 127   |

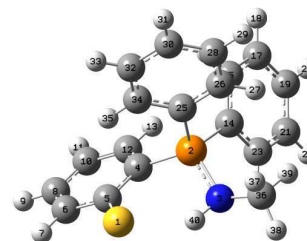
# Appendix 1. Crystallographic data

|        |      |      |      |     |
|--------|------|------|------|-----|
| H(42C) | 5266 | 1124 | 7016 | 127 |
| H(43A) | 6337 | 586  | 6809 | 122 |
| H(43B) | 5902 | 356  | 5852 | 122 |
| H(43C) | 5940 | 142  | 6691 | 122 |
| H(44A) | 4900 | 225  | 6055 | 147 |
| H(44B) | 4789 | 413  | 5148 | 147 |
| H(44C) | 4571 | 717  | 5647 | 147 |
| H(46)  | 4217 | 872  | 3378 | 50  |
| H(47)  | 4197 | 337  | 2395 | 60  |
| H(48)  | 4199 | 601  | 1195 | 53  |
| H(49)  | 4191 | 1407 | 947  | 50  |
| H(50)  | 4193 | 1947 | 1904 | 43  |
| H(52)  | 4079 | 2147 | 4837 | 55  |
| H(53)  | 3261 | 2148 | 4899 | 72  |
| H(54)  | 2386 | 1802 | 3778 | 69  |
| H(55)  | 2327 | 1437 | 2592 | 55  |
| H(56)  | 3154 | 1424 | 2529 | 45  |
| H(57A) | 4665 | 4073 | 1706 | 39  |
| H(57B) | 5363 | 4102 | 2420 | 39  |
| H(58A) | 4482 | 4264 | 2740 | 66  |
| H(58B) | 4977 | 4628 | 2895 | 66  |
| H(58C) | 5156 | 4183 | 3538 | 66  |

## Optimised Structures by DFT

### 1. Chapter 1

#### *Monodeprotonation of 2a*



Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 16               | 0              | -3.027033               | 0.242495  | 1.381663  |
| 2                | 15               | 0              | 0.111243                | -0.027919 | 0.477180  |
| 3                | 7                | 0              | 0.016833                | -0.084314 | 2.147051  |
| 4                | 6                | 0              | -1.152330               | -1.090448 | -0.204064 |
| 5                | 6                | 0              | -2.509005               | -0.934018 | 0.219214  |
| 6                | 6                | 0              | -3.440692               | -1.814298 | -0.391755 |
| 7                | 1                | 0              | -4.480482               | -1.723455 | -0.090916 |
| 8                | 6                | 0              | -3.062635               | -2.758578 | -1.328092 |
| 9                | 1                | 0              | -3.819307               | -3.408061 | -1.763674 |
| 10               | 6                | 0              | -1.721158               | -2.896958 | -1.718698 |
| 11               | 1                | 0              | -1.427871               | -3.644064 | -2.450292 |
| 12               | 6                | 0              | -0.773317               | -2.064520 | -1.149956 |
| 13               | 1                | 0              | 0.269782                | -2.164993 | -1.436947 |
| 14               | 6                | 0              | 1.755007                | -0.695474 | 0.092438  |
| 15               | 6                | 0              | 2.451512                | -0.317440 | -1.063302 |
| 16               | 1                | 0              | 2.034948                | 0.432207  | -1.729988 |
| 17               | 6                | 0              | 3.682330                | -0.901103 | -1.357241 |
| 18               | 1                | 0              | 4.218323                | -0.604640 | -2.254784 |
| 19               | 6                | 0              | 4.224447                | -1.859002 | -0.500836 |
| 20               | 1                | 0              | 5.186191                | -2.310118 | -0.731020 |
| 21               | 6                | 0              | 3.532842                | -2.240503 | 0.649039  |
| 22               | 1                | 0              | 3.952645                | -2.989114 | 1.315505  |
| 23               | 6                | 0              | 2.299081                | -1.666552 | 0.945146  |
| 24               | 1                | 0              | 1.749339                | -1.962248 | 1.834159  |
| 25               | 6                | 0              | 0.062526                | 1.642765  | -0.238232 |
| 26               | 6                | 0              | 1.122254                | 2.535712  | -0.016836 |
| 27               | 1                | 0              | 1.999328                | 2.221163  | 0.542974  |
| 28               | 6                | 0              | 1.066147                | 3.828924  | -0.532252 |
| 29               | 1                | 0              | 1.889844                | 4.515925  | -0.357300 |
| 30               | 6                | 0              | -0.042892               | 4.234946  | -1.273597 |
| 31               | 1                | 0              | -0.085757               | 5.243691  | -1.676322 |
| 32               | 6                | 0              | -1.095530               | 3.348477  | -1.500578 |
| 33               | 1                | 0              | -1.961386               | 3.664091  | -2.075861 |
| 34               | 6                | 0              | -1.049879               | 2.056566  | -0.982888 |
| 35               | 1                | 0              | -1.878107               | 1.373612  | -1.139647 |

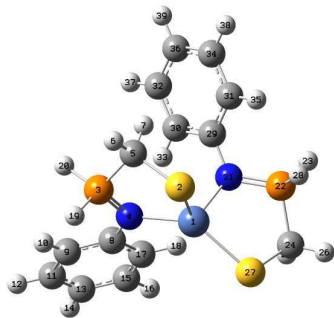
## Appendix 2. Optimised Structures

|    |   |   |           |           |          |
|----|---|---|-----------|-----------|----------|
| 36 | 6 | 0 | 0.807379  | 0.823746  | 2.974862 |
| 37 | 1 | 0 | 0.522347  | 1.878488  | 2.857221 |
| 38 | 1 | 0 | 0.664383  | 0.540415  | 4.021582 |
| 39 | 1 | 0 | 1.872259  | 0.716427  | 2.742441 |
| 40 | 1 | 0 | -0.996949 | -0.043713 | 2.364975 |

-----  
Rotational constants (GHz):      0.2835280      0.2437411  
0.1772657

Sum of electronic and zero-point Energies=      -1528.409669  
Sum of electronic and thermal Energies=      -1528.389762  
Sum of electronic and thermal Enthalpies=      -1528.388818  
Sum of electronic and thermal Free Energies=      -1528.458991

|                |         |         |   |
|----------------|---------|---------|---|
|                | 1       | 2       | 3 |
|                | A       | A       | A |
| Frequencies -- | 33.3922 | 43.4811 |   |
| 48.4936        |         |         |   |
| Red. masses -- | 4.1544  | 5.8284  |   |
| 4.5718         |         |         |   |
| Frc consts --  | 0.0027  | 0.0065  |   |
| 0.0063         |         |         |   |
| IR Inten    -- | 1.0634  | 1.6465  |   |
| 0.0481         |         |         |   |

**Complex 18, triplet**

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 28               | 0              | 0.201846                | 0.992948  | -0.488104 |
| 2                | 16               | 0              | 0.576118                | 2.372836  | 1.328532  |
| 3                | 15               | 0              | 2.174141                | -0.044016 | 1.598155  |
| 4                | 7                | 0              | 1.527014                | -0.402627 | 0.164202  |
| 5                | 6                | 0              | 1.050426                | 1.046309  | 2.492957  |
| 6                | 1                | 0              | 1.575560                | 1.450785  | 3.366623  |

## Appendix 2. Optimised Structures

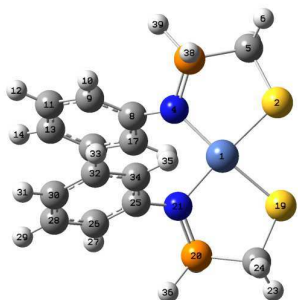
|    |    |   |           |           |           |
|----|----|---|-----------|-----------|-----------|
| 7  | 1  | 0 | 0.189287  | 0.460545  | 2.835260  |
| 8  | 6  | 0 | 2.016953  | -1.425088 | -0.662886 |
| 9  | 6  | 0 | 3.258980  | -2.055555 | -0.472662 |
| 10 | 1  | 0 | 3.918695  | -1.741138 | 0.335026  |
| 11 | 6  | 0 | 3.681906  | -3.072074 | -1.326750 |
| 12 | 1  | 0 | 4.648267  | -3.540568 | -1.156043 |
| 13 | 6  | 0 | 2.886132  | -3.478901 | -2.394861 |
| 14 | 1  | 0 | 3.220373  | -4.268511 | -3.061866 |
| 15 | 6  | 0 | 1.656707  | -2.850407 | -2.599467 |
| 16 | 1  | 0 | 1.024014  | -3.150028 | -3.431560 |
| 17 | 6  | 0 | 1.223278  | -1.840944 | -1.747621 |
| 18 | 1  | 0 | 0.263188  | -1.355921 | -1.908387 |
| 19 | 1  | 0 | 3.425934  | 0.620611  | 1.590956  |
| 20 | 1  | 0 | 2.470248  | -1.201857 | 2.359928  |
| 21 | 7  | 0 | -1.659915 | 0.181039  | -0.222650 |
| 22 | 15 | 0 | -2.716951 | 1.163443  | -0.944908 |
| 23 | 1  | 0 | -4.014687 | 0.595255  | -0.974207 |
| 24 | 6  | 0 | -2.102733 | 1.512554  | -2.603088 |
| 25 | 1  | 0 | -2.152103 | 0.598077  | -3.205079 |
| 26 | 1  | 0 | -2.737326 | 2.275198  | -3.068375 |
| 27 | 16 | 0 | -0.389616 | 2.128849  | -2.392422 |
| 28 | 1  | 0 | -2.962531 | 2.442275  | -0.385653 |
| 29 | 6  | 0 | -1.969300 | -0.476488 | 0.985560  |
| 30 | 6  | 0 | -1.413893 | -1.748080 | 1.209737  |
| 31 | 6  | 0 | -2.789146 | 0.079099  | 1.981430  |
| 32 | 6  | 0 | -1.682609 | -2.439410 | 2.387008  |
| 33 | 1  | 0 | -0.778908 | -2.180486 | 0.442460  |
| 34 | 6  | 0 | -3.061309 | -0.623351 | 3.155222  |
| 35 | 1  | 0 | -3.188495 | 1.083645  | 1.855027  |
| 36 | 6  | 0 | -2.510340 | -1.885509 | 3.366512  |
| 37 | 1  | 0 | -1.250621 | -3.426575 | 2.534935  |
| 38 | 1  | 0 | -3.700028 | -0.171960 | 3.910589  |
| 39 | 1  | 0 | -2.722744 | -2.432149 | 4.281291  |

-----  
Rotational constants (GHz):      0.2462247      0.1860907  
0.1582504

Sum of electronic and zero-point Energies=      -2301.563383  
Sum of electronic and thermal Energies=      -2301.540943  
Sum of electronic and thermal Enthalpies=      -2301.539999  
Sum of electronic and thermal Free Energies=      -2301.619293

|                |         |         |   |
|----------------|---------|---------|---|
|                | 1       | 2       | 3 |
|                | A       | A       | A |
| Frequencies -- | 22.6915 | 25.4058 |   |
| 31.6404        |         |         |   |
| Red. masses -- | 4.8206  | 5.3937  |   |
| 6.2897         |         |         |   |
| Frc consts --  | 0.0015  | 0.0021  |   |
| 0.0037         |         |         |   |
| IR Inten    -- | 1.0347  | 0.4589  |   |
| 2.3521         |         |         |   |



**Complex 18: singlet**

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 28               | 0              | -0.061401               | -0.008349 | 0.064248  |
| 2                | 16               | 0              | -0.059106               | 0.163614  | 2.284669  |
| 3                | 15               | 0              | 2.595656                | 0.127931  | 1.349255  |
| 4                | 7                | 0              | 1.853064                | -0.319605 | -0.007287 |
| 5                | 6                | 0              | 1.616389                | -0.422996 | 2.748687  |
| 6                | 1                | 0              | 1.943876                | 0.055055  | 3.678515  |
| 7                | 1                | 0              | 1.684988                | -1.512238 | 2.848417  |
| 8                | 6                | 0              | 2.536944                | -0.983353 | -1.047024 |
| 9                | 6                | 0              | 3.771832                | -0.539227 | -1.541873 |
| 10               | 1                | 0              | 4.199699                | 0.386945  | -1.164519 |
| 11               | 6                | 0              | 4.431643                | -1.247260 | -2.544986 |
| 12               | 1                | 0              | 5.388468                | -0.884187 | -2.912459 |
| 13               | 6                | 0              | 3.862342                | -2.395230 | -3.090609 |
| 14               | 1                | 0              | 4.374775                | -2.942738 | -3.877161 |
| 15               | 6                | 0              | 2.622691                | -2.831806 | -2.617890 |
| 16               | 1                | 0              | 2.169410                | -3.730772 | -3.029797 |
| 17               | 6                | 0              | 1.967590                | -2.139957 | -1.604545 |
| 18               | 1                | 0              | 1.014196                | -2.486677 | -1.214647 |
| 19               | 16               | 0              | -2.260299               | -0.304045 | 0.257919  |
| 20               | 15               | 0              | -1.590891               | -0.064424 | -2.465626 |
| 21               | 7                | 0              | -0.189610               | 0.407231  | -1.827836 |
| 22               | 6                | 0              | -2.910963               | 0.357011  | -1.325221 |
| 23               | 1                | 0              | -3.846608               | -0.146160 | -1.593100 |
| 24               | 1                | 0              | -3.063898               | 1.442134  | -1.313961 |
| 25               | 6                | 0              | 0.749047                | 1.156146  | -2.567687 |
| 26               | 6                | 0              | 1.136220                | 0.805881  | -3.869353 |
| 27               | 1                | 0              | 0.756805                | -0.111895 | -4.313276 |
| 28               | 6                | 0              | 2.037601                | 1.596839  | -4.579942 |
| 29               | 1                | 0              | 2.322503                | 1.305782  | -5.588138 |
| 30               | 6                | 0              | 2.588621                | 2.736091  | -3.998384 |
| 31               | 1                | 0              | 3.295946                | 3.348514  | -4.551221 |
| 32               | 6                | 0              | 2.224457                | 3.079520  | -2.694487 |
| 33               | 1                | 0              | 2.641127                | 3.970689  | -2.230260 |
| 34               | 6                | 0              | 1.311808                | 2.304483  | -1.986682 |
| 35               | 1                | 0              | 1.005003                | 2.578871  | -0.980885 |

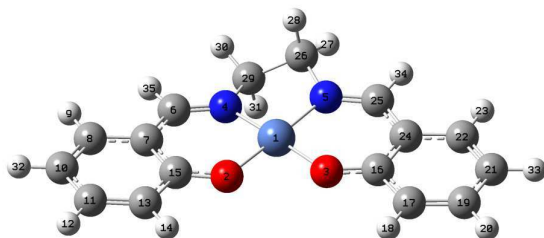
|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 36 | 1 | 0 | -1.756730 | 0.505437  | -3.751697 |
| 37 | 1 | 0 | -1.762368 | -1.448178 | -2.699822 |
| 38 | 1 | 0 | 2.761813  | 1.515075  | 1.566067  |
| 39 | 1 | 0 | 3.923408  | -0.365036 | 1.365847  |

-----  
 Rotational constants (GHZ):      0.2688150      0.2045036  
 0.1598595

Sum of electronic and zero-point Energies=      -2301.551138  
 Sum of electronic and thermal Energies=      -2301.529209  
 Sum of electronic and thermal Enthalpies=      -2301.528264  
 Sum of electronic and thermal Free Energies=      -2301.604702

|                | 1<br>A  | 2<br>A  | 3<br>A |
|----------------|---------|---------|--------|
| Frequencies -- | 23.9181 | 25.1861 |        |
| 37.5125        |         |         |        |
| Red. masses -- | 5.9688  | 6.6496  |        |
| 5.6170         |         |         |        |
| Frc consts --  | 0.0020  | 0.0025  |        |
| 0.0047         |         |         |        |
| IR Inten --    | 1.1717  | 2.8104  |        |
| 0.8091         |         |         |        |

## Chapter 3

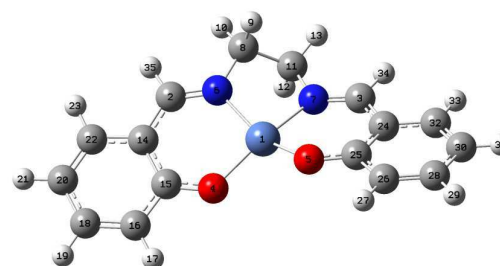
*[Ni(Salen)] singlet, square planar*

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 28               | 0              | 0.015742                | -0.046715 | 0.016601  |
| 2                | 8                | 0              | 0.016175                | -0.131133 | 1.862897  |
| 3                | 8                | 0              | 1.854780                | 0.031940  | 0.166905  |
| 4                | 7                | 0              | -1.830249               | -0.198028 | -0.119366 |
| 5                | 7                | 0              | 0.019572                | 0.118606  | -1.831654 |
| 6                | 6                | 0              | -2.689612               | -0.189780 | 0.856828  |
| 7                | 6                | 0              | -2.366292               | -0.099710 | 2.235819  |
| 8                | 6                | 0              | -3.411811               | -0.057880 | 3.191663  |
| 9                | 1                | 0              | -4.441013               | -0.070032 | 2.835425  |
| 10               | 6                | 0              | -3.145189               | -0.004454 | 4.539877  |
| 11               | 6                | 0              | -1.798295               | 0.001548  | 4.966531  |
| 12               | 1                | 0              | -1.577088               | 0.040919  | 6.031125  |
| 13               | 6                | 0              | -0.757342               | -0.042443 | 4.066165  |
| 14               | 1                | 0              | 0.278215                | -0.038927 | 4.392729  |
| 15               | 6                | 0              | -0.997002               | -0.090355 | 2.662624  |
| 16               | 6                | 0              | 2.729990                | -0.000911 | -0.782645 |
| 17               | 6                | 0              | 4.110790                | -0.052112 | -0.436183 |
| 18               | 1                | 0              | 4.356567                | -0.064709 | 0.621413  |
| 19               | 6                | 0              | 5.088885                | -0.088509 | -1.404844 |
| 20               | 1                | 0              | 6.133153                | -0.130811 | -1.102207 |
| 21               | 6                | 0              | 4.767345                | -0.071279 | -2.780535 |
| 22               | 6                | 0              | 3.443734                | -0.014028 | -3.149614 |
| 23               | 1                | 0              | 3.168165                | 0.007161  | -4.203107 |
| 24               | 6                | 0              | 2.409694                | 0.020396  | -2.181024 |
| 25               | 6                | 0              | 1.060486                | 0.116230  | -2.611335 |
| 26               | 6                | 0              | -1.311926               | 0.340690  | -2.386404 |
| 27               | 1                | 0              | -1.377239               | 0.007962  | -3.430244 |
| 28               | 1                | 0              | -1.535997               | 1.415783  | -2.351904 |
| 29               | 6                | 0              | -2.282300               | -0.411879 | -1.490642 |
| 30               | 1                | 0              | -3.316637               | -0.074199 | -1.634514 |
| 31               | 1                | 0              | -2.235130               | -1.486160 | -1.716148 |
| 32               | 1                | 0              | -3.952295               | 0.029104  | 5.265338  |
| 33               | 1                | 0              | 5.552881                | -0.099013 | -3.529506 |
| 34               | 1                | 0              | 0.886019                | 0.209138  | -3.688324 |

|                             |   |   |           |           |          |
|-----------------------------|---|---|-----------|-----------|----------|
| 35                          | 1 | 0 | -3.750217 | -0.271966 | 0.597390 |
| -----                       |   |   |           |           |          |
| Rotational constants (GHZ): |   |   | 0.6680831 | 0.1727332 |          |
| 0.1379416                   |   |   |           |           |          |

|  |              |
|--|--------------|
| Sum of electronic and zero-point Energies=   | -1046.919117 |
| Sum of electronic and thermal Energies=      | -1046.902607 |
| Sum of electronic and thermal Enthalpies=    | -1046.901663 |
| Sum of electronic and thermal Free Energies= | -1046.963265 |

|                |         |         |   |
|----------------|---------|---------|---|
|                | 1       | 2       | 3 |
|                | A       | A       | A |
| Frequencies -- | 30.8492 | 59.5601 |   |
| 84.2533        |         |         |   |
| Red. masses -- | 6.2817  | 4.2723  |   |
| 5.7138         |         |         |   |
| Frc consts --  | 0.0035  | 0.0089  |   |
| 0.0239         |         |         |   |
| IR Inten --    | 1.8948  | 0.0127  |   |
| 0.0919         |         |         |   |

*[Ni(Salen)] triplet, tetrahedral*

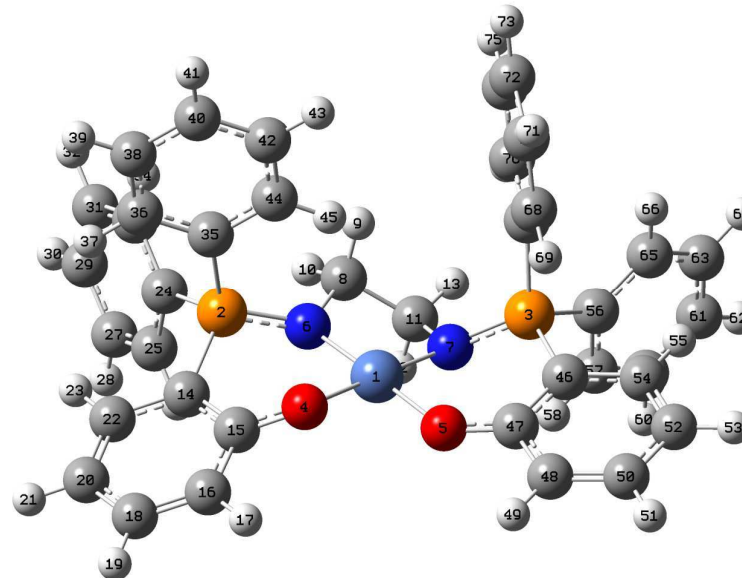
| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 28               | 0              | -0.439718               | -0.476050 | -0.156478 |
| 2                | 6                | 0              | -0.213068               | 0.276291  | 2.682256  |
| 3                | 6                | 0              | 1.863645                | -0.426269 | -1.986523 |
| 4                | 8                | 0              | -2.139610               | 0.085336  | 0.476245  |
| 5                | 8                | 0              | -0.806197               | -1.598057 | -1.644983 |
| 6                | 7                | 0              | 0.402299                | -0.087837 | 1.602616  |
| 7                | 7                | 0              | 1.379793                | -0.067044 | -0.839880 |
| 8                | 6                | 0              | 1.852221                | -0.069477 | 1.517601  |
| 9                | 1                | 0              | 2.227011                | -1.102133 | 1.537245  |
| 10               | 1                | 0              | 2.311583                | 0.482025  | 2.349865  |
| 11               | 6                | 0              | 2.213568                | 0.566884  | 0.166856  |
| 12               | 1                | 0              | 1.977377                | 1.639355  | 0.205246  |
| 13               | 1                | 0              | 3.285225                | 0.455293  | -0.049540 |
| 14               | 6                | 0              | -1.628994               | 0.425759  | 2.816973  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 15 | 6 | 0 | -2.519224 | 0.342150  | 1.690828  |
| 16 | 6 | 0 | -3.898349 | 0.580558  | 1.940498  |
| 17 | 1 | 0 | -4.570207 | 0.521685  | 1.089264  |
| 18 | 6 | 0 | -4.365053 | 0.862506  | 3.207427  |
| 19 | 1 | 0 | -5.429736 | 1.028342  | 3.357837  |
| 20 | 6 | 0 | -3.488363 | 0.945117  | 4.307696  |
| 21 | 1 | 0 | -3.867168 | 1.174158  | 5.299224  |
| 22 | 6 | 0 | -2.142745 | 0.736549  | 4.098733  |
| 23 | 1 | 0 | -1.444532 | 0.804750  | 4.932042  |
| 24 | 6 | 0 | 1.158085  | -1.162499 | -2.988668 |
| 25 | 6 | 0 | -0.142178 | -1.730157 | -2.751988 |
| 26 | 6 | 0 | -0.709993 | -2.501040 | -3.803274 |
| 27 | 1 | 0 | -1.689988 | -2.932946 | -3.622826 |
| 28 | 6 | 0 | -0.053388 | -2.682414 | -5.002328 |
| 29 | 1 | 0 | -0.527699 | -3.270050 | -5.785505 |
| 30 | 6 | 0 | 1.221338  | -2.125292 | -5.229041 |
| 31 | 1 | 0 | 1.730927  | -2.280263 | -6.175295 |
| 32 | 6 | 0 | 1.809116  | -1.387236 | -4.225554 |
| 33 | 1 | 0 | 2.797880  | -0.955065 | -4.374368 |
| 34 | 1 | 0 | 2.907306  | -0.171891 | -2.215514 |
| 35 | 1 | 0 | 0.387628  | 0.516598  | 3.569886  |

Rotational constants (GHZ): 0.7099586 0.1593090  
0.1333260

Sum of electronic and zero-point Energies= -1046.906914  
Sum of electronic and thermal Energies= -1046.889658  
Sum of electronic and thermal Enthalpies= -1046.888714  
Sum of electronic and thermal Free Energies= -1046.953803

|                | 1       | 2       | 3 |
|----------------|---------|---------|---|
|                | A       | A       | A |
| Frequencies -- | 19.2790 | 47.9351 |   |
| 62.5985        |         |         |   |
| Red. masses -- | 7.3292  | 4.7518  |   |
| 5.9456         |         |         |   |
| Frc consts --  | 0.0016  | 0.0064  |   |
| 0.0137         |         |         |   |
| IR Inten --    | 0.8226  | 0.0359  |   |
| 0.0885         |         |         |   |

*[Ni(phosphasalen)] square planar*

## Z-Matrix orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |           |           |
|---------------|---------------|-------------|-------------------------|-----------|-----------|
|               |               |             | X                       | Y         | Z         |
| 1             | 28            | 0           | 0.124220                | -0.131232 | 0.056752  |
| 2             | 15            | 0           | -0.054642               | -0.072813 | 3.120225  |
| 3             | 15            | 0           | 2.588596                | -0.051800 | -1.697128 |
| 4             | 8             | 0           | -1.446577               | -0.962411 | 0.679462  |
| 5             | 8             | 0           | -0.472384               | -0.676303 | -1.624262 |
| 6             | 7             | 0           | 0.686530                | 0.442558  | 1.771597  |
| 7             | 7             | 0           | 1.692988                | 0.718873  | -0.587608 |
| 8             | 6             | 0           | 2.079740                | 0.884578  | 1.793837  |
| 9             | 1             | 0           | 2.784738                | 0.043410  | 1.901627  |
| 10            | 1             | 0           | 2.273105                | 1.586790  | 2.617980  |
| 11            | 6             | 0           | 2.295023                | 1.560429  | 0.450215  |
| 12            | 1             | 0           | 1.767143                | 2.524235  | 0.454178  |
| 13            | 1             | 0           | 3.358906                | 1.771079  | 0.273815  |
| 14            | 6             | 0           | -1.812762               | -0.055426 | 2.873134  |
| 15            | 6             | 0           | -2.253778               | -0.561199 | 1.614661  |
| 16            | 6             | 0           | -3.659867               | -0.665248 | 1.432999  |
| 17            | 1             | 0           | -4.009304               | -1.047140 | 0.478028  |
| 18            | 6             | 0           | -4.542414               | -0.299047 | 2.431899  |
| 19            | 1             | 0           | -5.612234               | -0.391692 | 2.254447  |
| 20            | 6             | 0           | -4.088070               | 0.194544  | 3.666243  |

## Appendix 2. Optimised Structures

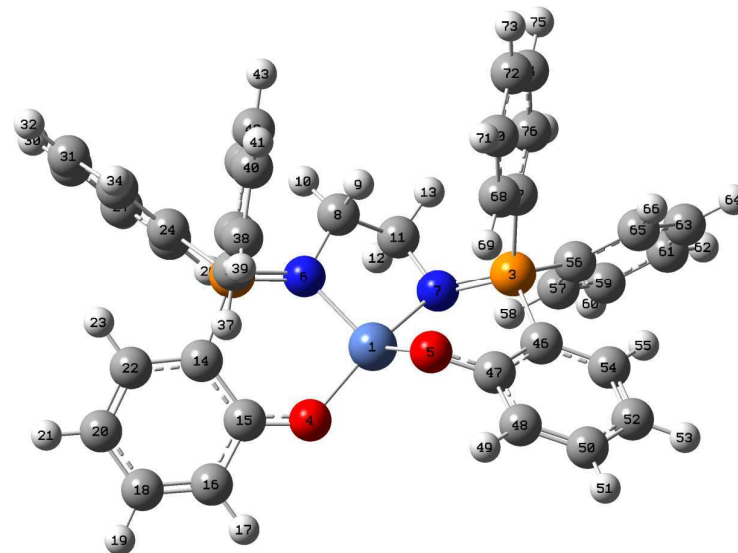
|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 21 | 1 | 0 | -4.792240 | 0.485643  | 4.440282  |
| 22 | 6 | 0 | -2.723529 | 0.307524  | 3.880242  |
| 23 | 1 | 0 | -2.355114 | 0.684675  | 4.831779  |
| 24 | 6 | 0 | 0.360262  | 1.040249  | 4.504647  |
| 25 | 6 | 0 | -0.111838 | 2.360570  | 4.434343  |
| 26 | 1 | 0 | -0.747921 | 2.660334  | 3.605571  |
| 27 | 6 | 0 | 0.228188  | 3.280096  | 5.422435  |
| 28 | 1 | 0 | -0.147549 | 4.298237  | 5.364160  |
| 29 | 6 | 0 | 1.048866  | 2.895139  | 6.483845  |
| 30 | 1 | 0 | 1.313412  | 3.614403  | 7.254830  |
| 31 | 6 | 0 | 1.532066  | 1.590054  | 6.552469  |
| 32 | 1 | 0 | 2.176775  | 1.288589  | 7.373975  |
| 33 | 6 | 0 | 1.192160  | 0.664672  | 5.565725  |
| 34 | 1 | 0 | 1.574828  | -0.349988 | 5.624180  |
| 35 | 6 | 0 | 0.431339  | -1.759327 | 3.641069  |
| 36 | 6 | 0 | -0.073963 | -2.338525 | 4.813910  |
| 37 | 1 | 0 | -0.752260 | -1.776862 | 5.451917  |
| 38 | 6 | 0 | 0.277302  | -3.640759 | 5.158124  |
| 39 | 1 | 0 | -0.118847 | -4.085324 | 6.067549  |
| 40 | 6 | 0 | 1.125853  | -4.377674 | 4.329432  |
| 41 | 1 | 0 | 1.394190  | -5.396613 | 4.597271  |
| 42 | 6 | 0 | 1.615459  | -3.813228 | 3.153487  |
| 43 | 1 | 0 | 2.262742  | -4.387957 | 2.496643  |
| 44 | 6 | 0 | 1.268302  | -2.507576 | 2.807432  |
| 45 | 1 | 0 | 1.621872  | -2.073656 | 1.876442  |
| 46 | 6 | 0 | 1.522734  | -0.611110 | -3.003789 |
| 47 | 6 | 0 | 0.127321  | -0.803329 | -2.760168 |
| 48 | 6 | 0 | -0.653974 | -1.196786 | -3.889294 |
| 49 | 1 | 0 | -1.717714 | -1.335234 | -3.718051 |
| 50 | 6 | 0 | -0.092181 | -1.406411 | -5.130225 |
| 51 | 1 | 0 | -0.730784 | -1.711935 | -5.956965 |
| 52 | 6 | 0 | 1.286766  | -1.228902 | -5.346444 |
| 53 | 1 | 0 | 1.722396  | -1.387506 | -6.328440 |
| 54 | 6 | 0 | 2.074326  | -0.827919 | -4.284158 |
| 55 | 1 | 0 | 3.138329  | -0.661668 | -4.441093 |
| 56 | 6 | 0 | 3.799674  | 1.115389  | -2.405692 |
| 57 | 6 | 0 | 3.362674  | 2.428142  | -2.637939 |
| 58 | 1 | 0 | 2.352015  | 2.710486  | -2.354928 |
| 59 | 6 | 0 | 4.216355  | 3.356650  | -3.225967 |
| 60 | 1 | 0 | 3.870954  | 4.372289  | -3.400252 |
| 61 | 6 | 0 | 5.509837  | 2.983196  | -3.594656 |
| 62 | 1 | 0 | 6.174792  | 3.709159  | -4.055635 |
| 63 | 6 | 0 | 5.946800  | 1.678363  | -3.375896 |
| 64 | 1 | 0 | 6.951806  | 1.382860  | -3.665852 |
| 65 | 6 | 0 | 5.096150  | 0.745307  | -2.782780 |
| 66 | 1 | 0 | 5.445060  | -0.269489 | -2.614418 |
| 67 | 6 | 0 | 3.577290  | -1.474326 | -1.083931 |
| 68 | 6 | 0 | 3.196318  | -2.780352 | -1.416192 |
| 69 | 1 | 0 | 2.367000  | -2.938037 | -2.100398 |
| 70 | 6 | 0 | 3.877033  | -3.871469 | -0.876081 |
| 71 | 1 | 0 | 3.574896  | -4.880352 | -1.145077 |
| 72 | 6 | 0 | 4.943035  | -3.668821 | -0.001118 |
| 73 | 1 | 0 | 5.477146  | -4.519825 | 0.414140  |
| 74 | 6 | 0 | 5.327163  | -2.370424 | 0.339703  |
| 75 | 1 | 0 | 6.158405  | -2.208304 | 1.021246  |
| 76 | 6 | 0 | 4.647277  | -1.279554 | -0.195494 |
| 77 | 1 | 0 | 4.957315  | -0.272457 | 0.073896  |

## Appendix 2. Optimised Structures

Rotational constants (GHz): 0.0989471 0.0495517  
0.0473300

Sum of electronic and zero-point Energies= -2578.008478  
Sum of electronic and thermal Energies= -2577.969521  
Sum of electronic and thermal Enthalpies= -2577.968577  
Sum of electronic and thermal Free Energies= -2578.084531

|                | 1      | 2       | 3 |
|----------------|--------|---------|---|
|                | A      | A       | A |
| Frequencies -- | 7.0978 | 13.3051 |   |
| 19.6091        |        |         |   |
| Red. masses -- | 5.3382 | 5.8200  |   |
| 4.7240         |        |         |   |
| Frc consts --  | 0.0002 | 0.0006  |   |
| 0.0011         |        |         |   |
| IR Inten --    | 0.0045 | 0.6007  |   |
| 0.1290         |        |         |   |

*[Ni(Phosphasalen)] triplet*

## Z-Matrix orientation:

| Center | Atomic | Atomic | Coordinates (Angstroms) |   |   |
|--------|--------|--------|-------------------------|---|---|
| Number | Number | Type   | X                       | Y | Z |

## Appendix 2. Optimised Structures

|    |    |   |           |           |           |
|----|----|---|-----------|-----------|-----------|
| 1  | 28 | 0 | 0.391424  | -0.586373 | 0.087925  |
| 2  | 15 | 0 | -0.031022 | -0.075297 | 3.117395  |
| 3  | 15 | 0 | 3.056662  | -0.159518 | -1.493694 |
| 4  | 8  | 0 | -1.425223 | -1.098519 | 0.405304  |
| 5  | 8  | 0 | 1.187057  | -2.302429 | -0.398357 |
| 6  | 7  | 0 | 0.665620  | 0.430601  | 1.748464  |
| 7  | 7  | 0 | 1.855088  | 0.559799  | -0.680194 |
| 8  | 6  | 0 | 1.963349  | 1.096551  | 1.718824  |
| 9  | 1  | 0 | 2.781299  | 0.401413  | 1.966678  |
| 10 | 1  | 0 | 2.012855  | 1.939049  | 2.427011  |
| 11 | 6  | 0 | 2.163599  | 1.615434  | 0.290424  |
| 12 | 1  | 0 | 1.471195  | 2.452902  | 0.123263  |
| 13 | 1  | 0 | 3.182859  | 2.016620  | 0.189747  |
| 14 | 6  | 0 | -1.685060 | -0.674607 | 2.785751  |
| 15 | 6  | 0 | -2.135382 | -1.086238 | 1.486917  |
| 16 | 6  | 0 | -3.491281 | -1.522115 | 1.404467  |
| 17 | 1  | 0 | -3.838870 | -1.826761 | 0.421142  |
| 18 | 6  | 0 | -4.322292 | -1.568715 | 2.503547  |
| 19 | 1  | 0 | -5.347001 | -1.915116 | 2.383332  |
| 20 | 6  | 0 | -3.863851 | -1.173898 | 3.771279  |
| 21 | 1  | 0 | -4.518355 | -1.204726 | 4.637291  |
| 22 | 6  | 0 | -2.560568 | -0.729265 | 3.892431  |
| 23 | 1  | 0 | -2.204948 | -0.403861 | 4.867900  |
| 24 | 6  | 0 | -0.164519 | 1.319905  | 4.294534  |
| 25 | 6  | 0 | -0.479234 | 2.576250  | 3.757035  |
| 26 | 1  | 0 | -0.600012 | 2.678181  | 2.681451  |
| 27 | 6  | 0 | -0.636056 | 3.678167  | 4.593202  |
| 28 | 1  | 0 | -0.878559 | 4.648659  | 4.168078  |
| 29 | 6  | 0 | -0.485639 | 3.535683  | 5.973309  |
| 30 | 1  | 0 | -0.610562 | 4.396178  | 6.625740  |
| 31 | 6  | 0 | -0.177384 | 2.289131  | 6.514993  |
| 32 | 1  | 0 | -0.061508 | 2.174268  | 7.589673  |
| 33 | 6  | 0 | -0.014576 | 1.183823  | 5.679852  |
| 34 | 1  | 0 | 0.231095  | 0.216350  | 6.108916  |
| 35 | 6  | 0 | 0.912286  | -1.371391 | 4.000565  |
| 36 | 6  | 0 | 0.461765  | -2.697300 | 3.988897  |
| 37 | 1  | 0 | -0.493121 | -2.935863 | 3.528876  |
| 38 | 6  | 0 | 1.232654  | -3.705789 | 4.564415  |
| 39 | 1  | 0 | 0.872587  | -4.731137 | 4.552308  |
| 40 | 6  | 0 | 2.459440  | -3.400850 | 5.151867  |
| 41 | 1  | 0 | 3.058238  | -4.188718 | 5.602021  |
| 42 | 6  | 0 | 2.919603  | -2.083598 | 5.161383  |
| 43 | 1  | 0 | 3.876707  | -1.842366 | 5.616846  |
| 44 | 6  | 0 | 2.152444  | -1.073030 | 4.587155  |
| 45 | 1  | 0 | 2.516252  | -0.048521 | 4.605622  |
| 46 | 6  | 0 | 2.425491  | -1.601842 | -2.345404 |
| 47 | 6  | 0 | 1.567153  | -2.498361 | -1.632372 |
| 48 | 6  | 0 | 1.152493  | -3.667309 | -2.323758 |
| 49 | 1  | 0 | 0.503477  | -4.352392 | -1.785454 |
| 50 | 6  | 0 | 1.545040  | -3.918538 | -3.625500 |
| 51 | 1  | 0 | 1.199133  | -4.824071 | -4.120364 |
| 52 | 6  | 0 | 2.369930  | -3.020836 | -4.318946 |
| 53 | 1  | 0 | 2.663222  | -3.215564 | -5.346368 |
| 54 | 6  | 0 | 2.801055  | -1.872683 | -3.673828 |
| 55 | 1  | 0 | 3.434850  | -1.169230 | -4.206531 |
| 56 | 6  | 0 | 3.761846  | 0.978726  | -2.740335 |
| 57 | 6  | 0 | 2.976765  | 2.068515  | -3.134502 |
| 58 | 1  | 0 | 2.004837  | 2.210362  | -2.669233 |

## Appendix 2. Optimised Structures

|    |   |   |          |           |           |
|----|---|---|----------|-----------|-----------|
| 59 | 6 | 0 | 3.437747 | 2.949513  | -4.111317 |
| 60 | 1 | 0 | 2.823162 | 3.794848  | -4.409891 |
| 61 | 6 | 0 | 4.681904 | 2.744203  | -4.705891 |
| 62 | 1 | 0 | 5.040392 | 3.430579  | -5.468912 |
| 63 | 6 | 0 | 5.467309 | 1.656065  | -4.323278 |
| 64 | 1 | 0 | 6.436627 | 1.492484  | -4.787173 |
| 65 | 6 | 0 | 5.011997 | 0.776758  | -3.342993 |
| 66 | 1 | 0 | 5.631025 | -0.065697 | -3.045192 |
| 67 | 6 | 0 | 4.479293 | -0.643490 | -0.440937 |
| 68 | 6 | 0 | 4.448647 | -1.885352 | 0.212647  |
| 69 | 1 | 0 | 3.611258 | -2.557919 | 0.053903  |
| 70 | 6 | 0 | 5.473093 | -2.241999 | 1.085734  |
| 71 | 1 | 0 | 5.440786 | -3.208091 | 1.582561  |
| 72 | 6 | 0 | 6.532652 | -1.365969 | 1.324709  |
| 73 | 1 | 0 | 7.332209 | -1.650082 | 2.004496  |
| 74 | 6 | 0 | 6.562760 | -0.124699 | 0.692123  |
| 75 | 1 | 0 | 7.383200 | 0.564232  | 0.877114  |
| 76 | 6 | 0 | 5.541119 | 0.236700  | -0.185631 |
| 77 | 1 | 0 | 5.581722 | 1.203214  | -0.680843 |

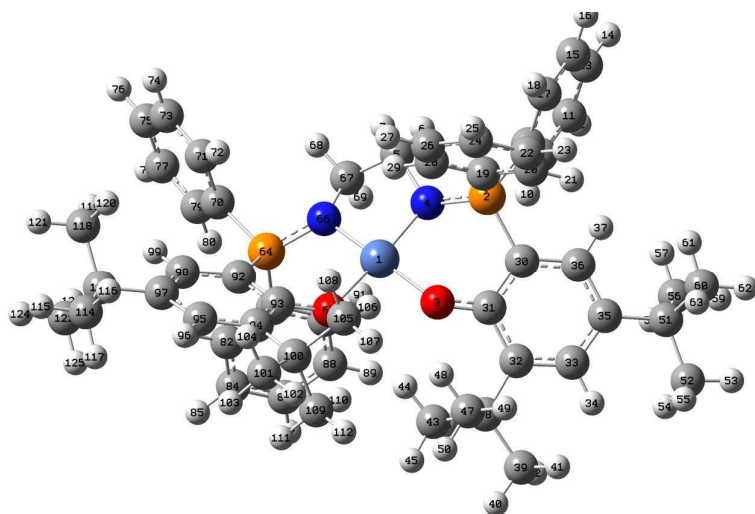
-----  
Rotational constants (GHZ):      0.1002885      0.0488261  
0.0465586

Sum of electronic and zero-point Energies=      -2578.011690  
Sum of electronic and thermal Energies=      -2577.972479  
Sum of electronic and thermal Enthalpies=      -2577.971534  
Sum of electronic and thermal Free Energies=      -2578.088748

|                |        |         |   |
|----------------|--------|---------|---|
|                | 1      | 2       | 3 |
|                | A      | A       | A |
| Frequencies -- | 6.5842 | 12.4026 |   |
| 19.7920        |        |         |   |
| Red. masses -- | 5.9642 | 6.1973  |   |
| 5.3852         |        |         |   |
| Frc consts --  | 0.0002 | 0.0006  |   |
| 0.0012         |        |         |   |
| IR Inten --    | 0.0957 | 0.3318  |   |
| 0.6315         |        |         |   |

## Chapter 4

## Complex 37a



Z-Matrix orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |          |
|------------------|------------------|----------------|-------------------------|-----------|----------|
|                  |                  |                | X                       | Y         | Z        |
| 1                | 28               | 0              | -0.014855               | 0.002040  | 0.010012 |
| 2                | 15               | 0              | -0.020430               | -0.056542 | 3.010462 |
| 3                | 8                | 0              | 1.754351                | -0.054966 | 0.712193 |
| 4                | 7                | 0              | -0.833078               | 0.382037  | 1.672302 |
| 5                | 6                | 0              | -2.293041               | 0.293298  | 1.604179 |
| 6                | 1                | 0              | -2.771883               | 0.845585  | 2.424324 |
| 7                | 1                | 0              | -2.658254               | -0.746250 | 1.640368 |
| 8                | 6                | 0              | -0.926259               | 0.551057  | 4.472485 |
| 9                | 6                | 0              | -1.114793               | 1.937827  | 4.587869 |
| 10               | 1                | 0              | -0.678319               | 2.602399  | 3.846986 |
| 11               | 6                | 0              | -1.852648               | 2.459435  | 5.646483 |
| 12               | 1                | 0              | -1.989890               | 3.534281  | 5.730968 |
| 13               | 6                | 0              | -2.414113               | 1.603854  | 6.596045 |
| 14               | 1                | 0              | -2.989944               | 2.012354  | 7.422647 |
| 15               | 6                | 0              | -2.238646               | 0.226537  | 6.482064 |
| 16               | 1                | 0              | -2.678756               | -0.442766 | 7.216681 |
| 17               | 6                | 0              | -1.499693               | -0.300665 | 5.422742 |
| 18               | 1                | 0              | -1.370928               | -1.375384 | 5.336827 |
| 19               | 6                | 0              | 0.173785                | -1.861967 | 3.229677 |
| 20               | 6                | 0              | 0.922046                | -2.382644 | 4.294913 |
| 21               | 1                | 0              | 1.393610                | -1.711930 | 5.009618 |
| 22               | 6                | 0              | 1.082120                | -3.759191 | 4.429496 |

|    |    |   |           |           |           |
|----|----|---|-----------|-----------|-----------|
| 23 | 1  | 0 | 1.666781  | -4.157259 | 5.254897  |
| 24 | 6  | 0 | 0.505684  | -4.623947 | 3.497323  |
| 25 | 1  | 0 | 0.637568  | -5.698110 | 3.600086  |
| 26 | 6  | 0 | -0.223209 | -4.110172 | 2.426605  |
| 27 | 1  | 0 | -0.655068 | -4.779990 | 1.687748  |
| 28 | 6  | 0 | -0.388116 | -2.732252 | 2.290001  |
| 29 | 1  | 0 | -0.923752 | -2.327030 | 1.435362  |
| 30 | 6  | 0 | 1.583852  | 0.699741  | 2.969473  |
| 31 | 6  | 0 | 2.271322  | 0.589652  | 1.727691  |
| 32 | 6  | 0 | 3.579052  | 1.176959  | 1.668329  |
| 33 | 6  | 0 | 4.077139  | 1.792026  | 2.814827  |
| 34 | 1  | 0 | 5.063912  | 2.233354  | 2.750738  |
| 35 | 6  | 0 | 3.403526  | 1.886606  | 4.044653  |
| 36 | 6  | 0 | 2.137651  | 1.318382  | 4.096832  |
| 37 | 1  | 0 | 1.560116  | 1.357383  | 5.017207  |
| 38 | 6  | 0 | 4.415337  | 1.101442  | 0.392193  |
| 39 | 6  | 0 | 5.759589  | 1.855008  | 0.512093  |
| 40 | 1  | 0 | 6.291670  | 1.763172  | -0.442926 |
| 41 | 1  | 0 | 6.397747  | 1.426197  | 1.295293  |
| 42 | 1  | 0 | 5.607812  | 2.922893  | 0.715868  |
| 43 | 6  | 0 | 3.645965  | 1.722100  | -0.802066 |
| 44 | 1  | 0 | 2.711856  | 1.184616  | -0.976361 |
| 45 | 1  | 0 | 4.266832  | 1.662239  | -1.705779 |
| 46 | 1  | 0 | 3.426739  | 2.779146  | -0.601238 |
| 47 | 6  | 0 | 4.743993  | -0.381624 | 0.084776  |
| 48 | 1  | 0 | 3.821531  | -0.952459 | -0.038192 |
| 49 | 1  | 0 | 5.334399  | -0.813764 | 0.903351  |
| 50 | 1  | 0 | 5.329519  | -0.445101 | -0.841427 |
| 51 | 6  | 0 | 3.995907  | 2.573310  | 5.275825  |
| 52 | 6  | 0 | 5.402393  | 3.153261  | 5.012025  |
| 53 | 1  | 0 | 5.770742  | 3.630345  | 5.928875  |
| 54 | 1  | 0 | 5.377068  | 3.910895  | 4.219178  |
| 55 | 1  | 0 | 6.111303  | 2.366056  | 4.727802  |
| 56 | 6  | 0 | 3.080179  | 3.741639  | 5.724008  |
| 57 | 1  | 0 | 2.075055  | 3.380513  | 5.970668  |
| 58 | 1  | 0 | 2.995837  | 4.487242  | 4.924111  |
| 59 | 1  | 0 | 3.501463  | 4.226826  | 6.614415  |
| 60 | 6  | 0 | 4.113610  | 1.559045  | 6.442824  |
| 61 | 1  | 0 | 3.132670  | 1.144544  | 6.703499  |
| 62 | 1  | 0 | 4.525071  | 2.056053  | 7.331285  |
| 63 | 1  | 0 | 4.777419  | 0.731946  | 6.163324  |
| 64 | 15 | 0 | -1.873765 | 0.515865  | -2.291493 |
| 65 | 8  | 0 | 0.746479  | -0.561238 | -1.641255 |
| 66 | 7  | 0 | -1.752958 | 0.243610  | -0.693387 |
| 67 | 6  | 0 | -2.654187 | 0.892812  | 0.260569  |
| 68 | 1  | 0 | -3.708377 | 0.705203  | 0.015022  |
| 69 | 1  | 0 | -2.509027 | 1.984582  | 0.308420  |
| 70 | 6  | 0 | -3.639445 | 0.549165  | -2.748933 |
| 71 | 6  | 0 | -4.391911 | -0.613426 | -2.515705 |
| 72 | 1  | 0 | -3.901083 | -1.501567 | -2.126606 |
| 73 | 6  | 0 | -5.757234 | -0.631048 | -2.785433 |
| 74 | 1  | 0 | -6.330978 | -1.536727 | -2.606984 |
| 75 | 6  | 0 | -6.386518 | 0.511261  | -3.283472 |
| 76 | 1  | 0 | -7.452850 | 0.496118  | -3.494251 |
| 77 | 6  | 0 | -5.647839 | 1.671002  | -3.507145 |
| 78 | 1  | 0 | -6.135445 | 2.563791  | -3.889880 |
| 79 | 6  | 0 | -4.278951 | 1.693022  | -3.238894 |
| 80 | 1  | 0 | -3.710073 | 2.601615  | -3.412138 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 81  | 6 | 0 | -1.163656 | 2.104452  | -2.855758 |
| 82  | 6 | 0 | -1.125739 | 2.430706  | -4.218739 |
| 83  | 1 | 0 | -1.523612 | 1.737415  | -4.956233 |
| 84  | 6 | 0 | -0.560900 | 3.633672  | -4.633871 |
| 85  | 1 | 0 | -0.530633 | 3.880085  | -5.692141 |
| 86  | 6 | 0 | -0.021706 | 4.513334  | -3.693429 |
| 87  | 1 | 0 | 0.424891  | 5.449135  | -4.019934 |
| 88  | 6 | 0 | -0.040171 | 4.184644  | -2.339394 |
| 89  | 1 | 0 | 0.397577  | 4.858110  | -1.607346 |
| 90  | 6 | 0 | -0.607732 | 2.982055  | -1.919468 |
| 91  | 1 | 0 | -0.590688 | 2.705856  | -0.868488 |
| 92  | 6 | 0 | -1.080917 | -0.817292 | -3.153831 |
| 93  | 6 | 0 | 0.195521  | -1.191966 | -2.647135 |
| 94  | 6 | 0 | 0.864016  | -2.261781 | -3.330895 |
| 95  | 6 | 0 | 0.232288  | -2.834947 | -4.432349 |
| 96  | 1 | 0 | 0.750178  | -3.642468 | -4.935167 |
| 97  | 6 | 0 | -1.019494 | -2.451199 | -4.943513 |
| 98  | 6 | 0 | -1.664864 | -1.419390 | -4.275020 |
| 99  | 1 | 0 | -2.638665 | -1.073657 | -4.613506 |
| 100 | 6 | 0 | 2.245503  | -2.736828 | -2.884993 |
| 101 | 6 | 0 | 2.754306  | -3.945963 | -3.702152 |
| 102 | 1 | 0 | 3.736454  | -4.238109 | -3.310091 |
| 103 | 1 | 0 | 2.876443  | -3.696716 | -4.764036 |
| 104 | 1 | 0 | 2.080620  | -4.807809 | -3.610256 |
| 105 | 6 | 0 | 2.222882  | -3.164803 | -1.395084 |
| 106 | 1 | 0 | 1.927985  | -2.325984 | -0.761671 |
| 107 | 1 | 0 | 3.225058  | -3.501614 | -1.098501 |
| 108 | 1 | 0 | 1.520619  | -3.996562 | -1.251192 |
| 109 | 6 | 0 | 3.266612  | -1.586477 | -3.077408 |
| 110 | 1 | 0 | 2.965555  | -0.717296 | -2.489481 |
| 111 | 1 | 0 | 3.324886  | -1.308174 | -4.137837 |
| 112 | 1 | 0 | 4.259856  | -1.915652 | -2.745798 |
| 113 | 6 | 0 | -1.663202 | -3.110133 | -6.163655 |
| 114 | 6 | 0 | -0.803909 | -4.256534 | -6.739882 |
| 115 | 1 | 0 | -1.320204 | -4.691116 | -7.605004 |
| 116 | 1 | 0 | -0.651949 | -5.050215 | -5.998112 |
| 117 | 1 | 0 | 0.174924  | -3.891856 | -7.074474 |
| 118 | 6 | 0 | -3.044964 | -3.701906 | -5.783317 |
| 119 | 1 | 0 | -3.717364 | -2.921870 | -5.407708 |
| 120 | 1 | 0 | -2.930932 | -4.466747 | -5.005387 |
| 121 | 1 | 0 | -3.509921 | -4.163773 | -6.664366 |
| 122 | 6 | 0 | -1.864173 | -2.058731 | -7.285587 |
| 123 | 1 | 0 | -2.507309 | -1.239572 | -6.943179 |
| 124 | 1 | 0 | -2.335923 | -2.526570 | -8.159726 |
| 125 | 1 | 0 | -0.897828 | -1.638723 | -7.589848 |

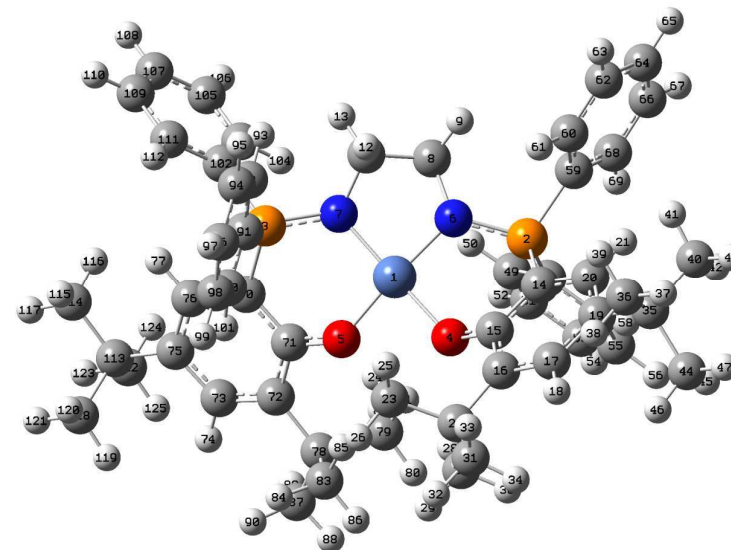
Rotational constants (GHz): 0.0557429 0.0282345  
0.0262850

Sum of electronic and zero-point Energies= -3202.971603  
Sum of electronic and thermal Energies= -3202.910930  
Sum of electronic and thermal Enthalpies= -3202.909985  
Sum of electronic and thermal Free Energies= -3203.069669

1 2 3

## Appendix 2. Optimised Structures

|                |        |         |   |
|----------------|--------|---------|---|
|                | A      | A       | A |
| Frequencies -- | 8.3015 | 12.7267 |   |
| 19.7535        |        |         |   |
| Red. masses -- | 4.6911 | 5.0398  |   |
| 4.1586         |        |         |   |
| Frc consts --  | 0.0002 | 0.0005  |   |
| 0.0010         |        |         |   |
| IR Inten --    | 0.1893 | 0.0662  |   |
| 0.0376         |        |         |   |

Complex [37a]<sup>+</sup>

## Z-Matrix orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |           |           |
|---------------|---------------|-------------|-------------------------|-----------|-----------|
|               |               |             | X                       | Y         | Z         |
| 1             | 28            | 0           | -0.027215               | -0.083833 | 0.057748  |
| 2             | 15            | 0           | -0.109982               | -0.204110 | 3.064512  |
| 3             | 15            | 0           | 1.914763                | 0.179430  | -2.260311 |
| 4             | 8             | 0           | -1.755362               | 0.131079  | 0.787887  |
| 5             | 8             | 0           | -0.860019               | -0.621487 | -1.467601 |
| 6             | 7             | 0           | 0.791705                | 0.009135  | 1.679750  |
| 7             | 7             | 0           | 1.728437                | -0.149652 | -0.657269 |
| 8             | 6             | 0           | 2.249561                | -0.149177 | 1.644983  |
| 9             | 1             | 0           | 2.727307                | 0.373813  | 2.480978  |
| 10            | 1             | 0           | 2.543375                | -1.208221 | 1.694303  |
| 11            | 6             | 0           | 2.661467                | 0.437509  | 0.313752  |

## Appendix 2. Optimised Structures

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 12 | 1 | 0 | 2.575533  | 1.533937  | 0.365832  |
| 13 | 1 | 0 | 3.701289  | 0.184626  | 0.069490  |
| 14 | 6 | 0 | -1.452362 | 0.946901  | 2.998057  |
| 15 | 6 | 0 | -2.112975 | 0.974969  | 1.747221  |
| 16 | 6 | 0 | -3.208342 | 1.881852  | 1.601753  |
| 17 | 6 | 0 | -3.536184 | 2.661108  | 2.707879  |
| 18 | 1 | 0 | -4.367036 | 3.349329  | 2.599541  |
| 19 | 6 | 0 | -2.885733 | 2.635063  | 3.956922  |
| 20 | 6 | 0 | -1.824507 | 1.752042  | 4.085012  |
| 21 | 1 | 0 | -1.275275 | 1.675384  | 5.017308  |
| 22 | 6 | 0 | -4.025588 | 1.958260  | 0.314258  |
| 23 | 6 | 0 | -3.111914 | 2.266783  | -0.898929 |
| 24 | 1 | 0 | -2.372445 | 1.476363  | -1.038245 |
| 25 | 1 | 0 | -2.597303 | 3.225414  | -0.754047 |
| 26 | 1 | 0 | -3.727983 | 2.338537  | -1.804450 |
| 27 | 6 | 0 | -4.749930 | 0.604356  | 0.097192  |
| 28 | 1 | 0 | -4.026086 | -0.212111 | 0.040098  |
| 29 | 1 | 0 | -5.322443 | 0.639825  | -0.838035 |
| 30 | 1 | 0 | -5.446296 | 0.412591  | 0.923131  |
| 31 | 6 | 0 | -5.107854 | 3.060215  | 0.361421  |
| 32 | 1 | 0 | -5.636787 | 3.064820  | -0.599024 |
| 33 | 1 | 0 | -4.667663 | 4.054352  | 0.510284  |
| 34 | 1 | 0 | -5.848932 | 2.871185  | 1.147731  |
| 35 | 6 | 0 | -3.352742 | 3.550948  | 5.085233  |
| 36 | 6 | 0 | -3.222963 | 5.032702  | 4.646231  |
| 37 | 1 | 0 | -3.570390 | 5.688226  | 5.454299  |
| 38 | 1 | 0 | -3.827455 | 5.237894  | 3.755473  |
| 39 | 1 | 0 | -2.177572 | 5.277564  | 4.422516  |
| 40 | 6 | 0 | -2.523594 | 3.360907  | 6.372981  |
| 41 | 1 | 0 | -1.464430 | 3.593799  | 6.206055  |
| 42 | 1 | 0 | -2.609145 | 2.336198  | 6.756099  |
| 43 | 1 | 0 | -2.901578 | 4.041961  | 7.144259  |
| 44 | 6 | 0 | -4.836453 | 3.256065  | 5.425927  |
| 45 | 1 | 0 | -4.956384 | 2.218483  | 5.760036  |
| 46 | 1 | 0 | -5.485017 | 3.420174  | 4.558027  |
| 47 | 1 | 0 | -5.168413 | 3.922757  | 6.231399  |
| 48 | 6 | 0 | -0.718802 | -1.904093 | 3.214268  |
| 49 | 6 | 0 | -0.079827 | -2.952752 | 2.541937  |
| 50 | 1 | 0 | 0.760845  | -2.749525 | 1.884729  |
| 51 | 6 | 0 | -0.541123 | -4.258107 | 2.696535  |
| 52 | 1 | 0 | -0.047783 | -5.070841 | 2.170844  |
| 53 | 6 | 0 | -1.638492 | -4.518493 | 3.517077  |
| 54 | 1 | 0 | -1.998242 | -5.537116 | 3.633439  |
| 55 | 6 | 0 | -2.282733 | -3.473601 | 4.180264  |
| 56 | 1 | 0 | -3.145794 | -3.675279 | 4.808372  |
| 57 | 6 | 0 | -1.827847 | -2.165935 | 4.030083  |
| 58 | 1 | 0 | -2.342599 | -1.350279 | 4.531456  |
| 59 | 6 | 0 | 0.936113  | 0.150533  | 4.499252  |
| 60 | 6 | 0 | 1.457879  | 1.446592  | 4.651731  |
| 61 | 1 | 0 | 1.208217  | 2.222333  | 3.932095  |
| 62 | 6 | 0 | 2.286236  | 1.738629  | 5.730853  |
| 63 | 1 | 0 | 2.685579  | 2.742032  | 5.848913  |
| 64 | 6 | 0 | 2.598292  | 0.745268  | 6.661549  |
| 65 | 1 | 0 | 3.242693  | 0.977278  | 7.505048  |
| 66 | 6 | 0 | 2.083954  | -0.541124 | 6.512521  |
| 67 | 1 | 0 | 2.325602  | -1.313198 | 7.237401  |
| 68 | 6 | 0 | 1.255444  | -0.843158 | 5.432543  |
| 69 | 1 | 0 | 0.856364  | -1.846638 | 5.320171  |

## Appendix 2. Optimised Structures

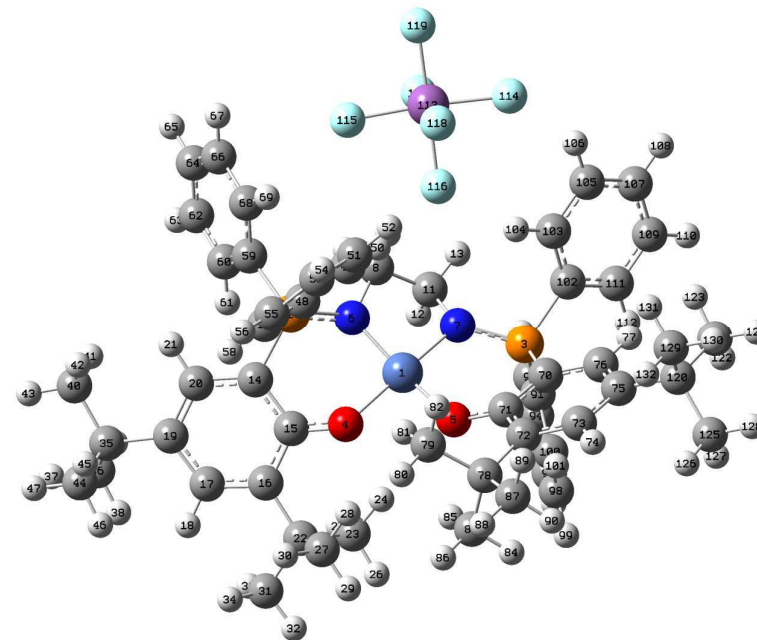
|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 70  | 6 | 0 | 0.837410  | -0.954230 | -3.119578 |
| 71  | 6 | 0 | -0.427210 | -1.243928 | -2.552181 |
| 72  | 6 | 0 | -1.259715 | -2.204627 | -3.210832 |
| 73  | 6 | 0 | -0.767014 | -2.770962 | -4.383340 |
| 74  | 1 | 0 | -1.392523 | -3.499455 | -4.885430 |
| 75  | 6 | 0 | 0.475264  | -2.474813 | -4.970318 |
| 76  | 6 | 0 | 1.275244  | -1.550826 | -4.306245 |
| 77  | 1 | 0 | 2.252866  | -1.293101 | -4.698032 |
| 78  | 6 | 0 | -2.644268 | -2.576228 | -2.682550 |
| 79  | 6 | 0 | -2.572925 | -3.046969 | -1.206341 |
| 80  | 1 | 0 | -3.575152 | -3.353273 | -0.881998 |
| 81  | 1 | 0 | -2.226043 | -2.243465 | -0.554557 |
| 82  | 1 | 0 | -1.902433 | -3.910810 | -1.112359 |
| 83  | 6 | 0 | -3.575609 | -1.341586 | -2.791102 |
| 84  | 1 | 0 | -3.677721 | -1.032533 | -3.839039 |
| 85  | 1 | 0 | -3.181276 | -0.510348 | -2.203363 |
| 86  | 1 | 0 | -4.569665 | -1.601838 | -2.407275 |
| 87  | 6 | 0 | -3.295151 | -3.719702 | -3.495231 |
| 88  | 1 | 0 | -4.268387 | -3.947622 | -3.045427 |
| 89  | 1 | 0 | -2.687814 | -4.633167 | -3.468293 |
| 90  | 1 | 0 | -3.472421 | -3.432064 | -4.538854 |
| 91  | 6 | 0 | 1.555279  | 1.894063  | -2.737910 |
| 92  | 6 | 0 | 2.384946  | 2.940198  | -2.298228 |
| 93  | 1 | 0 | 3.294113  | 2.726842  | -1.741755 |
| 94  | 6 | 0 | 2.059293  | 4.260529  | -2.595202 |
| 95  | 1 | 0 | 2.706953  | 5.064938  | -2.257800 |
| 96  | 6 | 0 | 0.907544  | 4.548386  | -3.329246 |
| 97  | 1 | 0 | 0.657414  | 5.579799  | -3.562003 |
| 98  | 6 | 0 | 0.081472  | 3.515136  | -3.768297 |
| 99  | 1 | 0 | -0.812757 | 3.737703  | -4.343410 |
| 100 | 6 | 0 | 0.400317  | 2.190904  | -3.474269 |
| 101 | 1 | 0 | -0.245680 | 1.389050  | -3.819796 |
| 102 | 6 | 0 | 3.627503  | -0.183810 | -2.731272 |
| 103 | 6 | 0 | 4.225868  | -1.333293 | -2.190880 |
| 104 | 1 | 0 | 3.672356  | -1.947081 | -1.485082 |
| 105 | 6 | 0 | 5.519905  | -1.683667 | -2.562840 |
| 106 | 1 | 0 | 5.981896  | -2.571459 | -2.140127 |
| 107 | 6 | 0 | 6.220278  | -0.898556 | -3.480737 |
| 108 | 1 | 0 | 7.230133  | -1.175095 | -3.771089 |
| 109 | 6 | 0 | 5.625360  | 0.236340  | -4.028939 |
| 110 | 1 | 0 | 6.167689  | 0.844325  | -4.747466 |
| 111 | 6 | 0 | 4.330778  | 0.597572  | -3.657267 |
| 112 | 1 | 0 | 3.872899  | 1.482307  | -4.089400 |
| 113 | 6 | 0 | 0.898417  | -3.160972 | -6.265359 |
| 114 | 6 | 0 | 2.284720  | -2.690144 | -6.753846 |
| 115 | 1 | 0 | 2.292442  | -1.612214 | -6.958560 |
| 116 | 1 | 0 | 3.068442  | -2.923703 | -6.022430 |
| 117 | 1 | 0 | 2.528230  | -3.211788 | -7.686499 |
| 118 | 6 | 0 | -0.133018 | -2.853980 | -7.382599 |
| 119 | 1 | 0 | -1.133043 | -3.211731 | -7.112996 |
| 120 | 1 | 0 | -0.186618 | -1.775555 | -7.573687 |
| 121 | 1 | 0 | 0.171106  | -3.357371 | -8.308325 |
| 122 | 6 | 0 | 0.962130  | -4.695698 | -6.048476 |
| 123 | 1 | 0 | 1.255504  | -5.184764 | -6.985417 |
| 124 | 1 | 0 | 1.700893  | -4.946245 | -5.277736 |
| 125 | 1 | 0 | -0.011218 | -5.096572 | -5.743966 |



Rotational constants (GHz):      0.0549741      0.0283287  
0.0269105

Sum of electronic and zero-point Energies=      -3202.773558  
Sum of electronic and thermal Energies=      -3202.712880  
Sum of electronic and thermal Enthalpies=      -3202.711936  
Sum of electronic and thermal Free Energies=      -3202.872181

|                |        |         |   |
|----------------|--------|---------|---|
|                | 1      | 2       | 3 |
|                | A      | A       | A |
| Frequencies -- | 8.7115 | 12.6680 |   |
| 21.1264        |        |         |   |
| Red. masses -- | 4.6569 | 5.0842  |   |
| 4.0743         |        |         |   |
| Frc consts --  | 0.0002 | 0.0005  |   |
| 0.0011         |        |         |   |
| IR Inten --    | 0.1320 | 0.0469  |   |
| 0.0343         |        |         |   |

**Complex [37a][SbF<sub>6</sub>]**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 28               | 0              | 0.575883                | -1.064578 | 0.400618  |
| 2                | 15               | 0              | 2.522586                | 1.150484  | -0.084205 |
| 3                | 15               | 0              | -2.230584               | -1.457325 | 1.598869  |
| 4                | 8                | 0              | 2.171575                | -1.711098 | -0.370663 |
| 5                | 8                | 0              | -0.257278               | -2.454266 | -0.444158 |
| 6                | 7                | 0              | 1.290688                | 0.528143  | 0.861413  |
| 7                | 7                | 0              | -0.926930               | -0.497335 | 1.368037  |
| 8                | 6                | 0              | 0.428023                | 1.406069  | 1.669942  |
| 9                | 1                | 0              | 1.031174                | 1.995890  | 2.369448  |
| 10               | 1                | 0              | -0.154502               | 2.090190  | 1.043999  |
| 11               | 6                | 0              | -0.506950               | 0.463965  | 2.393366  |
| 12               | 1                | 0              | 0.022543                | -0.032328 | 3.222091  |
| 13               | 1                | 0              | -1.364355               | 1.010249  | 2.805314  |
| 14               | 6                | 0              | 3.838880                | -0.037191 | -0.023484 |
| 15               | 6                | 0              | 3.426385                | -1.389224 | -0.118411 |
| 16               | 6                | 0              | 4.439521                | -2.394660 | 0.005474  |
| 17               | 6                | 0              | 5.753314                | -1.964260 | 0.152225  |

## Appendix 2. Optimised Structures

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 18 | 1 | 0 | 6.519788  | -2.727007 | 0.236632  |
| 19 | 6 | 0 | 6.176160  | -0.621482 | 0.200131  |
| 20 | 6 | 0 | 5.183763  | 0.341630  | 0.118429  |
| 21 | 1 | 0 | 5.431503  | 1.396878  | 0.165080  |
| 22 | 6 | 0 | 4.101440  | -3.882876 | -0.067181 |
| 23 | 6 | 0 | 3.018717  | -4.256176 | 0.978326  |
| 24 | 1 | 0 | 2.094301  | -3.708967 | 0.785722  |
| 25 | 1 | 0 | 3.371744  | -4.028036 | 1.992248  |
| 26 | 1 | 0 | 2.813263  | -5.332757 | 0.916392  |
| 27 | 6 | 0 | 3.588043  | -4.220105 | -1.490157 |
| 28 | 1 | 0 | 2.708335  | -3.619334 | -1.729304 |
| 29 | 1 | 0 | 3.319079  | -5.283005 | -1.542031 |
| 30 | 1 | 0 | 4.373262  | -4.022134 | -2.230943 |
| 31 | 6 | 0 | 5.327312  | -4.783809 | 0.206838  |
| 32 | 1 | 0 | 5.000978  | -5.830134 | 0.166820  |
| 33 | 1 | 0 | 5.751433  | -4.597228 | 1.201735  |
| 34 | 1 | 0 | 6.109557  | -4.649494 | -0.550619 |
| 35 | 6 | 0 | 7.658767  | -0.288017 | 0.346474  |
| 36 | 6 | 0 | 8.209467  | -0.891428 | 1.664463  |
| 37 | 1 | 0 | 9.278505  | -0.662071 | 1.758412  |
| 38 | 1 | 0 | 8.088996  | -1.980515 | 1.683366  |
| 39 | 1 | 0 | 7.683108  | -0.468150 | 2.528548  |
| 40 | 6 | 0 | 7.915930  | 1.233904  | 0.377547  |
| 41 | 1 | 0 | 7.407629  | 1.708069  | 1.226265  |
| 42 | 1 | 0 | 7.581829  | 1.713743  | -0.550779 |
| 43 | 1 | 0 | 8.992616  | 1.412651  | 0.483887  |
| 44 | 6 | 0 | 8.452649  | -0.880408 | -0.846509 |
| 45 | 1 | 0 | 8.098844  | -0.452258 | -1.792145 |
| 46 | 1 | 0 | 8.340537  | -1.969465 | -0.894859 |
| 47 | 1 | 0 | 9.519461  | -0.648392 | -0.734359 |
| 48 | 6 | 0 | 1.992678  | 1.438131  | -1.789520 |
| 49 | 6 | 0 | 0.686493  | 1.861282  | -2.071169 |
| 50 | 1 | 0 | -0.048691 | 1.995609  | -1.283659 |
| 51 | 6 | 0 | 0.320155  | 2.130357  | -3.388947 |
| 52 | 1 | 0 | -0.686355 | 2.481664  | -3.595727 |
| 53 | 6 | 0 | 1.245884  | 1.966634  | -4.418880 |
| 54 | 1 | 0 | 0.955963  | 2.179071  | -5.444694 |
| 55 | 6 | 0 | 2.542597  | 1.532946  | -4.139204 |
| 56 | 1 | 0 | 3.260168  | 1.397826  | -4.944083 |
| 57 | 6 | 0 | 2.921418  | 1.268548  | -2.826041 |
| 58 | 1 | 0 | 3.927771  | 0.921673  | -2.606908 |
| 59 | 6 | 0 | 3.035199  | 2.721999  | 0.649421  |
| 60 | 6 | 0 | 3.747588  | 2.718434  | 1.861288  |
| 61 | 1 | 0 | 4.055197  | 1.778253  | 2.311195  |
| 62 | 6 | 0 | 4.058493  | 3.922870  | 2.483401  |
| 63 | 1 | 0 | 4.613612  | 3.919559  | 3.417636  |
| 64 | 6 | 0 | 3.648951  | 5.130943  | 1.913771  |
| 65 | 1 | 0 | 3.883595  | 6.069433  | 2.409094  |
| 66 | 6 | 0 | 2.929134  | 5.135789  | 0.721603  |
| 67 | 1 | 0 | 2.583830  | 6.068733  | 0.287180  |
| 68 | 6 | 0 | 2.622463  | 3.934747  | 0.083424  |
| 69 | 1 | 0 | 2.040377  | 3.953856  | -0.831978 |
| 70 | 6 | 0 | -2.594150 | -2.227275 | 0.030898  |
| 71 | 6 | 0 | -1.520222 | -2.626111 | -0.798820 |
| 72 | 6 | 0 | -1.832850 | -3.263305 | -2.042179 |
| 73 | 6 | 0 | -3.178647 | -3.414985 | -2.360880 |
| 74 | 1 | 0 | -3.417349 | -3.883822 | -3.308935 |
| 75 | 6 | 0 | -4.254255 | -3.000657 | -1.556098 |

## Appendix 2. Optimised Structures

|     |    |   |           |           |           |
|-----|----|---|-----------|-----------|-----------|
| 76  | 6  | 0 | -3.931551 | -2.407596 | -0.342549 |
| 77  | 1  | 0 | -4.713506 | -2.060370 | 0.323795  |
| 78  | 6  | 0 | -0.739043 | -3.784762 | -2.972511 |
| 79  | 6  | 0 | 0.226921  | -2.645601 | -3.388787 |
| 80  | 1  | 0 | 0.981903  | -3.049394 | -4.076013 |
| 81  | 1  | 0 | 0.733347  | -2.223307 | -2.519573 |
| 82  | 1  | 0 | -0.323274 | -1.850683 | -3.907531 |
| 83  | 6  | 0 | 0.049321  | -4.907313 | -2.248475 |
| 84  | 1  | 0 | -0.619024 | -5.744479 | -2.008321 |
| 85  | 1  | 0 | 0.501433  | -4.526995 | -1.329698 |
| 86  | 1  | 0 | 0.845831  | -5.276369 | -2.906417 |
| 87  | 6  | 0 | -1.312722 | -4.394200 | -4.272018 |
| 88  | 1  | 0 | -0.473973 | -4.744558 | -4.885226 |
| 89  | 1  | 0 | -1.870407 | -3.650780 | -4.855353 |
| 90  | 1  | 0 | -1.961058 | -5.255372 | -4.066682 |
| 91  | 6  | 0 | -1.995690 | -2.740709 | 2.872685  |
| 92  | 6  | 0 | -1.851956 | -2.369411 | 4.219565  |
| 93  | 1  | 0 | -1.973011 | -1.331078 | 4.518192  |
| 94  | 6  | 0 | -1.571369 | -3.332433 | 5.185010  |
| 95  | 1  | 0 | -1.465664 | -3.037954 | 6.225714  |
| 96  | 6  | 0 | -1.429466 | -4.670944 | 4.816501  |
| 97  | 1  | 0 | -1.210985 | -5.421305 | 5.571767  |
| 98  | 6  | 0 | -1.570269 | -5.045666 | 3.481345  |
| 99  | 1  | 0 | -1.462977 | -6.087640 | 3.192276  |
| 100 | 6  | 0 | -1.851054 | -4.085828 | 2.510444  |
| 101 | 1  | 0 | -1.959913 | -4.381074 | 1.470725  |
| 102 | 6  | 0 | -3.637147 | -0.437167 | 2.103384  |
| 103 | 6  | 0 | -3.783083 | 0.823114  | 1.501694  |
| 104 | 1  | 0 | -3.041041 | 1.194588  | 0.799358  |
| 105 | 6  | 0 | -4.884641 | 1.616500  | 1.815955  |
| 106 | 1  | 0 | -4.977654 | 2.593886  | 1.351142  |
| 107 | 6  | 0 | -5.842826 | 1.151101  | 2.717400  |
| 108 | 1  | 0 | -6.701204 | 1.772082  | 2.960512  |
| 109 | 6  | 0 | -5.705388 | -0.105111 | 3.308781  |
| 110 | 1  | 0 | -6.454136 | -0.465400 | 4.009344  |
| 111 | 6  | 0 | -4.603307 | -0.902428 | 3.006911  |
| 112 | 1  | 0 | -4.497387 | -1.878753 | 3.471247  |
| 113 | 51 | 0 | -2.218381 | 4.685195  | -0.445536 |
| 114 | 9  | 0 | -4.048910 | 4.227354  | -0.089900 |
| 115 | 9  | 0 | -0.349103 | 5.009014  | -0.767083 |
| 116 | 9  | 0 | -1.764294 | 2.809997  | -0.208064 |
| 117 | 9  | 0 | -1.920415 | 4.922786  | 1.434310  |
| 118 | 9  | 0 | -2.463074 | 4.318735  | -2.310599 |
| 119 | 9  | 0 | -2.644176 | 6.528559  | -0.683142 |
| 120 | 6  | 0 | -5.690890 | -3.194098 | -2.032749 |
| 121 | 6  | 0 | -6.723167 | -2.682582 | -1.005279 |
| 122 | 1  | 0 | -6.640953 | -3.223231 | -0.054038 |
| 123 | 1  | 0 | -6.602521 | -1.608529 | -0.818838 |
| 124 | 1  | 0 | -7.731948 | -2.846272 | -1.402550 |
| 125 | 6  | 0 | -5.968044 | -4.699382 | -2.280405 |
| 126 | 1  | 0 | -5.289908 | -5.109910 | -3.037018 |
| 127 | 1  | 0 | -5.843639 | -5.270851 | -1.352518 |
| 128 | 1  | 0 | -6.997933 | -4.829820 | -2.635693 |
| 129 | 6  | 0 | -5.908684 | -2.416076 | -3.356792 |
| 130 | 1  | 0 | -6.938035 | -2.565275 | -3.706367 |
| 131 | 1  | 0 | -5.742733 | -1.343282 | -3.203001 |
| 132 | 1  | 0 | -5.225414 | -2.765151 | -4.139381 |

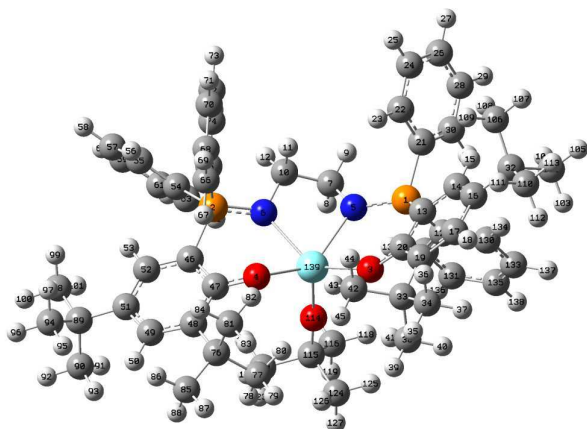
Rotational constants (GHz):      0.0311485      0.0267516  
0.0192758

Sum of electronic and zero-point Energies=      -3807.522404  
Sum of electronic and thermal Energies=      -3807.450943  
Sum of electronic and thermal Enthalpies=      -3807.449999  
Sum of electronic and thermal Free Energies=      -3807.636885

|                | 1      | 2       | 3 |
|----------------|--------|---------|---|
|                | A      | A       | A |
| Frequencies -- | 9.2656 | 11.1668 |   |
| 13.5524        |        |         |   |
| Red. masses -- | 4.9042 | 6.9776  |   |
| 9.2771         |        |         |   |
| Frc consts --  | 0.0002 | 0.0005  |   |
| 0.0010         |        |         |   |
| IR Inten --    | 0.2584 | 1.3010  |   |
| 1.0411         |        |         |   |

## Chapter 5

### Complex 45



Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 15               | 0              | -3.041670               | 1.100443  | 0.749695  |
| 2                | 15               | 0              | 2.646034                | 1.526886  | -0.673258 |
| 3                | 8                | 0              | -1.682441               | -1.546408 | 0.186293  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 4  | 8 | 0 | 1.694265  | -1.331294 | -0.557422 |
| 5  | 7 | 0 | -1.417653 | 1.290192  | 0.733246  |
| 6  | 7 | 0 | 1.266582  | 1.541357  | 0.224530  |
| 7  | 6 | 0 | -0.793209 | 2.584251  | 0.996913  |
| 8  | 1 | 0 | -0.445665 | 2.655586  | 2.041491  |
| 9  | 1 | 0 | -1.467606 | 3.436238  | 0.823905  |
| 10 | 6 | 0 | 0.416344  | 2.725643  | 0.078043  |
| 11 | 1 | 0 | 0.042199  | 2.836590  | -0.953835 |
| 12 | 1 | 0 | 0.945745  | 3.659718  | 0.334312  |
| 13 | 6 | 0 | -3.616466 | -0.260676 | -0.304621 |
| 14 | 6 | 0 | -4.863085 | -0.124345 | -0.928537 |
| 15 | 1 | 0 | -5.396951 | 0.818559  | -0.842015 |
| 16 | 6 | 0 | -5.424138 | -1.168087 | -1.657996 |
| 17 | 6 | 0 | -4.682007 | -2.357215 | -1.717257 |
| 18 | 1 | 0 | -5.105728 | -3.187885 | -2.267303 |
| 19 | 6 | 0 | -3.436384 | -2.549188 | -1.118417 |
| 20 | 6 | 0 | -2.855712 | -1.460660 | -0.392075 |
| 21 | 6 | 0 | -3.873733 | 2.630273  | 0.137699  |
| 22 | 6 | 0 | -3.581083 | 3.046736  | -1.169287 |
| 23 | 1 | 0 | -2.918296 | 2.448840  | -1.789742 |
| 24 | 6 | 0 | -4.140240 | 4.218292  | -1.671805 |
| 25 | 1 | 0 | -3.912582 | 4.532873  | -2.687010 |
| 26 | 6 | 0 | -4.992059 | 4.984868  | -0.873884 |
| 27 | 1 | 0 | -5.428612 | 5.899317  | -1.267472 |
| 28 | 6 | 0 | -5.282017 | 4.577284  | 0.426255  |
| 29 | 1 | 0 | -5.943638 | 5.172188  | 1.050563  |
| 30 | 6 | 0 | -4.724151 | 3.402678  | 0.933655  |
| 31 | 1 | 0 | -4.954834 | 3.089262  | 1.947612  |
| 32 | 6 | 0 | -6.784562 | -0.987794 | -2.345606 |
| 33 | 6 | 0 | -2.711634 | -3.899709 | -1.228292 |
| 34 | 6 | 0 | -3.528050 | -4.943776 | -2.006630 |
| 35 | 1 | 0 | -2.967060 | -5.885363 | -2.036100 |
| 36 | 1 | 0 | -3.710604 | -4.640292 | -3.044732 |
| 37 | 1 | 0 | -4.494188 | -5.153074 | -1.531545 |
| 38 | 6 | 0 | -2.462338 | -4.475100 | 0.181197  |
| 39 | 1 | 0 | -1.920240 | -5.427021 | 0.109710  |
| 40 | 1 | 0 | -3.414476 | -4.668149 | 0.691157  |
| 41 | 1 | 0 | -1.877884 | -3.787019 | 0.794446  |
| 42 | 6 | 0 | -1.375736 | -3.717419 | -1.973250 |
| 43 | 1 | 0 | -0.720375 | -3.016648 | -1.454042 |
| 44 | 1 | 0 | -1.548558 | -3.340231 | -2.989095 |
| 45 | 1 | 0 | -0.853462 | -4.679111 | -2.054787 |
| 46 | 6 | 0 | 3.634793  | 0.029210  | -0.414710 |
| 47 | 6 | 0 | 3.001774  | -1.244089 | -0.466360 |
| 48 | 6 | 0 | 3.852574  | -2.400303 | -0.443365 |
| 49 | 6 | 0 | 5.219286  | -2.201993 | -0.279396 |
| 50 | 1 | 0 | 5.855115  | -3.079992 | -0.238780 |
| 51 | 6 | 0 | 5.844938  | -0.946634 | -0.162602 |
| 52 | 6 | 0 | 5.023770  | 0.166731  | -0.255644 |
| 53 | 1 | 0 | 5.449204  | 1.161952  | -0.200988 |
| 54 | 6 | 0 | 3.709686  | 2.969550  | -0.222755 |
| 55 | 6 | 0 | 4.582726  | 3.590241  | -1.123520 |
| 56 | 1 | 0 | 4.639311  | 3.245825  | -2.152493 |
| 57 | 6 | 0 | 5.383345  | 4.651251  | -0.702041 |
| 58 | 1 | 0 | 6.061202  | 5.128156  | -1.405326 |
| 59 | 6 | 0 | 5.313638  | 5.098905  | 0.617064  |
| 60 | 1 | 0 | 5.936946  | 5.927841  | 0.942826  |
| 61 | 6 | 0 | 4.444937  | 4.482849  | 1.518048  |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 62  | 1 | 0 | 4.389226  | 4.829604  | 2.546736  |
| 63  | 6 | 0 | 3.645513  | 3.420280  | 1.101078  |
| 64  | 1 | 0 | 2.965311  | 2.931276  | 1.794302  |
| 65  | 6 | 0 | 2.326646  | 1.724309  | -2.484643 |
| 66  | 6 | 0 | 2.367073  | 0.610088  | -3.331149 |
| 67  | 1 | 0 | 2.662210  | -0.357082 | -2.937678 |
| 68  | 6 | 0 | 2.028101  | 0.739720  | -4.676774 |
| 69  | 1 | 0 | 2.067168  | -0.130881 | -5.326326 |
| 70  | 6 | 0 | 1.643411  | 1.978845  | -5.188205 |
| 71  | 1 | 0 | 1.381530  | 2.077048  | -6.238714 |
| 72  | 6 | 0 | 1.600741  | 3.093128  | -4.350950 |
| 73  | 1 | 0 | 1.307528  | 4.062874  | -4.745317 |
| 74  | 6 | 0 | 1.938757  | 2.968029  | -3.004222 |
| 75  | 1 | 0 | 1.917320  | 3.846166  | -2.364051 |
| 76  | 6 | 0 | 3.276006  | -3.813090 | -0.629945 |
| 77  | 6 | 0 | 2.296552  | -4.159431 | 0.507499  |
| 78  | 1 | 0 | 2.803380  | -4.127204 | 1.479184  |
| 79  | 1 | 0 | 1.899549  | -5.173184 | 0.366846  |
| 80  | 1 | 0 | 1.454656  | -3.466547 | 0.536794  |
| 81  | 6 | 0 | 2.553220  | -3.888204 | -1.989946 |
| 82  | 1 | 0 | 1.751172  | -3.149957 | -2.050846 |
| 83  | 1 | 0 | 2.117892  | -4.885485 | -2.132765 |
| 84  | 1 | 0 | 3.259337  | -3.709112 | -2.810767 |
| 85  | 6 | 0 | 4.366660  | -4.895910 | -0.631658 |
| 86  | 1 | 0 | 5.099216  | -4.747257 | -1.434363 |
| 87  | 1 | 0 | 3.898407  | -5.873956 | -0.793107 |
| 88  | 1 | 0 | 4.904424  | -4.946193 | 0.323054  |
| 89  | 6 | 0 | 7.360975  | -0.860827 | 0.048309  |
| 90  | 6 | 0 | 7.736002  | -1.571848 | 1.363585  |
| 91  | 1 | 0 | 7.238825  | -1.097933 | 2.217855  |
| 92  | 1 | 0 | 8.820042  | -1.528896 | 1.530595  |
| 93  | 1 | 0 | 7.442538  | -2.627324 | 1.351781  |
| 94  | 6 | 0 | 8.091418  | -1.543009 | -1.125312 |
| 95  | 1 | 0 | 7.814809  | -2.598739 | -1.220634 |
| 96  | 1 | 0 | 9.178340  | -1.496871 | -0.980140 |
| 97  | 1 | 0 | 7.852798  | -1.048811 | -2.074427 |
| 98  | 6 | 0 | 7.851353  | 0.590922  | 0.133858  |
| 99  | 1 | 0 | 7.640470  | 1.147654  | -0.787012 |
| 100 | 1 | 0 | 8.936919  | 0.607053  | 0.287220  |
| 101 | 1 | 0 | 7.391205  | 1.128106  | 0.971509  |
| 102 | 6 | 0 | -7.854804 | -0.628789 | -1.295737 |
| 103 | 1 | 0 | -7.945294 | -1.421754 | -0.543981 |
| 104 | 1 | 0 | -7.615851 | 0.304325  | -0.773048 |
| 105 | 1 | 0 | -8.834870 | -0.498221 | -1.772456 |
| 106 | 6 | 0 | -6.690142 | 0.149785  | -3.381663 |
| 107 | 1 | 0 | -7.658013 | 0.304416  | -3.876059 |
| 108 | 1 | 0 | -6.397325 | 1.097715  | -2.916618 |
| 109 | 1 | 0 | -5.947392 | -0.086484 | -4.152633 |
| 110 | 6 | 0 | -7.244542 | -2.258564 | -3.073343 |
| 111 | 1 | 0 | -6.545032 | -2.552358 | -3.864637 |
| 112 | 1 | 0 | -7.358691 | -3.104699 | -2.385512 |
| 113 | 1 | 0 | -8.219020 | -2.081885 | -3.543870 |
| 114 | 8 | 0 | 0.618466  | -0.930813 | 2.702248  |
| 115 | 6 | 0 | 1.046224  | -1.313322 | 3.976299  |
| 116 | 6 | 0 | 0.499792  | -0.319841 | 5.012781  |
| 117 | 1 | 0 | 0.852645  | 0.693071  | 4.783448  |
| 118 | 1 | 0 | -0.595625 | -0.318387 | 4.986432  |
| 119 | 1 | 0 | 0.821852  | -0.575495 | 6.030273  |

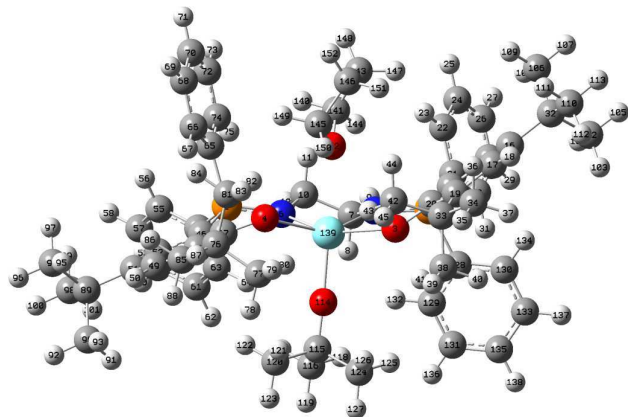
## Appendix 2. Optimised Structures

|     |    |   |           |           |          |
|-----|----|---|-----------|-----------|----------|
| 120 | 6  | 0 | 2.581644  | -1.309252 | 4.017394 |
| 121 | 1  | 0 | 2.979809  | -1.991796 | 3.258554 |
| 122 | 1  | 0 | 2.961319  | -0.304253 | 3.798451 |
| 123 | 1  | 0 | 2.964005  | -1.617901 | 4.998808 |
| 124 | 6  | 0 | 0.517220  | -2.722183 | 4.284070 |
| 125 | 1  | 0 | -0.577753 | -2.730935 | 4.232112 |
| 126 | 1  | 0 | 0.897602  | -3.436243 | 3.544883 |
| 127 | 1  | 0 | 0.820921  | -3.063043 | 5.282170 |
| 128 | 6  | 0 | -3.745219 | 0.807062  | 2.434069 |
| 129 | 6  | 0 | -2.973953 | 1.134365  | 3.553306 |
| 130 | 6  | 0 | -5.026402 | 0.268433  | 2.607158 |
| 131 | 6  | 0 | -3.487107 | 0.943932  | 4.836225 |
| 132 | 1  | 0 | -1.965756 | 1.514934  | 3.420480 |
| 133 | 6  | 0 | -5.535113 | 0.078499  | 3.890218 |
| 134 | 1  | 0 | -5.618399 | -0.016344 | 1.741301 |
| 135 | 6  | 0 | -4.767670 | 0.419362  | 5.004971 |
| 136 | 1  | 0 | -2.880861 | 1.196046  | 5.702271 |
| 137 | 1  | 0 | -6.528079 | -0.344380 | 4.019773 |
| 138 | 1  | 0 | -5.164831 | 0.266162  | 6.005247 |
| 139 | 39 | 0 | 0.134352  | -0.492134 | 0.768348 |

-----  
Rotational constants (GHZ):      0.0461968      0.0242741  
0.0226338

Sum of electronic and zero-point Energies=      -2638.893885  
Sum of electronic and thermal Energies=      -2638.824020  
Sum of electronic and thermal Enthalpies=      -2638.823076  
Sum of electronic and thermal Free Energies=      -2639.003943

|                | 1<br>A | 2<br>A  | 3<br>A |
|----------------|--------|---------|--------|
| Frequencies -- | 9.6572 | 11.8801 |        |
| 15.1770        |        |         |        |
| Red. masses -- | 4.9353 | 4.5005  |        |
| 4.6516         |        |         |        |
| Frc consts --  | 0.0003 | 0.0004  |        |
| 0.0006         |        |         |        |
| IR Inten --    | 0.0316 | 0.0448  |        |
| 0.0863         |        |         |        |

**Complex 45-THF**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 15               | 0              | -2.976916               | 1.314924  | 0.701790  |
| 2                | 15               | 0              | 2.873296                | 1.430304  | -0.621434 |
| 3                | 8                | 0              | -1.879829               | -1.472027 | 0.638844  |
| 4                | 8                | 0              | 1.829646                | -1.459837 | -0.468641 |
| 5                | 7                | 0              | -1.369244               | 1.437699  | 0.415928  |
| 6                | 7                | 0              | 1.337693                | 1.497557  | -0.050877 |
| 7                | 6                | 0              | -0.675855               | 2.713614  | 0.588325  |
| 8                | 1                | 0              | -0.355045               | 2.865458  | 1.632337  |
| 9                | 1                | 0              | -1.297215               | 3.581099  | 0.314352  |
| 10               | 6                | 0              | 0.572720                | 2.718905  | -0.293151 |
| 11               | 1                | 0              | 0.254058                | 2.798846  | -1.346174 |
| 12               | 1                | 0              | 1.144917                | 3.634457  | -0.062635 |
| 13               | 6                | 0              | -3.730100               | -0.156999 | -0.047966 |
| 14               | 6                | 0              | -5.000862               | -0.054829 | -0.627147 |
| 15               | 1                | 0              | -5.445915               | 0.928143  | -0.755729 |
| 16               | 6                | 0              | -5.703088               | -1.186875 | -1.032570 |
| 17               | 6                | 0              | -5.097537               | -2.426035 | -0.768406 |
| 18               | 1                | 0              | -5.647417               | -3.321223 | -1.031215 |
| 19               | 6                | 0              | -3.844691               | -2.589551 | -0.176943 |
| 20               | 6                | 0              | -3.087231               | -1.416648 | 0.148841  |
| 21               | 6                | 0              | -3.857890               | 2.800999  | 0.036630  |
| 22               | 6                | 0              | -3.851135               | 3.012218  | -1.349849 |
| 23               | 1                | 0              | -3.406114               | 2.269319  | -2.005847 |
| 24               | 6                | 0              | -4.426728               | 4.158103  | -1.891898 |
| 25               | 1                | 0              | -4.423405               | 4.306602  | -2.968732 |
| 26               | 6                | 0              | -5.006973               | 5.111812  | -1.053769 |
| 27               | 1                | 0              | -5.455298               | 6.007244  | -1.476671 |
| 28               | 6                | 0              | -5.009222               | 4.913627  | 0.324944  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 29 | 1 | 0 | -5.456692 | 5.654455  | 0.982529  |
| 30 | 6 | 0 | -4.437171 | 3.763132  | 0.869863  |
| 31 | 1 | 0 | -4.445017 | 3.616260  | 1.945615  |
| 32 | 6 | 0 | -7.079973 | -1.045599 | -1.696310 |
| 33 | 6 | 0 | -3.311787 | -3.989732 | 0.171774  |
| 34 | 6 | 0 | -4.314034 | -5.102506 | -0.172826 |
| 35 | 1 | 0 | -3.890860 | -6.069575 | 0.123776  |
| 36 | 1 | 0 | -4.526801 | -5.155013 | -1.247886 |
| 37 | 1 | 0 | -5.264083 | -4.982515 | 0.361558  |
| 38 | 6 | 0 | -3.040481 | -4.066604 | 1.688840  |
| 39 | 1 | 0 | -2.639577 | -5.054721 | 1.950515  |
| 40 | 1 | 0 | -3.969332 | -3.918920 | 2.253410  |
| 41 | 1 | 0 | -2.322518 | -3.304650 | 1.999304  |
| 42 | 6 | 0 | -2.013246 | -4.289643 | -0.599766 |
| 43 | 1 | 0 | -1.238777 | -3.560387 | -0.356694 |
| 44 | 1 | 0 | -2.191084 | -4.270648 | -1.682438 |
| 45 | 1 | 0 | -1.638965 | -5.287859 | -0.337998 |
| 46 | 6 | 0 | 3.758993  | -0.095547 | -0.193012 |
| 47 | 6 | 0 | 3.116943  | -1.367540 | -0.275365 |
| 48 | 6 | 0 | 3.961270  | -2.529403 | -0.167051 |
| 49 | 6 | 0 | 5.310584  | -2.340674 | 0.105830  |
| 50 | 1 | 0 | 5.934328  | -3.222700 | 0.208635  |
| 51 | 6 | 0 | 5.934900  | -1.088105 | 0.259492  |
| 52 | 6 | 0 | 5.132715  | 0.028143  | 0.081999  |
| 53 | 1 | 0 | 5.563959  | 1.019873  | 0.158292  |
| 54 | 6 | 0 | 3.847866  | 2.849226  | 0.056349  |
| 55 | 6 | 0 | 4.854199  | 3.512986  | -0.654188 |
| 56 | 1 | 0 | 5.089422  | 3.216568  | -1.672753 |
| 57 | 6 | 0 | 5.560279  | 4.556532  | -0.055962 |
| 58 | 1 | 0 | 6.342611  | 5.066742  | -0.612140 |
| 59 | 6 | 0 | 5.263433  | 4.943766  | 1.250283  |
| 60 | 1 | 0 | 5.814611  | 5.758094  | 1.713879  |
| 61 | 6 | 0 | 4.259005  | 4.286368  | 1.961380  |
| 62 | 1 | 0 | 4.024594  | 4.586286  | 2.979555  |
| 63 | 6 | 0 | 3.552784  | 3.242782  | 1.367435  |
| 64 | 1 | 0 | 2.765193  | 2.726277  | 1.910446  |
| 65 | 6 | 0 | 2.985544  | 1.633212  | -2.461129 |
| 66 | 6 | 0 | 3.348790  | 0.551882  | -3.271972 |
| 67 | 1 | 0 | 3.642606  | -0.387833 | -2.813180 |
| 68 | 6 | 0 | 3.343783  | 0.681428  | -4.660567 |
| 69 | 1 | 0 | 3.634887  | -0.162754 | -5.280683 |
| 70 | 6 | 0 | 2.976514  | 1.890110  | -5.251212 |
| 71 | 1 | 0 | 2.976952  | 1.990440  | -6.333737 |
| 72 | 6 | 0 | 2.619024  | 2.974524  | -4.449582 |
| 73 | 1 | 0 | 2.342007  | 3.922360  | -4.904419 |
| 74 | 6 | 0 | 2.623294  | 2.848497  | -3.061250 |
| 75 | 1 | 0 | 2.360489  | 3.705404  | -2.446353 |
| 76 | 6 | 0 | 3.392521  | -3.943026 | -0.379661 |
| 77 | 6 | 0 | 2.340005  | -4.277682 | 0.693693  |
| 78 | 1 | 0 | 2.796134  | -4.285939 | 1.690004  |
| 79 | 1 | 0 | 1.915983  | -5.273469 | 0.508337  |
| 80 | 1 | 0 | 1.526598  | -3.550673 | 0.697706  |
| 81 | 6 | 0 | 2.758703  | -4.033050 | -1.782416 |
| 82 | 1 | 0 | 1.972074  | -3.286436 | -1.900744 |
| 83 | 1 | 0 | 2.324902  | -5.029387 | -1.939434 |
| 84 | 1 | 0 | 3.516462  | -3.869949 | -2.559505 |
| 85 | 6 | 0 | 4.476518  | -5.030096 | -0.304021 |
| 86 | 1 | 0 | 5.260658  | -4.887540 | -1.057703 |

## Appendix 2. Optimised Structures

|     |    |   |           |           |           |
|-----|----|---|-----------|-----------|-----------|
| 87  | 1  | 0 | 4.016023  | -6.007627 | -0.490332 |
| 88  | 1  | 0 | 4.950391  | -5.077060 | 0.683901  |
| 89  | 6  | 0 | 7.429436  | -1.010233 | 0.591275  |
| 90  | 6  | 0 | 7.695104  | -1.712002 | 1.937883  |
| 91  | 1  | 0 | 7.137372  | -1.226552 | 2.747045  |
| 92  | 1  | 0 | 8.763243  | -1.675871 | 2.188194  |
| 93  | 1  | 0 | 7.394550  | -2.765207 | 1.912647  |
| 94  | 6  | 0 | 8.245986  | -1.707928 | -0.514674 |
| 95  | 1  | 0 | 7.970687  | -2.763038 | -0.620603 |
| 96  | 1  | 0 | 9.318798  | -1.666304 | -0.286254 |
| 97  | 1  | 0 | 8.084728  | -1.222364 | -1.484413 |
| 98  | 6  | 0 | 7.922311  | 0.438903  | 0.703241  |
| 99  | 1  | 0 | 7.793165  | 0.986918  | -0.237817 |
| 100 | 1  | 0 | 8.991408  | 0.449434  | 0.946640  |
| 101 | 1  | 0 | 7.397324  | 0.988209  | 1.493509  |
| 102 | 6  | 0 | -8.054254 | -0.342382 | -0.730288 |
| 103 | 1  | 0 | -8.165408 | -0.916739 | 0.196829  |
| 104 | 1  | 0 | -7.706549 | 0.661916  | -0.463031 |
| 105 | 1  | 0 | -9.046569 | -0.238268 | -1.188124 |
| 106 | 6  | 0 | -6.950670 | -0.205221 | -2.982149 |
| 107 | 1  | 0 | -7.928494 | -0.085579 | -3.466652 |
| 108 | 1  | 0 | -6.558335 | 0.796343  | -2.773264 |
| 109 | 1  | 0 | -6.273699 | -0.687935 | -3.696969 |
| 110 | 6  | 0 | -7.687097 | -2.403427 | -2.076595 |
| 111 | 1  | 0 | -7.048490 | -2.952992 | -2.778214 |
| 112 | 1  | 0 | -7.854240 | -3.037308 | -1.197906 |
| 113 | 1  | 0 | -8.658305 | -2.250947 | -2.562271 |
| 114 | 8  | 0 | 0.660279  | -0.633127 | 2.462654  |
| 115 | 6  | 0 | 1.115564  | -0.823536 | 3.767037  |
| 116 | 6  | 0 | 1.407168  | 0.541453  | 4.413788  |
| 117 | 1  | 0 | 2.169818  | 1.073364  | 3.833285  |
| 118 | 1  | 0 | 0.501157  | 1.158364  | 4.433211  |
| 119 | 1  | 0 | 1.770518  | 0.434488  | 5.444044  |
| 120 | 6  | 0 | 2.409151  | -1.651948 | 3.749950  |
| 121 | 1  | 0 | 2.218995  | -2.630180 | 3.297073  |
| 122 | 1  | 0 | 3.176023  | -1.145982 | 3.152994  |
| 123 | 1  | 0 | 2.802007  | -1.810500 | 4.762846  |
| 124 | 6  | 0 | 0.042778  | -1.565306 | 4.580051  |
| 125 | 1  | 0 | -0.891844 | -0.993774 | 4.587268  |
| 126 | 1  | 0 | -0.164161 | -2.539445 | 4.122357  |
| 127 | 1  | 0 | 0.360072  | -1.731112 | 5.617976  |
| 128 | 6  | 0 | -3.447189 | 1.263700  | 2.488476  |
| 129 | 6  | 0 | -2.464410 | 1.460116  | 3.460837  |
| 130 | 6  | 0 | -4.771621 | 1.023599  | 2.877274  |
| 131 | 6  | 0 | -2.806195 | 1.439985  | 4.813740  |
| 132 | 1  | 0 | -1.430698 | 1.595502  | 3.159154  |
| 133 | 6  | 0 | -5.109288 | 1.004097  | 4.228088  |
| 134 | 1  | 0 | -5.535578 | 0.839804  | 2.125865  |
| 135 | 6  | 0 | -4.127102 | 1.217354  | 5.197351  |
| 136 | 1  | 0 | -2.035551 | 1.586005  | 5.565978  |
| 137 | 1  | 0 | -6.137593 | 0.814335  | 4.525217  |
| 138 | 1  | 0 | -4.391483 | 1.198061  | 6.251661  |
| 139 | 39 | 0 | 0.087562  | -0.454157 | 0.500638  |
| 140 | 1  | 0 | 0.047229  | 0.909192  | -3.306537 |
| 141 | 6  | 0 | -0.877656 | 0.491061  | -2.883189 |
| 142 | 8  | 0 | -0.546773 | -0.608198 | -2.034936 |
| 143 | 6  | 0 | -1.773924 | -0.102384 | -3.980376 |
| 144 | 1  | 0 | -1.353710 | 1.243200  | -2.254220 |

## Appendix 2. Optimised Structures

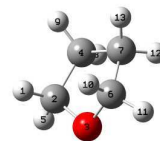
|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 145 | 6 | 0 | -0.299009 | -1.701007 | -2.919720 |
| 146 | 6 | 0 | -1.408563 | -1.606894 | -3.972897 |
| 147 | 1 | 0 | -2.831837 | 0.036229  | -3.738228 |
| 148 | 1 | 0 | -1.585268 | 0.371757  | -4.948846 |
| 149 | 1 | 0 | 0.697378  | -1.580624 | -3.367836 |
| 150 | 1 | 0 | -0.314542 | -2.619769 | -2.333651 |
| 151 | 1 | 0 | -2.270623 | -2.208153 | -3.670181 |
| 152 | 1 | 0 | -1.071016 | -1.967419 | -4.949641 |

Rotational constants (GHz): 0.0435340 0.0226522  
0.0213452

Sum of electronic and zero-point Energies= -2871.141187  
Sum of electronic and thermal Energies= -2871.064825  
Sum of electronic and thermal Enthalpies= -2871.063881  
Sum of electronic and thermal Free Energies= -2871.259119

|                |        |         |   |
|----------------|--------|---------|---|
|                | 1      | 2       | 3 |
|                | A      | A       | A |
| Frequencies -- | 8.8309 | 11.9787 |   |
| 16.4577        |        |         |   |
| Red. masses -- | 4.9587 | 4.3705  |   |
| 5.0753         |        |         |   |
| Frc consts --  | 0.0002 | 0.0004  |   |
| 0.0008         |        |         |   |
| IR Inten --    | 0.0318 | 0.0282  |   |
| 0.1121         |        |         |   |

## THF



Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |           |           |
|---------------|---------------|-------------|-------------------------|-----------|-----------|
|               |               |             | X                       | Y         | Z         |
| 1             | 1             | 0           | -1.334857               | -0.677937 | 1.210686  |
| 2             | 6             | 0           | -1.132251               | -0.459661 | 0.147912  |
| 3             | 8             | 0           | -0.009361               | -1.198963 | -0.297924 |
| 4             | 6             | 0           | -0.761285               | 1.024588  | -0.036518 |
| 5             | 1             | 0           | -1.997988               | -0.779510 | -0.439021 |
| 6             | 6             | 0           | 1.117655                | -0.480453 | 0.169223  |
| 7             | 6             | 0           | 0.786186                | 1.002566  | -0.064685 |
| 8             | 1             | 0           | -1.162015               | 1.414753  | -0.977020 |
| 9             | 1             | 0           | -1.159296               | 1.644355  | 0.773156  |
| 10            | 1             | 0           | 1.279041                | -0.676639 | 1.243699  |
| 11            | 1             | 0           | 1.993907                | -0.835328 | -0.380747 |

## Appendix 2. Optimised Structures

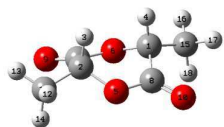
|    |   |   |          |          |           |
|----|---|---|----------|----------|-----------|
| 12 | 1 | 0 | 1.159698 | 1.331102 | -1.039516 |
| 13 | 1 | 0 | 1.234565 | 1.648667 | 0.696559  |

-----  
 Rotational constants (GHZ): 7.1794263 6.9294258  
 4.0047528

Sum of electronic and zero-point Energies= -232.248141  
 Sum of electronic and thermal Energies= -232.243221  
 Sum of electronic and thermal Enthalpies= -232.242276  
 Sum of electronic and thermal Free Energies= -232.277148

|                | 1       | 2        | 3 |
|----------------|---------|----------|---|
|                | A       | A        | A |
| Frequencies -- | 24.1180 | 282.4810 |   |
| 641.6987       |         |          |   |
| Red. masses -- | 1.5904  | 2.0693   |   |
| 2.3129         |         |          |   |
| Frc consts --  | 0.0005  | 0.0973   |   |
| 0.5611         |         |          |   |
| IR Inten --    | 0.0835  | 7.6377   |   |
| 3.3107         |         |          |   |

### (R,R)-LA



Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | 1.254239                | 0.466248  | 0.434192  |
| 2                | 6                | 0              | -1.254215               | -0.466266 | 0.434179  |
| 3                | 1                | 0              | -1.145206               | -0.463895 | 1.530401  |
| 4                | 1                | 0              | 1.145212                | 0.463917  | 1.530407  |
| 5                | 8                | 0              | -0.255738               | -1.349741 | -0.114353 |
| 6                | 8                | 0              | 0.255733                | 1.349744  | -0.114401 |
| 7                | 6                | 0              | -1.035197               | 0.960693  | -0.059221 |
| 8                | 6                | 0              | 1.035184                | -0.960681 | -0.059227 |
| 9                | 8                | 0              | -1.922040               | 1.708168  | -0.377719 |
| 10               | 8                | 0              | 1.922018                | -1.708166 | -0.377744 |
| 11               | 6                | 0              | -2.611609               | -1.010992 | 0.049286  |
| 12               | 1                | 0              | -2.725596               | -2.028734 | 0.431650  |
| 13               | 1                | 0              | -3.395455               | -0.375674 | 0.467474  |
| 14               | 1                | 0              | -2.721384               | -1.022891 | -1.038193 |
| 15               | 6                | 0              | 2.611624                | 1.010983  | 0.049297  |
| 16               | 1                | 0              | 2.725434                | 2.028856  | 0.431365  |

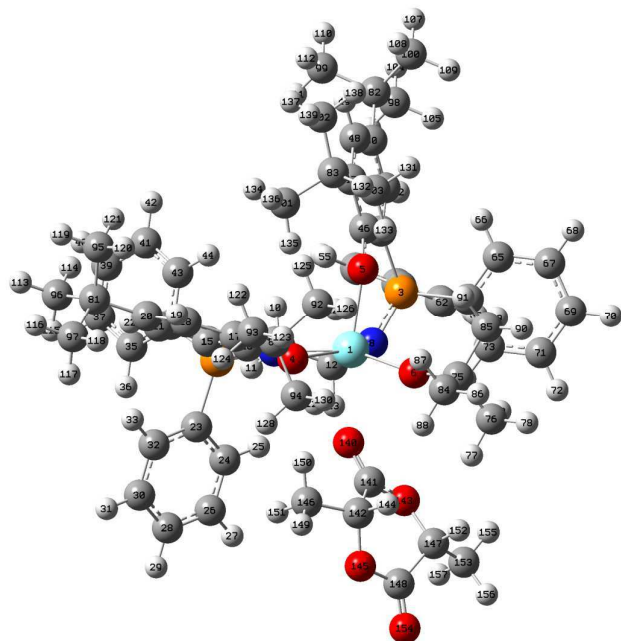
## Appendix 2. Optimised Structures

|    |   |   |          |          |           |
|----|---|---|----------|----------|-----------|
| 17 | 1 | 0 | 3.395530 | 0.375922 | 0.467770  |
| 18 | 1 | 0 | 2.721537 | 1.022552 | -1.038170 |

-----  
 Rotational constants (GHZ): 2.1988369 1.1957833  
 0.8179501

Sum of electronic and zero-point Energies= -534.017663  
 Sum of electronic and thermal Energies= -534.008238  
 Sum of electronic and thermal Enthalpies= -534.007294  
 Sum of electronic and thermal Free Energies= -534.052255

|                | 1       | 2        | 3 |
|----------------|---------|----------|---|
|                | A       | A        | A |
| Frequencies -- | 67.7468 | 131.3422 |   |
| 131.5655       |         |          |   |
| Red. masses -- | 5.1483  | 4.8822   |   |
| 4.7139         |         |          |   |
| Frc consts --  | 0.0139  | 0.0496   |   |
| 0.0481         |         |          |   |
| IR Inten --    | 6.4214  | 0.0079   |   |
| 0.2435         |         |          |   |

**Initiation : INT1**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | 0.017582                | 0.888824  | -0.645241 |
| 2                | 15               | 0              | -2.128598               | -0.922148 | 1.657367  |
| 3                | 15               | 0              | 3.239261                | 0.449173  | 0.654520  |
| 4                | 8                | 0              | -2.001922               | 0.173668  | -1.186908 |
| 5                | 8                | 0              | 1.357614                | -0.682214 | -1.355810 |
| 6                | 8                | 0              | 0.271157                | 2.347033  | -2.118365 |
| 7                | 7                | 0              | -0.670585               | -0.237795 | 1.385647  |
| 8                | 7                | 0              | 1.779582                | 1.112239  | 1.011518  |
| 9                | 6                | 0              | 0.290224                | -0.228704 | 2.495085  |
| 10               | 1                | 0              | 0.899700                | -1.148043 | 2.483660  |
| 11               | 1                | 0              | -0.179270               | -0.186259 | 3.492887  |
| 12               | 6                | 0              | 1.211084                | 0.983498  | 2.351118  |
| 13               | 1                | 0              | 0.618778                | 1.891128  | 2.534282  |
| 14               | 1                | 0              | 1.975929                | 0.944772  | 3.141616  |
| 15               | 6                | 0              | -2.996602               | -1.500170 | 0.172841  |
| 16               | 6                | 0              | -2.859828               | -0.806018 | -1.059463 |
| 17               | 6                | 0              | -3.706375               | -1.228892 | -2.143181 |
| 18               | 6                | 0              | -4.564974               | -2.301006 | -1.927028 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 19 | 1 | 0 | -5.194944 | -2.617536 | -2.751523 |
| 20 | 6 | 0 | -4.676234 | -3.016066 | -0.719814 |
| 21 | 6 | 0 | -3.876276 | -2.585615 | 0.328152  |
| 22 | 1 | 0 | -3.914514 | -3.095920 | 1.285105  |
| 23 | 6 | 0 | -3.298268 | 0.209527  | 2.553060  |
| 24 | 6 | 0 | -2.792216 | 1.371967  | 3.142185  |
| 25 | 1 | 0 | -1.738277 | 1.608602  | 3.034060  |
| 26 | 6 | 0 | -3.641363 | 2.238094  | 3.831670  |
| 27 | 1 | 0 | -3.239626 | 3.138486  | 4.290293  |
| 28 | 6 | 0 | -5.003360 | 1.953528  | 3.925768  |
| 29 | 1 | 0 | -5.665810 | 2.631000  | 4.458640  |
| 30 | 6 | 0 | -5.516522 | 0.803514  | 3.324429  |
| 31 | 1 | 0 | -6.580051 | 0.585954  | 3.382152  |
| 32 | 6 | 0 | -4.668723 | -0.065735 | 2.640102  |
| 33 | 1 | 0 | -5.077110 | -0.949805 | 2.157623  |
| 34 | 6 | 0 | -1.950298 | -2.395798 | 2.758002  |
| 35 | 6 | 0 | -2.545600 | -2.502207 | 4.017928  |
| 36 | 1 | 0 | -3.194967 | -1.712016 | 4.383753  |
| 37 | 6 | 0 | -2.308656 | -3.626437 | 4.810872  |
| 38 | 1 | 0 | -2.776637 | -3.703417 | 5.789030  |
| 39 | 6 | 0 | -1.476580 | -4.644587 | 4.350934  |
| 40 | 1 | 0 | -1.294217 | -5.519623 | 4.969743  |
| 41 | 6 | 0 | -0.875474 | -4.539891 | 3.094827  |
| 42 | 1 | 0 | -0.224004 | -5.331278 | 2.733023  |
| 43 | 6 | 0 | -1.108154 | -3.420244 | 2.301507  |
| 44 | 1 | 0 | -0.637585 | -3.335308 | 1.325019  |
| 45 | 6 | 0 | 3.319652  | -1.196440 | -0.126182 |
| 46 | 6 | 0 | 2.319848  | -1.526544 | -1.082929 |
| 47 | 6 | 0 | 2.436257  | -2.799488 | -1.739583 |
| 48 | 6 | 0 | 3.511512  | -3.614921 | -1.403248 |
| 49 | 1 | 0 | 3.590862  | -4.574279 | -1.903837 |
| 50 | 6 | 0 | 4.512561  | -3.288291 | -0.468950 |
| 51 | 6 | 0 | 4.393409  | -2.056812 | 0.159045  |
| 52 | 1 | 0 | 5.139774  | -1.742133 | 0.880101  |
| 53 | 6 | 0 | 4.312831  | 0.349251  | 2.158236  |
| 54 | 6 | 0 | 4.107487  | -0.677715 | 3.091668  |
| 55 | 1 | 0 | 3.376657  | -1.455872 | 2.888449  |
| 56 | 6 | 0 | 4.848408  | -0.717002 | 4.270810  |
| 57 | 1 | 0 | 4.680375  | -1.518368 | 4.985696  |
| 58 | 6 | 0 | 5.802640  | 0.267100  | 4.530579  |
| 59 | 1 | 0 | 6.382909  | 0.233757  | 5.449186  |
| 60 | 6 | 0 | 6.011351  | 1.290465  | 3.608327  |
| 61 | 1 | 0 | 6.756752  | 2.057352  | 3.802765  |
| 62 | 6 | 0 | 5.269257  | 1.333780  | 2.428217  |
| 63 | 1 | 0 | 5.441987  | 2.133968  | 1.714908  |
| 64 | 6 | 0 | 4.096166  | 1.616573  | -0.478546 |
| 65 | 6 | 0 | 5.047930  | 1.164890  | -1.398128 |
| 66 | 1 | 0 | 5.229754  | 0.099463  | -1.508696 |
| 67 | 6 | 0 | 5.751290  | 2.082203  | -2.177314 |
| 68 | 1 | 0 | 6.485252  | 1.728292  | -2.896618 |
| 69 | 6 | 0 | 5.511273  | 3.449048  | -2.036620 |
| 70 | 1 | 0 | 6.062547  | 4.162613  | -2.643953 |
| 71 | 6 | 0 | 4.556978  | 3.900411  | -1.124093 |
| 72 | 1 | 0 | 4.362628  | 4.965112  | -1.021698 |
| 73 | 6 | 0 | 3.843550  | 2.986723  | -0.349634 |
| 74 | 1 | 0 | 3.079348  | 3.317392  | 0.348540  |
| 75 | 6 | 0 | 0.589660  | 3.094461  | -3.249782 |
| 76 | 6 | 0 | 0.956869  | 4.529510  | -2.833546 |



## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 77  | 1 | 0 | 0.095067  | 5.010583  | -2.350936 |
| 78  | 1 | 0 | 1.247749  | 5.146664  | -3.693174 |
| 79  | 1 | 0 | 1.785616  | 4.509748  | -2.118398 |
| 80  | 6 | 0 | -3.668974 | -0.517201 | -3.506247 |
| 81  | 6 | 0 | -5.644778 | -4.199777 | -0.613105 |
| 82  | 6 | 0 | 5.657780  | -4.269368 | -0.190526 |
| 83  | 6 | 0 | 1.413767  | -3.240814 | -2.797451 |
| 84  | 6 | 0 | -0.616464 | 3.140585  | -4.201547 |
| 85  | 6 | 0 | 1.786392  | 2.455303  | -3.972155 |
| 86  | 1 | 0 | -0.406570 | 3.736877  | -5.099082 |
| 87  | 1 | 0 | -0.889288 | 2.127669  | -4.514093 |
| 88  | 1 | 0 | -1.485057 | 3.578143  | -3.693523 |
| 89  | 1 | 0 | 2.651535  | 2.415131  | -3.301914 |
| 90  | 1 | 0 | 2.067713  | 3.014548  | -4.874215 |
| 91  | 1 | 0 | 1.538718  | 1.428782  | -4.264455 |
| 92  | 6 | 0 | -2.280269 | -0.685255 | -4.150580 |
| 93  | 6 | 0 | -4.702443 | -1.082606 | -4.493582 |
| 94  | 6 | 0 | -3.981233 | 0.981118  | -3.328932 |
| 95  | 6 | 0 | -5.262433 | -5.277021 | -1.647384 |
| 96  | 6 | 0 | -5.617966 | -4.846738 | 0.778446  |
| 97  | 6 | 0 | -7.083069 | -3.718845 | -0.889866 |
| 98  | 6 | 0 | 6.648495  | -3.723507 | 0.846773  |
| 99  | 6 | 0 | 5.083282  | -5.594753 | 0.347950  |
| 100 | 6 | 0 | 6.435369  | -4.545919 | -1.492426 |
| 101 | 6 | 0 | 0.014541  | -3.335527 | -2.160066 |
| 102 | 6 | 0 | 1.738231  | -4.621576 | -3.389714 |
| 103 | 6 | 0 | 1.404875  | -2.233261 | -3.964710 |
| 104 | 1 | 0 | 7.446312  | -4.455759 | 1.018512  |
| 105 | 1 | 0 | 7.121295  | -2.793879 | 0.508252  |
| 106 | 1 | 0 | 6.165193  | -3.528343 | 1.811375  |
| 107 | 1 | 0 | 7.258357  | -5.248770 | -1.308511 |
| 108 | 1 | 0 | 5.793551  | -4.981472 | -2.266003 |
| 109 | 1 | 0 | 6.862111  | -3.620186 | -1.895851 |
| 110 | 1 | 0 | 5.889355  | -6.311696 | 0.551060  |
| 111 | 1 | 0 | 4.531108  | -5.429797 | 1.280723  |
| 112 | 1 | 0 | 4.396757  | -6.060011 | -0.367828 |
| 113 | 1 | 0 | -6.319423 | -5.688929 | 0.809875  |
| 114 | 1 | 0 | -4.623721 | -5.234732 | 1.029161  |
| 115 | 1 | 0 | -5.917008 | -4.140842 | 1.562777  |
| 116 | 1 | 0 | -7.789089 | -4.557034 | -0.828524 |
| 117 | 1 | 0 | -7.389179 | -2.961110 | -0.158901 |
| 118 | 1 | 0 | -7.178750 | -3.276133 | -1.887247 |
| 119 | 1 | 0 | -5.953809 | -6.127823 | -1.591696 |
| 120 | 1 | 0 | -5.295477 | -4.887696 | -2.670778 |
| 121 | 1 | 0 | -4.247576 | -5.649290 | -1.465602 |
| 122 | 1 | 0 | -4.522716 | -2.139453 | -4.724984 |
| 123 | 1 | 0 | -4.635008 | -0.527486 | -5.436638 |
| 124 | 1 | 0 | -5.729982 | -0.978418 | -4.123894 |
| 125 | 1 | 0 | -2.061091 | -1.744483 | -4.327378 |
| 126 | 1 | 0 | -2.249112 | -0.168000 | -5.118562 |
| 127 | 1 | 0 | -1.495273 | -0.272423 | -3.514792 |
| 128 | 1 | 0 | -4.972384 | 1.120917  | -2.879198 |
| 129 | 1 | 0 | -3.233810 | 1.457465  | -2.693154 |
| 130 | 1 | 0 | -3.977777 | 1.483856  | -4.304778 |
| 131 | 1 | 0 | 2.387236  | -2.203837 | -4.452717 |
| 132 | 1 | 0 | 0.663575  | -2.532613 | -4.716634 |
| 133 | 1 | 0 | 1.162630  | -1.227362 | -3.617784 |
| 134 | 1 | 0 | 0.008305  | -4.089109 | -1.362187 |

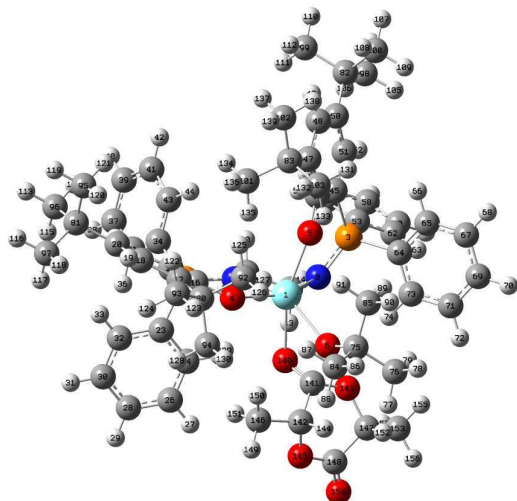
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 135 | 1 | 0 | -0.299672 | -2.380312 | -1.736929 |
| 136 | 1 | 0 | -0.727003 | -3.637717 | -2.910172 |
| 137 | 1 | 0 | 1.727880  | -5.412725 | -2.629776 |
| 138 | 1 | 0 | 2.712008  | -4.638716 | -3.894223 |
| 139 | 1 | 0 | 0.977557  | -4.876951 | -4.136864 |
| 140 | 8 | 0 | -0.939918 | 2.875589  | 0.585829  |
| 141 | 6 | 0 | -1.220340 | 4.044878  | 0.431638  |
| 142 | 6 | 0 | -2.506540 | 4.524246  | -0.221088 |
| 143 | 8 | 0 | -0.385362 | 4.993507  | 0.855103  |
| 144 | 1 | 0 | -2.260793 | 4.776306  | -1.264307 |
| 145 | 8 | 0 | -2.994773 | 5.711997  | 0.437792  |
| 146 | 6 | 0 | -3.611959 | 3.492785  | -0.178234 |
| 147 | 6 | 0 | -0.662431 | 6.364315  | 0.478834  |
| 148 | 6 | 0 | -2.127143 | 6.697954  | 0.734867  |
| 149 | 1 | 0 | -4.491038 | 3.881708  | -0.698793 |
| 150 | 1 | 0 | -3.283689 | 2.570981  | -0.662694 |
| 151 | 1 | 0 | -3.879605 | 3.265026  | 0.856857  |
| 152 | 1 | 0 | -0.471351 | 6.452823  | -0.600314 |
| 153 | 6 | 0 | 0.283080  | 7.252980  | 1.254091  |
| 154 | 8 | 0 | -2.507571 | 7.754151  | 1.167765  |
| 155 | 1 | 0 | 1.318146  | 6.986217  | 1.024977  |
| 156 | 1 | 0 | 0.108291  | 8.295602  | 0.979489  |
| 157 | 1 | 0 | 0.113469  | 7.147774  | 2.329077  |

-----  
Rotational constants (GHZ):      0.0290047      0.0251375  
0.0200209

Sum of electronic and zero-point Energies=      -3172.904876  
Sum of electronic and thermal Energies=      -3172.823590  
Sum of electronic and thermal Enthalpies=      -3172.822646  
Sum of electronic and thermal Free Energies=      -3173.028573

|                | 1<br>A | 2<br>A  | 3<br>A |
|----------------|--------|---------|--------|
| Frequencies -- | 8.7438 | 12.8063 |        |
| 13.3140        |        |         |        |
| Red. masses -- | 4.7748 | 5.6960  |        |
| 5.3789         |        |         |        |
| Frc consts --  | 0.0002 | 0.0006  |        |
| 0.0006         |        |         |        |
| IR Inten --    | 0.0481 | 0.1189  |        |
| 0.1216         |        |         |        |

*Intitiation TS1*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | 0.165743                | 0.981483  | -0.441731 |
| 2                | 15               | 0              | -2.355979               | -0.275323 | 1.731502  |
| 3                | 15               | 0              | 3.105326                | -0.595413 | 0.641867  |
| 4                | 8                | 0              | -1.928837               | 0.824687  | -1.070582 |
| 5                | 8                | 0              | 1.029264                | -0.775642 | -1.450449 |
| 6                | 8                | 0              | 0.783152                | 2.943333  | -1.545788 |
| 7                | 7                | 0              | -0.760331               | 0.010707  | 1.484442  |
| 8                | 7                | 0              | 1.940741                | 0.471657  | 1.066950  |
| 9                | 6                | 0              | 0.136432                | -0.221941 | 2.626043  |
| 10               | 1                | 0              | 0.379229                | -1.294042 | 2.708582  |
| 11               | 1                | 0              | -0.301433               | 0.073269  | 3.594848  |
| 12               | 6                | 0              | 1.426325                | 0.579097  | 2.428641  |
| 13               | 1                | 0              | 1.208504                | 1.640378  | 2.602604  |
| 14               | 1                | 0              | 2.154968                | 0.271025  | 3.192924  |
| 15               | 6                | 0              | -3.317749               | -0.595905 | 0.227020  |
| 16               | 6                | 0              | -3.024020               | 0.109070  | -0.970321 |
| 17               | 6                | 0              | -3.978158               | 0.005948  | -2.039301 |
| 18               | 6                | 0              | -5.065409               | -0.844462 | -1.867938 |
| 19               | 1                | 0              | -5.770802               | -0.930195 | -2.687478 |
| 20               | 6                | 0              | -5.322889               | -1.601805 | -0.710923 |
| 21               | 6                | 0              | -4.435282               | -1.439530 | 0.342812  |
| 22               | 1                | 0              | -4.593546               | -1.977455 | 1.271810  |
| 23               | 6                | 0              | -3.187233               | 1.129848  | 2.602471  |
| 24               | 6                | 0              | -2.421373               | 2.248784  | 2.941154  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 25 | 1 | 0 | -1.368740 | 2.277693  | 2.675972  |
| 26 | 6 | 0 | -3.021520 | 3.339287  | 3.572715  |
| 27 | 1 | 0 | -2.421959 | 4.209239  | 3.828218  |
| 28 | 6 | 0 | -4.384682 | 3.317239  | 3.861546  |
| 29 | 1 | 0 | -4.851341 | 4.168781  | 4.350408  |
| 30 | 6 | 0 | -5.155190 | 2.206952  | 3.510314  |
| 31 | 1 | 0 | -6.221595 | 2.193674  | 3.721012  |
| 32 | 6 | 0 | -4.560933 | 1.117274  | 2.878652  |
| 33 | 1 | 0 | -5.169866 | 0.265014  | 2.587548  |
| 34 | 6 | 0 | -2.570292 | -1.751612 | 2.818334  |
| 35 | 6 | 0 | -3.083386 | -1.679913 | 4.116165  |
| 36 | 1 | 0 | -3.436887 | -0.732039 | 4.511179  |
| 37 | 6 | 0 | -3.143137 | -2.826833 | 4.909502  |
| 38 | 1 | 0 | -3.546506 | -2.763619 | 5.916897  |
| 39 | 6 | 0 | -2.687003 | -4.045816 | 4.413072  |
| 40 | 1 | 0 | -2.735758 | -4.938131 | 5.032109  |
| 41 | 6 | 0 | -2.164549 | -4.120432 | 3.120255  |
| 42 | 1 | 0 | -1.804708 | -5.068955 | 2.729896  |
| 43 | 6 | 0 | -2.103387 | -2.979103 | 2.325717  |
| 44 | 1 | 0 | -1.694546 | -3.036528 | 1.319939  |
| 45 | 6 | 0 | 2.620519  | -2.088528 | -0.279667 |
| 46 | 6 | 0 | 1.610369  | -1.942205 | -1.268777 |
| 47 | 6 | 0 | 1.290252  | -3.106127 | -2.047189 |
| 48 | 6 | 0 | 1.988515  | -4.281790 | -1.785611 |
| 49 | 1 | 0 | 1.740416  | -5.155393 | -2.379056 |
| 50 | 6 | 0 | 2.995962  | -4.428032 | -0.815463 |
| 51 | 6 | 0 | 3.299440  | -3.298771 | -0.067950 |
| 52 | 1 | 0 | 4.074685  | -3.339518 | 0.689605  |
| 53 | 6 | 0 | 4.065708  | -1.168903 | 2.110541  |
| 54 | 6 | 0 | 3.498868  | -2.108457 | 2.984647  |
| 55 | 1 | 0 | 2.533640  | -2.551382 | 2.753870  |
| 56 | 6 | 0 | 4.173505  | -2.487708 | 4.142870  |
| 57 | 1 | 0 | 3.725461  | -3.217206 | 4.812567  |
| 58 | 6 | 0 | 5.418490  | -1.932917 | 4.440989  |
| 59 | 1 | 0 | 5.944580  | -2.230851 | 5.344334  |
| 60 | 6 | 0 | 5.985844  | -0.997434 | 3.578201  |
| 61 | 1 | 0 | 6.956380  | -0.563605 | 3.804470  |
| 62 | 6 | 0 | 5.312683  | -0.614599 | 2.418093  |
| 63 | 1 | 0 | 5.763022  | 0.114724  | 1.751438  |
| 64 | 6 | 0 | 4.315599  | 0.283627  | -0.430822 |
| 65 | 6 | 0 | 5.123680  | -0.423572 | -1.328532 |
| 66 | 1 | 0 | 4.992053  | -1.495737 | -1.446822 |
| 67 | 6 | 0 | 6.087425  | 0.249958  | -2.076288 |
| 68 | 1 | 0 | 6.710389  | -0.300873 | -2.776286 |
| 69 | 6 | 0 | 6.249630  | 1.627799  | -1.927759 |
| 70 | 1 | 0 | 7.003727  | 2.151850  | -2.509814 |
| 71 | 6 | 0 | 5.439728  | 2.333760  | -1.038311 |
| 72 | 1 | 0 | 5.562606  | 3.408309  | -0.929075 |
| 73 | 6 | 0 | 4.467037  | 1.667170  | -0.292390 |
| 74 | 1 | 0 | 3.808099  | 2.208589  | 0.381175  |
| 75 | 6 | 0 | 1.228878  | 3.269197  | -2.859301 |
| 76 | 6 | 0 | 2.387793  | 4.273260  | -2.828280 |
| 77 | 1 | 0 | 2.051340  | 5.265190  | -2.505507 |
| 78 | 1 | 0 | 2.818178  | 4.393352  | -3.829556 |
| 79 | 1 | 0 | 3.175014  | 3.926699  | -2.152470 |
| 80 | 6 | 0 | -3.835565 | 0.845283  | -3.320177 |
| 81 | 6 | 0 | -6.541109 | -2.531021 | -0.653138 |
| 82 | 6 | 0 | 3.694370  | -5.779487 | -0.625205 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 83  | 6 | 0 | 0.213850  | -3.069715 | -3.141572 |
| 84  | 6 | 0 | 0.068797  | 3.839070  | -3.688500 |
| 85  | 6 | 0 | 1.722616  | 1.974043  | -3.516483 |
| 86  | 1 | 0 | 0.380404  | 4.030596  | -4.722932 |
| 87  | 1 | 0 | -0.766870 | 3.132435  | -3.707073 |
| 88  | 1 | 0 | -0.296979 | 4.785167  | -3.273421 |
| 89  | 1 | 0 | 2.546060  | 1.535610  | -2.943006 |
| 90  | 1 | 0 | 2.074947  | 2.159782  | -4.538746 |
| 91  | 1 | 0 | 0.914406  | 1.236790  | -3.577146 |
| 92  | 6 | 0 | -2.539190 | 0.487801  | -4.069696 |
| 93  | 6 | 0 | -4.999564 | 0.629833  | -4.300710 |
| 94  | 6 | 0 | -3.828861 | 2.338404  | -2.939097 |
| 95  | 6 | 0 | -6.443947 | -3.580573 | -1.777780 |
| 96  | 6 | 0 | -6.638447 | -3.276638 | 0.684766  |
| 97  | 6 | 0 | -7.831620 | -1.707862 | -0.836573 |
| 98  | 6 | 0 | 4.767576  | -5.725632 | 0.470501  |
| 99  | 6 | 0 | 2.655716  | -6.845838 | -0.224231 |
| 100 | 6 | 0 | 4.375375  | -6.204465 | -1.940987 |
| 101 | 6 | 0 | -1.145824 | -2.719556 | -2.510782 |
| 102 | 6 | 0 | 0.048686  | -4.420113 | -3.856530 |
| 103 | 6 | 0 | 0.596404  | -2.030657 | -4.213397 |
| 104 | 1 | 0 | 5.239429  | -6.709600 | 0.577104  |
| 105 | 1 | 0 | 5.558519  | -5.004725 | 0.231414  |
| 106 | 1 | 0 | 4.342958  | -5.455081 | 1.444492  |
| 107 | 1 | 0 | 4.870219  | -7.176901 | -1.821895 |
| 108 | 1 | 0 | 3.655491  | -6.296184 | -2.761586 |
| 109 | 1 | 0 | 5.132789  | -5.471628 | -2.243060 |
| 110 | 1 | 0 | 3.137387  | -7.823373 | -0.092580 |
| 111 | 1 | 0 | 2.166195  | -6.577422 | 0.719416  |
| 112 | 1 | 0 | 1.874718  | -6.959609 | -0.984122 |
| 113 | 1 | 0 | -7.512669 | -3.938293 | 0.677227  |
| 114 | 1 | 0 | -5.754309 | -3.897753 | 0.870665  |
| 115 | 1 | 0 | -6.756096 | -2.587394 | 1.529711  |
| 116 | 1 | 0 | -8.713309 | -2.360663 | -0.801222 |
| 117 | 1 | 0 | -7.931585 | -0.956491 | -0.044519 |
| 118 | 1 | 0 | -7.846424 | -1.182005 | -1.797424 |
| 119 | 1 | 0 | -7.313897 | -4.249621 | -1.756992 |
| 120 | 1 | 0 | -6.407521 | -3.113162 | -2.767791 |
| 121 | 1 | 0 | -5.540532 | -4.191030 | -1.664665 |
| 122 | 1 | 0 | -5.056026 | -0.405683 | -4.657664 |
| 123 | 1 | 0 | -4.849232 | 1.269566  | -5.178397 |
| 124 | 1 | 0 | -5.967712 | 0.898589  | -3.861435 |
| 125 | 1 | 0 | -2.561639 | -0.553834 | -4.408550 |
| 126 | 1 | 0 | -2.427823 | 1.127498  | -4.955161 |
| 127 | 1 | 0 | -1.662681 | 0.618339  | -3.432976 |
| 128 | 1 | 0 | -4.776128 | 2.621076  | -2.463711 |
| 129 | 1 | 0 | -3.017539 | 2.554141  | -2.242062 |
| 130 | 1 | 0 | -3.700045 | 2.960342  | -3.834709 |
| 131 | 1 | 0 | 1.532697  | -2.316793 | -4.708908 |
| 132 | 1 | 0 | -0.186429 | -1.968280 | -4.980073 |
| 133 | 1 | 0 | 0.731278  | -1.042740 | -3.771321 |
| 134 | 1 | 0 | -1.425315 | -3.470527 | -1.761317 |
| 135 | 1 | 0 | -1.124557 | -1.742307 | -2.027230 |
| 136 | 1 | 0 | -1.931011 | -2.705370 | -3.276632 |
| 137 | 1 | 0 | -0.271052 | -5.216042 | -3.172827 |
| 138 | 1 | 0 | 0.970110  | -4.741929 | -4.356939 |
| 139 | 1 | 0 | -0.724925 | -4.322296 | -4.627149 |
| 140 | 8 | 0 | 0.100496  | 2.976513  | 0.744530  |

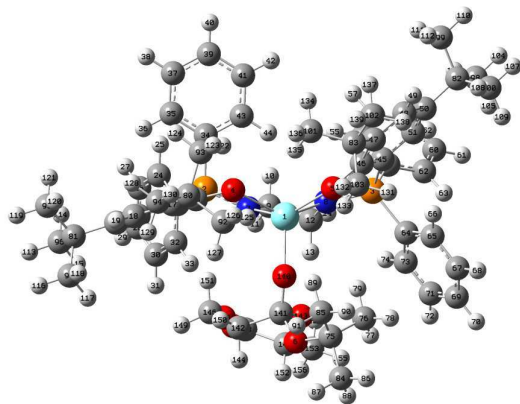
## Appendix 2. Optimised Structures

|     |   |   |           |          |           |
|-----|---|---|-----------|----------|-----------|
| 141 | 6 | 0 | 0.613319  | 3.917796 | 0.092331  |
| 142 | 6 | 0 | -0.223570 | 5.126930 | -0.332471 |
| 143 | 8 | 0 | 1.895162  | 4.253320 | 0.433886  |
| 144 | 1 | 0 | 0.178825  | 5.550848 | -1.257391 |
| 145 | 8 | 0 | -0.084751 | 6.128281 | 0.710947  |
| 146 | 6 | 0 | -1.695733 | 4.835239 | -0.468778 |
| 147 | 6 | 0 | 2.265300  | 5.638902 | 0.409505  |
| 148 | 6 | 0 | 1.167597  | 6.485392 | 1.051557  |
| 149 | 1 | 0 | -2.234149 | 5.756881 | -0.709828 |
| 150 | 1 | 0 | -1.853217 | 4.109395 | -1.267829 |
| 151 | 1 | 0 | -2.089377 | 4.417624 | 0.460590  |
| 152 | 1 | 0 | 2.381684  | 5.971163 | -0.632620 |
| 153 | 6 | 0 | 3.585352  | 5.777763 | 1.137645  |
| 154 | 8 | 0 | 1.372762  | 7.403173 | 1.805722  |
| 155 | 1 | 0 | 4.354079  | 5.182961 | 0.636691  |
| 156 | 1 | 0 | 3.891900  | 6.826346 | 1.149028  |
| 157 | 1 | 0 | 3.487179  | 5.435999 | 2.171558  |

-----  
Rotational constants (GHz):      0.0295061      0.0259839  
0.0206903

Sum of electronic and zero-point Energies=      -3172.890542  
Sum of electronic and thermal Energies=      -3172.811164  
Sum of electronic and thermal Enthalpies=      -3172.810220  
Sum of electronic and thermal Free Energies=      -3173.007842

|                | 1         | 2       | 3 |
|----------------|-----------|---------|---|
|                | A         | A       | A |
| Frequencies -- | -160.6767 | 13.0077 |   |
| 13.9389        |           |         |   |
| Red. masses -- | 8.1828    | 5.1629  |   |
| 4.4952         |           |         |   |
| Frc consts --  | 0.1245    | 0.0005  |   |
| 0.0005         |           |         |   |
| IR Inten --    | 64.6273   | 0.0448  |   |
| 0.0748         |           |         |   |

*Initiation INT2*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.046787               | 0.259134  | -0.492984 |
| 2                | 15               | 0              | -2.460002               | -1.221958 | 1.515114  |
| 3                | 15               | 0              | 3.097951                | 0.320632  | 1.202916  |
| 4                | 8                | 0              | -1.538208               | -1.142025 | -1.275216 |
| 5                | 8                | 0              | 1.789081                | -0.328037 | -1.488570 |
| 6                | 8                | 0              | -0.811559               | 4.401457  | -1.865901 |
| 7                | 7                | 0              | -1.181206               | -0.187158 | 1.504742  |
| 8                | 7                | 0              | 1.464860                | 0.273841  | 1.319330  |
| 9                | 6                | 0              | -0.466666               | 0.011268  | 2.769519  |
| 10               | 1                | 0              | -0.160734               | -0.941930 | 3.233110  |
| 11               | 1                | 0              | -1.080467               | 0.544312  | 3.510808  |
| 12               | 6                | 0              | 0.790305                | 0.835893  | 2.493709  |
| 13               | 1                | 0              | 0.493563                | 1.879828  | 2.310125  |
| 14               | 1                | 0              | 1.415455                | 0.829380  | 3.400704  |
| 15               | 6                | 0              | -3.501929               | -1.075927 | 0.042064  |
| 16               | 6                | 0              | -2.855404               | -1.170568 | -1.217653 |
| 17               | 6                | 0              | -3.687196               | -1.305647 | -2.375138 |
| 18               | 6                | 0              | -5.066620               | -1.242293 | -2.190037 |
| 19               | 1                | 0              | -5.695944               | -1.323188 | -3.069969 |
| 20               | 6                | 0              | -5.712094               | -1.085262 | -0.949524 |
| 21               | 6                | 0              | -4.896569               | -1.026783 | 0.173168  |
| 22               | 1                | 0              | -5.327246               | -0.936632 | 1.164492  |
| 23               | 6                | 0              | -3.505678               | -0.914460 | 2.996972  |
| 24               | 6                | 0              | -3.853026               | -1.903634 | 3.922685  |
| 25               | 1                | 0              | -3.531531               | -2.930203 | 3.775317  |
| 26               | 6                | 0              | -4.606271               | -1.570186 | 5.048253  |
| 27               | 1                | 0              | -4.874762               | -2.343180 | 5.763879  |
| 28               | 6                | 0              | -5.005801               | -0.251183 | 5.258005  |
| 29               | 1                | 0              | -5.588928               | 0.005749  | 6.138934  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 30 | 6 | 0 | -4.647354 | 0.740504  | 4.344179  |
| 31 | 1 | 0 | -4.934861 | 1.775269  | 4.507292  |
| 32 | 6 | 0 | -3.898630 | 0.414482  | 3.216129  |
| 33 | 1 | 0 | -3.607779 | 1.198803  | 2.522519  |
| 34 | 6 | 0 | -1.945043 | -2.997666 | 1.562597  |
| 35 | 6 | 0 | -2.894024 | -4.025274 | 1.489388  |
| 36 | 1 | 0 | -3.952978 | -3.786275 | 1.427454  |
| 37 | 6 | 0 | -2.483440 | -5.356220 | 1.466797  |
| 38 | 1 | 0 | -3.224602 | -6.149110 | 1.407359  |
| 39 | 6 | 0 | -1.123687 | -5.668878 | 1.502694  |
| 40 | 1 | 0 | -0.804454 | -6.707681 | 1.476855  |
| 41 | 6 | 0 | -0.175460 | -4.648494 | 1.553707  |
| 42 | 1 | 0 | 0.884882  | -4.888191 | 1.559043  |
| 43 | 6 | 0 | -0.584218 | -3.315082 | 1.582433  |
| 44 | 1 | 0 | 0.151930  | -2.515338 | 1.591700  |
| 45 | 6 | 0 | 3.701000  | -0.745513 | -0.134714 |
| 46 | 6 | 0 | 2.967415  | -0.888187 | -1.343568 |
| 47 | 6 | 0 | 3.578099  | -1.653607 | -2.393912 |
| 48 | 6 | 0 | 4.821570  | -2.227135 | -2.150448 |
| 49 | 1 | 0 | 5.272872  | -2.809821 | -2.946256 |
| 50 | 6 | 0 | 5.541584  | -2.112300 | -0.946961 |
| 51 | 6 | 0 | 4.955883  | -1.350653 | 0.052414  |
| 52 | 1 | 0 | 5.464541  | -1.216379 | 1.001112  |
| 53 | 6 | 0 | 3.856430  | -0.286988 | 2.775942  |
| 54 | 6 | 0 | 3.263958  | -1.399711 | 3.386963  |
| 55 | 1 | 0 | 2.380689  | -1.846961 | 2.939239  |
| 56 | 6 | 0 | 3.798158  | -1.923416 | 4.561178  |
| 57 | 1 | 0 | 3.330483  | -2.785119 | 5.030451  |
| 58 | 6 | 0 | 4.929469  | -1.340674 | 5.134107  |
| 59 | 1 | 0 | 5.346353  | -1.749203 | 6.051113  |
| 60 | 6 | 0 | 5.523025  | -0.233318 | 4.531042  |
| 61 | 1 | 0 | 6.403423  | 0.223887  | 4.975130  |
| 62 | 6 | 0 | 4.988374  | 0.295237  | 3.355691  |
| 63 | 1 | 0 | 5.454110  | 1.160152  | 2.892499  |
| 64 | 6 | 0 | 3.843895  | 1.994584  | 0.954805  |
| 65 | 6 | 0 | 4.674051  | 2.256830  | -0.140112 |
| 66 | 1 | 0 | 4.892989  | 1.467228  | -0.853099 |
| 67 | 6 | 0 | 5.219998  | 3.528240  | -0.316706 |
| 68 | 1 | 0 | 5.863611  | 3.722903  | -1.170663 |
| 69 | 6 | 0 | 4.941788  | 4.543184  | 0.596572  |
| 70 | 1 | 0 | 5.369155  | 5.533024  | 0.458044  |
| 71 | 6 | 0 | 4.112456  | 4.288027  | 1.689739  |
| 72 | 1 | 0 | 3.892154  | 5.076666  | 2.404508  |
| 73 | 6 | 0 | 3.564296  | 3.020792  | 1.868901  |
| 74 | 1 | 0 | 2.924012  | 2.832880  | 2.726460  |
| 75 | 6 | 0 | 0.385106  | 4.479302  | -2.671764 |
| 76 | 6 | 0 | 1.665106  | 4.243289  | -1.870505 |
| 77 | 1 | 0 | 1.725299  | 4.925497  | -1.017919 |
| 78 | 1 | 0 | 2.534455  | 4.417192  | -2.516060 |
| 79 | 1 | 0 | 1.718042  | 3.220266  | -1.493615 |
| 80 | 6 | 0 | -3.084685 | -1.563237 | -3.765450 |
| 81 | 6 | 0 | -7.242142 | -1.008881 | -0.883614 |
| 82 | 6 | 0 | 6.896758  | -2.812022 | -0.791497 |
| 83 | 6 | 0 | 2.882130  | -1.832868 | -3.752126 |
| 84 | 6 | 0 | 0.355806  | 5.920794  | -3.186615 |
| 85 | 6 | 0 | 0.282837  | 3.508057  | -3.851629 |
| 86 | 1 | 0 | 1.196263  | 6.104778  | -3.865494 |
| 87 | 1 | 0 | -0.576246 | 6.113568  | -3.728864 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 88  | 1 | 0 | 0.419915  | 6.627894  | -2.352461 |
| 89  | 1 | 0 | 0.278567  | 2.473583  | -3.504601 |
| 90  | 1 | 0 | 1.128938  | 3.647708  | -4.535696 |
| 91  | 1 | 0 | -0.642144 | 3.690169  | -4.410453 |
| 92  | 6 | 0 | -2.163185 | -0.404848 | -4.192974 |
| 93  | 6 | 0 | -2.287934 | -2.882743 | -3.720979 |
| 94  | 6 | 0 | -4.161253 | -1.710227 | -4.852261 |
| 95  | 6 | 0 | -7.853120 | -2.302642 | -1.457449 |
| 96  | 6 | 0 | -7.749435 | -0.838830 | 0.554854  |
| 97  | 6 | 0 | -7.734718 | 0.195767  | -1.709621 |
| 98  | 6 | 0 | 7.521307  | -2.563551 | 0.588320  |
| 99  | 6 | 0 | 6.713412  | -4.332595 | -0.966374 |
| 100 | 6 | 0 | 7.877311  | -2.291924 | -1.861184 |
| 101 | 6 | 0 | 1.552692  | -2.586873 | -3.563063 |
| 102 | 6 | 0 | 3.729381  | -2.647683 | -4.742664 |
| 103 | 6 | 0 | 2.628070  | -0.455604 | -4.398326 |
| 104 | 1 | 0 | 8.483162  | -3.084851 | 0.658418  |
| 105 | 1 | 0 | 7.710553  | -1.497939 | 0.764757  |
| 106 | 1 | 0 | 6.883059  | -2.936703 | 1.397900  |
| 107 | 1 | 0 | 8.850196  | -2.790805 | -1.765741 |
| 108 | 1 | 0 | 7.509129  | -2.475331 | -2.876499 |
| 109 | 1 | 0 | 8.036212  | -1.212470 | -1.753921 |
| 110 | 1 | 0 | 7.676066  | -4.850716 | -0.868963 |
| 111 | 1 | 0 | 6.031872  | -4.732866 | -0.206735 |
| 112 | 1 | 0 | 6.299834  | -4.582188 | -1.949609 |
| 113 | 1 | 0 | -8.844175 | -0.777966 | 0.557432  |
| 114 | 1 | 0 | -7.465690 | -1.686332 | 1.190246  |
| 115 | 1 | 0 | -7.365661 | 0.078572  | 1.016177  |
| 116 | 1 | 0 | -8.830036 | 0.260240  | -1.681145 |
| 117 | 1 | 0 | -7.327522 | 1.132820  | -1.312625 |
| 118 | 1 | 0 | -7.433550 | 0.119647  | -2.760245 |
| 119 | 1 | 0 | -8.949217 | -2.257942 | -1.424234 |
| 120 | 1 | 0 | -7.558980 | -2.465360 | -2.500156 |
| 121 | 1 | 0 | -7.530150 | -3.176864 | -0.879958 |
| 122 | 1 | 0 | -1.502580 | -2.842918 | -2.963518 |
| 123 | 1 | 0 | -1.822154 | -3.078288 | -4.695462 |
| 124 | 1 | 0 | -2.951521 | -3.724735 | -3.488244 |
| 125 | 1 | 0 | -1.325417 | -0.285201 | -3.504964 |
| 126 | 1 | 0 | -1.757286 | -0.598921 | -5.194332 |
| 127 | 1 | 0 | -2.715506 | 0.541266  | -4.229978 |
| 128 | 1 | 0 | -4.844157 | -2.543747 | -4.648918 |
| 129 | 1 | 0 | -4.755384 | -0.796185 | -4.973645 |
| 130 | 1 | 0 | -3.673749 | -1.914110 | -5.812799 |
| 131 | 1 | 0 | 3.577252  | 0.060695  | -4.589846 |
| 132 | 1 | 0 | 2.113785  | -0.579996 | -5.359854 |
| 133 | 1 | 0 | 2.014392  | 0.178998  | -3.757078 |
| 134 | 1 | 0 | 1.730631  | -3.584273 | -3.142033 |
| 135 | 1 | 0 | 0.876263  | -2.050136 | -2.896691 |
| 136 | 1 | 0 | 1.050007  | -2.714259 | -4.529959 |
| 137 | 1 | 0 | 3.916145  | -3.668846 | -4.388805 |
| 138 | 1 | 0 | 4.694394  | -2.171403 | -4.954762 |
| 139 | 1 | 0 | 3.188127  | -2.726892 | -5.692723 |
| 140 | 8 | 0 | -0.606054 | 2.178162  | -1.211232 |
| 141 | 6 | 0 | -1.039392 | 3.400378  | -0.898063 |
| 142 | 6 | 0 | -2.585003 | 3.520535  | -0.703339 |
| 143 | 8 | 0 | -0.392891 | 3.774041  | 0.345282  |
| 144 | 1 | 0 | -2.843391 | 4.576201  | -0.843389 |
| 145 | 8 | 0 | -2.972339 | 3.149392  | 0.638545  |

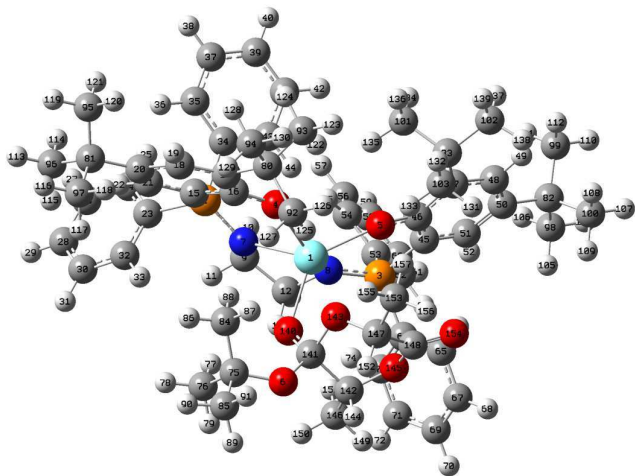
## Appendix 2. Optimised Structures

|     |   |   |           |          |           |
|-----|---|---|-----------|----------|-----------|
| 146 | 6 | 0 | -3.388447 | 2.676888 | -1.661828 |
| 147 | 6 | 0 | -1.157393 | 4.631748 | 1.178088  |
| 148 | 6 | 0 | -2.361640 | 3.813849 | 1.637178  |
| 149 | 1 | 0 | -4.458305 | 2.856554 | -1.516226 |
| 150 | 1 | 0 | -3.120309 | 2.944945 | -2.687400 |
| 151 | 1 | 0 | -3.187469 | 1.613863 | -1.515074 |
| 152 | 1 | 0 | -1.505534 | 5.507148 | 0.605311  |
| 153 | 6 | 0 | -0.303676 | 5.103631 | 2.336097  |
| 154 | 8 | 0 | -2.731566 | 3.682033 | 2.782177  |
| 155 | 1 | 0 | 0.562253  | 5.651593 | 1.953662  |
| 156 | 1 | 0 | -0.884690 | 5.758717 | 2.991308  |
| 157 | 1 | 0 | 0.045016  | 4.254004 | 2.929507  |

-----  
Rotational constants (GHZ):      0.0346172      0.0216966  
0.0209529

Sum of electronic and zero-point Energies=      -3172.908615  
Sum of electronic and thermal Energies=      -3172.828667  
Sum of electronic and thermal Enthalpies=      -3172.827723  
Sum of electronic and thermal Free Energies=      -3173.030221

|                |        |         |   |
|----------------|--------|---------|---|
|                | 1      | 2       | 3 |
|                | A      | A       | A |
| Frequencies -- | 8.8772 | 12.2809 |   |
| 13.0579        |        |         |   |
| Red. masses -- | 4.7560 | 5.1340  |   |
| 4.4053         |        |         |   |
| Frc consts --  | 0.0002 | 0.0005  |   |
| 0.0004         |        |         |   |
| IR Inten --    | 0.0205 | 0.2605  |   |
| 0.0594         |        |         |   |

*Initiation INT3*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.129274               | -0.639372 | -0.132199 |
| 2                | 15               | 0              | -2.608639               | 1.833224  | -0.575665 |
| 3                | 15               | 0              | 3.029329                | 0.796290  | -1.159601 |
| 4                | 8                | 0              | -1.846761               | -0.425480 | 1.219697  |
| 5                | 8                | 0              | 1.497323                | -0.460741 | 1.290124  |
| 6                | 8                | 0              | -1.137864               | -4.155685 | -2.163474 |
| 7                | 7                | 0              | -1.274629               | 1.113466  | -1.205676 |
| 8                | 7                | 0              | 1.400688                | 0.724863  | -1.301641 |
| 9                | 6                | 0              | -0.530319               | 1.894474  | -2.200967 |
| 10               | 1                | 0              | -0.268590               | 2.899866  | -1.828591 |
| 11               | 1                | 0              | -1.109344               | 2.040549  | -3.126206 |
| 12               | 6                | 0              | 0.767336                | 1.162437  | -2.547227 |
| 13               | 1                | 0              | 0.533333                | 0.295926  | -3.184115 |
| 14               | 1                | 0              | 1.391788                | 1.847913  | -3.142431 |
| 15               | 6                | 0              | -3.716066               | 0.706179  | 0.305473  |
| 16               | 6                | 0              | -3.143565               | -0.216380 | 1.221753  |
| 17               | 6                | 0              | -4.037270               | -0.868064 | 2.135661  |
| 18               | 6                | 0              | -5.401776               | -0.639619 | 1.985484  |
| 19               | 1                | 0              | -6.074833               | -1.156203 | 2.661590  |
| 20               | 6                | 0              | -5.979805               | 0.215546  | 1.028991  |
| 21               | 6                | 0              | -5.101866               | 0.910768  | 0.209860  |
| 22               | 1                | 0              | -5.480023               | 1.620558  | -0.517697 |
| 23               | 6                | 0              | -3.582090               | 2.639000  | -1.918871 |
| 24               | 6                | 0              | -3.718289               | 4.024633  | -2.042056 |
| 25               | 1                | 0              | -3.295429               | 4.683451  | -1.289542 |
| 26               | 6                | 0              | -4.395210               | 4.567388  | -3.135042 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 27 | 1 | 0 | -4.498786 | 5.645871  | -3.222146 |
| 28 | 6 | 0 | -4.932586 | 3.731229  | -4.111092 |
| 29 | 1 | 0 | -5.459944 | 4.155850  | -4.961497 |
| 30 | 6 | 0 | -4.787426 | 2.347110  | -3.999956 |
| 31 | 1 | 0 | -5.198635 | 1.691608  | -4.763196 |
| 32 | 6 | 0 | -4.112035 | 1.801621  | -2.911829 |
| 33 | 1 | 0 | -3.991277 | 0.724430  | -2.830187 |
| 34 | 6 | 0 | -2.185179 | 3.160841  | 0.641279  |
| 35 | 6 | 0 | -3.176784 | 3.925897  | 1.269056  |
| 36 | 1 | 0 | -4.224242 | 3.773687  | 1.020297  |
| 37 | 6 | 0 | -2.825639 | 4.869416  | 2.231378  |
| 38 | 1 | 0 | -3.599036 | 5.459143  | 2.716844  |
| 39 | 6 | 0 | -1.485857 | 5.046266  | 2.582116  |
| 40 | 1 | 0 | -1.215114 | 5.778210  | 3.338817  |
| 41 | 6 | 0 | -0.498494 | 4.273098  | 1.974331  |
| 42 | 1 | 0 | 0.543434  | 4.392912  | 2.259515  |
| 43 | 6 | 0 | -0.847095 | 3.330991  | 1.006113  |
| 44 | 1 | 0 | -0.085893 | 2.705343  | 0.546657  |
| 45 | 6 | 0 | 3.565714  | 0.469447  | 0.540942  |
| 46 | 6 | 0 | 2.709008  | -0.037266 | 1.555827  |
| 47 | 6 | 0 | 3.236569  | -0.058596 | 2.894822  |
| 48 | 6 | 0 | 4.566872  | 0.291949  | 3.087433  |
| 49 | 1 | 0 | 4.960311  | 0.242135  | 4.096952  |
| 50 | 6 | 0 | 5.444872  | 0.714232  | 2.071133  |
| 51 | 6 | 0 | 4.902318  | 0.821685  | 0.802905  |
| 52 | 1 | 0 | 5.514217  | 1.188328  | -0.015400 |
| 53 | 6 | 0 | 3.624231  | 2.502969  | -1.582853 |
| 54 | 6 | 0 | 2.826217  | 3.578345  | -1.173805 |
| 55 | 1 | 0 | 1.885964  | 3.380536  | -0.667581 |
| 56 | 6 | 0 | 3.228971  | 4.889159  | -1.416211 |
| 57 | 1 | 0 | 2.598866  | 5.715366  | -1.096695 |
| 58 | 6 | 0 | 4.437338  | 5.139465  | -2.067037 |
| 59 | 1 | 0 | 4.752679  | 6.162382  | -2.256507 |
| 60 | 6 | 0 | 5.239455  | 4.074752  | -2.473714 |
| 61 | 1 | 0 | 6.182176  | 4.263537  | -2.980903 |
| 62 | 6 | 0 | 4.835463  | 2.760971  | -2.234736 |
| 63 | 1 | 0 | 5.465332  | 1.938926  | -2.562110 |
| 64 | 6 | 0 | 3.992740  | -0.302355 | -2.294092 |
| 65 | 6 | 0 | 4.654716  | -1.428860 | -1.795807 |
| 66 | 1 | 0 | 4.629881  | -1.650381 | -0.733477 |
| 67 | 6 | 0 | 5.340555  | -2.277431 | -2.664405 |
| 68 | 1 | 0 | 5.849108  | -3.151060 | -2.266220 |
| 69 | 6 | 0 | 5.364673  | -2.011755 | -4.031898 |
| 70 | 1 | 0 | 5.903607  | -2.673015 | -4.705964 |
| 71 | 6 | 0 | 4.692095  | -0.898020 | -4.537942 |
| 72 | 1 | 0 | 4.703817  | -0.689463 | -5.604782 |
| 73 | 6 | 0 | 4.008094  | -0.046608 | -3.674030 |
| 74 | 1 | 0 | 3.498436  | 0.825545  | -4.076204 |
| 75 | 6 | 0 | -2.533625 | -3.852693 | -2.395203 |
| 76 | 6 | 0 | -2.681654 | -2.960138 | -3.630853 |
| 77 | 1 | 0 | -2.210802 | -1.990069 | -3.461180 |
| 78 | 1 | 0 | -3.743629 | -2.811156 | -3.862785 |
| 79 | 1 | 0 | -2.208304 | -3.433549 | -4.498919 |
| 80 | 6 | 0 | -3.508628 | -1.755047 | 3.274146  |
| 81 | 6 | 0 | -7.504377 | 0.354593  | 0.943245  |
| 82 | 6 | 0 | 6.904496  | 1.047299  | 2.398572  |
| 83 | 6 | 0 | 2.345120  | -0.420869 | 4.094111  |
| 84 | 6 | 0 | -3.213408 | -3.235065 | -1.175278 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 85  | 6 | 0 | -3.132791 | -5.233151 | -2.674495 |
| 86  | 1 | 0 | -4.298250 | -3.202940 | -1.332826 |
| 87  | 1 | 0 | -3.014073 | -3.832293 | -0.281451 |
| 88  | 1 | 0 | -2.870101 | -2.214783 | -0.994908 |
| 89  | 1 | 0 | -2.614713 | -5.712628 | -3.512011 |
| 90  | 1 | 0 | -4.195536 | -5.146472 | -2.927169 |
| 91  | 1 | 0 | -3.036046 | -5.879611 | -1.795438 |
| 92  | 6 | 0 | -2.794936 | -2.993980 | 2.705869  |
| 93  | 6 | 0 | -2.532456 | -0.936642 | 4.142115  |
| 94  | 6 | 0 | -4.629694 | -2.256134 | 4.198142  |
| 95  | 6 | 0 | -8.063867 | 0.846131  | 2.292681  |
| 96  | 6 | 0 | -7.934049 | 1.352371  | -0.140931 |
| 97  | 6 | 0 | -8.124468 | -1.016152 | 0.606234  |
| 98  | 6 | 0 | 7.685453  | 1.501289  | 1.157552  |
| 99  | 6 | 0 | 6.961098  | 2.182227  | 3.440031  |
| 100 | 6 | 0 | 7.599181  | -0.203928 | 2.970898  |
| 101 | 6 | 0 | 1.189364  | 0.595689  | 4.184809  |
| 102 | 6 | 0 | 3.105401  | -0.366279 | 5.429003  |
| 103 | 6 | 0 | 1.782772  | -1.845883 | 3.948854  |
| 104 | 1 | 0 | 8.723338  | 1.722521  | 1.433318  |
| 105 | 1 | 0 | 7.708104  | 0.723391  | 0.384989  |
| 106 | 1 | 0 | 7.260002  | 2.410966  | 0.717096  |
| 107 | 1 | 0 | 8.645025  | 0.016441  | 3.220930  |
| 108 | 1 | 0 | 7.106259  | -0.560207 | 3.882027  |
| 109 | 1 | 0 | 7.586594  | -1.024072 | 2.243833  |
| 110 | 1 | 0 | 8.002734  | 2.428656  | 3.683153  |
| 111 | 1 | 0 | 6.476320  | 3.088110  | 3.057659  |
| 112 | 1 | 0 | 6.460284  | 1.904075  | 4.373728  |
| 113 | 1 | 0 | -9.028230 | 1.413427  | -0.176089 |
| 114 | 1 | 0 | -7.554388 | 2.361358  | 0.060462  |
| 115 | 1 | 0 | -7.587624 | 1.049207  | -1.135973 |
| 116 | 1 | 0 | -9.218182 | -0.942142 | 0.549657  |
| 117 | 1 | 0 | -7.757133 | -1.384375 | -0.358852 |
| 118 | 1 | 0 | -7.879797 | -1.768589 | 1.363987  |
| 119 | 1 | 0 | -9.156179 | 0.940735  | 2.243848  |
| 120 | 1 | 0 | -7.827453 | 0.155154  | 3.108949  |
| 121 | 1 | 0 | -7.647897 | 1.825948  | 2.554709  |
| 122 | 1 | 0 | -1.694194 | -0.565357 | 3.550804  |
| 123 | 1 | 0 | -2.137258 | -1.561001 | 4.953805  |
| 124 | 1 | 0 | -3.044839 | -0.078560 | 4.594673  |
| 125 | 1 | 0 | -1.984891 | -2.714989 | 2.030978  |
| 126 | 1 | 0 | -2.374724 | -3.593447 | 3.524129  |
| 127 | 1 | 0 | -3.500595 | -3.625896 | 2.153038  |
| 128 | 1 | 0 | -5.178953 | -1.430665 | 4.666855  |
| 129 | 1 | 0 | -5.347981 | -2.897772 | 3.673371  |
| 130 | 1 | 0 | -4.186565 | -2.854911 | 5.002742  |
| 131 | 1 | 0 | 2.593702  | -2.579728 | 3.872529  |
| 132 | 1 | 0 | 1.170430  | -2.100437 | 4.823665  |
| 133 | 1 | 0 | 1.162946  | -1.923813 | 3.055742  |
| 134 | 1 | 0 | 1.579229  | 1.608487  | 4.346660  |
| 135 | 1 | 0 | 0.587676  | 0.598165  | 3.273402  |
| 136 | 1 | 0 | 0.532600  | 0.348168  | 5.028244  |
| 137 | 1 | 0 | 3.508119  | 0.632111  | 5.638644  |
| 138 | 1 | 0 | 3.929793  | -1.088695 | 5.466024  |
| 139 | 1 | 0 | 2.414278  | -0.616910 | 6.242276  |
| 140 | 8 | 0 | -0.440558 | -1.951314 | -1.864430 |
| 141 | 6 | 0 | -0.209138 | -3.234695 | -1.653739 |
| 142 | 6 | 0 | 1.135447  | -3.787446 | -2.223402 |

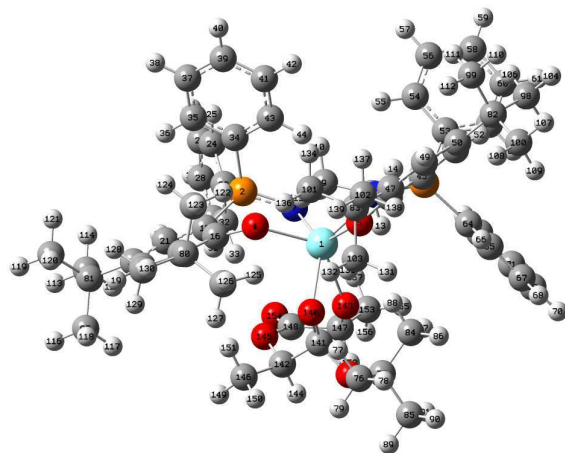
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 143 | 8 | 0 | -0.145522 | -3.368915 | -0.170853 |
| 144 | 1 | 0 | 1.017922  | -4.867759 | -2.362824 |
| 145 | 8 | 0 | 2.228612  | -3.580440 | -1.302787 |
| 146 | 6 | 0 | 1.512910  | -3.144845 | -3.536669 |
| 147 | 6 | 0 | 0.641061  | -4.478565 | 0.266062  |
| 148 | 6 | 0 | 2.087524  | -4.128677 | -0.074831 |
| 149 | 1 | 0 | 2.442905  | -3.577305 | -3.916770 |
| 150 | 1 | 0 | 0.714865  | -3.317327 | -4.264740 |
| 151 | 1 | 0 | 1.643762  | -2.068096 | -3.411488 |
| 152 | 1 | 0 | 0.337395  | -5.364747 | -0.311952 |
| 153 | 6 | 0 | 0.427663  | -4.755410 | 1.736493  |
| 154 | 8 | 0 | 3.035953  | -4.248103 | 0.661901  |
| 155 | 1 | 0 | -0.616868 | -5.023240 | 1.915992  |
| 156 | 1 | 0 | 1.069532  | -5.584097 | 2.049308  |
| 157 | 1 | 0 | 0.683324  | -3.884800 | 2.343073  |

-----  
Rotational constants (GHZ): 0.0361859 0.0217221  
0.0205308

Sum of electronic and zero-point Energies= -3172.903791  
Sum of electronic and thermal Energies= -3172.823927  
Sum of electronic and thermal Enthalpies= -3172.822983  
Sum of electronic and thermal Free Energies= -3173.023821

|                | 1<br>A | 2<br>A  | 3<br>A |
|----------------|--------|---------|--------|
| Frequencies -- | 9.7985 | 11.4469 |        |
| 15.2780        |        |         |        |
| Red. masses -- | 4.7686 | 4.5840  |        |
| 4.6697         |        |         |        |
| Frc consts --  | 0.0003 | 0.0004  |        |
| 0.0006         |        |         |        |
| IR Inten --    | 0.1104 | 0.0352  |        |
| 0.7425         |        |         |        |

*Initiation TS2'*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.100642               | -0.504935 | -0.366193 |
| 2                | 15               | 0              | -2.562528               | 1.918362  | 0.111291  |
| 3                | 15               | 0              | 3.082089                | 1.174289  | -0.820284 |
| 4                | 8                | 0              | -1.587404               | -0.549553 | 1.267869  |
| 5                | 8                | 0              | 1.675233                | -1.054623 | 0.777783  |
| 6                | 8                | 0              | -0.165965               | -3.866905 | -2.649192 |
| 7                | 7                | 0              | -1.241830               | 1.521788  | -0.788274 |
| 8                | 7                | 0              | 1.446772                | 1.270790  | -0.865501 |
| 9                | 6                | 0              | -0.500827               | 2.661495  | -1.335821 |
| 10               | 1                | 0              | -0.328997               | 3.447175  | -0.580215 |
| 11               | 1                | 0              | -1.038326               | 3.142756  | -2.168602 |
| 12               | 6                | 0              | 0.860722                | 2.190054  | -1.844831 |
| 13               | 1                | 0              | 0.730049                | 1.693193  | -2.814228 |
| 14               | 1                | 0              | 1.479277                | 3.084649  | -2.025850 |
| 15               | 6                | 0              | -3.580953               | 0.499037  | 0.564358  |
| 16               | 6                | 0              | -2.903158               | -0.526835 | 1.274830  |
| 17               | 6                | 0              | -3.712571               | -1.456838 | 2.005663  |
| 18               | 6                | 0              | -5.091364               | -1.396030 | 1.814850  |
| 19               | 1                | 0              | -5.702274               | -2.124661 | 2.337993  |
| 20               | 6                | 0              | -5.760158               | -0.449978 | 1.014567  |
| 21               | 6                | 0              | -4.975012               | 0.534127  | 0.428690  |
| 22               | 1                | 0              | -5.429525               | 1.339053  | -0.138283 |
| 23               | 6                | 0              | -3.608873               | 3.145025  | -0.781832 |
| 24               | 6                | 0              | -3.815148               | 4.451138  | -0.324630 |
| 25               | 1                | 0              | -3.395312               | 4.772539  | 0.623672  |
| 26               | 6                | 0              | -4.557521               | 5.351038  | -1.089233 |
| 27               | 1                | 0              | -4.714016               | 6.363741  | -0.726241 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 28 | 6 | 0 | -5.092954 | 4.953981  | -2.313016 |
| 29 | 1 | 0 | -5.672449 | 5.656640  | -2.906832 |
| 30 | 6 | 0 | -4.876826 | 3.656624  | -2.778920 |
| 31 | 1 | 0 | -5.282080 | 3.343392  | -3.737448 |
| 32 | 6 | 0 | -4.132944 | 2.752870  | -2.023279 |
| 33 | 1 | 0 | -3.953949 | 1.751049  | -2.406865 |
| 34 | 6 | 0 | -2.106326 | 2.692967  | 1.730370  |
| 35 | 6 | 0 | -3.094268 | 3.120257  | 2.626418  |
| 36 | 1 | 0 | -4.145121 | 3.033996  | 2.360619  |
| 37 | 6 | 0 | -2.736050 | 3.634175  | 3.870634  |
| 38 | 1 | 0 | -3.507983 | 3.962107  | 4.562202  |
| 39 | 6 | 0 | -1.390540 | 3.712259  | 4.233454  |
| 40 | 1 | 0 | -1.112643 | 4.106474  | 5.207731  |
| 41 | 6 | 0 | -0.405542 | 3.268001  | 3.353102  |
| 42 | 1 | 0 | 0.641959  | 3.305430  | 3.641667  |
| 43 | 6 | 0 | -0.761639 | 2.757454  | 2.104498  |
| 44 | 1 | 0 | 0.000502  | 2.383421  | 1.425579  |
| 45 | 6 | 0 | 3.667478  | 0.239879  | 0.613772  |
| 46 | 6 | 0 | 2.865657  | -0.756824 | 1.233249  |
| 47 | 6 | 0 | 3.433374  | -1.427104 | 2.373625  |
| 48 | 6 | 0 | 4.725939  | -1.092846 | 2.759244  |
| 49 | 1 | 0 | 5.146308  | -1.612680 | 3.613362  |
| 50 | 6 | 0 | 5.533686  | -0.125982 | 2.130774  |
| 51 | 6 | 0 | 4.968680  | 0.539876  | 1.056147  |
| 52 | 1 | 0 | 5.529510  | 1.314228  | 0.542834  |
| 53 | 6 | 0 | 3.811260  | 2.871472  | -0.694345 |
| 54 | 6 | 0 | 3.176031  | 3.778449  | 0.163715  |
| 55 | 1 | 0 | 2.279479  | 3.470866  | 0.694984  |
| 56 | 6 | 0 | 3.683804  | 5.064521  | 0.326795  |
| 57 | 1 | 0 | 3.182557  | 5.762835  | 0.992102  |
| 58 | 6 | 0 | 4.832203  | 5.455132  | -0.363524 |
| 59 | 1 | 0 | 5.228563  | 6.459248  | -0.235843 |
| 60 | 6 | 0 | 5.469225  | 4.557158  | -1.217761 |
| 61 | 1 | 0 | 6.363395  | 4.857516  | -1.757910 |
| 62 | 6 | 0 | 4.960076  | 3.268909  | -1.386010 |
| 63 | 1 | 0 | 5.458697  | 2.576091  | -2.057653 |
| 64 | 6 | 0 | 3.880702  | 0.459302  | -2.332875 |
| 65 | 6 | 0 | 4.649549  | -0.706304 | -2.253191 |
| 66 | 1 | 0 | 4.811880  | -1.178866 | -1.288698 |
| 67 | 6 | 0 | 5.209742  | -1.259055 | -3.405257 |
| 68 | 1 | 0 | 5.808842  | -2.163036 | -3.331382 |
| 69 | 6 | 0 | 5.003708  | -0.655348 | -4.644072 |
| 70 | 1 | 0 | 5.441583  | -1.086686 | -5.540698 |
| 71 | 6 | 0 | 4.237860  | 0.508282  | -4.731484 |
| 72 | 1 | 0 | 4.078484  | 0.986426  | -5.694643 |
| 73 | 6 | 0 | 3.680047  | 1.064813  | -3.582874 |
| 74 | 1 | 0 | 3.099456  | 1.979902  | -3.661863 |
| 75 | 6 | 0 | 1.108734  | -4.487852 | -2.281091 |
| 76 | 6 | 0 | 0.886095  | -5.439243 | -1.107212 |
| 77 | 1 | 0 | 0.573932  | -4.895694 | -0.214143 |
| 78 | 1 | 0 | 1.816674  | -5.973637 | -0.884595 |
| 79 | 1 | 0 | 0.119570  | -6.181440 | -1.357730 |
| 80 | 6 | 0 | -3.096862 | -2.406500 | 3.045542  |
| 81 | 6 | 0 | -7.284542 | -0.511598 | 0.861893  |
| 82 | 6 | 0 | 6.948400  | 0.152174  | 2.651426  |
| 83 | 6 | 0 | 2.630239  | -2.474127 | 3.160361  |
| 84 | 6 | 0 | 2.174391  | -3.437380 | -1.989369 |
| 85 | 6 | 0 | 1.467564  | -5.269532 | -3.543877 |



## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 86  | 1 | 0 | 3.151259  | -3.930203 | -1.917382 |
| 87  | 1 | 0 | 2.216098  | -2.702855 | -2.798283 |
| 88  | 1 | 0 | 1.988595  | -2.915489 | -1.048749 |
| 89  | 1 | 0 | 0.674838  | -5.981554 | -3.796703 |
| 90  | 1 | 0 | 2.397000  | -5.827637 | -3.388382 |
| 91  | 1 | 0 | 1.607351  | -4.590918 | -4.391988 |
| 92  | 6 | 0 | -2.112408 | -3.398744 | 2.402759  |
| 93  | 6 | 0 | -2.366268 | -1.545638 | 4.096919  |
| 94  | 6 | 0 | -4.159441 | -3.232511 | 3.787489  |
| 95  | 6 | 0 | -7.957432 | -0.380897 | 2.242376  |
| 96  | 6 | 0 | -7.819613 | 0.611630  | -0.036543 |
| 97  | 6 | 0 | -7.681167 | -1.859936 | 0.228683  |
| 98  | 6 | 0 | 7.665641  | 1.230464  | 1.828132  |
| 99  | 6 | 0 | 6.876926  | 0.634499  | 4.113769  |
| 100 | 6 | 0 | 7.788447  | -1.138537 | 2.582986  |
| 101 | 6 | 0 | 1.371180  | -1.811125 | 3.749622  |
| 102 | 6 | 0 | 3.425836  | -3.066399 | 4.334928  |
| 103 | 6 | 0 | 2.231004  | -3.645896 | 2.243070  |
| 104 | 1 | 0 | 8.672331  | 1.395704  | 2.229932  |
| 105 | 1 | 0 | 7.773927  | 0.935034  | 0.777552  |
| 106 | 1 | 0 | 7.135568  | 2.189520  | 1.861685  |
| 107 | 1 | 0 | 8.803271  | -0.956908 | 2.959695  |
| 108 | 1 | 0 | 7.350466  | -1.942782 | 3.184204  |
| 109 | 1 | 0 | 7.867521  | -1.499058 | 1.550611  |
| 110 | 1 | 0 | 7.883738  | 0.829865  | 4.504799  |
| 111 | 1 | 0 | 6.295012  | 1.560252  | 4.190933  |
| 112 | 1 | 0 | 6.406166  | -0.109986 | 4.765095  |
| 113 | 1 | 0 | -8.907845 | 0.520692  | -0.135678 |
| 114 | 1 | 0 | -7.608962 | 1.603433  | 0.381217  |
| 115 | 1 | 0 | -7.389047 | 0.566009  | -1.043557 |
| 116 | 1 | 0 | -8.771010 | -1.927410 | 0.115035  |
| 117 | 1 | 0 | -7.226275 | -1.972859 | -0.762148 |
| 118 | 1 | 0 | -7.357201 | -2.707214 | 0.843303  |
| 119 | 1 | 0 | -9.049587 | -0.429815 | 2.144258  |
| 120 | 1 | 0 | -7.649902 | -1.181444 | 2.923929  |
| 121 | 1 | 0 | -7.700057 | 0.575212  | 2.713131  |
| 122 | 1 | 0 | -1.584601 | -0.940340 | 3.633423  |
| 123 | 1 | 0 | -1.904925 | -2.186894 | 4.859124  |
| 124 | 1 | 0 | -3.072075 | -0.873891 | 4.601062  |
| 125 | 1 | 0 | -1.334852 | -2.888910 | 1.834760  |
| 126 | 1 | 0 | -1.635128 | -4.006665 | 3.182811  |
| 127 | 1 | 0 | -2.638031 | -4.082069 | 1.725061  |
| 128 | 1 | 0 | -4.879273 | -2.600145 | 4.321152  |
| 129 | 1 | 0 | -4.714210 | -3.896712 | 3.113294  |
| 130 | 1 | 0 | -3.662662 | -3.865374 | 4.532589  |
| 131 | 1 | 0 | 3.123511  | -4.142293 | 1.841040  |
| 132 | 1 | 0 | 1.659583  | -4.390326 | 2.812421  |
| 133 | 1 | 0 | 1.616911  | -3.302587 | 1.409935  |
| 134 | 1 | 0 | 1.647697  | -1.008203 | 4.444504  |
| 135 | 1 | 0 | 0.737466  | -1.389633 | 2.967981  |
| 136 | 1 | 0 | 0.781198  | -2.549660 | 4.305950  |
| 137 | 1 | 0 | 3.715226  | -2.303473 | 5.067811  |
| 138 | 1 | 0 | 4.330665  | -3.591023 | 4.003807  |
| 139 | 1 | 0 | 2.796758  | -3.796963 | 4.856832  |
| 140 | 8 | 0 | -0.552556 | -2.781052 | -0.667780 |
| 141 | 6 | 0 | -0.832322 | -2.993319 | -1.875808 |
| 142 | 6 | 0 | -2.291159 | -2.995809 | -2.395020 |
| 143 | 8 | 0 | -0.293242 | -1.242658 | -2.571968 |

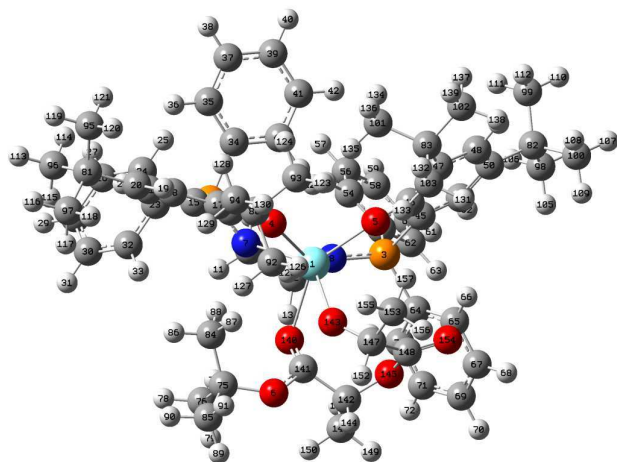
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 144 | 1 | 0 | -2.273070 | -3.407585 | -3.409228 |
| 145 | 8 | 0 | -2.921978 | -1.710758 | -2.438286 |
| 146 | 6 | 0 | -3.154546 | -3.868223 | -1.501945 |
| 147 | 6 | 0 | -1.005611 | -1.018721 | -3.753647 |
| 148 | 6 | 0 | -2.466579 | -0.818076 | -3.355037 |
| 149 | 1 | 0 | -4.164183 | -3.933832 | -1.917830 |
| 150 | 1 | 0 | -2.733119 | -4.876036 | -1.434041 |
| 151 | 1 | 0 | -3.208548 | -3.437168 | -0.499767 |
| 152 | 1 | 0 | -0.946616 | -1.930943 | -4.377541 |
| 153 | 6 | 0 | -0.502453 | 0.135503  | -4.606720 |
| 154 | 8 | 0 | -3.183910 | 0.084204  | -3.718166 |
| 155 | 1 | 0 | 0.576259  | 0.030688  | -4.758115 |
| 156 | 1 | 0 | -0.999276 | 0.126579  | -5.583017 |
| 157 | 1 | 0 | -0.717092 | 1.097103  | -4.135704 |

-----  
Rotational constants (GHz): 0.0365939 0.0220377  
0.0209976

Sum of electronic and zero-point Energies= -3172.896914  
Sum of electronic and thermal Energies= -3172.817498  
Sum of electronic and thermal Enthalpies= -3172.816554  
Sum of electronic and thermal Free Energies= -3173.015406

|                | 1        | 2      | 3 |
|----------------|----------|--------|---|
|                | A        | A      | A |
| Frequencies -- | 180.0881 | 5.8141 |   |
| 11.0607        |          |        |   |
| Red. masses -- | 9.5350   | 4.5713 |   |
| 5.1993         |          |        |   |
| Frc consts --  | 0.1822   | 0.0001 |   |
| 0.0004         |          |        |   |
| IR Inten --    | 81.3810  | 0.0308 |   |
| 0.2104         |          |        |   |

*Initiation TS2*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | 0.119109                | 0.899206  | 0.184346  |
| 2                | 15               | 0              | 2.431335                | -1.428767 | -1.168328 |
| 3                | 15               | 0              | -3.041307               | -0.118891 | -1.239196 |
| 4                | 8                | 0              | 1.879649                | 0.178480  | 1.273034  |
| 5                | 8                | 0              | -1.405913               | -0.000818 | 1.429326  |
| 6                | 8                | 0              | 1.399600                | 4.563809  | -0.781018 |
| 7                | 7                | 0              | 1.253359                | -0.341862 | -1.523007 |
| 8                | 7                | 0              | -1.421855               | 0.023271  | -1.411169 |
| 9                | 6                | 0              | 0.492249                | -0.640634 | -2.746047 |
| 10               | 1                | 0              | 0.254670                | -1.714637 | -2.834660 |
| 11               | 1                | 0              | 1.057702                | -0.371228 | -3.652127 |
| 12               | 6                | 0              | -0.829034               | 0.134572  | -2.743602 |
| 13               | 1                | 0              | -0.632741               | 1.185722  | -2.992976 |
| 14               | 1                | 0              | -1.464696               | -0.279950 | -3.542205 |
| 15               | 6                | 0              | 3.630942                | -0.844211 | 0.051870  |
| 16               | 6                | 0              | 3.143585                | -0.162421 | 1.198775  |
| 17               | 6                | 0              | 4.088349                | 0.111213  | 2.245229  |
| 18               | 6                | 0              | 5.411212                | -0.271441 | 2.045433  |
| 19               | 1                | 0              | 6.121127                | -0.056042 | 2.836897  |
| 20               | 6                | 0              | 5.903926                | -0.920641 | 0.898278  |
| 21               | 6                | 0              | 4.978022                | -1.212296 | -0.092780 |
| 22               | 1                | 0              | 5.288614                | -1.728643 | -0.994815 |
| 23               | 6                | 0              | 3.370504                | -1.860827 | -2.699911 |
| 24               | 6                | 0              | 3.316447                | -3.121531 | -3.301063 |
| 25               | 1                | 0              | 2.762032                | -3.927092 | -2.829082 |
| 26               | 6                | 0              | 3.971970                | -3.350613 | -4.511760 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 27 | 1 | 0 | 3.925597  | -4.334922 | -4.970607 |
| 28 | 6 | 0 | 4.680229  | -2.322896 | -5.129984 |
| 29 | 1 | 0 | 5.190680  | -2.503246 | -6.072624 |
| 30 | 6 | 0 | 4.730221  | -1.058961 | -4.539173 |
| 31 | 1 | 0 | 5.278242  | -0.252803 | -5.020165 |
| 32 | 6 | 0 | 4.075899  | -0.826754 | -3.332715 |
| 33 | 1 | 0 | 4.109705  | 0.159174  | -2.876431 |
| 34 | 6 | 0 | 1.765376  | -3.029201 | -0.519246 |
| 35 | 6 | 0 | 2.620063  | -4.080681 | -0.162917 |
| 36 | 1 | 0 | 3.695916  | -3.973669 | -0.279541 |
| 37 | 6 | 0 | 2.095942  | -5.259745 | 0.361163  |
| 38 | 1 | 0 | 2.763822  | -6.071384 | 0.638504  |
| 39 | 6 | 0 | 0.717811  | -5.392734 | 0.541951  |
| 40 | 1 | 0 | 0.311113  | -6.311857 | 0.956216  |
| 41 | 6 | 0 | -0.133350 | -4.341172 | 0.207898  |
| 42 | 1 | 0 | -1.204449 | -4.430803 | 0.368246  |
| 43 | 6 | 0 | 0.388310  | -3.159101 | -0.319879 |
| 44 | 1 | 0 | -0.270426 | -2.325991 | -0.556372 |
| 45 | 6 | 0 | -3.462974 | -0.689674 | 0.431576  |
| 46 | 6 | 0 | -2.554384 | -0.626754 | 1.523880  |
| 47 | 6 | 0 | -2.957625 | -1.285479 | 2.739135  |
| 48 | 6 | 0 | -4.234552 | -1.830539 | 2.801933  |
| 49 | 1 | 0 | -4.536765 | -2.300942 | 3.731369  |
| 50 | 6 | 0 | -5.167969 | -1.824387 | 1.748755  |
| 51 | 6 | 0 | -4.740178 | -1.264617 | 0.557343  |
| 52 | 1 | 0 | -5.395471 | -1.273792 | -0.307673 |
| 53 | 6 | 0 | -3.706866 | -1.395765 | -2.410803 |
| 54 | 6 | 0 | -2.932302 | -2.540907 | -2.634776 |
| 55 | 1 | 0 | -1.962581 | -2.633357 | -2.154788 |
| 56 | 6 | 0 | -3.397063 | -3.555513 | -3.467839 |
| 57 | 1 | 0 | -2.784850 | -4.437883 | -3.636155 |
| 58 | 6 | 0 | -4.644199 | -3.439215 | -4.082522 |
| 59 | 1 | 0 | -5.007625 | -4.231643 | -4.731930 |
| 60 | 6 | 0 | -5.422774 | -2.304826 | -3.861606 |
| 61 | 1 | 0 | -6.395806 | -2.208878 | -4.336598 |
| 62 | 6 | 0 | -4.956358 | -1.285114 | -3.031548 |
| 63 | 1 | 0 | -5.568671 | -0.402987 | -2.869630 |
| 64 | 6 | 0 | -4.040656 | 1.388650  | -1.618087 |
| 65 | 6 | 0 | -4.673381 | 2.095572  | -0.592128 |
| 66 | 1 | 0 | -4.604821 | 1.745884  | 0.433201  |
| 67 | 6 | 0 | -5.379382 | 3.263354  | -0.879931 |
| 68 | 1 | 0 | -5.854272 | 3.811723  | -0.071570 |
| 69 | 6 | 0 | -5.459743 | 3.728497  | -2.190010 |
| 70 | 1 | 0 | -6.015527 | 4.636070  | -2.412764 |
| 71 | 6 | 0 | -4.820232 | 3.032993  | -3.218501 |
| 72 | 1 | 0 | -4.877938 | 3.394831  | -4.242201 |
| 73 | 6 | 0 | -4.109323 | 1.870050  | -2.934675 |
| 74 | 1 | 0 | -3.621050 | 1.329549  | -3.742181 |
| 75 | 6 | 0 | 2.718595  | 4.197647  | -1.310072 |
| 76 | 6 | 0 | 2.630386  | 4.097101  | -2.832053 |
| 77 | 1 | 0 | 1.965986  | 3.282401  | -3.128666 |
| 78 | 1 | 0 | 3.627013  | 3.903920  | -3.245776 |
| 79 | 1 | 0 | 2.261615  | 5.035301  | -3.261910 |
| 80 | 6 | 0 | 3.660312  | 0.790845  | 3.555506  |
| 81 | 6 | 0 | 7.390849  | -1.281094 | 0.797925  |
| 82 | 6 | 0 | -6.556834 | -2.442198 | 1.943676  |
| 83 | 6 | 0 | -2.002227 | -1.410807 | 3.937751  |
| 84 | 6 | 0 | 3.249770  | 2.913542  | -0.683824 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 85  | 6 | 0 | 3.577614  | 5.389804  | -0.894026 |
| 86  | 1 | 0 | 4.321574  | 2.825600  | -0.897787 |
| 87  | 1 | 0 | 3.122873  | 2.932675  | 0.401414  |
| 88  | 1 | 0 | 2.751422  | 2.027776  | -1.084676 |
| 89  | 1 | 0 | 3.161034  | 6.323329  | -1.286932 |
| 90  | 1 | 0 | 4.595237  | 5.273592  | -1.281682 |
| 91  | 1 | 0 | 3.627989  | 5.465219  | 0.197075  |
| 92  | 6 | 0 | 3.163294  | 2.219484  | 3.268564  |
| 93  | 6 | 0 | 2.544862  | -0.030165 | 4.230420  |
| 94  | 6 | 0 | 4.815082  | 0.903869  | 4.564053  |
| 95  | 6 | 0 | 7.773201  | -2.232481 | 1.949168  |
| 96  | 6 | 0 | 7.729347  | -1.977355 | -0.526958 |
| 97  | 6 | 0 | 8.242807  | 0.000034  | 0.894508  |
| 98  | 6 | 0 | -7.423679 | -2.325142 | 0.682403  |
| 99  | 6 | 0 | -6.416442 | -3.937616 | 2.290695  |
| 100 | 6 | 0 | -7.285817 | -1.720009 | 3.093954  |
| 101 | 6 | 0 | -0.742018 | -2.188203 | 3.508678  |
| 102 | 6 | 0 | -2.629834 | -2.177067 | 5.113180  |
| 103 | 6 | 0 | -1.604637 | -0.019510 | 4.459696  |
| 104 | 1 | 0 | -8.409454 | -2.767669 | 0.868463  |
| 105 | 1 | 0 | -7.580123 | -1.279123 | 0.393004  |
| 106 | 1 | 0 | -6.979771 | -2.854344 | -0.169200 |
| 107 | 1 | 0 | -8.278867 | -2.158698 | 3.256014  |
| 108 | 1 | 0 | -6.732159 | -1.793676 | 4.036332  |
| 109 | 1 | 0 | -7.415486 | -0.655463 | 2.867059  |
| 110 | 1 | 0 | -7.404073 | -4.392185 | 2.441676  |
| 111 | 1 | 0 | -5.911074 | -4.479574 | 1.482676  |
| 112 | 1 | 0 | -5.836999 | -4.089063 | 3.207912  |
| 113 | 1 | 0 | 8.800448  | -2.208917 | -0.561208 |
| 114 | 1 | 0 | 7.184843  | -2.922279 | -0.641147 |
| 115 | 1 | 0 | 7.499405  | -1.343440 | -1.391487 |
| 116 | 1 | 0 | 9.311685  | -0.242322 | 0.834093  |
| 117 | 1 | 0 | 8.002945  | 0.690460  | 0.077322  |
| 118 | 1 | 0 | 8.075504  | 0.530409  | 1.838207  |
| 119 | 1 | 0 | 8.839143  | -2.489482 | 1.898810  |
| 120 | 1 | 0 | 7.586074  | -1.781000 | 2.929486  |
| 121 | 1 | 0 | 7.195098  | -3.162408 | 1.895632  |
| 122 | 1 | 0 | 1.677618  | -0.132319 | 3.577232  |
| 123 | 1 | 0 | 2.227239  | 0.460854  | 5.159343  |
| 124 | 1 | 0 | 2.905990  | -1.034183 | 4.485642  |
| 125 | 1 | 0 | 2.313074  | 2.223367  | 2.583794  |
| 126 | 1 | 0 | 2.853454  | 2.702625  | 4.204853  |
| 127 | 1 | 0 | 3.966801  | 2.826350  | 2.831993  |
| 128 | 1 | 0 | 5.222199  | -0.076739 | 4.838970  |
| 129 | 1 | 0 | 5.636162  | 1.528602  | 4.191531  |
| 130 | 1 | 0 | 4.441120  | 1.372882  | 5.481837  |
| 131 | 1 | 0 | -2.489747 | 0.552120  | 4.763982  |
| 132 | 1 | 0 | -0.943920 | -0.116972 | 5.330668  |
| 133 | 1 | 0 | -1.078865 | 0.541827  | 3.688120  |
| 134 | 1 | 0 | -1.004949 | -3.201122 | 3.180518  |
| 135 | 1 | 0 | -0.218994 | -1.686430 | 2.692307  |
| 136 | 1 | 0 | -0.048485 | -2.277725 | 4.354467  |
| 137 | 1 | 0 | -2.915125 | -3.200306 | 4.839573  |
| 138 | 1 | 0 | -3.512171 | -1.666981 | 5.518558  |
| 139 | 1 | 0 | -1.893821 | -2.248542 | 5.922476  |
| 140 | 8 | 0 | 0.325280  | 2.640911  | -1.390501 |
| 141 | 6 | 0 | 0.333019  | 3.751995  | -0.804541 |
| 142 | 6 | 0 | -0.910943 | 4.653711  | -0.729946 |

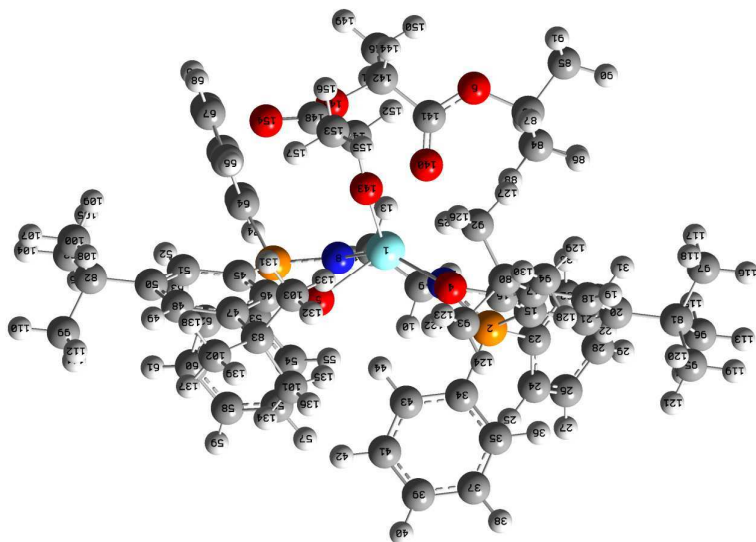
## Appendix 2. Optimised Structures

|     |   |   |           |          |           |
|-----|---|---|-----------|----------|-----------|
| 143 | 8 | 0 | 0.214056  | 3.035371 | 1.060036  |
| 144 | 1 | 0 | -0.617988 | 5.579557 | -0.224142 |
| 145 | 8 | 0 | -2.019660 | 4.073436 | -0.047306 |
| 146 | 6 | 0 | -1.386644 | 4.971356 | -2.139241 |
| 147 | 6 | 0 | -0.521649 | 3.912328 | 1.863575  |
| 148 | 6 | 0 | -1.945106 | 3.927679 | 1.306355  |
| 149 | 1 | 0 | -2.243226 | 5.649620 | -2.093667 |
| 150 | 1 | 0 | -0.585293 | 5.449391 | -2.711054 |
| 151 | 1 | 0 | -1.690949 | 4.052277 | -2.646338 |
| 152 | 1 | 0 | -0.106074 | 4.933201 | 1.761667  |
| 153 | 6 | 0 | -0.510568 | 3.566010 | 3.342623  |
| 154 | 8 | 0 | -2.960285 | 3.740047 | 1.931614  |
| 155 | 1 | 0 | 0.520236  | 3.548480 | 3.705108  |
| 156 | 1 | 0 | -1.075599 | 4.312450 | 3.911025  |
| 157 | 1 | 0 | -0.968856 | 2.591460 | 3.517894  |

-----  
Rotational constants (GHZ):      0.0359933      0.0223956  
0.0210857

Sum of electronic and zero-point Energies=      -3172.896536  
Sum of electronic and thermal Energies=      -3172.817048  
Sum of electronic and thermal Enthalpies=      -3172.816104  
Sum of electronic and thermal Free Energies=      -3173.014311

|                | 1         | 2      | 3 |
|----------------|-----------|--------|---|
|                | A         | A      | A |
| Frequencies -- | -158.3357 | 7.4137 |   |
| 13.8111        |           |        |   |
| Red. masses -- | 8.0557    | 4.6918 |   |
| 4.5893         |           |        |   |
| Frc consts --  | 0.1190    | 0.0002 |   |
| 0.0005         |           |        |   |
| IR Inten --    | 70.8579   | 0.0692 |   |
| 0.0282         |           |        |   |

*Intitiation INT4*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.007816               | 0.549001  | 0.347095  |
| 2                | 15               | 0              | 2.602962                | -1.541913 | -0.849551 |
| 3                | 15               | 0              | -2.998289               | -0.561696 | -1.327891 |
| 4                | 8                | 0              | 1.824352                | 0.059702  | 1.455281  |
| 5                | 8                | 0              | -1.486947               | -0.622519 | 1.424441  |
| 6                | 8                | 0              | 1.678567                | 4.398581  | -1.728207 |
| 7                | 7                | 0              | 1.320468                | -0.636935 | -1.331491 |
| 8                | 7                | 0              | -1.390778               | -0.272688 | -1.398460 |
| 9                | 6                | 0              | 0.610011                | -1.110241 | -2.524646 |
| 10               | 1                | 0              | 0.365814                | -2.185147 | -2.470683 |
| 11               | 1                | 0              | 1.206935                | -0.976801 | -3.441909 |
| 12               | 6                | 0              | -0.699508               | -0.332146 | -2.685185 |
| 13               | 1                | 0              | -0.468976               | 0.684995  | -3.037150 |
| 14               | 1                | 0              | -1.284331               | -0.815592 | -3.483955 |
| 15               | 6                | 0              | 3.729211                | -0.666901 | 0.265213  |
| 16               | 6                | 0              | 3.128477                | -0.031548 | 1.383779  |
| 17               | 6                | 0              | 4.001312                | 0.466743  | 2.406733  |
| 18               | 6                | 0              | 5.372738                | 0.353859  | 2.197843  |
| 19               | 1                | 0              | 6.032070                | 0.742790  | 2.966874  |
| 20               | 6                | 0              | 5.975129                | -0.239362 | 1.071445  |
| 21               | 6                | 0              | 5.119718                | -0.769385 | 0.114054  |
| 22               | 1                | 0              | 5.520105                | -1.272898 | -0.759336 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 23 | 6 | 0 | 3.576763  | -2.115143 | -2.312846 |
| 24 | 6 | 0 | 3.613875  | -3.452376 | -2.720439 |
| 25 | 1 | 0 | 3.121187  | -4.216174 | -2.126647 |
| 26 | 6 | 0 | 4.282418  | -3.813186 | -3.890914 |
| 27 | 1 | 0 | 4.306075  | -4.856123 | -4.196359 |
| 28 | 6 | 0 | 4.915075  | -2.842890 | -4.664653 |
| 29 | 1 | 0 | 5.436562  | -3.126277 | -5.575353 |
| 30 | 6 | 0 | 4.873547  | -1.504849 | -4.270039 |
| 31 | 1 | 0 | 5.361142  | -0.742668 | -4.872537 |
| 32 | 6 | 0 | 4.204301  | -1.142101 | -3.104272 |
| 33 | 1 | 0 | 4.167658  | -0.099069 | -2.803092 |
| 34 | 6 | 0 | 2.133680  | -3.086009 | 0.056971  |
| 35 | 6 | 0 | 3.113884  | -3.970076 | 0.526882  |
| 36 | 1 | 0 | 4.165773  | -3.768560 | 0.338289  |
| 37 | 6 | 0 | 2.745673  | -5.099619 | 1.253149  |
| 38 | 1 | 0 | 3.510479  | -5.781121 | 1.617067  |
| 39 | 6 | 0 | 1.398504  | -5.347503 | 1.525028  |
| 40 | 1 | 0 | 1.113142  | -6.225676 | 2.098775  |
| 41 | 6 | 0 | 0.422577  | -4.459729 | 1.077109  |
| 42 | 1 | 0 | -0.625065 | -4.633593 | 1.306563  |
| 43 | 6 | 0 | 0.789584  | -3.329142 | 0.345583  |
| 44 | 1 | 0 | 0.032129  | -2.618330 | 0.026105  |
| 45 | 6 | 0 | -3.629712 | -0.500769 | 0.370487  |
| 46 | 6 | 0 | -2.792504 | -0.636975 | 1.515335  |
| 47 | 6 | 0 | -3.448907 | -0.800672 | 2.785737  |
| 48 | 6 | 0 | -4.836418 | -0.765096 | 2.823617  |
| 49 | 1 | 0 | -5.318767 | -0.872665 | 3.789528  |
| 50 | 6 | 0 | -5.668822 | -0.592407 | 1.700305  |
| 51 | 6 | 0 | -5.032347 | -0.476864 | 0.477080  |
| 52 | 1 | 0 | -5.620361 | -0.352198 | -0.426553 |
| 53 | 6 | 0 | -3.437402 | -2.244514 | -1.985528 |
| 54 | 6 | 0 | -2.461595 | -3.245077 | -1.961646 |
| 55 | 1 | 0 | -1.459954 | -3.001228 | -1.623795 |
| 56 | 6 | 0 | -2.769118 | -4.545734 | -2.358477 |
| 57 | 1 | 0 | -1.998484 | -5.312214 | -2.336351 |
| 58 | 6 | 0 | -4.060228 | -4.860076 | -2.778344 |
| 59 | 1 | 0 | -4.302747 | -5.873955 | -3.086611 |
| 60 | 6 | 0 | -5.042191 | -3.869367 | -2.799444 |
| 61 | 1 | 0 | -6.051971 | -4.108448 | -3.123453 |
| 62 | 6 | 0 | -4.734089 | -2.568809 | -2.406251 |
| 63 | 1 | 0 | -5.507715 | -1.806873 | -2.433354 |
| 64 | 6 | 0 | -3.992976 | 0.599646  | -2.369945 |
| 65 | 6 | 0 | -4.399809 | 1.826736  | -1.831317 |
| 66 | 1 | 0 | -4.211660 | 2.065576  | -0.788780 |
| 67 | 6 | 0 | -5.038159 | 2.765421  | -2.639597 |
| 68 | 1 | 0 | -5.349346 | 3.712194  | -2.206708 |
| 69 | 6 | 0 | -5.264791 | 2.495699  | -3.988830 |
| 70 | 1 | 0 | -5.765794 | 3.229640  | -4.615573 |
| 71 | 6 | 0 | -4.843848 | 1.283591  | -4.535200 |
| 72 | 1 | 0 | -5.013196 | 1.068708  | -5.587475 |
| 73 | 6 | 0 | -4.209725 | 0.338521  | -3.730149 |
| 74 | 1 | 0 | -3.895642 | -0.607226 | -4.163515 |
| 75 | 6 | 0 | 3.071888  | 3.904503  | -1.792309 |
| 76 | 6 | 0 | 3.184296  | 2.784553  | -2.822245 |
| 77 | 1 | 0 | 2.669199  | 1.879980  | -2.491704 |
| 78 | 1 | 0 | 4.244739  | 2.552969  | -2.974042 |
| 79 | 1 | 0 | 2.769356  | 3.103828  | -3.785196 |
| 80 | 6 | 0 | 3.439495  | 1.065670  | 3.704986  |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 81  | 6 | 0 | 7.503396  | -0.301926 | 0.961540  |
| 82  | 6 | 0 | -7.191069 | -0.536647 | 1.868889  |
| 83  | 6 | 0 | -2.630338 | -0.996989 | 4.072551  |
| 84  | 6 | 0 | 3.512601  | 3.471430  | -0.399833 |
| 85  | 6 | 0 | 3.836469  | 5.143186  | -2.248963 |
| 86  | 1 | 0 | 4.573839  | 3.201760  | -0.419507 |
| 87  | 1 | 0 | 3.382214  | 4.290477  | 0.315207  |
| 88  | 1 | 0 | 2.954165  | 2.603160  | -0.047385 |
| 89  | 1 | 0 | 3.492211  | 5.475273  | -3.234114 |
| 90  | 1 | 0 | 4.905149  | 4.914648  | -2.314752 |
| 91  | 1 | 0 | 3.702617  | 5.965613  | -1.538882 |
| 92  | 6 | 0 | 2.613072  | 2.331438  | 3.405777  |
| 93  | 6 | 0 | 2.555229  | 0.017113  | 4.410763  |
| 94  | 6 | 0 | 4.548934  | 1.465690  | 4.690407  |
| 95  | 6 | 0 | 8.079290  | -1.092216 | 2.153396  |
| 96  | 6 | 0 | 7.962522  | -0.991067 | -0.330823 |
| 97  | 6 | 0 | 8.083769  | 1.126130  | 0.972897  |
| 98  | 6 | 0 | -7.915403 | -0.362801 | 0.527176  |
| 99  | 6 | 0 | -7.692606 | -1.842907 | 2.515626  |
| 100 | 6 | 0 | -7.564890 | 0.655203  | 2.772372  |
| 101 | 6 | 0 | -1.713022 | -2.228968 | 3.934618  |
| 102 | 6 | 0 | -3.520867 | -1.236485 | 5.302526  |
| 103 | 6 | 0 | -1.791643 | 0.264473  | 4.356637  |
| 104 | 1 | 0 | -8.998645 | -0.325016 | 0.692611  |
| 105 | 1 | 0 | -7.624845 | 0.567301  | 0.024722  |
| 106 | 1 | 0 | -7.714710 | -1.199111 | -0.153484 |
| 107 | 1 | 0 | -8.652816 | 0.708939  | 2.909455  |
| 108 | 1 | 0 | -7.107671 | 0.570675  | 3.764240  |
| 109 | 1 | 0 | -7.227598 | 1.599805  | 2.330449  |
| 110 | 1 | 0 | -8.781748 | -1.812556 | 2.649698  |
| 111 | 1 | 0 | -7.449778 | -2.708180 | 1.887659  |
| 112 | 1 | 0 | -7.242489 | -2.009237 | 3.500310  |
| 113 | 1 | 0 | 9.057943  | -1.004991 | -0.375685 |
| 114 | 1 | 0 | 7.617786  | -2.030626 | -0.383646 |
| 115 | 1 | 0 | 7.601162  | -0.466486 | -1.223330 |
| 116 | 1 | 0 | 9.179347  | 1.098138  | 0.911537  |
| 117 | 1 | 0 | 7.710132  | 1.705895  | 0.120345  |
| 118 | 1 | 0 | 7.815426  | 1.667361  | 1.886873  |
| 119 | 1 | 0 | 9.173603  | -1.147515 | 2.087254  |
| 120 | 1 | 0 | 7.827585  | -0.625309 | 3.111756  |
| 121 | 1 | 0 | 7.686206  | -2.115429 | 2.168530  |
| 122 | 1 | 0 | 1.729036  | -0.300481 | 3.772165  |
| 123 | 1 | 0 | 2.138126  | 0.438735  | 5.334399  |
| 124 | 1 | 0 | 3.146266  | -0.867305 | 4.679838  |
| 125 | 1 | 0 | 1.759270  | 2.122093  | 2.758146  |
| 126 | 1 | 0 | 2.230929  | 2.755288  | 4.343912  |
| 127 | 1 | 0 | 3.238855  | 3.094991  | 2.926035  |
| 128 | 1 | 0 | 5.172503  | 0.611744  | 4.982154  |
| 129 | 1 | 0 | 5.202378  | 2.249552  | 4.287238  |
| 130 | 1 | 0 | 4.089736  | 1.862133  | 5.603509  |
| 131 | 1 | 0 | -2.446058 | 1.127810  | 4.527449  |
| 132 | 1 | 0 | -1.183076 | 0.116655  | 5.258601  |
| 133 | 1 | 0 | -1.127919 | 0.505556  | 3.525710  |
| 134 | 1 | 0 | -2.311483 | -3.137465 | 3.787378  |
| 135 | 1 | 0 | -1.027845 | -2.122656 | 3.092350  |
| 136 | 1 | 0 | -1.122337 | -2.360714 | 4.850531  |
| 137 | 1 | 0 | -4.150965 | -2.127704 | 5.191669  |
| 138 | 1 | 0 | -4.168187 | -0.378833 | 5.522185  |

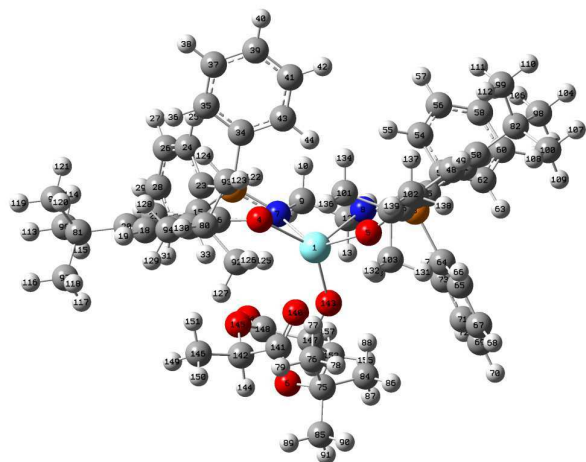
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 139 | 1 | 0 | -2.881685 | -1.392934 | 6.179680  |
| 140 | 8 | 0 | 0.681029  | 2.425821  | -1.234167 |
| 141 | 6 | 0 | 0.638968  | 3.622771  | -1.455571 |
| 142 | 6 | 0 | -0.637863 | 4.465660  | -1.525850 |
| 143 | 8 | 0 | -0.488761 | 2.373291  | 1.302614  |
| 144 | 1 | 0 | -0.442775 | 5.399121  | -0.984358 |
| 145 | 8 | 0 | -1.774768 | 3.810280  | -0.999753 |
| 146 | 6 | 0 | -0.962798 | 4.791119  | -2.983502 |
| 147 | 6 | 0 | -0.861283 | 3.698682  | 1.323017  |
| 148 | 6 | 0 | -2.046038 | 3.790725  | 0.351880  |
| 149 | 1 | 0 | -1.860574 | 5.413852  | -3.019810 |
| 150 | 1 | 0 | -0.133235 | 5.327354  | -3.451729 |
| 151 | 1 | 0 | -1.161850 | 3.870200  | -3.540218 |
| 152 | 1 | 0 | -0.037249 | 4.350743  | 0.966779  |
| 153 | 6 | 0 | -1.265570 | 4.178180  | 2.712307  |
| 154 | 8 | 0 | -3.202886 | 3.677518  | 0.675207  |
| 155 | 1 | 0 | -0.427286 | 4.022208  | 3.397803  |
| 156 | 1 | 0 | -1.529585 | 5.243293  | 2.709480  |
| 157 | 1 | 0 | -2.125414 | 3.604362  | 3.066047  |

-----  
Rotational constants (GHZ):      0.0371176      0.0212310  
0.0206406

Sum of electronic and zero-point Energies=      -3172.902932  
Sum of electronic and thermal Energies=      -3172.822041  
Sum of electronic and thermal Enthalpies=      -3172.821097  
Sum of electronic and thermal Free Energies=      -3173.025017

|                |        |        |   |
|----------------|--------|--------|---|
|                | 1      | 2      | 3 |
|                | A      | A      | A |
| Frequencies -- | 8.1447 | 8.8934 |   |
| 17.1171        |        |        |   |
| Red. masses -- | 4.6412 | 4.6930 |   |
| 4.0396         |        |        |   |
| Frc consts --  | 0.0002 | 0.0002 |   |
| 0.0007         |        |        |   |
| IR Inten --    | 0.0810 | 0.1797 |   |
| 0.0408         |        |        |   |

*Intitiation INT4'*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.009741               | 0.392165  | -0.471004 |
| 2                | 15               | 0              | 2.349633                | -2.151915 | 0.077613  |
| 3                | 15               | 0              | -3.198993               | -1.066313 | -0.936260 |
| 4                | 8                | 0              | 1.524118                | 0.450629  | 1.171541  |
| 5                | 8                | 0              | -1.788697               | 1.128784  | 0.600053  |
| 6                | 8                | 0              | 1.341065                | 4.645144  | -1.956675 |
| 7                | 7                | 0              | 1.084553                | -1.661410 | -0.839269 |
| 8                | 7                | 0              | -1.591241               | -1.374206 | -0.886738 |
| 9                | 6                | 0              | 0.327492                | -2.728050 | -1.502508 |
| 10               | 1                | 0              | 0.132062                | -3.580823 | -0.829648 |
| 11               | 1                | 0              | 0.866306                | -3.130680 | -2.373908 |
| 12               | 6                | 0              | -1.014202               | -2.170316 | -1.975660 |
| 13               | 1                | 0              | -0.842307               | -1.548459 | -2.865506 |
| 14               | 1                | 0              | -1.651363               | -3.018831 | -2.276560 |
| 15               | 6                | 0              | 3.440960                | -0.810560 | 0.600451  |
| 16               | 6                | 0              | 2.823310                | 0.288663  | 1.257113  |
| 17               | 6                | 0              | 3.686921                | 1.144341  | 2.023346  |
| 18               | 6                | 0              | 5.062272                | 0.943111  | 1.919779  |
| 19               | 1                | 0              | 5.710494                | 1.613810  | 2.474959  |
| 20               | 6                | 0              | 5.678752                | -0.075034 | 1.168871  |
| 21               | 6                | 0              | 4.830277                | -0.980437 | 0.544834  |
| 22               | 1                | 0              | 5.232698                | -1.832022 | 0.006810  |
| 23               | 6                | 0              | 3.363793                | -3.380335 | -0.850702 |
| 24               | 6                | 0              | 3.651196                | -4.668250 | -0.388650 |
| 25               | 1                | 0              | 3.297829                | -4.992265 | 0.585683  |
| 26               | 6                | 0              | 4.385660                | -5.548207 | -1.184138 |
| 27               | 1                | 0              | 4.605848                | -6.548022 | -0.818374 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 28 | 6 | 0 | 4.829999  | -5.148616 | -2.443138 |
| 29 | 1 | 0 | 5.401486  | -5.836495 | -3.061551 |
| 30 | 6 | 0 | 4.531405  | -3.869014 | -2.913289 |
| 31 | 1 | 0 | 4.863308  | -3.556643 | -3.900002 |
| 32 | 6 | 0 | 3.796789  | -2.985263 | -2.126078 |
| 33 | 1 | 0 | 3.545686  | -1.998130 | -2.509018 |
| 34 | 6 | 0 | 1.815016  | -2.960931 | 1.655344  |
| 35 | 6 | 0 | 2.750050  | -3.414885 | 2.594394  |
| 36 | 1 | 0 | 3.814612  | -3.321905 | 2.392965  |
| 37 | 6 | 0 | 2.321095  | -3.958556 | 3.803193  |
| 38 | 1 | 0 | 3.051927  | -4.307357 | 4.528528  |
| 39 | 6 | 0 | 0.957085  | -4.038062 | 4.088324  |
| 40 | 1 | 0 | 0.623597  | -4.455456 | 5.035208  |
| 41 | 6 | 0 | 0.024687  | -3.564607 | 3.166765  |
| 42 | 1 | 0 | -1.037375 | -3.602184 | 3.396163  |
| 43 | 6 | 0 | 0.450317  | -3.024849 | 1.952386  |
| 44 | 1 | 0 | -0.272802 | -2.626401 | 1.244257  |
| 45 | 6 | 0 | -3.742571 | -0.229170 | 0.574758  |
| 46 | 6 | 0 | -2.941265 | 0.803902  | 1.135343  |
| 47 | 6 | 0 | -3.472062 | 1.477944  | 2.289281  |
| 48 | 6 | 0 | -4.705774 | 1.068961  | 2.784162  |
| 49 | 1 | 0 | -5.092533 | 1.582794  | 3.657631  |
| 50 | 6 | 0 | -5.492964 | 0.038464  | 2.240011  |
| 51 | 6 | 0 | -4.983407 | -0.598135 | 1.118774  |
| 52 | 1 | 0 | -5.543548 | -1.398728 | 0.648663  |
| 53 | 6 | 0 | -4.141622 | -2.652647 | -1.064051 |
| 54 | 6 | 0 | -3.610291 | -3.769005 | -0.406512 |
| 55 | 1 | 0 | -2.666667 | -3.671817 | 0.123940  |
| 56 | 6 | 0 | -4.280225 | -4.989681 | -0.442015 |
| 57 | 1 | 0 | -3.858104 | -5.852651 | 0.066677  |
| 58 | 6 | 0 | -5.487855 | -5.103988 | -1.131399 |
| 59 | 1 | 0 | -6.010284 | -6.056920 | -1.159564 |
| 60 | 6 | 0 | -6.023341 | -3.995421 | -1.785636 |
| 61 | 1 | 0 | -6.964008 | -4.080517 | -2.323702 |
| 62 | 6 | 0 | -5.352239 | -2.772954 | -1.755316 |
| 63 | 1 | 0 | -5.772024 | -1.914393 | -2.271870 |
| 64 | 6 | 0 | -3.793703 | -0.071713 | -2.378958 |
| 65 | 6 | 0 | -4.288037 | 1.223529  | -2.193420 |
| 66 | 1 | 0 | -4.366371 | 1.631564  | -1.189775 |
| 67 | 6 | 0 | -4.685674 | 1.986931  | -3.290635 |
| 68 | 1 | 0 | -5.074245 | 2.990402  | -3.135638 |
| 69 | 6 | 0 | -4.593381 | 1.462896  | -4.579043 |
| 70 | 1 | 0 | -4.908815 | 2.056764  | -5.433395 |
| 71 | 6 | 0 | -4.100940 | 0.171273  | -4.770741 |
| 72 | 1 | 0 | -4.029821 | -0.243244 | -5.773188 |
| 73 | 6 | 0 | -3.700433 | -0.592679 | -3.677016 |
| 74 | 1 | 0 | -3.325216 | -1.599979 | -3.836765 |
| 75 | 6 | 0 | 0.241837  | 5.508281  | -1.472183 |
| 76 | 6 | 0 | 0.375482  | 5.713787  | 0.031987  |
| 77 | 1 | 0 | 0.211219  | 4.786398  | 0.581939  |
| 78 | 1 | 0 | -0.368405 | 6.446790  | 0.362782  |
| 79 | 1 | 0 | 1.368988  | 6.103119  | 0.279135  |
| 80 | 6 | 0 | 3.116806  | 2.178422  | 3.006194  |
| 81 | 6 | 0 | 7.207704  | -0.175178 | 1.110654  |
| 82 | 6 | 0 | -6.834038 | -0.329838 | 2.885625  |
| 83 | 6 | 0 | -2.704853 | 2.626112  | 2.961194  |
| 84 | 6 | 0 | -1.098658 | 4.900947  | -1.873714 |
| 85 | 6 | 0 | 0.495182  | 6.810958  | -2.224904 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 86  | 1 | 0 | -1.899958 | 5.603078  | -1.617969 |
| 87  | 1 | 0 | -1.132016 | 4.725722  | -2.954470 |
| 88  | 1 | 0 | -1.290811 | 3.957298  | -1.360593 |
| 89  | 1 | 0 | 1.479540  | 7.219885  | -1.974885 |
| 90  | 1 | 0 | -0.265405 | 7.550002  | -1.952867 |
| 91  | 1 | 0 | 0.450025  | 6.650057  | -3.306909 |
| 92  | 6 | 0 | 2.282525  | 3.243517  | 2.275970  |
| 93  | 6 | 0 | 2.237234  | 1.431841  | 4.029947  |
| 94  | 6 | 0 | 4.212297  | 2.915794  | 3.792641  |
| 95  | 6 | 0 | 7.775317  | -0.369250 | 2.530645  |
| 96  | 6 | 0 | 7.674960  | -1.354779 | 0.246920  |
| 97  | 6 | 0 | 7.787609  | 1.118565  | 0.506106  |
| 98  | 6 | 0 | -7.540694 | -1.470534 | 2.141201  |
| 99  | 6 | 0 | -6.599976 | -0.781338 | 4.340795  |
| 100 | 6 | 0 | -7.768434 | 0.896186  | 2.878450  |
| 101 | 6 | 0 | -1.353706 | 2.109816  | 3.486489  |
| 102 | 6 | 0 | -3.461624 | 3.226498  | 4.156924  |
| 103 | 6 | 0 | -2.479489 | 3.762503  | 1.945561  |
| 104 | 1 | 0 | -8.491604 | -1.702346 | 2.635439  |
| 105 | 1 | 0 | -7.765421 | -1.201362 | 1.102249  |
| 106 | 1 | 0 | -6.939300 | -2.387104 | 2.134317  |
| 107 | 1 | 0 | -8.731417 | 0.649784  | 3.344000  |
| 108 | 1 | 0 | -7.339107 | 1.739193  | 3.430976  |
| 109 | 1 | 0 | -7.962002 | 1.233040  | 1.853265  |
| 110 | 1 | 0 | -7.551532 | -1.043038 | 4.821514  |
| 111 | 1 | 0 | -5.946674 | -1.660955 | 4.375844  |
| 112 | 1 | 0 | -6.130090 | 0.006120  | 4.940224  |
| 113 | 1 | 0 | 8.770713  | -1.380501 | 0.214631  |
| 114 | 1 | 0 | 7.335106  | -2.315618 | 0.651321  |
| 115 | 1 | 0 | 7.313476  | -1.272017 | -0.784651 |
| 116 | 1 | 0 | 8.883950  | 1.072197  | 0.473843  |
| 117 | 1 | 0 | 7.422350  | 1.267604  | -0.516683 |
| 118 | 1 | 0 | 7.508576  | 2.000981  | 1.092697  |
| 119 | 1 | 0 | 8.870414  | -0.440336 | 2.502077  |
| 120 | 1 | 0 | 7.514051  | 0.464444  | 3.191484  |
| 121 | 1 | 0 | 7.386097  | -1.288509 | 2.983861  |
| 122 | 1 | 0 | 1.430379  | 0.889766  | 3.532566  |
| 123 | 1 | 0 | 1.794465  | 2.139978  | 4.742171  |
| 124 | 1 | 0 | 2.838584  | 0.711470  | 4.597959  |
| 125 | 1 | 0 | 1.472200  | 2.787030  | 1.708079  |
| 126 | 1 | 0 | 1.852042  | 3.947911  | 2.999924  |
| 127 | 1 | 0 | 2.911065  | 3.818970  | 1.584471  |
| 128 | 1 | 0 | 4.834153  | 2.230759  | 4.381131  |
| 129 | 1 | 0 | 4.869237  | 3.503873  | 3.139452  |
| 130 | 1 | 0 | 3.739745  | 3.613686  | 4.494145  |
| 131 | 1 | 0 | -3.439343 | 4.170746  | 1.603943  |
| 132 | 1 | 0 | -1.912399 | 4.579054  | 2.411334  |
| 133 | 1 | 0 | -1.926122 | 3.401502  | 1.076906  |
| 134 | 1 | 0 | -1.505659 | 1.329367  | 4.242208  |
| 135 | 1 | 0 | -0.745413 | 1.692784  | 2.682851  |
| 136 | 1 | 0 | -0.791132 | 2.927343  | 3.954944  |
| 137 | 1 | 0 | -3.624910 | 2.492743  | 4.955420  |
| 138 | 1 | 0 | -4.433219 | 3.645942  | 3.867927  |
| 139 | 1 | 0 | -2.865518 | 4.042787  | 4.581934  |
| 140 | 8 | 0 | 0.810020  | 2.774352  | -0.789769 |
| 141 | 6 | 0 | 1.501605  | 3.382005  | -1.589590 |
| 142 | 6 | 0 | 2.736516  | 2.810568  | -2.291800 |
| 143 | 8 | 0 | -0.127044 | 0.828963  | -2.556978 |

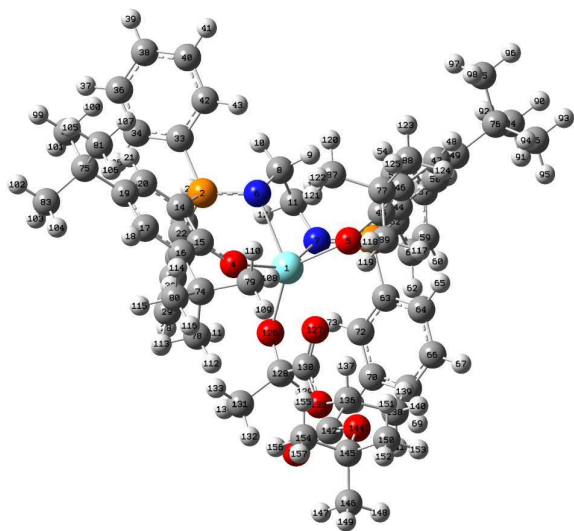
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 144 | 1 | 0 | 2.763061  | 3.234811  | -3.302269 |
| 145 | 8 | 0 | 2.738685  | 1.392508  | -2.355191 |
| 146 | 6 | 0 | 4.001592  | 3.217014  | -1.540651 |
| 147 | 6 | 0 | 0.619293  | 1.255339  | -3.633680 |
| 148 | 6 | 0 | 2.043543  | 0.750999  | -3.363558 |
| 149 | 1 | 0 | 4.874406  | 2.854136  | -2.090225 |
| 150 | 1 | 0 | 4.061922  | 4.306054  | -1.453822 |
| 151 | 1 | 0 | 4.010360  | 2.768122  | -0.543442 |
| 152 | 1 | 0 | 0.634377  | 2.364192  | -3.696417 |
| 153 | 6 | 0 | 0.100031  | 0.734535  | -4.969049 |
| 154 | 8 | 0 | 2.525030  | -0.252059 | -3.827284 |
| 155 | 1 | 0 | -0.944786 | 1.037586  | -5.084408 |
| 156 | 1 | 0 | 0.682803  | 1.134027  | -5.808508 |
| 157 | 1 | 0 | 0.159413  | -0.356782 | -4.996941 |

-----  
Rotational constants (GHZ):      0.0347683      0.0224534  
0.0205511

Sum of electronic and zero-point Energies=      -3172.906435  
Sum of electronic and thermal Energies=      -3172.825861  
Sum of electronic and thermal Enthalpies=      -3172.824917  
Sum of electronic and thermal Free Energies=      -3173.027356

|                | 1      | 2       | 3 |
|----------------|--------|---------|---|
|                | A      | A       | A |
| Frequencies -- | 7.1350 | 10.3199 |   |
| 17.6332        |        |         |   |
| Red. masses -- | 4.3746 | 5.1171  |   |
| 5.4090         |        |         |   |
| Frc consts --  | 0.0001 | 0.0003  |   |
| 0.0010         |        |         |   |
| IR Inten --    | 0.0365 | 0.1816  |   |
| 0.0792         |        |         |   |

*Intitiation P*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.055144               | -0.046995 | -0.789074 |
| 2                | 15               | 0              | 0.764252                | -3.351957 | -0.511074 |
| 3                | 15               | 0              | -3.367181               | 0.264608  | -0.903634 |
| 4                | 8                | 0              | 1.942830                | -0.646691 | -0.175997 |
| 5                | 8                | 0              | -1.187643               | 0.779638  | 0.874697  |
| 6                | 7                | 0              | -0.418445               | -2.329791 | -0.002028 |
| 7                | 7                | 0              | -2.235141               | -0.760145 | -1.517149 |
| 8                | 6                | 0              | -1.808823               | -2.774197 | -0.158425 |
| 9                | 1                | 0              | -2.372367               | -2.407199 | 0.713618  |
| 10               | 1                | 0              | -1.909883               | -3.872713 | -0.152290 |
| 11               | 6                | 0              | -2.449561               | -2.197799 | -1.424835 |
| 12               | 1                | 0              | -1.965610               | -2.658982 | -2.294327 |
| 13               | 1                | 0              | -3.517767               | -2.471159 | -1.471881 |
| 14               | 6                | 0              | 2.376128                | -2.935283 | 0.194771  |
| 15               | 6                | 0              | 2.748708                | -1.572952 | 0.278480  |
| 16               | 6                | 0              | 4.035179                | -1.270121 | 0.832650  |
| 17               | 6                | 0              | 4.819739                | -2.340614 | 1.252013  |
| 18               | 1                | 0              | 5.794169                | -2.110900 | 1.672255  |
| 19               | 6                | 0              | 4.461539                | -3.700798 | 1.169011  |
| 20               | 6                | 0              | 3.213672                | -3.973545 | 0.626437  |
| 21               | 1                | 0              | 2.864340                | -4.993879 | 0.513414  |
| 22               | 6                | 0              | 0.884721                | -3.280959 | -2.340340 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 23 | 6 | 0 | -0.109255 | -3.909774 | -3.143274 |
| 24 | 1 | 0 | -0.793676 | -4.643835 | -2.694532 |
| 25 | 6 | 0 | -0.210228 | -3.594515 | -4.510606 |
| 26 | 1 | 0 | -0.970301 | -4.090300 | -5.130185 |
| 27 | 6 | 0 | 0.672103  | -2.656424 | -5.088240 |
| 28 | 1 | 0 | 0.588912  | -2.413952 | -6.157123 |
| 29 | 6 | 0 | 1.676908  | -2.050363 | -4.308505 |
| 30 | 1 | 0 | 2.373389  | -1.329423 | -4.760154 |
| 31 | 6 | 0 | 1.791817  | -2.358161 | -2.933289 |
| 32 | 1 | 0 | 2.568110  | -1.879229 | -2.320712 |
| 33 | 6 | 0 | 0.445753  | -5.081179 | -0.020951 |
| 34 | 6 | 0 | 0.992419  | -6.175944 | -0.738268 |
| 35 | 1 | 0 | 1.558991  | -5.997507 | -1.662901 |
| 36 | 6 | 0 | 0.810544  | -7.485422 | -0.254677 |
| 37 | 1 | 0 | 1.234580  | -8.334525 | -0.806274 |
| 38 | 6 | 0 | 0.087957  | -7.704169 | 0.933006  |
| 39 | 1 | 0 | -0.053797 | -8.728581 | 1.302976  |
| 40 | 6 | 0 | -0.445347 | -6.619834 | 1.654701  |
| 41 | 1 | 0 | -0.998883 | -6.795920 | 2.586367  |
| 42 | 6 | 0 | -0.261760 | -5.306367 | 1.188612  |
| 43 | 1 | 0 | -0.648023 | -4.445231 | 1.753159  |
| 44 | 6 | 0 | -3.522135 | 0.493435  | 0.892005  |
| 45 | 6 | 0 | -2.296021 | 0.716060  | 1.567373  |
| 46 | 6 | 0 | -2.331524 | 0.887492  | 2.988641  |
| 47 | 6 | 0 | -3.582385 | 0.870545  | 3.597787  |
| 48 | 1 | 0 | -3.614838 | 1.009327  | 4.674161  |
| 49 | 6 | 0 | -4.815187 | 0.684729  | 2.937441  |
| 50 | 6 | 0 | -4.753345 | 0.488342  | 1.564502  |
| 51 | 1 | 0 | -5.653387 | 0.305199  | 0.988756  |
| 52 | 6 | 0 | -5.031685 | -0.200310 | -1.492443 |
| 53 | 6 | 0 | -5.673038 | -1.324072 | -0.898003 |
| 54 | 1 | 0 | -5.221448 | -1.810481 | -0.022562 |
| 55 | 6 | 0 | -6.896655 | -1.788783 | -1.416542 |
| 56 | 1 | 0 | -7.389757 | -2.654262 | -0.954890 |
| 57 | 6 | 0 | -7.483214 | -1.144307 | -2.520510 |
| 58 | 1 | 0 | -8.438308 | -1.508508 | -2.922128 |
| 59 | 6 | 0 | -6.853975 | -0.032782 | -3.111628 |
| 60 | 1 | 0 | -7.318847 | 0.470609  | -3.969405 |
| 61 | 6 | 0 | -5.629717 | 0.439213  | -2.606273 |
| 62 | 1 | 0 | -5.141699 | 1.308264  | -3.068095 |
| 63 | 6 | 0 | -2.876983 | 1.878109  | -1.604313 |
| 64 | 6 | 0 | -3.012979 | 3.071947  | -0.850867 |
| 65 | 1 | 0 | -3.386719 | 3.019248  | 0.182840  |
| 66 | 6 | 0 | -2.676124 | 4.310879  | -1.438271 |
| 67 | 1 | 0 | -2.826857 | 5.241087  | -0.873734 |
| 68 | 6 | 0 | -2.204219 | 4.357345  | -2.768360 |
| 69 | 1 | 0 | -1.969486 | 5.327143  | -3.229625 |
| 70 | 6 | 0 | -2.057549 | 3.169199  | -3.520477 |
| 71 | 1 | 0 | -1.719981 | 3.212757  | -4.565580 |
| 72 | 6 | 0 | -2.383514 | 1.922393  | -2.941517 |
| 73 | 1 | 0 | -2.253244 | 0.982999  | -3.496422 |
| 74 | 6 | 0 | 4.529719  | 0.187401  | 0.927550  |
| 75 | 6 | 0 | 5.427666  | -4.788548 | 1.672884  |
| 76 | 6 | 0 | -6.130123 | 0.693139  | 3.738970  |
| 77 | 6 | 0 | -1.029203 | 1.069283  | 3.791489  |
| 78 | 6 | 0 | 4.579517  | 0.807292  | -0.506670 |
| 79 | 6 | 0 | 3.557174  | 1.014125  | 1.827725  |
| 80 | 6 | 0 | 5.958360  | 0.284052  | 1.544996  |



## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 81  | 6 | 0 | 5.684229  | -4.577848 | 3.200169  |
| 82  | 6 | 0 | 4.842361  | -6.216624 | 1.458459  |
| 83  | 6 | 0 | 6.780462  | -4.683774 | 0.897046  |
| 84  | 6 | 0 | -7.365891 | 0.476915  | 2.814425  |
| 85  | 6 | 0 | -6.094967 | -0.453313 | 4.800918  |
| 86  | 6 | 0 | -6.285818 | 2.069218  | 4.463884  |
| 87  | 6 | 0 | -0.129588 | -0.195043 | 3.596100  |
| 88  | 6 | 0 | -1.301635 | 1.234944  | 5.318149  |
| 89  | 6 | 0 | -0.274502 | 2.344643  | 3.292740  |
| 90  | 1 | 0 | -8.284632 | 0.498545  | 3.420925  |
| 91  | 1 | 0 | -7.437242 | 1.271204  | 2.057415  |
| 92  | 1 | 0 | -7.315027 | -0.497843 | 2.308062  |
| 93  | 1 | 0 | -7.217934 | 2.083006  | 5.049277  |
| 94  | 1 | 0 | -5.444908 | 2.249842  | 5.148823  |
| 95  | 1 | 0 | -6.316015 | 2.886731  | 3.729788  |
| 96  | 1 | 0 | -7.030732 | -0.459231 | 5.380686  |
| 97  | 1 | 0 | -5.977557 | -1.428281 | 4.306727  |
| 98  | 1 | 0 | -5.256597 | -0.316597 | 5.499116  |
| 99  | 1 | 0 | 5.560476  | -6.965515 | 1.827033  |
| 100 | 1 | 0 | 3.901118  | -6.344802 | 2.012300  |
| 101 | 1 | 0 | 4.661537  | -6.412273 | 0.391721  |
| 102 | 1 | 0 | 7.479460  | -5.455621 | 1.254028  |
| 103 | 1 | 0 | 6.615814  | -4.825300 | -0.180472 |
| 104 | 1 | 0 | 7.246709  | -3.699659 | 1.049183  |
| 105 | 1 | 0 | 6.381014  | -5.342997 | 3.575331  |
| 106 | 1 | 0 | 6.121447  | -3.587242 | 3.390515  |
| 107 | 1 | 0 | 4.740343  | -4.652092 | 3.758724  |
| 108 | 1 | 0 | 2.540214  | 0.993968  | 1.411252  |
| 109 | 1 | 0 | 3.902770  | 2.060494  | 1.878191  |
| 110 | 1 | 0 | 3.533698  | 0.594418  | 2.845374  |
| 111 | 1 | 0 | 3.582822  | 0.758217  | -0.967621 |
| 112 | 1 | 0 | 4.899295  | 1.860803  | -0.445762 |
| 113 | 1 | 0 | 5.292046  | 0.252604  | -1.136739 |
| 114 | 1 | 0 | 5.979236  | -0.110964 | 2.571095  |
| 115 | 1 | 0 | 6.697025  | -0.254637 | 0.933979  |
| 116 | 1 | 0 | 6.257259  | 1.343873  | 1.582143  |
| 117 | 1 | 0 | -0.896963 | 3.238384  | 3.454969  |
| 118 | 1 | 0 | 0.666480  | 2.455938  | 3.855778  |
| 119 | 1 | 0 | -0.046842 | 2.256380  | 2.221716  |
| 120 | 1 | 0 | -0.648567 | -1.091382 | 3.972308  |
| 121 | 1 | 0 | 0.103352  | -0.347109 | 2.531679  |
| 122 | 1 | 0 | 0.815711  | -0.067127 | 4.150772  |
| 123 | 1 | 0 | -1.803569 | 0.349274  | 5.734074  |
| 124 | 1 | 0 | -1.911790 | 2.126642  | 5.523458  |
| 125 | 1 | 0 | -0.338413 | 1.355070  | 5.839326  |
| 126 | 8 | 0 | 0.488649  | 0.762906  | -2.722748 |
| 127 | 8 | 0 | 0.859191  | 2.276883  | -0.592484 |
| 128 | 6 | 0 | 1.005196  | 1.995439  | -2.983546 |
| 129 | 1 | 0 | 0.282684  | 2.632458  | -3.535852 |
| 130 | 6 | 0 | 1.181798  | 2.755959  | -1.672619 |
| 131 | 6 | 0 | 2.313666  | 1.965812  | -3.787900 |
| 132 | 1 | 0 | 2.697086  | 2.972873  | -3.984194 |
| 133 | 1 | 0 | 3.075308  | 1.395135  | -3.247115 |
| 134 | 1 | 0 | 2.120462  | 1.464095  | -4.741521 |
| 135 | 8 | 0 | 1.648892  | 4.003173  | -1.800006 |
| 136 | 6 | 0 | 1.668187  | 4.818534  | -0.622789 |
| 137 | 1 | 0 | 1.554623  | 4.172292  | 0.253406  |
| 138 | 6 | 0 | 0.510333  | 5.806506  | -0.696226 |

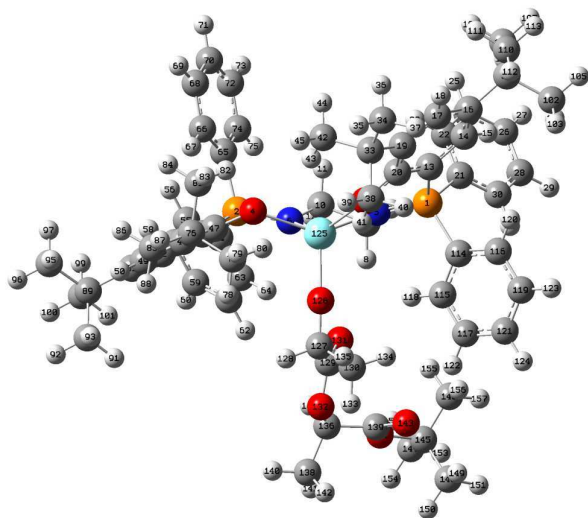
## Appendix 2. Optimised Structures

|     |   |   |           |          |           |
|-----|---|---|-----------|----------|-----------|
| 139 | 1 | 0 | -0.420284 | 5.254110 | -0.854662 |
| 140 | 1 | 0 | 0.440457  | 6.380135 | 0.231509  |
| 141 | 1 | 0 | 0.647265  | 6.501253 | -1.532421 |
| 142 | 6 | 0 | 3.035494  | 5.491618 | -0.551676 |
| 143 | 8 | 0 | 3.938018  | 5.315005 | -1.335147 |
| 144 | 8 | 0 | 3.060989  | 6.290942 | 0.526263  |
| 145 | 6 | 0 | 4.257655  | 7.064664 | 0.879039  |
| 146 | 6 | 0 | 4.584959  | 8.055725 | -0.236335 |
| 147 | 1 | 0 | 4.891113  | 7.538138 | -1.147443 |
| 148 | 1 | 0 | 3.713437  | 8.681573 | -0.458553 |
| 149 | 1 | 0 | 5.400846  | 8.712709 | 0.085777  |
| 150 | 6 | 0 | 3.822574  | 7.797358 | 2.145193  |
| 151 | 1 | 0 | 3.541911  | 7.083965 | 2.926982  |
| 152 | 1 | 0 | 4.642467  | 8.418899 | 2.520459  |
| 153 | 1 | 0 | 2.962073  | 8.443560 | 1.942521  |
| 154 | 6 | 0 | 5.421014  | 6.119596 | 1.173637  |
| 155 | 1 | 0 | 5.133625  | 5.389318 | 1.938007  |
| 156 | 1 | 0 | 5.735480  | 5.586847 | 0.274245  |
| 157 | 1 | 0 | 6.271451  | 6.695096 | 1.556531  |

-----  
Rotational constants (GHZ):      0.0258497      0.0255342  
0.0181036

Sum of electronic and zero-point Energies=      -3154.452675  
Sum of electronic and thermal Energies=      -3154.373325  
Sum of electronic and thermal Enthalpies=      -3154.372381  
Sum of electronic and thermal Free Energies=      -3154.573052

|                | 1      | 2       | 3 |
|----------------|--------|---------|---|
|                | A      | A       | A |
| Frequencies -- | 8.9615 | 11.9962 |   |
| 13.4847        |        |         |   |
| Red. masses -- | 4.8869 | 4.8938  |   |
| 4.5457         |        |         |   |
| Frc consts --  | 0.0002 | 0.0004  |   |
| 0.0005         |        |         |   |
| IR Inten --    | 0.2833 | 0.3373  |   |
| 0.2848         |        |         |   |

**Intitiation P'**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 15               | 0              | 3.077088                | 0.576670  | 0.633863  |
| 2                | 15               | 0              | -2.466922               | -1.216713 | 1.781129  |
| 3                | 8                | 0              | 1.989419                | -1.462569 | -1.292768 |
| 4                | 8                | 0              | -1.314867               | -2.423945 | -0.755847 |
| 5                | 7                | 0              | 1.489793                | 0.317376  | 0.933487  |
| 6                | 7                | 0              | -1.104931               | -0.383893 | 1.398678  |
| 7                | 6                | 0              | 0.753986                | 1.088392  | 1.935714  |
| 8                | 1                | 0              | 0.273325                | 1.972468  | 1.490238  |
| 9                | 1                | 0              | 1.390670                | 1.438345  | 2.762297  |
| 10               | 6                | 0              | -0.335776               | 0.186105  | 2.507703  |
| 11               | 1                | 0              | 0.150315                | -0.600836 | 3.108657  |
| 12               | 1                | 0              | -0.960558               | 0.784236  | 3.192883  |
| 13               | 6                | 0              | 3.908243                | -0.903740 | -0.013076 |
| 14               | 6                | 0              | 5.228600                | -1.156437 | 0.375817  |
| 15               | 1                | 0              | 5.697639                | -0.505827 | 1.109063  |
| 16               | 6                | 0              | 5.944906                | -2.226829 | -0.152870 |
| 17               | 6                | 0              | 5.279790                | -3.016020 | -1.102705 |
| 18               | 1                | 0              | 5.821904                | -3.846892 | -1.536196 |
| 19               | 6                | 0              | 3.967752                | -2.807972 | -1.531417 |
| 20               | 6                | 0              | 3.232490                | -1.721947 | -0.961169 |
| 21               | 6                | 0              | 3.958755                | 1.044270  | 2.186443  |
| 22               | 6                | 0              | 3.920683                | 0.135582  | 3.254230  |
| 23               | 1                | 0              | 3.416941                | -0.819742 | 3.130438  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 24 | 6 | 0 | 4.528223  | 0.453595  | 4.465776  |
| 25 | 1 | 0 | 4.498274  | -0.257104 | 5.287676  |
| 26 | 6 | 0 | 5.174313  | 1.681473  | 4.622972  |
| 27 | 1 | 0 | 5.648951  | 1.928457  | 5.569294  |
| 28 | 6 | 0 | 5.209074  | 2.589607  | 3.567204  |
| 29 | 1 | 0 | 5.709160  | 3.547291  | 3.686708  |
| 30 | 6 | 0 | 4.601891  | 2.274240  | 2.350651  |
| 31 | 1 | 0 | 4.632929  | 2.985712  | 1.530610  |
| 32 | 6 | 0 | 7.384792  | -2.494110 | 0.307749  |
| 33 | 6 | 0 | 3.332954  | -3.717803 | -2.594981 |
| 34 | 6 | 0 | 4.309167  | -4.785956 | -3.113425 |
| 35 | 1 | 0 | 3.804788  | -5.388251 | -3.878243 |
| 36 | 1 | 0 | 4.636181  | -5.471310 | -2.321920 |
| 37 | 1 | 0 | 5.198541  | -4.343410 | -3.578483 |
| 38 | 6 | 0 | 2.893626  | -2.875051 | -3.809868 |
| 39 | 1 | 0 | 2.415525  | -3.517195 | -4.561017 |
| 40 | 1 | 0 | 3.762240  | -2.396694 | -4.279395 |
| 41 | 1 | 0 | 2.187903  | -2.095215 | -3.518435 |
| 42 | 6 | 0 | 2.122792  | -4.459715 | -1.995272 |
| 43 | 1 | 0 | 1.359345  | -3.763836 | -1.643955 |
| 44 | 1 | 0 | 2.434909  | -5.086100 | -1.150128 |
| 45 | 1 | 0 | 1.667928  | -5.114094 | -2.749957 |
| 46 | 6 | 0 | -3.348661 | -1.825407 | 0.317466  |
| 47 | 6 | 0 | -2.626268 | -2.430844 | -0.749729 |
| 48 | 6 | 0 | -3.394748 | -3.056571 | -1.789839 |
| 49 | 6 | 0 | -4.780447 | -2.962457 | -1.726296 |
| 50 | 1 | 0 | -5.354686 | -3.420064 | -2.525016 |
| 51 | 6 | 0 | -5.499519 | -2.317432 | -0.702231 |
| 52 | 6 | 0 | -4.752732 | -1.766791 | 0.327725  |
| 53 | 1 | 0 | -5.249840 | -1.275718 | 1.156256  |
| 54 | 6 | 0 | -3.627183 | -0.115081 | 2.705832  |
| 55 | 6 | 0 | -4.504436 | -0.570810 | 3.696135  |
| 56 | 1 | 0 | -4.510794 | -1.620124 | 3.978350  |
| 57 | 6 | 0 | -5.373015 | 0.321646  | 4.323992  |
| 58 | 1 | 0 | -6.053930 | -0.037608 | 5.091407  |
| 59 | 6 | 0 | -5.365646 | 1.670273  | 3.969297  |
| 60 | 1 | 0 | -6.041647 | 2.364721  | 4.461976  |
| 61 | 6 | 0 | -4.489977 | 2.128142  | 2.984204  |
| 62 | 1 | 0 | -4.480141 | 3.179767  | 2.709062  |
| 63 | 6 | 0 | -3.622230 | 1.240207  | 2.351772  |
| 64 | 1 | 0 | -2.933179 | 1.588421  | 1.585364  |
| 65 | 6 | 0 | -2.159195 | -2.649096 | 2.907951  |
| 66 | 6 | 0 | -2.202446 | -3.957263 | 2.412315  |
| 67 | 1 | 0 | -2.498654 | -4.135917 | 1.383090  |
| 68 | 6 | 0 | -1.870394 | -5.030836 | 3.236944  |
| 69 | 1 | 0 | -1.909692 | -6.042987 | 2.842712  |
| 70 | 6 | 0 | -1.492747 | -4.808640 | 4.560571  |
| 71 | 1 | 0 | -1.235638 | -5.647820 | 5.202018  |
| 72 | 6 | 0 | -1.450714 | -3.507974 | 5.062419  |
| 73 | 1 | 0 | -1.162910 | -3.329512 | 6.095465  |
| 74 | 6 | 0 | -1.781014 | -2.431494 | 4.241098  |
| 75 | 1 | 0 | -1.758177 | -1.423027 | 4.645966  |
| 76 | 6 | 0 | -2.706895 | -3.833633 | -2.924019 |
| 77 | 6 | 0 | -1.803397 | -2.903258 | -3.756659 |
| 78 | 1 | 0 | -2.385333 | -2.081456 | -4.190724 |
| 79 | 1 | 0 | -1.344083 | -3.465679 | -4.579953 |
| 80 | 1 | 0 | -1.003592 | -2.473870 | -3.152389 |
| 81 | 6 | 0 | -1.869879 | -4.979968 | -2.320613 |

## Appendix 2. Optimised Structures

|     |    |   |           |           |           |
|-----|----|---|-----------|-----------|-----------|
| 82  | 1  | 0 | -1.120537 | -4.598088 | -1.624619 |
| 83  | 1  | 0 | -1.353981 | -5.531490 | -3.117146 |
| 84  | 1  | 0 | -2.516621 | -5.688075 | -1.786876 |
| 85  | 6  | 0 | -3.717361 | -4.468441 | -3.893058 |
| 86  | 1  | 0 | -4.391885 | -5.170623 | -3.388129 |
| 87  | 1  | 0 | -3.172188 | -5.032298 | -4.658913 |
| 88  | 1  | 0 | -4.324404 | -3.716495 | -4.412220 |
| 89  | 6  | 0 | -7.030512 | -2.257523 | -0.759714 |
| 90  | 6  | 0 | -7.468337 | -1.513731 | -2.036949 |
| 91  | 1  | 0 | -7.082987 | -0.487395 | -2.041094 |
| 92  | 1  | 0 | -8.563161 | -1.468205 | -2.101408 |
| 93  | 1  | 0 | -7.101997 | -2.010140 | -2.942139 |
| 94  | 6  | 0 | -7.608290 | -3.686681 | -0.780047 |
| 95  | 1  | 0 | -7.253084 | -4.258455 | -1.644437 |
| 96  | 1  | 0 | -8.704418 | -3.657515 | -0.828830 |
| 97  | 1  | 0 | -7.321660 | -4.236949 | 0.123833  |
| 98  | 6  | 0 | -7.626446 | -1.520704 | 0.447393  |
| 99  | 1  | 0 | -7.379695 | -2.019291 | 1.392293  |
| 100 | 1  | 0 | -8.719447 | -1.495423 | 0.363225  |
| 101 | 1  | 0 | -7.274694 | -0.484032 | 0.505826  |
| 102 | 6  | 0 | 8.266262  | -1.269181 | -0.006649 |
| 103 | 1  | 0 | 8.281155  | -1.065763 | -1.083880 |
| 104 | 1  | 0 | 7.904036  | -0.367554 | 0.499993  |
| 105 | 1  | 0 | 9.299489  | -1.441317 | 0.321592  |
| 106 | 6  | 0 | 7.399502  | -2.752785 | 1.827464  |
| 107 | 1  | 0 | 8.423341  | -2.936429 | 2.178650  |
| 108 | 1  | 0 | 7.002713  | -1.899555 | 2.388790  |
| 109 | 1  | 0 | 6.790578  | -3.629042 | 2.079035  |
| 110 | 6  | 0 | 8.003901  | -3.714353 | -0.387641 |
| 111 | 1  | 0 | 7.440832  | -4.631642 | -0.179397 |
| 112 | 1  | 0 | 8.054938  | -3.582950 | -1.474873 |
| 113 | 1  | 0 | 9.027586  | -3.865809 | -0.025008 |
| 114 | 6  | 0 | 3.408722  | 1.946298  | -0.558331 |
| 115 | 6  | 0 | 2.380459  | 2.843061  | -0.863646 |
| 116 | 6  | 0 | 4.662774  | 2.089174  | -1.166585 |
| 117 | 6  | 0 | 2.608249  | 3.887627  | -1.761600 |
| 118 | 1  | 0 | 1.394016  | 2.715512  | -0.427436 |
| 119 | 6  | 0 | 4.887553  | 3.134211  | -2.059625 |
| 120 | 1  | 0 | 5.455511  | 1.376158  | -0.954958 |
| 121 | 6  | 0 | 3.861494  | 4.033832  | -2.354950 |
| 122 | 1  | 0 | 1.798389  | 4.571264  | -2.001841 |
| 123 | 1  | 0 | 5.860521  | 3.239620  | -2.533129 |
| 124 | 1  | 0 | 4.037037  | 4.844120  | -3.058461 |
| 125 | 39 | 0 | 0.061007  | -0.704588 | -0.634321 |
| 126 | 8  | 0 | -0.636856 | 0.639469  | -2.031109 |
| 127 | 6  | 0 | -1.227332 | 1.666798  | -2.708980 |
| 128 | 1  | 0 | -2.214465 | 1.365899  | -3.109335 |
| 129 | 6  | 0 | -1.527925 | 2.844326  | -1.775827 |
| 130 | 6  | 0 | -0.375252 | 2.143098  | -3.897152 |
| 131 | 8  | 0 | -1.182739 | 2.957941  | -0.618740 |
| 132 | 8  | 0 | -2.285167 | 3.778764  | -2.402912 |
| 133 | 1  | 0 | -0.858781 | 2.959278  | -4.442894 |
| 134 | 1  | 0 | 0.605494  | 2.477663  | -3.544980 |
| 135 | 1  | 0 | -0.224146 | 1.297237  | -4.575022 |
| 136 | 6  | 0 | -2.657085 | 4.909245  | -1.623955 |
| 137 | 1  | 0 | -3.049180 | 4.576129  | -0.657764 |
| 138 | 6  | 0 | -3.721909 | 5.662224  | -2.410901 |
| 139 | 6  | 0 | -1.441577 | 5.800272  | -1.353417 |

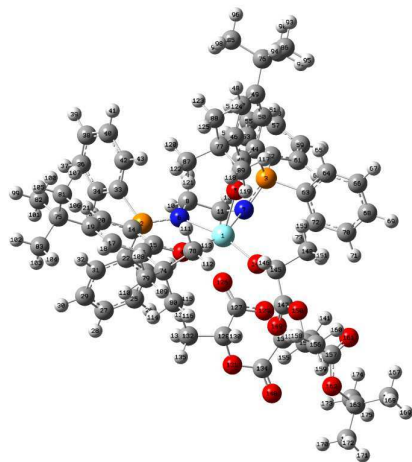
## Appendix 2. Optimised Structures

|     |   |   |           |          |           |
|-----|---|---|-----------|----------|-----------|
| 140 | 1 | 0 | -4.577004 | 5.006037 | -2.597762 |
| 141 | 1 | 0 | -4.060945 | 6.534298 | -1.845023 |
| 142 | 1 | 0 | -3.322348 | 5.994550 | -3.374230 |
| 143 | 8 | 0 | -0.403137 | 5.751443 | -1.972411 |
| 144 | 8 | 0 | -1.747535 | 6.654904 | -0.370642 |
| 145 | 6 | 0 | -0.803061 | 7.682776 | 0.089083  |
| 146 | 6 | 0 | -0.469508 | 8.637067 | -1.055886 |
| 147 | 6 | 0 | -1.593279 | 8.400819 | 1.179652  |
| 148 | 6 | 0 | 0.441302  | 7.017030 | 0.671982  |
| 149 | 1 | 0 | 0.093328  | 8.131112 | -1.842724 |
| 150 | 1 | 0 | -1.386578 | 9.054289 | -1.486571 |
| 151 | 1 | 0 | 0.132867  | 9.468393 | -0.672851 |
| 152 | 1 | 0 | -1.867058 | 7.705727 | 1.980067  |
| 153 | 1 | 0 | -0.989471 | 9.206152 | 1.610780  |
| 154 | 1 | 0 | -2.510987 | 8.836992 | 0.771197  |
| 155 | 1 | 0 | 0.159342  | 6.292592 | 1.443544  |
| 156 | 1 | 0 | 1.015347  | 6.502056 | -0.100160 |
| 157 | 1 | 0 | 1.079483  | 7.778338 | 1.134642  |

-----  
Rotational constants (GHZ):      0.0271963      0.0225333  
0.0172943

Sum of electronic and zero-point Energies=      -3172.928365  
Sum of electronic and thermal Energies=      -3172.847135  
Sum of electronic and thermal Enthalpies=      -3172.846191  
Sum of electronic and thermal Free Energies=      -3173.054954

|                | 1      | 2      | 3 |
|----------------|--------|--------|---|
|                | A      | A      | A |
| Frequencies -- | 5.6844 | 9.1766 |   |
| 9.6599         |        |        |   |
| Red. masses -- | 4.4482 | 4.7610 |   |
| 4.9915         |        |        |   |
| Frc consts --  | 0.0001 | 0.0002 |   |
| 0.0003         |        |        |   |
| IR Inten --    | 0.0368 | 0.0548 |   |
| 0.0026         |        |        |   |

**Propagation : INT1**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.007996               | 0.010434  | 0.138441  |
| 2                | 15               | 0              | 2.612689                | -2.142813 | 1.418463  |
| 3                | 15               | 0              | 1.055295                | 3.250232  | 0.934458  |
| 4                | 8                | 0              | 0.318276                | -2.045883 | -0.580577 |
| 5                | 8                | 0              | 1.037971                | 1.277947  | -1.295366 |
| 6                | 7                | 0              | 1.897877                | -0.672670 | 1.448566  |
| 7                | 7                | 0              | 0.610111                | 1.823400  | 1.611568  |
| 8                | 6                | 0              | 2.421859                | 0.309919  | 2.405281  |
| 9                | 1                | 0              | 3.261208                | 0.869839  | 1.959994  |
| 10               | 1                | 0              | 2.808507                | -0.137830 | 3.337050  |
| 11               | 6                | 0              | 1.307253                | 1.288460  | 2.777603  |
| 12               | 1                | 0              | 0.560266                | 0.750081  | 3.378297  |
| 13               | 1                | 0              | 1.723884                | 2.072847  | 3.427144  |
| 14               | 6                | 0              | 2.417753                | -3.060367 | -0.134182 |
| 15               | 6                | 0              | 1.225337                | -2.933697 | -0.896095 |
| 16               | 6                | 0              | 1.064276                | -3.823148 | -2.013813 |
| 17               | 6                | 0              | 2.099132                | -4.705025 | -2.304670 |
| 18               | 1                | 0              | 1.976662                | -5.363683 | -3.158022 |
| 19               | 6                | 0              | 3.301906                | -4.804673 | -1.579952 |
| 20               | 6                | 0              | 3.432454                | -3.969170 | -0.480385 |
| 21               | 1                | 0              | 4.335131                | -4.001158 | 0.121085  |
| 22               | 6                | 0              | 2.003427                | -3.248466 | 2.778537  |
| 23               | 6                | 0              | 1.167919                | -2.705541 | 3.758140  |
| 24               | 1                | 0              | 0.867519                | -1.664925 | 3.682372  |
| 25               | 6                | 0              | 0.697013                | -3.504723 | 4.800535  |
| 26               | 1                | 0              | 0.049250                | -3.074846 | 5.560755  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 27 | 6 | 0 | 1.049532  | -4.852041 | 4.862001  |
| 28 | 1 | 0 | 0.678737  | -5.475729 | 5.671559  |
| 29 | 6 | 0 | 1.870133  | -5.402891 | 3.876221  |
| 30 | 1 | 0 | 2.135267  | -6.456514 | 3.912986  |
| 31 | 6 | 0 | 2.345462  | -4.605563 | 2.837249  |
| 32 | 1 | 0 | 2.969839  | -5.044405 | 2.063386  |
| 33 | 6 | 0 | 4.431781  | -1.987070 | 1.706992  |
| 34 | 6 | 0 | 5.070263  | -2.470124 | 2.852540  |
| 35 | 1 | 0 | 4.506539  | -3.022382 | 3.598658  |
| 36 | 6 | 0 | 6.434892  | -2.245455 | 3.041492  |
| 37 | 1 | 0 | 6.924678  | -2.626618 | 3.933960  |
| 38 | 6 | 0 | 7.165310  | -1.536301 | 2.090736  |
| 39 | 1 | 0 | 8.228397  | -1.363541 | 2.238646  |
| 40 | 6 | 0 | 6.530594  | -1.045984 | 0.947602  |
| 41 | 1 | 0 | 7.096453  | -0.490644 | 0.203964  |
| 42 | 6 | 0 | 5.169648  | -1.266826 | 0.756076  |
| 43 | 1 | 0 | 4.675457  | -0.882771 | -0.132732 |
| 44 | 6 | 0 | 2.125187  | 3.246422  | -0.543634 |
| 45 | 6 | 0 | 1.931736  | 2.214043  | -1.501545 |
| 46 | 6 | 0 | 2.731793  | 2.265119  | -2.693508 |
| 47 | 6 | 0 | 3.632878  | 3.315865  | -2.832696 |
| 48 | 1 | 0 | 4.233394  | 3.348267  | -3.736001 |
| 49 | 6 | 0 | 3.820491  | 4.348783  | -1.895153 |
| 50 | 6 | 0 | 3.041329  | 4.291396  | -0.748010 |
| 51 | 1 | 0 | 3.130384  | 5.063587  | 0.008495  |
| 52 | 6 | 0 | 1.898141  | 4.341050  | 2.166254  |
| 53 | 6 | 0 | 3.239041  | 4.099794  | 2.500481  |
| 54 | 1 | 0 | 3.797735  | 3.327388  | 1.978697  |
| 55 | 6 | 0 | 3.865307  | 4.855310  | 3.489047  |
| 56 | 1 | 0 | 4.904874  | 4.659586  | 3.738936  |
| 57 | 6 | 0 | 3.160123  | 5.858933  | 4.153876  |
| 58 | 1 | 0 | 3.650089  | 6.450325  | 4.923202  |
| 59 | 6 | 0 | 1.827309  | 6.102438  | 3.828350  |
| 60 | 1 | 0 | 1.274198  | 6.885308  | 4.340857  |
| 61 | 6 | 0 | 1.196622  | 5.346116  | 2.840549  |
| 62 | 1 | 0 | 0.157996  | 5.543404  | 2.592532  |
| 63 | 6 | 0 | -0.488660 | 4.130323  | 0.464502  |
| 64 | 6 | 0 | -0.484471 | 5.101411  | -0.542936 |
| 65 | 1 | 0 | 0.422659  | 5.288235  | -1.111494 |
| 66 | 6 | 0 | -1.646433 | 5.817991  | -0.822064 |
| 67 | 1 | 0 | -1.642453 | 6.567923  | -1.608867 |
| 68 | 6 | 0 | -2.812323 | 5.569630  | -0.097005 |
| 69 | 1 | 0 | -3.718464 | 6.128378  | -0.317379 |
| 70 | 6 | 0 | -2.819309 | 4.596201  | 0.901961  |
| 71 | 1 | 0 | -3.731483 | 4.393897  | 1.457483  |
| 72 | 6 | 0 | -1.661245 | 3.871658  | 1.181858  |
| 73 | 1 | 0 | -1.656329 | 3.093232  | 1.939685  |
| 74 | 6 | 0 | -0.217436 | -3.803545 | -2.863854 |
| 75 | 6 | 0 | 4.384149  | -5.797815 | -2.019921 |
| 76 | 6 | 0 | 4.841775  | 5.459732  | -2.166286 |
| 77 | 6 | 0 | 2.589359  | 1.200236  | -3.790996 |
| 78 | 6 | 0 | -0.361525 | -2.443853 | -3.573056 |
| 79 | 6 | 0 | -0.216764 | -4.891172 | -3.949933 |
| 80 | 6 | 0 | -1.447860 | -4.053116 | -1.969308 |
| 81 | 6 | 0 | 4.856567  | -5.447597 | -3.445019 |
| 82 | 6 | 0 | 5.607454  | -5.769356 | -1.093734 |
| 83 | 6 | 0 | 3.812754  | -7.229462 | -2.012502 |
| 84 | 6 | 0 | 4.879200  | 6.497989  | -1.036345 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 85  | 6 | 0 | 6.249497  | 4.845525  | -2.299051 |
| 86  | 6 | 0 | 4.482918  | 6.191548  | -3.474621 |
| 87  | 6 | 0 | 2.960997  | -0.183097 | -3.223591 |
| 88  | 6 | 0 | 3.514470  | 1.461479  | -4.989998 |
| 89  | 6 | 0 | 1.142996  | 1.189865  | -4.325336 |
| 90  | 1 | 0 | 5.620728  | 7.272043  | -1.267266 |
| 91  | 1 | 0 | 3.910758  | 6.996410  | -0.909584 |
| 92  | 1 | 0 | 5.159118  | 6.047792  | -0.076614 |
| 93  | 1 | 0 | 5.213525  | 6.982924  | -3.686053 |
| 94  | 1 | 0 | 4.472937  | 5.510859  | -4.332771 |
| 95  | 1 | 0 | 3.491132  | 6.653370  | -3.404403 |
| 96  | 1 | 0 | 6.993861  | 5.625408  | -2.505808 |
| 97  | 1 | 0 | 6.539700  | 4.333223  | -1.374147 |
| 98  | 1 | 0 | 6.298050  | 4.114819  | -3.113908 |
| 99  | 1 | 0 | 6.356666  | -6.488144 | -1.446101 |
| 100 | 1 | 0 | 6.081193  | -4.780929 | -1.073929 |
| 101 | 1 | 0 | 5.346308  | -6.044595 | -0.064734 |
| 102 | 1 | 0 | 4.576390  | -7.950653 | -2.331200 |
| 103 | 1 | 0 | 3.475821  | -7.511000 | -1.007885 |
| 104 | 1 | 0 | 2.958002  | -7.331102 | -2.690011 |
| 105 | 1 | 0 | 5.624836  | -6.155533 | -3.782133 |
| 106 | 1 | 0 | 4.032292  | -5.482338 | -4.165743 |
| 107 | 1 | 0 | 5.283794  | -4.438562 | -3.476895 |
| 108 | 1 | 0 | 0.594736  | -4.756810 | -4.675460 |
| 109 | 1 | 0 | -1.160444 | -4.841242 | -4.505993 |
| 110 | 1 | 0 | -0.138242 | -5.899617 | -3.525652 |
| 111 | 1 | 0 | 0.481471  | -2.267801 | -4.251032 |
| 112 | 1 | 0 | -1.284040 | -2.424562 | -4.168734 |
| 113 | 1 | 0 | -0.399522 | -1.624790 | -2.852646 |
| 114 | 1 | 0 | -1.369781 | -5.023389 | -1.462985 |
| 115 | 1 | 0 | -1.543944 | -3.269944 | -1.215628 |
| 116 | 1 | 0 | -2.360251 | -4.064205 | -2.580226 |
| 117 | 1 | 0 | 0.892991  | 2.159209  | -4.774656 |
| 118 | 1 | 0 | 1.032230  | 0.420584  | -5.100244 |
| 119 | 1 | 0 | 0.428199  | 0.985323  | -3.526819 |
| 120 | 1 | 0 | 4.005173  | -0.189346 | -2.885751 |
| 121 | 1 | 0 | 2.324183  | -0.457557 | -2.381550 |
| 122 | 1 | 0 | 2.855627  | -0.954325 | -3.996902 |
| 123 | 1 | 0 | 4.574852  | 1.444006  | -4.709407 |
| 124 | 1 | 0 | 3.301366  | 2.420195  | -5.478437 |
| 125 | 1 | 0 | 3.362177  | 0.672932  | -5.736393 |
| 126 | 8 | 0 | -1.320770 | -0.721053 | 2.090097  |
| 127 | 6 | 0 | -2.523779 | -0.860469 | 2.240501  |
| 128 | 6 | 0 | -3.256000 | -2.152250 | 1.942270  |
| 129 | 8 | 0 | -3.253940 | 0.141052  | 2.706092  |
| 130 | 1 | 0 | -3.700237 | -2.015872 | 0.947104  |
| 131 | 8 | 0 | -4.318797 | -2.360507 | 2.900662  |
| 132 | 6 | 0 | -2.361374 | -3.371549 | 1.978568  |
| 133 | 6 | 0 | -4.700721 | 0.016933  | 2.633974  |
| 134 | 6 | 0 | -5.142482 | -1.333990 | 3.179168  |
| 135 | 1 | 0 | -2.952212 | -4.259062 | 1.736202  |
| 136 | 1 | 0 | -1.559905 | -3.265451 | 1.244426  |
| 137 | 1 | 0 | -1.913365 | -3.500643 | 2.967494  |
| 138 | 1 | 0 | -4.968116 | 0.063279  | 1.570774  |
| 139 | 6 | 0 | -5.291924 | 1.176357  | 3.402462  |
| 140 | 8 | 0 | -6.151475 | -1.499274 | 3.817305  |
| 141 | 1 | 0 | -4.968086 | 2.121134  | 2.958073  |
| 142 | 1 | 0 | -6.381605 | 1.116557  | 3.364154  |

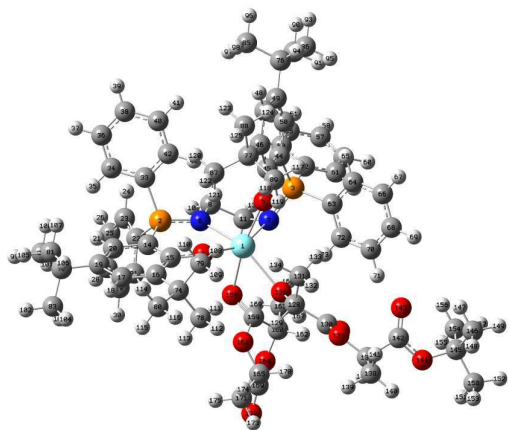
## Appendix 2. Optimised Structures

|     |   |   |            |           |           |
|-----|---|---|------------|-----------|-----------|
| 143 | 1 | 0 | -4.982261  | 1.145955  | 4.451080  |
| 144 | 8 | 0 | -1.964307  | 0.226008  | -0.661694 |
| 145 | 6 | 0 | -2.787438  | 0.452210  | -1.729983 |
| 146 | 1 | 0 | -2.401917  | -0.022862 | -2.653511 |
| 147 | 6 | 0 | -4.166028  | -0.181527 | -1.531312 |
| 148 | 6 | 0 | -2.965866  | 1.950024  | -2.036147 |
| 149 | 8 | 0 | -4.595124  | -0.695991 | -0.515131 |
| 150 | 8 | 0 | -4.898152  | -0.136048 | -2.665757 |
| 151 | 1 | 0 | -3.608981  | 2.113652  | -2.906703 |
| 152 | 1 | 0 | -3.397399  | 2.463417  | -1.171591 |
| 153 | 1 | 0 | -1.979131  | 2.380035  | -2.230716 |
| 154 | 6 | 0 | -6.197346  | -0.717407 | -2.598936 |
| 155 | 1 | 0 | -6.126603  | -1.720174 | -2.165996 |
| 156 | 6 | 0 | -6.731706  | -0.776573 | -4.023375 |
| 157 | 6 | 0 | -7.113593  | 0.119271  | -1.701149 |
| 158 | 1 | 0 | -6.058953  | -1.371465 | -4.648054 |
| 159 | 1 | 0 | -7.723264  | -1.237517 | -4.032156 |
| 160 | 1 | 0 | -6.801654  | 0.229786  | -4.448074 |
| 161 | 8 | 0 | -6.900833  | 1.266609  | -1.383526 |
| 162 | 8 | 0 | -8.185409  | -0.616200 | -1.381402 |
| 163 | 6 | 0 | -9.285056  | -0.072146 | -0.572132 |
| 164 | 6 | 0 | -9.937144  | 1.099502  | -1.303231 |
| 165 | 6 | 0 | -10.244831 | -1.254120 | -0.472319 |
| 166 | 6 | 0 | -8.768273  | 0.324064  | 0.809417  |
| 167 | 1 | 0 | -9.248335  | 1.941898  | -1.393322 |
| 168 | 1 | 0 | -10.259880 | 0.794689  | -2.304942 |
| 169 | 1 | 0 | -10.822541 | 1.428626  | -0.747853 |
| 170 | 1 | 0 | -9.758168  | -2.106957 | 0.011709  |
| 171 | 1 | 0 | -11.123665 | -0.975571 | 0.118710  |
| 172 | 1 | 0 | -10.580853 | -1.565830 | -1.466858 |
| 173 | 1 | 0 | -8.254948  | -0.518532 | 1.284972  |
| 174 | 1 | 0 | -8.080855  | 1.169644  | 0.742609  |
| 175 | 1 | 0 | -9.613403  | 0.607833  | 1.446582  |

-----  
Rotational constants (GHZ):      0.0238129      0.0177112  
0.0144158

Sum of electronic and zero-point Energies=      -3706.945550  
Sum of electronic and thermal Energies=      -3706.852831  
Sum of electronic and thermal Enthalpies=      -3706.851887  
Sum of electronic and thermal Free Energies=      -3707.087665

|                | 1      | 2      | 3 |
|----------------|--------|--------|---|
|                | A      | A      | A |
| Frequencies -- | 5.4830 | 7.1954 |   |
| 7.9403         |        |        |   |
| Red. masses -- | 5.2716 | 5.0952 |   |
| 4.7057         |        |        |   |
| Frc consts --  | 0.0001 | 0.0002 |   |
| 0.0002         |        |        |   |
| IR Inten --    | 0.1682 | 0.2483 |   |
| 0.0901         |        |        |   |

**Propagation : TSI**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | 0.146853                | -0.299792 | 0.158811  |
| 2                | 15               | 0              | 3.625983                | -0.666283 | 0.934652  |
| 3                | 15               | 0              | -0.557866               | 2.949471  | 1.124399  |
| 4                | 8                | 0              | 1.372997                | -1.577555 | -1.076199 |
| 5                | 8                | 0              | 0.108097                | 1.419879  | -1.227686 |
| 6                | 7                | 0              | 2.198447                | 0.102913  | 1.190765  |
| 7                | 7                | 0              | -0.213278               | 1.460196  | 1.739019  |
| 8                | 6                | 0              | 2.208581                | 1.124585  | 2.246140  |
| 9                | 1                | 0              | 2.577157                | 2.088071  | 1.853626  |
| 10               | 1                | 0              | 2.862425                | 0.858002  | 3.092524  |
| 11               | 6                | 0              | 0.789785                | 1.299716  | 2.791931  |
| 12               | 1                | 0              | 0.529771                | 0.388170  | 3.344857  |
| 13               | 1                | 0              | 0.782959                | 2.123388  | 3.521968  |
| 14               | 6                | 0              | 3.562083                | -2.033144 | -0.261643 |
| 15               | 6                | 0              | 2.464823                | -2.297259 | -1.123987 |
| 16               | 6                | 0              | 2.608542                | -3.390555 | -2.049612 |
| 17               | 6                | 0              | 3.803665                | -4.098391 | -2.054539 |
| 18               | 1                | 0              | 3.903493                | -4.918275 | -2.757552 |
| 19               | 6                | 0              | 4.898980                | -3.836240 | -1.209971 |
| 20               | 6                | 0              | 4.745298                | -2.791829 | -0.315134 |
| 21               | 1                | 0              | 5.549924                | -2.553831 | 0.373133  |
| 22               | 6                | 0              | 4.274840                | -1.382889 | 2.510155  |
| 23               | 6                | 0              | 5.116373                | -0.664809 | 3.368274  |
| 24               | 1                | 0              | 5.504252                | 0.304794  | 3.068591  |
| 25               | 6                | 0              | 5.466196                | -1.192090 | 4.611857  |
| 26               | 1                | 0              | 6.123155                | -0.629244 | 5.270113  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 27 | 6 | 0 | 4.972360  | -2.433273 | 5.007908  |
| 28 | 1 | 0 | 5.245544  | -2.843667 | 5.976759  |
| 29 | 6 | 0 | 4.122314  | -3.147417 | 4.161744  |
| 30 | 1 | 0 | 3.728803  | -4.112451 | 4.469945  |
| 31 | 6 | 0 | 3.770800  | -2.625288 | 2.919865  |
| 32 | 1 | 0 | 3.100494  | -3.178170 | 2.267326  |
| 33 | 6 | 0 | 4.913596  | 0.527006  | 0.342856  |
| 34 | 6 | 0 | 6.292024  | 0.309598  | 0.465364  |
| 35 | 1 | 0 | 6.666896  | -0.569941 | 0.981278  |
| 36 | 6 | 0 | 7.196512  | 1.225535  | -0.068430 |
| 37 | 1 | 0 | 8.264423  | 1.048567  | 0.031860  |
| 38 | 6 | 0 | 6.733517  | 2.363991  | -0.728540 |
| 39 | 1 | 0 | 7.441446  | 3.076684  | -1.144239 |
| 40 | 6 | 0 | 5.362895  | 2.584663  | -0.855104 |
| 41 | 1 | 0 | 4.992050  | 3.466333  | -1.370694 |
| 42 | 6 | 0 | 4.455425  | 1.670461  | -0.321447 |
| 43 | 1 | 0 | 3.386912  | 1.835923  | -0.430155 |
| 44 | 6 | 0 | 0.413726  | 3.568360  | -0.288670 |
| 45 | 6 | 0 | 0.553888  | 2.649860  | -1.365572 |
| 46 | 6 | 0 | 1.157009  | 3.138116  | -2.571964 |
| 47 | 6 | 0 | 1.594984  | 4.460840  | -2.587843 |
| 48 | 1 | 0 | 2.054826  | 4.825581  | -3.500341 |
| 49 | 6 | 0 | 1.471970  | 5.370379  | -1.521217 |
| 50 | 6 | 0 | 0.854158  | 4.896750  | -0.370224 |
| 51 | 1 | 0 | 0.691261  | 5.557962  | 0.473689  |
| 52 | 6 | 0 | -0.493035 | 4.242202  | 2.439110  |
| 53 | 6 | 0 | 0.742188  | 4.699064  | 2.922739  |
| 54 | 1 | 0 | 1.666891  | 4.350002  | 2.470836  |
| 55 | 6 | 0 | 0.792786  | 5.613363  | 3.973143  |
| 56 | 1 | 0 | 1.755508  | 5.961883  | 4.337952  |
| 57 | 6 | 0 | -0.387538 | 6.078430  | 4.552473  |
| 58 | 1 | 0 | -0.347308 | 6.792954  | 5.370628  |
| 59 | 6 | 0 | -1.618068 | 5.625098  | 4.080338  |
| 60 | 1 | 0 | -2.540876 | 5.984968  | 4.527821  |
| 61 | 6 | 0 | -1.672430 | 4.709410  | 3.030371  |
| 62 | 1 | 0 | -2.635129 | 4.360882  | 2.668154  |
| 63 | 6 | 0 | -2.284164 | 2.915749  | 0.504965  |
| 64 | 6 | 0 | -2.705252 | 3.886519  | -0.413088 |
| 65 | 1 | 0 | -2.006428 | 4.639257  | -0.767365 |
| 66 | 6 | 0 | -4.013313 | 3.870358  | -0.890136 |
| 67 | 1 | 0 | -4.334019 | 4.621171  | -1.607896 |
| 68 | 6 | 0 | -4.900572 | 2.880260  | -0.465268 |
| 69 | 1 | 0 | -5.911056 | 2.845473  | -0.862697 |
| 70 | 6 | 0 | -4.484729 | 1.916324  | 0.451511  |
| 71 | 1 | 0 | -5.162404 | 1.127980  | 0.762086  |
| 72 | 6 | 0 | -3.179725 | 1.937101  | 0.943641  |
| 73 | 1 | 0 | -2.844154 | 1.176564  | 1.638975  |
| 74 | 6 | 0 | 1.465718  | -3.782277 | -3.002238 |
| 75 | 6 | 0 | 6.169986  | -4.687139 | -1.305767 |
| 76 | 6 | 0 | 1.983971  | 6.808031  | -1.672756 |
| 77 | 6 | 0 | 1.299373  | 2.249188  | -3.817050 |
| 78 | 6 | 0 | 0.238680  | -4.223647 | -2.181930 |
| 79 | 6 | 0 | 1.098403  | -2.598832 | -3.917326 |
| 80 | 6 | 0 | 1.841783  | -4.956956 | -3.920170 |
| 81 | 6 | 0 | 6.760060  | -4.575909 | -2.725556 |
| 82 | 6 | 0 | 7.243979  | -4.234450 | -0.307092 |
| 83 | 6 | 0 | 5.832527  | -6.161747 | -1.009446 |
| 84 | 6 | 0 | 1.748032  | 7.642101  | -0.406142 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 85  | 6 | 0 | 3.498662  | 6.792104  | -1.958424 |
| 86  | 6 | 0 | 1.255980  | 7.500294  | -2.842133 |
| 87  | 6 | 0 | 2.245699  | 1.072129  | -3.517595 |
| 88  | 6 | 0 | 1.883890  | 3.008860  | -5.019033 |
| 89  | 6 | 0 | -0.085796 | 1.723640  | -4.244034 |
| 90  | 1 | 0 | 2.136703  | 8.656930  | -0.551702 |
| 91  | 1 | 0 | 0.681373  | 7.729237  | -0.167864 |
| 92  | 1 | 0 | 2.258401  | 7.214099  | 0.464792  |
| 93  | 1 | 0 | 1.612478  | 8.531477  | -2.961688 |
| 94  | 1 | 0 | 1.422017  | 6.979537  | -3.791463 |
| 95  | 1 | 0 | 0.174775  | 7.531981  | -2.664026 |
| 96  | 1 | 0 | 3.879057  | 7.813992  | -2.084250 |
| 97  | 1 | 0 | 4.046680  | 6.325838  | -1.130899 |
| 98  | 1 | 0 | 3.733976  | 6.236236  | -2.872923 |
| 99  | 1 | 0 | 8.134789  | -4.865334 | -0.409101 |
| 100 | 1 | 0 | 7.552482  | -3.197261 | -0.485568 |
| 101 | 1 | 0 | 6.897469  | -4.317873 | 0.729931  |
| 102 | 1 | 0 | 6.731891  | -6.785912 | -1.089005 |
| 103 | 1 | 0 | 5.427303  | -6.274259 | 0.002901  |
| 104 | 1 | 0 | 5.090420  | -6.557766 | -1.711198 |
| 105 | 1 | 0 | 7.669630  | -5.184109 | -2.812513 |
| 106 | 1 | 0 | 6.054544  | -4.923413 | -3.488197 |
| 107 | 1 | 0 | 7.019237  | -3.537003 | -2.960276 |
| 108 | 1 | 0 | 0.792372  | -1.726571 | -3.339035 |
| 109 | 1 | 0 | 0.276179  | -2.883310 | -4.587349 |
| 110 | 1 | 0 | 1.955175  | -2.312920 | -4.539263 |
| 111 | 1 | 0 | -0.083500 | -3.445565 | -1.489174 |
| 112 | 1 | 0 | -0.595727 | -4.466212 | -2.854165 |
| 113 | 1 | 0 | 0.470265  | -5.118995 | -1.592846 |
| 114 | 1 | 0 | 2.696084  | -4.721156 | -4.566304 |
| 115 | 1 | 0 | 2.073485  | -5.869077 | -3.357060 |
| 116 | 1 | 0 | 0.991225  | -5.185122 | -4.573608 |
| 117 | 1 | 0 | -0.745772 | 2.555384  | -4.520778 |
| 118 | 1 | 0 | 0.014694  | 1.066643  | -5.117650 |
| 119 | 1 | 0 | -0.560445 | 1.162987  | -3.437467 |
| 120 | 1 | 0 | 3.246166  | 1.437651  | -3.256294 |
| 121 | 1 | 0 | 1.881021  | 0.452464  | -2.696372 |
| 122 | 1 | 0 | 2.344326  | 0.434541  | -4.405198 |
| 123 | 1 | 0 | 2.901667  | 3.371506  | -4.829336 |
| 124 | 1 | 0 | 1.261193  | 3.862218  | -5.314670 |
| 125 | 1 | 0 | 1.937553  | 2.328835  | -5.877277 |
| 126 | 8 | 0 | -2.037363 | -1.287566 | 0.296106  |
| 127 | 8 | 0 | -4.810569 | -1.602344 | 0.649918  |
| 128 | 6 | 0 | -2.809636 | -1.747796 | -0.772239 |
| 129 | 1 | 0 | -2.525534 | -2.784405 | -1.023502 |
| 130 | 6 | 0 | -4.301319 | -1.820187 | -0.428839 |
| 131 | 6 | 0 | -2.581434 | -0.880649 | -2.014861 |
| 132 | 1 | 0 | -3.217620 | -1.203672 | -2.843206 |
| 133 | 1 | 0 | -2.796976 | 0.169054  | -1.793311 |
| 134 | 1 | 0 | -1.539470 | -0.966369 | -2.342073 |
| 135 | 8 | 0 | -5.009131 | -2.260890 | -1.491749 |
| 136 | 6 | 0 | -6.395273 | -2.518099 | -1.269363 |
| 137 | 1 | 0 | -6.513136 | -3.090210 | -0.343403 |
| 138 | 6 | 0 | -6.895342 | -3.312440 | -2.468180 |
| 139 | 1 | 0 | -6.324194 | -4.240384 | -2.564855 |
| 140 | 1 | 0 | -7.952082 | -3.559455 | -2.337218 |
| 141 | 1 | 0 | -6.775908 | -2.732970 | -3.389069 |
| 142 | 6 | 0 | -7.171462 | -1.207979 | -1.107592 |

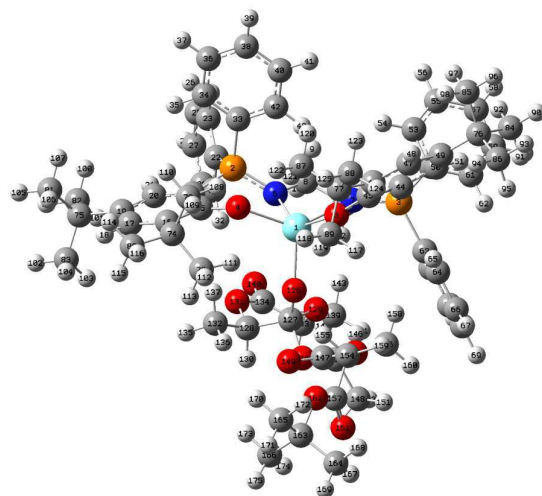
## Appendix 2. Optimised Structures

|     |   |   |            |           |           |
|-----|---|---|------------|-----------|-----------|
| 143 | 8 | 0 | -6.747454  | -0.115754 | -1.406804 |
| 144 | 8 | 0 | -8.385733  | -1.497203 | -0.627918 |
| 145 | 6 | 0 | -9.404955  | -0.461137 | -0.404346 |
| 146 | 6 | 0 | -9.748050  | 0.226926  | -1.723898 |
| 147 | 1 | 0 | -8.899242  | 0.796734  | -2.107150 |
| 148 | 1 | 0 | -10.047838 | -0.512270 | -2.474981 |
| 149 | 1 | 0 | -10.589212 | 0.911868  | -1.569496 |
| 150 | 6 | 0 | -10.593386 | -1.266209 | 0.113278  |
| 151 | 1 | 0 | -10.332694 | -1.790832 | 1.038141  |
| 152 | 1 | 0 | -11.436849 | -0.598843 | 0.318764  |
| 153 | 1 | 0 | -10.911533 | -2.007697 | -0.627015 |
| 154 | 6 | 0 | -8.914602  | 0.523119  | 0.654520  |
| 155 | 1 | 0 | -8.613741  | -0.010784 | 1.562154  |
| 156 | 1 | 0 | -8.066075  | 1.105181  | 0.290639  |
| 157 | 1 | 0 | -9.725507  | 1.212030  | 0.916109  |
| 158 | 8 | 0 | -0.229574  | -1.956050 | 1.693880  |
| 159 | 6 | 0 | -1.407266  | -2.406525 | 1.571777  |
| 160 | 6 | 0 | -2.425622  | -2.191315 | 2.708857  |
| 161 | 8 | 0 | -1.509410  | -3.650338 | 0.996681  |
| 162 | 1 | 0 | -3.416482  | -2.022284 | 2.282043  |
| 163 | 6 | 0 | -2.040938  | -1.074623 | 3.648613  |
| 164 | 8 | 0 | -2.471050  | -3.397935 | 3.519354  |
| 165 | 6 | 0 | -2.638061  | -4.457443 | 1.364109  |
| 166 | 1 | 0 | -1.910819  | -0.139575 | 3.097939  |
| 167 | 1 | 0 | -2.819828  | -0.942645 | 4.406012  |
| 168 | 1 | 0 | -1.096359  | -1.313905 | 4.143961  |
| 169 | 6 | 0 | -2.700290  | -4.558712 | 2.885271  |
| 170 | 1 | 0 | -3.566773  | -3.972960 | 1.027093  |
| 171 | 6 | 0 | -2.480596  | -5.808203 | 0.701644  |
| 172 | 8 | 0 | -2.919389  | -5.577514 | 3.493285  |
| 173 | 1 | 0 | -3.317380  | -6.454531 | 0.977546  |
| 174 | 1 | 0 | -2.451946  | -5.693973 | -0.385747 |
| 175 | 1 | 0 | -1.554632  | -6.285410 | 1.033166  |

-----  
Rotational constants (GHZ):      0.0246569      0.0181830  
0.0141582

Sum of electronic and zero-point Energies=      -3706.926246  
Sum of electronic and thermal Energies=      -3706.835655  
Sum of electronic and thermal Enthalpies=      -3706.834711  
Sum of electronic and thermal Free Energies=      -3707.060596

|                | 1         | 2      | 3 |
|----------------|-----------|--------|---|
|                | A         | A      | A |
| Frequencies -- | -151.9668 | 6.5556 |   |
| 7.5380         |           |        |   |
| Red. masses -- | 8.6808    | 4.8934 |   |
| 4.5524         |           |        |   |
| Frc consts --  | 0.1181    | 0.0001 |   |
| 0.0002         |           |        |   |
| IR Inten --    | 54.4441   | 0.0530 |   |
| 0.2015         |           |        |   |

**Propagation : INT2**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.382446               | -0.155730 | -0.024264 |
| 2                | 15               | 0              | -3.742024               | -0.957516 | -0.261233 |
| 3                | 15               | 0              | 1.544091                | -2.975892 | 0.934636  |
| 4                | 8                | 0              | -1.699378               | 0.720110  | -1.533307 |
| 5                | 8                | 0              | 1.364516                | -0.744445 | -1.162397 |
| 6                | 7                | 0              | -2.379603               | -1.164044 | 0.639393  |
| 7                | 7                | 0              | 0.059649                | -2.283533 | 0.901121  |
| 8                | 6                | 0              | -2.295372               | -2.366824 | 1.474538  |
| 9                | 1                | 0              | -2.528495               | -3.287408 | 0.913246  |
| 10               | 1                | 0              | -2.993645               | -2.326040 | 2.323545  |
| 11               | 6                | 0              | -0.871197               | -2.481796 | 2.017529  |
| 12               | 1                | 0              | -0.724238               | -1.712393 | 2.790307  |
| 13               | 1                | 0              | -0.763246               | -3.463715 | 2.505654  |
| 14               | 6                | 0              | -3.960837               | 0.740599  | -0.849348 |
| 15               | 6                | 0              | -2.867702               | 1.332148  | -1.532070 |
| 16               | 6                | 0              | -3.103709               | 2.575009  | -2.202122 |
| 17               | 6                | 0              | -4.360923               | 3.157804  | -2.054290 |
| 18               | 1                | 0              | -4.533116               | 4.111092  | -2.542867 |
| 19               | 6                | 0              | -5.429574               | 2.606697  | -1.323777 |
| 20               | 6                | 0              | -5.210387               | 1.365099  | -0.741142 |
| 21               | 1                | 0              | -6.000232               | 0.866138  | -0.190976 |
| 22               | 6                | 0              | -5.229008               | -1.418242 | 0.718797  |
| 23               | 6                | 0              | -6.166663               | -2.364843 | 0.293853  |
| 24               | 1                | 0              | -6.057213               | -2.848839 | -0.672020 |
| 25               | 6                | 0              | -7.244889               | -2.694847 | 1.114817  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 26 | 1 | 0 | -7.971686 | -3.430007 | 0.778625  |
| 27 | 6 | 0 | -7.386243 | -2.088226 | 2.361936  |
| 28 | 1 | 0 | -8.226154 | -2.349671 | 3.000911  |
| 29 | 6 | 0 | -6.445541 | -1.152217 | 2.793495  |
| 30 | 1 | 0 | -6.537243 | -0.684016 | 3.769472  |
| 31 | 6 | 0 | -5.367656 | -0.815630 | 1.978232  |
| 32 | 1 | 0 | -4.634540 | -0.096409 | 2.333950  |
| 33 | 6 | 0 | -3.752891 | -2.008554 | -1.783251 |
| 34 | 6 | 0 | -4.755652 | -1.860347 | -2.749586 |
| 35 | 1 | 0 | -5.546566 | -1.128205 | -2.605512 |
| 36 | 6 | 0 | -4.728339 | -2.631694 | -3.909358 |
| 37 | 1 | 0 | -5.507569 | -2.509832 | -4.657389 |
| 38 | 6 | 0 | -3.694736 | -3.546374 | -4.116558 |
| 39 | 1 | 0 | -3.671104 | -4.142511 | -5.025275 |
| 40 | 6 | 0 | -2.684291 | -3.682591 | -3.165953 |
| 41 | 1 | 0 | -1.866521 | -4.378899 | -3.333708 |
| 42 | 6 | 0 | -2.711309 | -2.914576 | -2.001561 |
| 43 | 1 | 0 | -1.909651 | -2.998564 | -1.271979 |
| 44 | 6 | 0 | 2.357196  | -2.853831 | -0.683411 |
| 45 | 6 | 0 | 2.147472  | -1.731459 | -1.529703 |
| 46 | 6 | 0 | 2.836297  | -1.724170 | -2.789896 |
| 47 | 6 | 0 | 3.683709  | -2.787647 | -3.081617 |
| 48 | 1 | 0 | 4.205986  | -2.769812 | -4.032133 |
| 49 | 6 | 0 | 3.913305  | -3.890928 | -2.238929 |
| 50 | 6 | 0 | 3.223829  | -3.902311 | -1.036487 |
| 51 | 1 | 0 | 3.344775  | -4.733473 | -0.350153 |
| 52 | 6 | 0 | 1.386407  | -4.773623 | 1.335192  |
| 53 | 6 | 0 | 0.309005  | -5.464350 | 0.765667  |
| 54 | 1 | 0 | -0.395845 | -4.926320 | 0.137428  |
| 55 | 6 | 0 | 0.139652  | -6.824592 | 1.010302  |
| 56 | 1 | 0 | -0.701123 | -7.352841 | 0.568143  |
| 57 | 6 | 0 | 1.046351  | -7.505859 | 1.823654  |
| 58 | 1 | 0 | 0.913592  | -8.567601 | 2.015222  |
| 59 | 6 | 0 | 2.120828  | -6.823962 | 2.392082  |
| 60 | 1 | 0 | 2.828135  | -7.351456 | 3.026767  |
| 61 | 6 | 0 | 2.291119  | -5.460251 | 2.151782  |
| 62 | 1 | 0 | 3.126909  | -4.932862 | 2.602292  |
| 63 | 6 | 0 | 2.711154  | -2.321684 | 2.209757  |
| 64 | 6 | 0 | 3.909975  | -1.705731 | 1.835004  |
| 65 | 1 | 0 | 4.175892  | -1.636612 | 0.784018  |
| 66 | 6 | 0 | 4.763545  | -1.184544 | 2.807406  |
| 67 | 1 | 0 | 5.690949  | -0.704439 | 2.507357  |
| 68 | 6 | 0 | 4.427424  | -1.277703 | 4.156625  |
| 69 | 1 | 0 | 5.095192  | -0.873717 | 4.913171  |
| 70 | 6 | 0 | 3.231460  | -1.889141 | 4.536347  |
| 71 | 1 | 0 | 2.965486  | -1.962802 | 5.587645  |
| 72 | 6 | 0 | 2.374255  | -2.406090 | 3.568822  |
| 73 | 1 | 0 | 1.446717  | -2.882016 | 3.875478  |
| 74 | 6 | 0 | -2.030178 | 3.222102  | -3.092678 |
| 75 | 6 | 0 | -6.759390 | 3.362344  | -1.214768 |
| 76 | 6 | 0 | 4.873685  | -5.004691 | -2.672756 |
| 77 | 6 | 0 | 2.628661  | -0.584579 | -3.800284 |
| 78 | 6 | 0 | -0.776462 | 3.584354  | -2.274968 |
| 79 | 6 | 0 | -1.658028 | 2.235807  | -4.217731 |
| 80 | 6 | 0 | -2.524786 | 4.515521  | -3.759225 |
| 81 | 6 | 0 | -7.354978 | 3.574926  | -2.620583 |
| 82 | 6 | 0 | -7.788696 | 2.598332  | -0.370900 |
| 83 | 6 | 0 | -6.519972 | 4.732658  | -0.550720 |



## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 84  | 6 | 0 | 4.989268  | -6.113305 | -1.617780 |
| 85  | 6 | 0 | 4.369694  | -5.641981 | -3.982858 |
| 86  | 6 | 0 | 6.279122  | -4.414601 | -2.901869 |
| 87  | 6 | 0 | 1.151082  | -0.549385 | -4.235927 |
| 88  | 6 | 0 | 3.472784  | -0.765761 | -5.072184 |
| 89  | 6 | 0 | 3.033774  | 0.766419  | -3.178520 |
| 90  | 1 | 0 | 5.685346  | -6.884963 | -1.967029 |
| 91  | 1 | 0 | 5.373205  | -5.729879 | -0.664794 |
| 92  | 1 | 0 | 4.025021  | -6.599433 | -1.428479 |
| 93  | 1 | 0 | 6.977448  | -5.196888 | -3.225704 |
| 94  | 1 | 0 | 6.273189  | -3.635691 | -3.672140 |
| 95  | 1 | 0 | 6.670653  | -3.969194 | -1.979753 |
| 96  | 1 | 0 | 5.050303  | -6.438292 | -4.310527 |
| 97  | 1 | 0 | 3.373990  | -6.079609 | -3.845580 |
| 98  | 1 | 0 | 4.302770  | -4.908371 | -4.793715 |
| 99  | 1 | 0 | -8.718716 | 3.175672  | -0.308398 |
| 100 | 1 | 0 | -8.035183 | 1.624541  | -0.810831 |
| 101 | 1 | 0 | -7.432462 | 2.431043  | 0.652220  |
| 102 | 1 | 0 | -7.462157 | 5.289515  | -0.466640 |
| 103 | 1 | 0 | -6.104576 | 4.610264  | 0.456192  |
| 104 | 1 | 0 | -5.820744 | 5.347803  | -1.127644 |
| 105 | 1 | 0 | -8.303674 | 4.123388  | -2.558236 |
| 106 | 1 | 0 | -6.681452 | 4.148993  | -3.266304 |
| 107 | 1 | 0 | -7.549498 | 2.614183  | -3.111918 |
| 108 | 1 | 0 | -1.290245 | 1.292866  | -3.809231 |
| 109 | 1 | 0 | -0.875899 | 2.667775  | -4.855666 |
| 110 | 1 | 0 | -2.529821 | 2.023420  | -4.849011 |
| 111 | 1 | 0 | -0.337064 | 2.706308  | -1.799903 |
| 112 | 1 | 0 | -0.017848 | 4.032339  | -2.929786 |
| 113 | 1 | 0 | -1.015019 | 4.312708  | -1.492064 |
| 114 | 1 | 0 | -3.402079 | 4.346169  | -4.395199 |
| 115 | 1 | 0 | -2.773202 | 5.291627  | -3.024995 |
| 116 | 1 | 0 | -1.728611 | 4.914982  | -4.398555 |
| 117 | 1 | 0 | 4.103481  | 0.768650  | -2.934879 |
| 118 | 1 | 0 | 2.850644  | 1.579711  | -3.892377 |
| 119 | 1 | 0 | 2.469281  | 0.971063  | -2.267408 |
| 120 | 1 | 0 | 0.869461  | -1.493157 | -4.719115 |
| 121 | 1 | 0 | 0.484889  | -0.385478 | -3.387352 |
| 122 | 1 | 0 | 0.988697  | 0.260635  | -4.957700 |
| 123 | 1 | 0 | 3.216390  | -1.683170 | -5.615837 |
| 124 | 1 | 0 | 4.548587  | -0.778684 | -4.858424 |
| 125 | 1 | 0 | 3.283616  | 0.076521  | -5.747847 |
| 126 | 8 | 0 | 0.109339  | 1.320636  | 1.424252  |
| 127 | 6 | 0 | -0.109439 | 1.841607  | 2.628245  |
| 128 | 6 | 0 | -1.366715 | 2.746776  | 2.761600  |
| 129 | 8 | 0 | -0.213556 | 0.743706  | 3.562096  |
| 130 | 1 | 0 | -1.196307 | 3.404073  | 3.622161  |
| 131 | 8 | 0 | -2.543782 | 1.955271  | 3.036627  |
| 132 | 6 | 0 | -1.639278 | 3.584999  | 1.537733  |
| 133 | 6 | 0 | -1.067050 | 0.986761  | 4.671812  |
| 134 | 6 | 0 | -2.475371 | 1.137220  | 4.101487  |
| 135 | 1 | 0 | -2.471715 | 4.269990  | 1.727773  |
| 136 | 1 | 0 | -0.741688 | 4.160073  | 1.294776  |
| 137 | 1 | 0 | -1.892697 | 2.955809  | 0.681865  |
| 138 | 1 | 0 | -0.775491 | 1.921143  | 5.179446  |
| 139 | 6 | 0 | -0.960989 | -0.164506 | 5.649220  |
| 140 | 8 | 0 | -3.456678 | 0.544918  | 4.491304  |
| 141 | 1 | 0 | 0.070356  | -0.252181 | 6.003089  |

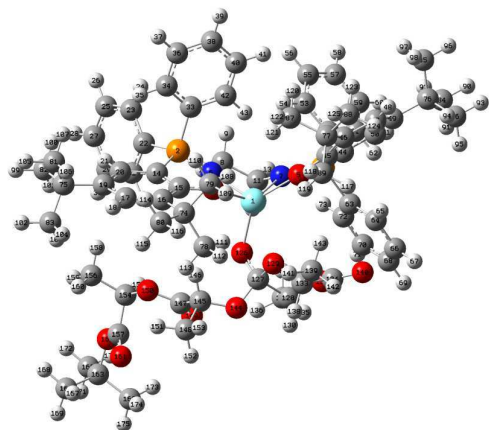
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 142 | 1 | 0 | -1.621225 | 0.005605  | 6.504141  |
| 143 | 1 | 0 | -1.258436 | -1.103057 | 5.173567  |
| 144 | 8 | 0 | 0.920673  | 2.711903  | 3.075075  |
| 145 | 6 | 0 | 2.241477  | 2.336787  | 2.765378  |
| 146 | 1 | 0 | 2.324195  | 1.251281  | 2.642207  |
| 147 | 6 | 0 | 2.686423  | 3.001786  | 1.466754  |
| 148 | 6 | 0 | 3.139803  | 2.798844  | 3.912519  |
| 149 | 8 | 0 | 2.117820  | 3.889516  | 0.879369  |
| 150 | 8 | 0 | 3.876589  | 2.486400  | 1.067664  |
| 151 | 1 | 0 | 4.188405  | 2.581148  | 3.695149  |
| 152 | 1 | 0 | 3.033497  | 3.877629  | 4.062806  |
| 153 | 1 | 0 | 2.844492  | 2.284516  | 4.831710  |
| 154 | 6 | 0 | 4.477693  | 3.135195  | -0.050363 |
| 155 | 1 | 0 | 3.760838  | 3.190729  | -0.874058 |
| 156 | 6 | 0 | 5.698968  | 2.315265  | -0.440834 |
| 157 | 6 | 0 | 4.888228  | 4.558548  | 0.338120  |
| 158 | 1 | 0 | 5.396055  | 1.297111  | -0.701007 |
| 159 | 1 | 0 | 6.191758  | 2.768034  | -1.306090 |
| 160 | 1 | 0 | 6.410145  | 2.271494  | 0.390400  |
| 161 | 8 | 0 | 5.087136  | 4.917681  | 1.476244  |
| 162 | 8 | 0 | 5.043152  | 5.287460  | -0.772249 |
| 163 | 6 | 0 | 5.469418  | 6.692349  | -0.717674 |
| 164 | 6 | 0 | 6.867938  | 6.789777  | -0.111395 |
| 165 | 6 | 0 | 5.486556  | 7.094214  | -2.189775 |
| 166 | 6 | 0 | 4.442208  | 7.514682  | 0.057394  |
| 167 | 1 | 0 | 6.863801  | 6.490914  | 0.938618  |
| 168 | 1 | 0 | 7.569324  | 6.152074  | -0.661159 |
| 169 | 1 | 0 | 7.224711  | 7.823641  | -0.180450 |
| 170 | 1 | 0 | 4.491919  | 6.979435  | -2.632670 |
| 171 | 1 | 0 | 5.792767  | 8.140916  | -2.290030 |
| 172 | 1 | 0 | 6.189451  | 6.471821  | -2.753687 |
| 173 | 1 | 0 | 3.441977  | 7.368571  | -0.363670 |
| 174 | 1 | 0 | 4.422984  | 7.231952  | 1.111362  |
| 175 | 1 | 0 | 4.695033  | 8.578444  | -0.018124 |

-----  
Rotational constants (GHZ): 0.0229056 0.0194457  
0.0155023

Sum of electronic and zero-point Energies= -3706.942966  
Sum of electronic and thermal Energies= -3706.851953  
Sum of electronic and thermal Enthalpies= -3706.851009  
Sum of electronic and thermal Free Energies= -3707.080496

|                | 1      | 2      | 3 |
|----------------|--------|--------|---|
|                | A      | A      | A |
| Frequencies -- | 5.6684 | 7.1784 |   |
| 8.4950         |        |        |   |
| Red. masses -- | 5.1422 | 5.1340 |   |
| 4.9532         |        |        |   |
| Frc consts --  | 0.0001 | 0.0002 |   |
| 0.0002         |        |        |   |
| IR Inten --    | 0.0666 | 0.0599 |   |
| 0.1287         |        |        |   |

**Propagation : INT3**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.541011               | -0.052198 | -0.532413 |
| 2                | 15               | 0              | 1.086504                | 2.271455  | 1.522258  |
| 3                | 15               | 0              | -3.360782               | -1.302639 | 1.337569  |
| 4                | 8                | 0              | 0.509670                | 1.692074  | -1.324359 |
| 5                | 8                | 0              | -2.564404               | 0.375852  | -1.198192 |
| 6                | 7                | 0              | 0.407612                | 0.778055  | 1.459373  |
| 7                | 7                | 0              | -1.822656               | -0.744747 | 1.320339  |
| 8                | 6                | 0              | -0.089633               | 0.216196  | 2.721355  |
| 9                | 1                | 0              | -0.736374               | 0.921534  | 3.270040  |
| 10               | 1                | 0              | 0.731929                | -0.052934 | 3.403165  |
| 11               | 6                | 0              | -0.903895               | -1.043709 | 2.419093  |
| 12               | 1                | 0              | -0.214103               | -1.854426 | 2.137935  |
| 13               | 1                | 0              | -1.410504               | -1.354067 | 3.346590  |
| 14               | 6                | 0              | 2.129860                | 2.666204  | 0.097132  |
| 15               | 6                | 0              | 1.614568                | 2.391758  | -1.196067 |
| 16               | 6                | 0              | 2.332293                | 2.926579  | -2.315670 |
| 17               | 6                | 0              | 3.515883                | 3.613548  | -2.059457 |
| 18               | 1                | 0              | 4.062304                | 4.006928  | -2.910073 |
| 19               | 6                | 0              | 4.057799                | 3.846318  | -0.781961 |
| 20               | 6                | 0              | 3.326088                | 3.371179  | 0.298142  |
| 21               | 1                | 0              | 3.671772                | 3.541928  | 1.311986  |
| 22               | 6                | 0              | 2.139763                | 2.417421  | 3.029973  |
| 23               | 6                | 0              | 1.979515                | 3.408720  | 4.001571  |
| 24               | 1                | 0              | 1.219216                | 4.174493  | 3.881064  |
| 25               | 6                | 0              | 2.794352                | 3.416030  | 5.134639  |
| 26               | 1                | 0              | 2.664829                | 4.191778  | 5.884894  |
| 27               | 6                | 0              | 3.766112                | 2.432649  | 5.305428  |
| 28               | 1                | 0              | 4.398739                | 2.440190  | 6.189338  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 29 | 6 | 0 | 3.920999  | 1.432013  | 4.344296  |
| 30 | 1 | 0 | 4.670498  | 0.656569  | 4.479312  |
| 31 | 6 | 0 | 3.110263  | 1.421312  | 3.212675  |
| 32 | 1 | 0 | 3.215598  | 0.635039  | 2.469011  |
| 33 | 6 | 0 | -0.162805 | 3.630756  | 1.623624  |
| 34 | 6 | 0 | 0.222160  | 4.976788  | 1.572012  |
| 35 | 1 | 0 | 1.272070  | 5.240348  | 1.469107  |
| 36 | 6 | 0 | -0.741970 | 5.980864  | 1.624883  |
| 37 | 1 | 0 | -0.438348 | 7.023735  | 1.581833  |
| 38 | 6 | 0 | -2.094646 | 5.647955  | 1.716275  |
| 39 | 1 | 0 | -2.845674 | 6.433052  | 1.750456  |
| 40 | 6 | 0 | -2.482538 | 4.309710  | 1.742861  |
| 41 | 1 | 0 | -3.535840 | 4.045879  | 1.787952  |
| 42 | 6 | 0 | -1.518964 | 3.301928  | 1.694268  |
| 43 | 1 | 0 | -1.818237 | 2.256898  | 1.680212  |
| 44 | 6 | 0 | -4.385582 | -0.426581 | 0.121692  |
| 45 | 6 | 0 | -3.847603 | 0.363133  | -0.932239 |
| 46 | 6 | 0 | -4.782165 | 1.152509  | -1.691029 |
| 47 | 6 | 0 | -6.138862 | 0.997458  | -1.432805 |
| 48 | 1 | 0 | -6.835209 | 1.576839  | -2.029140 |
| 49 | 6 | 0 | -6.682031 | 0.150971  | -0.448205 |
| 50 | 6 | 0 | -5.771341 | -0.533154 | 0.338229  |
| 51 | 1 | 0 | -6.124895 | -1.162713 | 1.148762  |
| 52 | 6 | 0 | -4.135100 | -0.983607 | 2.993313  |
| 53 | 6 | 0 | -3.869078 | 0.246778  | 3.607391  |
| 54 | 1 | 0 | -3.201554 | 0.952411  | 3.121888  |
| 55 | 6 | 0 | -4.453232 | 0.566757  | 4.830080  |
| 56 | 1 | 0 | -4.236802 | 1.523845  | 5.297898  |
| 57 | 6 | 0 | -5.314533 | -0.338706 | 5.450943  |
| 58 | 1 | 0 | -5.771722 | -0.089016 | 6.405053  |
| 59 | 6 | 0 | -5.587522 | -1.563279 | 4.844690  |
| 60 | 1 | 0 | -6.258399 | -2.272256 | 5.323041  |
| 61 | 6 | 0 | -4.999511 | -1.887056 | 3.621514  |
| 62 | 1 | 0 | -5.215747 | -2.845603 | 3.159369  |
| 63 | 6 | 0 | -3.566614 | -3.120439 | 1.092428  |
| 64 | 6 | 0 | -4.167283 | -3.620955 | -0.065601 |
| 65 | 1 | 0 | -4.541462 | -2.940713 | -0.824146 |
| 66 | 6 | 0 | -4.268145 | -4.997929 | -0.261333 |
| 67 | 1 | 0 | -4.717488 | -5.373562 | -1.175696 |
| 68 | 6 | 0 | -3.774261 | -5.879177 | 0.696792  |
| 69 | 1 | 0 | -3.855223 | -6.952328 | 0.542649  |
| 70 | 6 | 0 | -3.163820 | -5.385683 | 1.851713  |
| 71 | 1 | 0 | -2.771087 | -6.070940 | 2.598744  |
| 72 | 6 | 0 | -3.055932 | -4.012105 | 2.048649  |
| 73 | 1 | 0 | -2.583392 | -3.636182 | 2.953002  |
| 74 | 6 | 0 | 1.798958  | 2.780868  | -3.749488 |
| 75 | 6 | 0 | 5.377299  | 4.613955  | -0.634300 |
| 76 | 6 | 0 | -8.200803 | 0.049621  | -0.269357 |
| 77 | 6 | 0 | -4.302029 | 2.172264  | -2.738126 |
| 78 | 6 | 0 | 1.748928  | 1.295435  | -4.152362 |
| 79 | 6 | 0 | 0.390523  | 3.400978  | -3.839944 |
| 80 | 6 | 0 | 2.682630  | 3.501532  | -4.780119 |
| 81 | 6 | 0 | 5.221955  | 6.030031  | -1.223520 |
| 82 | 6 | 0 | 5.804213  | 4.752440  | 0.833351  |
| 83 | 6 | 0 | 6.497163  | 3.870898  | -1.388899 |
| 84 | 6 | 0 | -8.586652 | -0.925966 | 0.850926  |
| 85 | 6 | 0 | -8.776110 | 1.435877  | 0.082841  |
| 86 | 6 | 0 | -8.841565 | -0.448697 | -1.579609 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 87  | 6 | 0 | -3.413937 | 3.227693  | -2.049277 |
| 88  | 6 | 0 | -5.467005 | 2.922253  | -3.404242 |
| 89  | 6 | 0 | -3.508624 | 1.479243  | -3.859697 |
| 90  | 1 | 0 | -9.678411 | -0.975788 | 0.939042  |
| 91  | 1 | 0 | -8.224790 | -1.940791 | 0.647006  |
| 92  | 1 | 0 | -8.191487 | -0.609311 | 1.823476  |
| 93  | 1 | 0 | -9.931932 | -0.516701 | -1.473705 |
| 94  | 1 | 0 | -8.630435 | 0.224663  | -2.417485 |
| 95  | 1 | 0 | -8.461872 | -1.441530 | -1.847151 |
| 96  | 1 | 0 | -9.865164 | 1.380143  | 0.207809  |
| 97  | 1 | 0 | -8.344336 | 1.811893  | 1.017836  |
| 98  | 1 | 0 | -8.569299 | 2.173413  | -0.700480 |
| 99  | 1 | 0 | 6.752501  | 5.299418  | 0.893205  |
| 100 | 1 | 0 | 5.066149  | 5.308730  | 1.423504  |
| 101 | 1 | 0 | 5.954544  | 3.775302  | 1.307251  |
| 102 | 1 | 0 | 7.448662  | 4.409714  | -1.293684 |
| 103 | 1 | 0 | 6.634481  | 2.860616  | -0.986805 |
| 104 | 1 | 0 | 6.274891  | 3.776036  | -2.457267 |
| 105 | 1 | 0 | 6.161853  | 6.589693  | -1.133739 |
| 106 | 1 | 0 | 4.951936  | 6.001325  | -2.284688 |
| 107 | 1 | 0 | 4.440212  | 6.589405  | -0.696290 |
| 108 | 1 | 0 | -0.299657 | 2.921874  | -3.143697 |
| 109 | 1 | 0 | -0.005197 | 3.288879  | -4.857681 |
| 110 | 1 | 0 | 0.426983  | 4.472681  | -3.608207 |
| 111 | 1 | 0 | 1.106310  | 0.716386  | -3.487038 |
| 112 | 1 | 0 | 1.361598  | 1.196657  | -5.175204 |
| 113 | 1 | 0 | 2.754099  | 0.857257  | -4.132135 |
| 114 | 1 | 0 | 2.755388  | 4.577922  | -4.582746 |
| 115 | 1 | 0 | 3.697252  | 3.086913  | -4.821799 |
| 116 | 1 | 0 | 2.240386  | 3.379974  | -5.775927 |
| 117 | 1 | 0 | -4.121055 | 0.715953  | -4.355259 |
| 118 | 1 | 0 | -3.204526 | 2.214190  | -4.616089 |
| 119 | 1 | 0 | -2.612368 | 1.003678  | -3.461814 |
| 120 | 1 | 0 | -3.981243 | 3.771033  | -1.283788 |
| 121 | 1 | 0 | -2.544010 | 2.770294  | -1.573600 |
| 122 | 1 | 0 | -3.055435 | 3.959216  | -2.784739 |
| 123 | 1 | 0 | -6.069962 | 3.484000  | -2.680551 |
| 124 | 1 | 0 | -6.130723 | 2.248758  | -3.960277 |
| 125 | 1 | 0 | -5.060976 | 3.644956  | -4.121560 |
| 126 | 8 | 0 | 0.823762  | -1.783916 | -0.559498 |
| 127 | 6 | 0 | 0.736971  | -2.504804 | -1.659369 |
| 128 | 6 | 0 | 0.101293  | -3.921202 | -1.541970 |
| 129 | 8 | 0 | -0.106318 | -1.701707 | -2.577823 |
| 130 | 1 | 0 | 0.531028  | -4.538424 | -2.339018 |
| 131 | 8 | 0 | -1.329804 | -3.888105 | -1.741469 |
| 132 | 6 | 0 | 0.368194  | -4.562257 | -0.201505 |
| 133 | 6 | 0 | -0.736331 | -2.477141 | -3.600519 |
| 134 | 6 | 0 | -1.772197 | -3.347958 | -2.894208 |
| 135 | 1 | 0 | -0.044704 | -5.575488 | -0.181545 |
| 136 | 1 | 0 | 1.447921  | -4.600773 | -0.034780 |
| 137 | 1 | 0 | -0.088662 | -3.972880 | 0.596944  |
| 138 | 1 | 0 | 0.028506  | -3.121210 | -4.060409 |
| 139 | 6 | 0 | -1.345135 | -1.586163 | -4.657972 |
| 140 | 8 | 0 | -2.911218 | -3.513128 | -3.262165 |
| 141 | 1 | 0 | -0.571813 | -0.951963 | -5.100205 |
| 142 | 1 | 0 | -1.794200 | -2.202620 | -5.441955 |
| 143 | 1 | 0 | -2.129166 | -0.957828 | -4.232904 |
| 144 | 8 | 0 | 1.963673  | -2.774139 | -2.313195 |

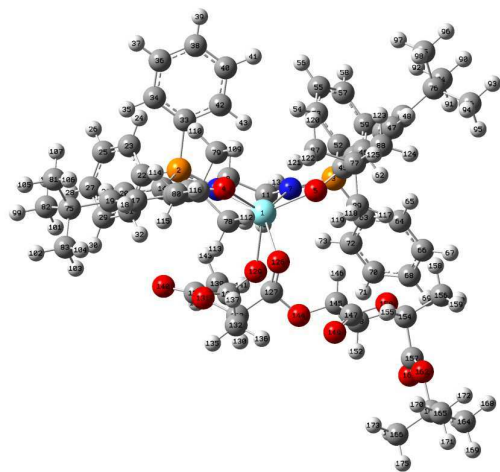
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 145 | 6 | 0 | 3.037752  | -1.894382 | -2.075923 |
| 146 | 1 | 0 | 2.693709  | -0.861084 | -1.962568 |
| 147 | 6 | 0 | 3.778358  | -2.295925 | -0.805073 |
| 148 | 6 | 0 | 3.986587  | -2.002202 | -3.268739 |
| 149 | 8 | 0 | 3.683291  | -3.345508 | -0.215778 |
| 150 | 8 | 0 | 4.642950  | -1.316566 | -0.444610 |
| 151 | 1 | 0 | 4.865200  | -1.369625 | -3.119340 |
| 152 | 1 | 0 | 4.320438  | -3.036992 | -3.392341 |
| 153 | 1 | 0 | 3.463996  | -1.689625 | -4.177367 |
| 154 | 6 | 0 | 5.515255  | -1.641988 | 0.633419  |
| 155 | 1 | 0 | 4.929440  | -2.003048 | 1.484114  |
| 156 | 6 | 0 | 6.283719  | -0.376173 | 0.985569  |
| 157 | 6 | 0 | 6.478941  | -2.753462 | 0.205712  |
| 158 | 1 | 0 | 5.587765  | 0.423365  | 1.254893  |
| 159 | 1 | 0 | 6.953481  | -0.567000 | 1.829343  |
| 160 | 1 | 0 | 6.877719  | -0.042467 | 0.128970  |
| 161 | 8 | 0 | 6.761184  | -2.997432 | -0.944725 |
| 162 | 8 | 0 | 6.980194  | -3.340917 | 1.297894  |
| 163 | 6 | 0 | 7.961959  | -4.430475 | 1.201858  |
| 164 | 6 | 0 | 9.239050  | -3.924282 | 0.534577  |
| 165 | 6 | 0 | 8.216457  | -4.782356 | 2.664803  |
| 166 | 6 | 0 | 7.347454  | -5.614294 | 0.457945  |
| 167 | 1 | 0 | 9.058185  | -3.655053 | -0.507728 |
| 168 | 1 | 0 | 9.628969  | -3.049330 | 1.066739  |
| 169 | 1 | 0 | 10.003716 | -4.708585 | 0.567049  |
| 170 | 1 | 0 | 7.289335  | -5.101334 | 3.152094  |
| 171 | 1 | 0 | 8.943299  | -5.598579 | 2.733453  |
| 172 | 1 | 0 | 8.613475  | -3.918480 | 3.208565  |
| 173 | 1 | 0 | 6.397464  | -5.901968 | 0.920400  |
| 174 | 1 | 0 | 7.166696  | -5.372337 | -0.590890 |
| 175 | 1 | 0 | 8.028860  | -6.471033 | 0.510139  |

-----  
Rotational constants (GHz): 0.0277360 0.0168430  
0.0148835

Sum of electronic and zero-point Energies= -3706.939125  
Sum of electronic and thermal Energies= -3706.848040  
Sum of electronic and thermal Enthalpies= -3706.847096  
Sum of electronic and thermal Free Energies= -3707.075061

|                | 1      | 2      | 3 |
|----------------|--------|--------|---|
|                | A      | A      | A |
| Frequencies -- | 6.3823 | 8.0733 |   |
| 12.8231        |        |        |   |
| Red. masses -- | 5.0850 | 4.7045 |   |
| 4.9709         |        |        |   |
| Frc consts --  | 0.0001 | 0.0002 |   |
| 0.0005         |        |        |   |
| IR Inten --    | 0.0731 | 0.0584 |   |
| 0.0252         |        |        |   |

**Propagation : TS2'**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.622986               | -0.104832 | -0.250622 |
| 2                | 15               | 0              | -4.152950               | 0.042306  | -0.389782 |
| 3                | 15               | 0              | 0.616101                | 3.194763  | -1.087253 |
| 4                | 8                | 0              | -1.935656               | -0.947879 | 1.292989  |
| 5                | 8                | 0              | 0.854861                | 0.965325  | 0.964007  |
| 6                | 7                | 0              | -2.748115               | 0.514481  | -1.105157 |
| 7                | 7                | 0              | -0.548428               | 2.060849  | -1.261639 |
| 8                | 6                | 0              | -2.856360               | 1.716217  | -1.938517 |
| 9                | 1                | 0              | -3.300131               | 2.563594  | -1.387708 |
| 10               | 1                | 0              | -3.489481               | 1.553467  | -2.826188 |
| 11               | 6                | 0              | -1.462025               | 2.131202  | -2.402468 |
| 12               | 1                | 0              | -1.137311               | 1.448895  | -3.199909 |
| 13               | 1                | 0              | -1.531456               | 3.136853  | -2.846106 |
| 14               | 6                | 0              | -4.059001               | -1.557970 | 0.440543  |
| 15               | 6                | 0              | -2.972500               | -1.759747 | 1.332156  |
| 16               | 6                | 0              | -3.091174               | -2.839240 | 2.267841  |
| 17               | 6                | 0              | -4.178326               | -3.697779 | 2.131094  |
| 18               | 1                | 0              | -4.245487               | -4.537186 | 2.815392  |
| 19               | 6                | 0              | -5.207673               | -3.557883 | 1.182209  |
| 20               | 6                | 0              | -5.147667               | -2.439232 | 0.364555  |
| 21               | 1                | 0              | -5.940303               | -2.236346 | -0.346588 |
| 22               | 6                | 0              | -5.508481               | -0.020659 | -1.637666 |
| 23               | 6                | 0              | -6.543024               | 0.919565  | -1.688433 |
| 24               | 1                | 0              | -6.621487               | 1.688943  | -0.925828 |
| 25               | 6                | 0              | -7.478595               | 0.876111  | -2.722657 |
| 26               | 1                | 0              | -8.280494               | 1.609433  | -2.753581 |
| 27               | 6                | 0              | -7.383486               | -0.101373 | -3.711118 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 28 | 1 | 0 | -8.114988 | -0.135214 | -4.514742 |
| 29 | 6 | 0 | -6.344900 | -1.032679 | -3.671186 |
| 30 | 1 | 0 | -6.262147 | -1.794043 | -4.442403 |
| 31 | 6 | 0 | -5.404610 | -0.993591 | -2.644197 |
| 32 | 1 | 0 | -4.592714 | -1.717588 | -2.629803 |
| 33 | 6 | 0 | -4.694321 | 1.224780  | 0.927844  |
| 34 | 6 | 0 | -5.927486 | 1.078369  | 1.575558  |
| 35 | 1 | 0 | -6.613761 | 0.292184  | 1.270629  |
| 36 | 6 | 0 | -6.270029 | 1.924105  | 2.627752  |
| 37 | 1 | 0 | -7.228037 | 1.804120  | 3.127239  |
| 38 | 6 | 0 | -5.378758 | 2.912419  | 3.049173  |
| 39 | 1 | 0 | -5.644292 | 3.566453  | 3.875947  |
| 40 | 6 | 0 | -4.142961 | 3.049719  | 2.419537  |
| 41 | 1 | 0 | -3.438166 | 3.805157  | 2.757978  |
| 42 | 6 | 0 | -3.800497 | 2.208138  | 1.360805  |
| 43 | 1 | 0 | -2.830270 | 2.295600  | 0.878706  |
| 44 | 6 | 0 | 1.246103  | 3.281175  | 0.604780  |
| 45 | 6 | 0 | 1.329689  | 2.104587  | 1.396756  |
| 46 | 6 | 0 | 1.974614  | 2.228684  | 2.676514  |
| 47 | 6 | 0 | 2.426876  | 3.484255  | 3.066329  |
| 48 | 1 | 0 | 2.904363  | 3.567832  | 4.037116  |
| 49 | 6 | 0 | 2.312068  | 4.659992  | 2.299564  |
| 50 | 6 | 0 | 1.719244  | 4.526755  | 1.053680  |
| 51 | 1 | 0 | 1.610127  | 5.391222  | 0.406789  |
| 52 | 6 | 0 | -0.046598 | 4.870859  | -1.503188 |
| 53 | 6 | 0 | -1.235810 | 5.266710  | -0.874959 |
| 54 | 1 | 0 | -1.726903 | 4.592389  | -0.178606 |
| 55 | 6 | 0 | -1.789319 | 6.515341  | -1.143126 |
| 56 | 1 | 0 | -2.711958 | 6.813677  | -0.651988 |
| 57 | 6 | 0 | -1.161009 | 7.380183  | -2.041064 |
| 58 | 1 | 0 | -1.593747 | 8.355176  | -2.250270 |
| 59 | 6 | 0 | 0.020217  | 6.991879  | -2.669194 |
| 60 | 1 | 0 | 0.512207  | 7.661788  | -3.369627 |
| 61 | 6 | 0 | 0.577461  | 5.740143  | -2.403032 |
| 62 | 1 | 0 | 1.498061  | 5.444241  | -2.897268 |
| 63 | 6 | 0 | 2.079909  | 3.009412  | -2.211893 |
| 64 | 6 | 0 | 3.382454  | 3.246181  | -1.758518 |
| 65 | 1 | 0 | 3.552386  | 3.512675  | -0.719097 |
| 66 | 6 | 0 | 4.461024  | 3.141474  | -2.637434 |
| 67 | 1 | 0 | 5.469305  | 3.327412  | -2.276230 |
| 68 | 6 | 0 | 4.247549  | 2.800093  | -3.971935 |
| 69 | 1 | 0 | 5.088855  | 2.720859  | -4.655673 |
| 70 | 6 | 0 | 2.951903  | 2.552025  | -4.427550 |
| 71 | 1 | 0 | 2.781170  | 2.277295  | -5.465381 |
| 72 | 6 | 0 | 1.872713  | 2.652350  | -3.551899 |
| 73 | 1 | 0 | 0.868827  | 2.450569  | -3.913807 |
| 74 | 6 | 0 | -2.102649 | -3.000979 | 3.432071  |
| 75 | 6 | 0 | -6.331515 | -4.597164 | 1.107075  |
| 76 | 6 | 0 | 2.828570  | 5.994542  | 2.849623  |
| 77 | 6 | 0 | 2.161427  | 1.007731  | 3.589802  |
| 78 | 6 | 0 | -0.676662 | -3.266519 | 2.919200  |
| 79 | 6 | 0 | -2.139206 | -1.713032 | 4.279681  |
| 80 | 6 | 0 | -2.474125 | -4.166477 | 4.362060  |
| 81 | 6 | 0 | -7.065229 | -4.678666 | 2.460199  |
| 82 | 6 | 0 | -7.364703 | -4.251845 | 0.025577  |
| 83 | 6 | 0 | -5.728649 | -5.975324 | 0.770381  |
| 84 | 6 | 0 | 2.604886  | 7.150583  | 1.865230  |
| 85 | 6 | 0 | 2.090222  | 6.332637  | 4.159873  |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 86  | 6 | 0 | 4.340562  | 5.891496  | 3.130995  |
| 87  | 6 | 0 | 0.786145  | 0.468499  | 4.019930  |
| 88  | 6 | 0 | 2.944587  | 1.345913  | 4.868270  |
| 89  | 6 | 0 | 2.947740  | -0.091659 | 2.848443  |
| 90  | 1 | 0 | 2.982070  | 8.084573  | 2.298183  |
| 91  | 1 | 0 | 3.134502  | 6.988465  | 0.918737  |
| 92  | 1 | 0 | 1.541447  | 7.295306  | 1.641418  |
| 93  | 1 | 0 | 4.721917  | 6.835884  | 3.540167  |
| 94  | 1 | 0 | 4.566986  | 5.100604  | 3.854295  |
| 95  | 1 | 0 | 4.895117  | 5.670688  | 2.211221  |
| 96  | 1 | 0 | 2.453103  | 7.282666  | 4.572881  |
| 97  | 1 | 0 | 1.011770  | 6.425398  | 3.986534  |
| 98  | 1 | 0 | 2.239569  | 5.559937  | 4.921716  |
| 99  | 1 | 0 | -8.141306 | -5.025332 | -0.005751 |
| 100 | 1 | 0 | -7.861460 | -3.294768 | 0.226273  |
| 101 | 1 | 0 | -6.908496 | -4.198795 | -0.969721 |
| 102 | 1 | 0 | -6.515914 | -6.739000 | 0.721692  |
| 103 | 1 | 0 | -5.214074 | -5.948671 | -0.196812 |
| 104 | 1 | 0 | -5.001156 | -6.293808 | 1.525219  |
| 105 | 1 | 0 | -7.866248 | -5.427894 | 2.418197  |
| 106 | 1 | 0 | -6.389909 | -4.961713 | 3.274884  |
| 107 | 1 | 0 | -7.514515 | -3.712967 | 2.720498  |
| 108 | 1 | 0 | -1.886294 | -0.837553 | 3.679071  |
| 109 | 1 | 0 | -1.424197 | -1.783994 | 5.109213  |
| 110 | 1 | 0 | -3.138994 | -1.563602 | 4.706152  |
| 111 | 1 | 0 | -0.333145 | -2.486521 | 2.239621  |
| 112 | 1 | 0 | 0.022577  | -3.324784 | 3.763893  |
| 113 | 1 | 0 | -0.639448 | -4.225442 | 2.388583  |
| 114 | 1 | 0 | -3.469381 | -4.043514 | 4.806092  |
| 115 | 1 | 0 | -2.440375 | -5.134974 | 3.848205  |
| 116 | 1 | 0 | -1.750967 | -4.209595 | 5.185334  |
| 117 | 1 | 0 | 3.935948  | 0.279828  | 2.549291  |
| 118 | 1 | 0 | 3.095322  | -0.955963 | 3.508959  |
| 119 | 1 | 0 | 2.417325  | -0.427013 | 1.956089  |
| 120 | 1 | 0 | 0.231558  | 1.226456  | 4.587216  |
| 121 | 1 | 0 | 0.187010  | 0.175832  | 3.156953  |
| 122 | 1 | 0 | 0.910002  | -0.411245 | 4.663633  |
| 123 | 1 | 0 | 2.424033  | 2.080814  | 5.494276  |
| 124 | 1 | 0 | 3.950353  | 1.726441  | 4.650508  |
| 125 | 1 | 0 | 3.060065  | 0.434296  | 5.466211  |
| 126 | 8 | 0 | 0.940573  | -1.861325 | -0.063345 |
| 127 | 6 | 0 | 1.076366  | -2.409343 | -1.182323 |
| 128 | 6 | 0 | 0.421010  | -3.743811 | -1.560530 |
| 129 | 8 | 0 | -0.118218 | -1.218677 | -2.202826 |
| 130 | 1 | 0 | 0.778907  | -4.013783 | -2.559453 |
| 131 | 8 | 0 | -1.009282 | -3.705477 | -1.571249 |
| 132 | 6 | 0 | 0.838907  | -4.813010 | -0.566388 |
| 133 | 6 | 0 | -0.752760 | -1.935655 | -3.222512 |
| 134 | 6 | 0 | -1.625625 | -2.999356 | -2.551840 |
| 135 | 1 | 0 | 0.423155  | -5.778460 | -0.869822 |
| 136 | 1 | 0 | 1.929905  | -4.877746 | -0.531516 |
| 137 | 1 | 0 | 0.469201  | -4.559221 | 0.429473  |
| 138 | 1 | 0 | 0.013842  | -2.462763 | -3.822061 |
| 139 | 6 | 0 | -1.565025 | -1.084675 | -4.185280 |
| 140 | 8 | 0 | -2.797012 | -3.196318 | -2.777059 |
| 141 | 1 | 0 | -0.909868 | -0.347985 | -4.661091 |
| 142 | 1 | 0 | -2.006260 | -1.714675 | -4.964899 |
| 143 | 1 | 0 | -2.372574 | -0.568813 | -3.661300 |

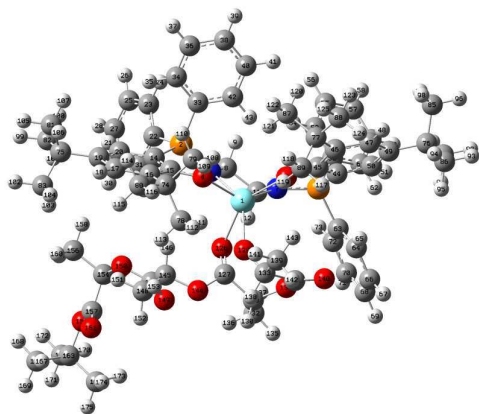
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 144 | 8 | 0 | 2.230445  | -2.325788 | -1.881658 |
| 145 | 6 | 0 | 3.243857  | -1.435686 | -1.427755 |
| 146 | 1 | 0 | 2.800502  | -0.625436 | -0.840382 |
| 147 | 6 | 0 | 4.194188  | -2.217862 | -0.526767 |
| 148 | 6 | 0 | 3.963298  | -0.889879 | -2.653962 |
| 149 | 8 | 0 | 4.115630  | -3.394047 | -0.266359 |
| 150 | 8 | 0 | 5.168370  | -1.405908 | -0.066022 |
| 151 | 1 | 0 | 4.752705  | -0.199656 | -2.350075 |
| 152 | 1 | 0 | 4.413816  | -1.704693 | -3.228713 |
| 153 | 1 | 0 | 3.247380  | -0.356456 | -3.284044 |
| 154 | 6 | 0 | 6.207370  | -2.051751 | 0.669617  |
| 155 | 1 | 0 | 5.766145  | -2.717288 | 1.417293  |
| 156 | 6 | 0 | 7.040754  | -0.962648 | 1.328507  |
| 157 | 6 | 0 | 7.049997  | -2.897612 | -0.291284 |
| 158 | 1 | 0 | 6.414129  | -0.369260 | 2.000121  |
| 159 | 1 | 0 | 7.850893  | -1.414163 | 1.907554  |
| 160 | 1 | 0 | 7.471098  | -0.297824 | 0.572705  |
| 161 | 8 | 0 | 7.011584  | -2.793115 | -1.495810 |
| 162 | 8 | 0 | 7.833540  | -3.713880 | 0.419521  |
| 163 | 6 | 0 | 8.766093  | -4.646697 | -0.231960 |
| 164 | 6 | 0 | 9.803707  | -3.868161 | -1.037814 |
| 165 | 6 | 0 | 9.417091  | -5.352632 | 0.953648  |
| 166 | 6 | 0 | 7.984103  | -5.636495 | -1.092558 |
| 167 | 1 | 0 | 9.342738  | -3.351642 | -1.881934 |
| 168 | 1 | 0 | 10.308526 | -3.132122 | -0.402181 |
| 169 | 1 | 0 | 10.561458 | -4.560319 | -1.422007 |
| 170 | 1 | 0 | 8.663936  | -5.869125 | 1.557358  |
| 171 | 1 | 0 | 10.143077 | -6.091427 | 0.598154  |
| 172 | 1 | 0 | 9.940011  | -4.634306 | 1.593842  |
| 173 | 1 | 0 | 7.213735  | -6.135448 | -0.495133 |
| 174 | 1 | 0 | 7.504746  | -5.135524 | -1.935622 |
| 175 | 1 | 0 | 8.666449  | -6.401767 | -1.479578 |

-----  
Rotational constants (GHZ):      0.0247085      0.0175735  
0.0138712

Sum of electronic and zero-point Energies=      -3706.929707  
Sum of electronic and thermal Energies=      -3706.839110  
Sum of electronic and thermal Enthalpies=      -3706.838166  
Sum of electronic and thermal Free Energies=      -3707.064660

|                | 1         | 2      | 3 |
|----------------|-----------|--------|---|
|                | A         | A      | A |
| Frequencies -- | -166.3810 | 5.3813 |   |
| 9.2927         |           |        |   |
| Red. masses -- | 9.2434    | 4.7056 |   |
| 4.6704         |           |        |   |
| Frc consts --  | 0.1508    | 0.0001 |   |
| 0.0002         |           |        |   |
| IR Inten --    | 102.8254  | 0.2094 |   |
| 0.0283         |           |        |   |

**Propagation : TS2**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.666224               | 0.032669  | -0.664017 |
| 2                | 15               | 0              | 1.058174                | 2.128293  | 1.614525  |
| 3                | 15               | 0              | -3.364022               | -1.496336 | 1.194720  |
| 4                | 8                | 0              | 0.349223                | 1.890450  | -1.236090 |
| 5                | 8                | 0              | -2.710185               | 0.594549  | -1.076011 |
| 6                | 7                | 0              | 0.366282                | 0.657757  | 1.413012  |
| 7                | 7                | 0              | -1.843443               | -0.896317 | 1.174917  |
| 8                | 6                | 0              | -0.089701               | -0.034673 | 2.623268  |
| 9                | 1                | 0              | -0.729431               | 0.603835  | 3.256078  |
| 10               | 1                | 0              | 0.751518                | -0.358014 | 3.256581  |
| 11               | 6                | 0              | -0.897451               | -1.272597 | 2.226852  |
| 12               | 1                | 0              | -0.209336               | -2.049433 | 1.864954  |
| 13               | 1                | 0              | -1.383111               | -1.661882 | 3.135895  |
| 14               | 6                | 0              | 2.053155                | 2.670963  | 0.203953  |
| 15               | 6                | 0              | 1.464115                | 2.564590  | -1.083016 |
| 16               | 6                | 0              | 2.125687                | 3.234410  | -2.164876 |
| 17               | 6                | 0              | 3.339022                | 3.860981  | -1.893613 |
| 18               | 1                | 0              | 3.846204                | 4.352439  | -2.717439 |
| 19               | 6                | 0              | 3.959203                | 3.915158  | -0.630962 |
| 20               | 6                | 0              | 3.275819                | 3.322792  | 0.422756  |
| 21               | 1                | 0              | 3.680375                | 3.357500  | 1.428893  |
| 22               | 6                | 0              | 2.161739                | 2.114582  | 3.096146  |
| 23               | 6                | 0              | 2.012513                | 2.981233  | 4.182316  |
| 24               | 1                | 0              | 1.244570                | 3.748679  | 4.166064  |
| 25               | 6                | 0              | 2.845314                | 2.860667  | 5.295813  |
| 26               | 1                | 0              | 2.723188                | 3.540785  | 6.134872  |
| 27               | 6                | 0              | 3.823947                | 1.870372  | 5.334385  |
| 28               | 1                | 0              | 4.469219                | 1.775418  | 6.204018  |
| 29               | 6                | 0              | 3.968805                | 0.993353  | 4.257789  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 30 | 1 | 0 | 4.721934  | 0.210278  | 4.291655  |
| 31 | 6 | 0 | 3.141741  | 1.111939  | 3.143970  |
| 32 | 1 | 0 | 3.242167  | 0.421693  | 2.309757  |
| 33 | 6 | 0 | -0.164797 | 3.485570  | 1.909878  |
| 34 | 6 | 0 | 0.238406  | 4.824855  | 1.989967  |
| 35 | 1 | 0 | 1.287776  | 5.085879  | 1.875499  |
| 36 | 6 | 0 | -0.706633 | 5.828035  | 2.192450  |
| 37 | 1 | 0 | -0.388573 | 6.865938  | 2.250225  |
| 38 | 6 | 0 | -2.059407 | 5.502137  | 2.305213  |
| 39 | 1 | 0 | -2.796066 | 6.286911  | 2.457352  |
| 40 | 6 | 0 | -2.466516 | 4.173428  | 2.201943  |
| 41 | 1 | 0 | -3.521079 | 3.918220  | 2.263170  |
| 42 | 6 | 0 | -1.521901 | 3.166600  | 2.000843  |
| 43 | 1 | 0 | -1.837809 | 2.133481  | 1.881797  |
| 44 | 6 | 0 | -4.449360 | -0.582144 | 0.062964  |
| 45 | 6 | 0 | -3.985216 | 0.417987  | -0.835940 |
| 46 | 6 | 0 | -4.986498 | 1.233515  | -1.472400 |
| 47 | 6 | 0 | -6.323172 | 0.910160  | -1.274261 |
| 48 | 1 | 0 | -7.069565 | 1.512791  | -1.780501 |
| 49 | 6 | 0 | -6.787021 | -0.139919 | -0.459026 |
| 50 | 6 | 0 | -5.819682 | -0.854622 | 0.225680  |
| 51 | 1 | 0 | -6.115928 | -1.641860 | 0.912644  |
| 52 | 6 | 0 | -4.112983 | -1.300822 | 2.883393  |
| 53 | 6 | 0 | -3.839437 | -0.117358 | 3.579649  |
| 54 | 1 | 0 | -3.174453 | 0.618347  | 3.137234  |
| 55 | 6 | 0 | -4.411022 | 0.116187  | 4.827777  |
| 56 | 1 | 0 | -4.188009 | 1.037435  | 5.360126  |
| 57 | 6 | 0 | -5.268244 | -0.829521 | 5.391419  |
| 58 | 1 | 0 | -5.715856 | -0.647171 | 6.365169  |
| 59 | 6 | 0 | -5.549221 | -2.008078 | 4.702928  |
| 60 | 1 | 0 | -6.216494 | -2.748517 | 5.136730  |
| 61 | 6 | 0 | -4.972892 | -2.245268 | 3.454723  |
| 62 | 1 | 0 | -5.192766 | -3.170131 | 2.929649  |
| 63 | 6 | 0 | -3.515219 | -3.305333 | 0.851478  |
| 64 | 6 | 0 | -4.066422 | -3.761469 | -0.348458 |
| 65 | 1 | 0 | -4.444960 | -3.054419 | -1.079030 |
| 66 | 6 | 0 | -4.107379 | -5.127962 | -0.623913 |
| 67 | 1 | 0 | -4.523826 | -5.467814 | -1.567638 |
| 68 | 6 | 0 | -3.600254 | -6.043543 | 0.294319  |
| 69 | 1 | 0 | -3.635601 | -7.108558 | 0.078244  |
| 70 | 6 | 0 | -3.036116 | -5.593651 | 1.489992  |
| 71 | 1 | 0 | -2.633812 | -6.304920 | 2.207181  |
| 72 | 6 | 0 | -2.990206 | -4.230399 | 1.767599  |
| 73 | 1 | 0 | -2.555685 | -3.888981 | 2.704007  |
| 74 | 6 | 0 | 1.499888  | 3.290762  | -3.566814 |
| 75 | 6 | 0 | 5.308329  | 4.625202  | -0.467734 |
| 76 | 6 | 0 | -8.289100 | -0.419995 | -0.341334 |
| 77 | 6 | 0 | -4.596810 | 2.449493  | -2.330903 |
| 78 | 6 | 0 | 1.403766  | 1.876186  | -4.167511 |
| 79 | 6 | 0 | 0.095630  | 3.921734  | -3.476792 |
| 80 | 6 | 0 | 2.323600  | 4.147873  | -4.540964 |
| 81 | 6 | 0 | 5.172801  | 6.104034  | -0.881035 |
| 82 | 6 | 0 | 5.812226  | 4.582422  | 0.981428  |
| 83 | 6 | 0 | 6.362897  | 3.943040  | -1.361198 |
| 84 | 6 | 0 | -8.584112 | -1.610103 | 0.581790  |
| 85 | 6 | 0 | -9.005858 | 0.818865  | 0.230790  |
| 86 | 6 | 0 | -8.863266 | -0.741468 | -1.735303 |
| 87 | 6 | 0 | -3.778624 | 3.439253  | -1.477986 |

## Appendix 2. Optimised Structures

|     |   |   |            |           |           |
|-----|---|---|------------|-----------|-----------|
| 88  | 6 | 0 | -5.824609  | 3.211993  | -2.856027 |
| 89  | 6 | 0 | -3.773161  | 2.015128  | -3.556302 |
| 90  | 1 | 0 | -9.665660  | -1.784920 | 0.626848  |
| 91  | 1 | 0 | -8.114808  | -2.531974 | 0.218023  |
| 92  | 1 | 0 | -8.236409  | -1.428005 | 1.605654  |
| 93  | 1 | 0 | -9.941509  | -0.937057 | -1.671561 |
| 94  | 1 | 0 | -8.716484  | 0.087234  | -2.436681 |
| 95  | 1 | 0 | -8.379665  | -1.627647 | -2.162327 |
| 96  | 1 | 0 | -10.085154 | 0.636266  | 0.312355  |
| 97  | 1 | 0 | -8.624606  | 1.063271  | 1.229217  |
| 98  | 1 | 0 | -8.865183  | 1.699710  | -0.405172 |
| 99  | 1 | 0 | 6.780011   | 5.092670  | 1.053178  |
| 100 | 1 | 0 | 5.122262   | 5.087051  | 1.668313  |
| 101 | 1 | 0 | 5.952952   | 3.553840  | 1.334095  |
| 102 | 1 | 0 | 7.335131   | 4.442906  | -1.261995 |
| 103 | 1 | 0 | 6.489416   | 2.890723  | -1.081071 |
| 104 | 1 | 0 | 6.079718   | 3.973543  | -2.418960 |
| 105 | 1 | 0 | 6.133426   | 6.623966  | -0.772643 |
| 106 | 1 | 0 | 4.854968   | 6.208963  | -1.924001 |
| 107 | 1 | 0 | 4.434276   | 6.617961  | -0.254683 |
| 108 | 1 | 0 | -0.555187  | 3.347468  | -2.815477 |
| 109 | 1 | 0 | -0.363890  | 3.958069  | -4.472927 |
| 110 | 1 | 0 | 0.158014   | 4.948809  | -3.096036 |
| 111 | 1 | 0 | 0.817974   | 1.201982  | -3.539722 |
| 112 | 1 | 0 | 0.931661   | 1.921874  | -5.158166 |
| 113 | 1 | 0 | 2.405617   | 1.448156  | -4.296883 |
| 114 | 1 | 0 | 2.428867   | 5.182963  | -4.193877 |
| 115 | 1 | 0 | 3.325873   | 3.736860  | -4.714307 |
| 116 | 1 | 0 | 1.812584   | 4.177071  | -5.510499 |
| 117 | 1 | 0 | -4.341174  | 1.311801  | -4.177496 |
| 118 | 1 | 0 | -3.527331  | 2.889265  | -4.173063 |
| 119 | 1 | 0 | -2.842122  | 1.537000  | -3.252188 |
| 120 | 1 | 0 | -4.371925  | 3.796666  | -0.627274 |
| 121 | 1 | 0 | -2.865822  | 2.978958  | -1.095391 |
| 122 | 1 | 0 | -3.495448  | 4.311966  | -2.080534 |
| 123 | 1 | 0 | -6.462186  | 3.584111  | -2.044725 |
| 124 | 1 | 0 | -6.439289  | 2.599554  | -3.527059 |
| 125 | 1 | 0 | -5.484179  | 4.081862  | -3.429958 |
| 126 | 8 | 0 | 0.879344   | -1.774276 | -0.412483 |
| 127 | 6 | 0 | 1.022224   | -2.358363 | -1.503170 |
| 128 | 6 | 0 | 0.313721   | -3.657955 | -1.901323 |
| 129 | 8 | 0 | -0.233146  | -1.083900 | -2.580883 |
| 130 | 1 | 0 | 0.706855   | -3.952074 | -2.880077 |
| 131 | 8 | 0 | -1.107110  | -3.572519 | -1.970711 |
| 132 | 6 | 0 | 0.644075   | -4.728717 | -0.872013 |
| 133 | 6 | 0 | -0.796438  | -1.805910 | -3.630610 |
| 134 | 6 | 0 | -1.680049  | -2.884058 | -3.000998 |
| 135 | 1 | 0 | 0.220065   | -5.685146 | -1.190806 |
| 136 | 1 | 0 | 1.728066   | -4.823988 | -0.763800 |
| 137 | 1 | 0 | 0.214690   | -4.454487 | 0.095294  |
| 138 | 1 | 0 | 0.006024   | -2.316342 | -4.199163 |
| 139 | 6 | 0 | -1.586144  | -0.958213 | -4.615143 |
| 140 | 8 | 0 | -2.836211  | -3.100675 | -3.273077 |
| 141 | 1 | 0 | -0.936786  | -0.177333 | -5.021431 |
| 142 | 1 | 0 | -1.960887  | -1.574364 | -5.439386 |
| 143 | 1 | 0 | -2.440966  | -0.491242 | -4.122519 |
| 144 | 8 | 0 | 2.161389   | -2.285122 | -2.213269 |
| 145 | 6 | 0 | 3.178325   | -1.386197 | -1.780013 |

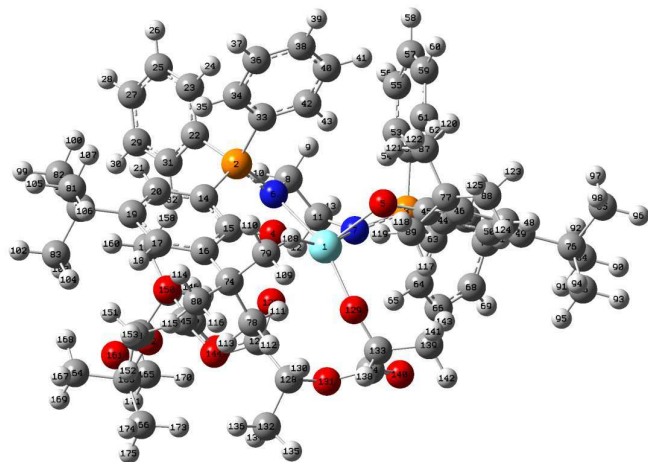
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 146 | 1 | 0 | 2.732135  | -0.459204 | -1.407067 |
| 147 | 6 | 0 | 3.966954  | -2.045454 | -0.653562 |
| 148 | 6 | 0 | 4.074526  | -1.109916 | -2.980629 |
| 149 | 8 | 0 | 3.829316  | -3.178304 | -0.260345 |
| 150 | 8 | 0 | 4.886668  | -1.184504 | -0.169492 |
| 151 | 1 | 0 | 4.862195  | -0.405822 | -2.703902 |
| 152 | 1 | 0 | 4.541095  | -2.034274 | -3.333286 |
| 153 | 1 | 0 | 3.474328  | -0.680447 | -3.786481 |
| 154 | 6 | 0 | 5.819795  | -1.739595 | 0.757678  |
| 155 | 1 | 0 | 5.279428  | -2.266353 | 1.550118  |
| 156 | 6 | 0 | 6.637824  | -0.584874 | 1.316816  |
| 157 | 6 | 0 | 6.718361  | -2.749203 | 0.033971  |
| 158 | 1 | 0 | 5.981851  | 0.140760  | 1.806034  |
| 159 | 1 | 0 | 7.360338  | -0.960464 | 2.046668  |
| 160 | 1 | 0 | 7.177760  | -0.074839 | 0.512862  |
| 161 | 8 | 0 | 6.827963  | -2.814424 | -1.168565 |
| 162 | 8 | 0 | 7.366534  | -3.482136 | 0.943103  |
| 163 | 6 | 0 | 8.328055  | -4.525313 | 0.548373  |
| 164 | 6 | 0 | 9.491488  | -3.897470 | -0.215497 |
| 165 | 6 | 0 | 8.793675  | -5.076450 | 1.892706  |
| 166 | 6 | 0 | 7.612425  | -5.602380 | -0.263411 |
| 167 | 1 | 0 | 9.162593  | -3.493817 | -1.174965 |
| 168 | 1 | 0 | 9.946958  | -3.093108 | 0.372802  |
| 169 | 1 | 0 | 10.258767 | -4.657735 | -0.399822 |
| 170 | 1 | 0 | 7.948017  | -5.479665 | 2.459240  |
| 171 | 1 | 0 | 9.520737  | -5.880194 | 1.736578  |
| 172 | 1 | 0 | 9.268553  | -4.291728 | 2.491083  |
| 173 | 1 | 0 | 6.747564  | -5.984742 | 0.288952  |
| 174 | 1 | 0 | 7.271810  | -5.213114 | -1.224587 |
| 175 | 1 | 0 | 8.299050  | -6.436813 | -0.445133 |

-----  
Rotational constants (GHZ):      0.0281900      0.0165329  
0.0145127

Sum of electronic and zero-point Energies=      -3706.929471  
Sum of electronic and thermal Energies=      -3706.838571  
Sum of electronic and thermal Enthalpies=      -3706.837627  
Sum of electronic and thermal Free Energies=      -3707.064193

|                | 1<br>A    | 2<br>A | 3<br>A |
|----------------|-----------|--------|--------|
| Frequencies -- | -134.4429 | 7.9741 |        |
| 8.9059         |           |        |        |
| Red. masses -- | 8.1778    | 4.9368 |        |
| 4.6802         |           |        |        |
| Frc consts --  | 0.0871    | 0.0002 |        |
| 0.0002         |           |        |        |
| IR Inten --    | 80.8760   | 0.0705 |        |
| 0.0467         |           |        |        |

**Propagation : INT4**

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | 0.948516                | -0.502162 | -0.739817 |
| 2                | 15               | 0              | -1.101772               | -2.169938 | 1.621574  |
| 3                | 15               | 0              | 2.860319                | 1.708938  | 1.230009  |
| 4                | 8                | 0              | -0.055227               | -2.424027 | -1.117466 |
| 5                | 8                | 0              | 2.948155                | -1.072344 | -0.044814 |
| 6                | 7                | 0              | -0.447081               | -0.721326 | 1.237564  |
| 7                | 7                | 0              | 1.359189                | 1.318447  | 0.704044  |
| 8                | 6                | 0              | -0.269308               | 0.309364  | 2.262165  |
| 9                | 1                | 0              | 0.478236                | 0.029192  | 3.022049  |
| 10               | 1                | 0              | -1.203734               | 0.530571  | 2.803981  |
| 11               | 6                | 0              | 0.205068                | 1.588122  | 1.564349  |
| 12               | 1                | 0              | -0.610113               | 1.959250  | 0.928281  |
| 13               | 1                | 0              | 0.385642                | 2.367285  | 2.321158  |
| 14               | 6                | 0              | -1.929908               | -2.969492 | 0.216297  |
| 15               | 6                | 0              | -1.203568               | -3.042343 | -1.002298 |
| 16               | 6                | 0              | -1.769968               | -3.825671 | -2.062347 |
| 17               | 6                | 0              | -3.006950               | -4.424329 | -1.839715 |
| 18               | 1                | 0              | -3.435242               | -5.012450 | -2.644862 |
| 19               | 6                | 0              | -3.741950               | -4.338828 | -0.642021 |
| 20               | 6                | 0              | -3.168519               | -3.605443 | 0.389473  |
| 21               | 1                | 0              | -3.672426               | -3.523153 | 1.346330  |
| 22               | 6                | 0              | -2.358748               | -2.013679 | 2.968192  |
| 23               | 6                | 0              | -2.232058               | -2.672266 | 4.195184  |
| 24               | 1                | 0              | -1.385048               | -3.327122 | 4.375236  |
| 25               | 6                | 0              | -3.193075               | -2.496205 | 5.191585  |
| 26               | 1                | 0              | -3.084695               | -3.014769 | 6.140725  |
| 27               | 6                | 0              | -4.287144               | -1.663712 | 4.969115  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 28 | 1 | 0 | -5.039008 | -1.532248 | 5.743216  |
| 29 | 6 | 0 | -4.415521 | -0.996902 | 3.749655  |
| 30 | 1 | 0 | -5.268400 | -0.347859 | 3.570858  |
| 31 | 6 | 0 | -3.453991 | -1.163475 | 2.756009  |
| 32 | 1 | 0 | -3.554711 | -0.632162 | 1.813289  |
| 33 | 6 | 0 | 0.110839  | -3.415017 | 2.252152  |
| 34 | 6 | 0 | -0.226708 | -4.772687 | 2.324949  |
| 35 | 1 | 0 | -1.204724 | -5.108044 | 1.988501  |
| 36 | 6 | 0 | 0.696168  | -5.696044 | 2.810592  |
| 37 | 1 | 0 | 0.432126  | -6.749430 | 2.860316  |
| 38 | 6 | 0 | 1.960715  | -5.269745 | 3.220270  |
| 39 | 1 | 0 | 2.682481  | -5.991904 | 3.593789  |
| 40 | 6 | 0 | 2.302661  | -3.921315 | 3.136841  |
| 41 | 1 | 0 | 3.291730  | -3.588651 | 3.438879  |
| 42 | 6 | 0 | 1.381690  | -2.993111 | 2.650584  |
| 43 | 1 | 0 | 1.660118  | -1.947916 | 2.556327  |
| 44 | 6 | 0 | 4.162446  | 0.962258  | 0.208587  |
| 45 | 6 | 0 | 4.062841  | -0.398637 | -0.205064 |
| 46 | 6 | 0 | 5.236009  | -0.997387 | -0.777883 |
| 47 | 6 | 0 | 6.351024  | -0.191095 | -0.979175 |
| 48 | 1 | 0 | 7.225995  | -0.643220 | -1.434216 |
| 49 | 6 | 0 | 6.431603  | 1.173006  | -0.640484 |
| 50 | 6 | 0 | 5.320037  | 1.724626  | -0.021687 |
| 51 | 1 | 0 | 5.329444  | 2.763413  | 0.287988  |
| 52 | 6 | 0 | 3.213547  | 1.221330  | 2.987550  |
| 53 | 6 | 0 | 2.641120  | 1.923703  | 4.058023  |
| 54 | 1 | 0 | 2.042381  | 2.811472  | 3.872581  |
| 55 | 6 | 0 | 2.852781  | 1.505901  | 5.370762  |
| 56 | 1 | 0 | 2.405117  | 2.060775  | 6.191483  |
| 57 | 6 | 0 | 3.643955  | 0.387016  | 5.629753  |
| 58 | 1 | 0 | 3.813978  | 0.065203  | 6.654105  |
| 59 | 6 | 0 | 4.226190  | -0.309136 | 4.571288  |
| 60 | 1 | 0 | 4.857810  | -1.171832 | 4.768136  |
| 61 | 6 | 0 | 4.012113  | 0.102824  | 3.256509  |
| 62 | 1 | 0 | 4.475527  | -0.438444 | 2.436967  |
| 63 | 6 | 0 | 3.086300  | 3.541875  | 1.215588  |
| 64 | 6 | 0 | 2.375688  | 4.255917  | 0.243500  |
| 65 | 1 | 0 | 1.723174  | 3.727675  | -0.445442 |
| 66 | 6 | 0 | 2.520686  | 5.639124  | 0.151022  |
| 67 | 1 | 0 | 1.973115  | 6.183218  | -0.613592 |
| 68 | 6 | 0 | 3.369207  | 6.314475  | 1.027516  |
| 69 | 1 | 0 | 3.480245  | 7.393598  | 0.954243  |
| 70 | 6 | 0 | 4.080660  | 5.606063  | 1.996533  |
| 71 | 1 | 0 | 4.745013  | 6.130024  | 2.679173  |
| 72 | 6 | 0 | 3.942117  | 4.222397  | 2.091508  |
| 73 | 1 | 0 | 4.498906  | 3.675141  | 2.847443  |
| 74 | 6 | 0 | -1.013660 | -4.030348 | -3.384495 |
| 75 | 6 | 0 | -5.088269 | -5.062620 | -0.513485 |
| 76 | 6 | 0 | 7.706813  | 1.967640  | -0.944577 |
| 77 | 6 | 0 | 5.264736  | -2.493247 | -1.137575 |
| 78 | 6 | 0 | -0.782760 | -2.678815 | -4.089068 |
| 79 | 6 | 0 | 0.343089  | -4.706634 | -3.100481 |
| 80 | 6 | 0 | -1.781727 | -4.931236 | -4.364113 |
| 81 | 6 | 0 | -4.883626 | -6.576658 | -0.719863 |
| 82 | 6 | 0 | -5.728127 | -4.854771 | 0.866136  |
| 83 | 6 | 0 | -6.069421 | -4.535647 | -1.579046 |
| 84 | 6 | 0 | 7.595641  | 3.431667  | -0.497316 |
| 85 | 6 | 0 | 8.904081  | 1.332610  | -0.209968 |



## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 86  | 6 | 0 | 7.974945  | 1.952160  | -2.462444 |
| 87  | 6 | 0 | 4.946694  | -3.331044 | 0.117341  |
| 88  | 6 | 0 | 6.642676  | -2.942956 | -1.649558 |
| 89  | 6 | 0 | 4.241671  | -2.809876 | -2.245135 |
| 90  | 1 | 0 | 8.523486  | 3.963775  | -0.738779 |
| 91  | 1 | 0 | 6.774230  | 3.951125  | -1.004336 |
| 92  | 1 | 0 | 7.439034  | 3.517803  | 0.584667  |
| 93  | 1 | 0 | 8.889764  | 2.511450  | -2.697593 |
| 94  | 1 | 0 | 8.101857  | 0.932588  | -2.843031 |
| 95  | 1 | 0 | 7.143338  | 2.410862  | -3.009247 |
| 96  | 1 | 0 | 9.826074  | 1.887708  | -0.426040 |
| 97  | 1 | 0 | 8.746655  | 1.342535  | 0.875052  |
| 98  | 1 | 0 | 9.064909  | 0.292342  | -0.513966 |
| 99  | 1 | 0 | -6.687559 | -5.383236 | 0.912854  |
| 100 | 1 | 0 | -5.096169 | -5.247371 | 1.671571  |
| 101 | 1 | 0 | -5.923244 | -3.795497 | 1.071304  |
| 102 | 1 | 0 | -7.033708 | -5.054905 | -1.506122 |
| 103 | 1 | 0 | -6.250829 | -3.462662 | -1.445844 |
| 104 | 1 | 0 | -5.687545 | -4.686705 | -2.594735 |
| 105 | 1 | 0 | -5.839414 | -7.109944 | -0.636508 |
| 106 | 1 | 0 | -4.463413 | -6.800311 | -1.706471 |
| 107 | 1 | 0 | -4.199141 | -6.983759 | 0.033457  |
| 108 | 1 | 0 | 0.946895  | -4.107438 | -2.416383 |
| 109 | 1 | 0 | 0.902295  | -4.837386 | -4.036129 |
| 110 | 1 | 0 | 0.193015  | -5.697692 | -2.654778 |
| 111 | 1 | 0 | -0.164074 | -2.014226 | -3.482318 |
| 112 | 1 | 0 | -0.270966 | -2.838387 | -5.047253 |
| 113 | 1 | 0 | -1.740972 | -2.185443 | -4.299170 |
| 114 | 1 | 0 | -1.955133 | -5.933842 | -3.955022 |
| 115 | 1 | 0 | -2.749964 | -4.502950 | -4.652070 |
| 116 | 1 | 0 | -1.191187 | -5.049960 | -5.280116 |
| 117 | 1 | 0 | 4.469440  | -2.246889 | -3.157732 |
| 118 | 1 | 0 | 4.274688  | -3.879723 | -2.490335 |
| 119 | 1 | 0 | 3.225823  | -2.561076 | -1.936178 |
| 120 | 1 | 0 | 5.700045  | -3.158024 | 0.897056  |
| 121 | 1 | 0 | 3.961910  | -3.080706 | 0.516144  |
| 122 | 1 | 0 | 4.959324  | -4.400386 | -0.130597 |
| 123 | 1 | 0 | 7.435407  | -2.774531 | -0.910244 |
| 124 | 1 | 0 | 6.924976  | -2.437766 | -2.581214 |
| 125 | 1 | 0 | 6.612197  | -4.018652 | -1.859474 |
| 126 | 8 | 0 | -1.142901 | 0.745881  | -1.467210 |
| 127 | 6 | 0 | -1.676996 | 0.941466  | -2.546914 |
| 128 | 6 | 0 | -0.916013 | 1.303510  | -3.819949 |
| 129 | 8 | 0 | 1.523306  | 0.118937  | -2.674158 |
| 130 | 1 | 0 | -0.314927 | 0.420508  | -4.054787 |
| 131 | 8 | 0 | -0.085285 | 2.411582  | -3.481672 |
| 132 | 6 | 0 | -1.789724 | 1.698079  | -4.997926 |
| 133 | 6 | 0 | 1.936309  | 0.971985  | -3.679509 |
| 134 | 6 | 0 | 1.280885  | 2.339600  | -3.441535 |
| 135 | 1 | 0 | -1.146481 | 1.943086  | -5.848503 |
| 136 | 1 | 0 | -2.452732 | 0.877219  | -5.285294 |
| 137 | 1 | 0 | -2.397898 | 2.573178  | -4.754056 |
| 138 | 1 | 0 | 1.593167  | 0.608343  | -4.671611 |
| 139 | 6 | 0 | 3.450543  | 1.119625  | -3.761724 |
| 140 | 8 | 0 | 1.873345  | 3.356966  | -3.175743 |
| 141 | 1 | 0 | 3.890798  | 0.132876  | -3.932223 |
| 142 | 1 | 0 | 3.739434  | 1.786326  | -4.582349 |
| 143 | 1 | 0 | 3.848493  | 1.524031  | -2.827822 |

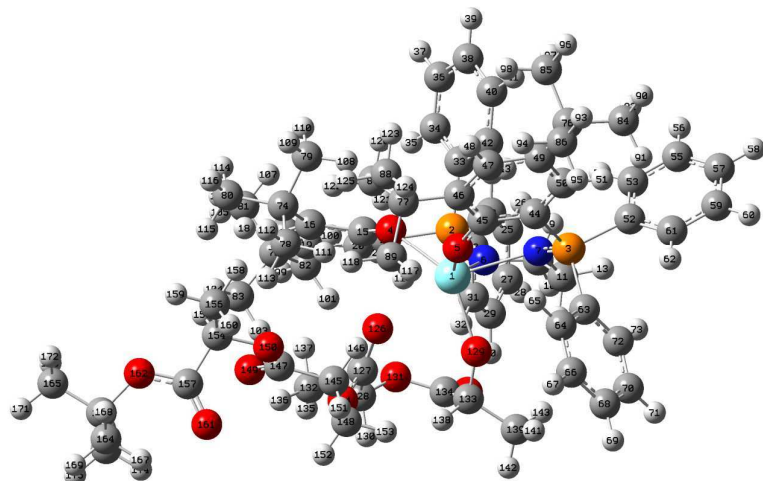
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 144 | 8 | 0 | -2.989670 | 0.835064  | -2.730629 |
| 145 | 6 | 0 | -3.797260 | 0.620628  | -1.563932 |
| 146 | 1 | 0 | -3.296593 | -0.093493 | -0.902989 |
| 147 | 6 | 0 | -3.930292 | 1.962471  | -0.849986 |
| 148 | 6 | 0 | -5.144328 | 0.093078  | -2.032437 |
| 149 | 8 | 0 | -3.535435 | 3.017883  | -1.278745 |
| 150 | 8 | 0 | -4.570819 | 1.808800  | 0.326183  |
| 151 | 1 | 0 | -5.802136 | -0.046548 | -1.171518 |
| 152 | 1 | 0 | -5.618543 | 0.800193  | -2.718695 |
| 153 | 1 | 0 | -5.008011 | -0.866879 | -2.537842 |
| 154 | 6 | 0 | -4.899438 | 3.031534  | 0.994600  |
| 155 | 1 | 0 | -4.020484 | 3.682307  | 1.009207  |
| 156 | 6 | 0 | -5.343734 | 2.679669  | 2.404954  |
| 157 | 6 | 0 | -6.010955 | 3.739678  | 0.210945  |
| 158 | 1 | 0 | -4.536674 | 2.166534  | 2.935678  |
| 159 | 1 | 0 | -5.598185 | 3.593007  | 2.949282  |
| 160 | 1 | 0 | -6.222419 | 2.026836  | 2.380107  |
| 161 | 8 | 0 | -6.668145 | 3.206380  | -0.653444 |
| 162 | 8 | 0 | -6.134132 | 4.987962  | 0.664118  |
| 163 | 6 | 0 | -7.128132 | 5.919822  | 0.102915  |
| 164 | 6 | 0 | -8.536313 | 5.382807  | 0.347305  |
| 165 | 6 | 0 | -6.883333 | 7.193185  | 0.906591  |
| 166 | 6 | 0 | -6.839530 | 6.146547  | -1.378959 |
| 167 | 1 | 0 | -8.713383 | 4.464733  | -0.216273 |
| 168 | 1 | 0 | -8.691039 | 5.183057  | 1.413505  |
| 169 | 1 | 0 | -9.271209 | 6.132520  | 0.033606  |
| 170 | 1 | 0 | -5.857876 | 7.549300  | 0.764830  |
| 171 | 1 | 0 | -7.571665 | 7.979553  | 0.579875  |
| 172 | 1 | 0 | -7.043522 | 7.015705  | 1.975259  |
| 173 | 1 | 0 | -5.801409 | 6.464635  | -1.521689 |
| 174 | 1 | 0 | -7.012141 | 5.239337  | -1.960999 |
| 175 | 1 | 0 | -7.495120 | 6.937743  | -1.759602 |

-----  
Rotational constants (GHZ):      0.0250008      0.0179506  
0.0150027

Sum of electronic and zero-point Energies=      -3706.939641  
Sum of electronic and thermal Energies=      -3706.847652  
Sum of electronic and thermal Enthalpies=      -3706.846708  
Sum of electronic and thermal Free Energies=      -3707.078130

|                | 1      | 2      | 3 |
|----------------|--------|--------|---|
|                | A      | A      | A |
| Frequencies -- | 5.5889 | 9.8541 |   |
| 11.5039        |        |        |   |
| Red. masses -- | 5.1116 | 4.7133 |   |
| 4.3657         |        |        |   |
| Frc consts --  | 0.0001 | 0.0003 |   |
| 0.0003         |        |        |   |
| IR Inten --    | 0.0164 | 0.0693 |   |
| 0.2655         |        |        |   |

*Propagation : INT4'*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | -0.824712               | 0.166482  | 0.524902  |
| 2                | 15               | 0              | -1.845634               | 3.415603  | -0.308544 |
| 3                | 15               | 0              | -3.685556               | -1.910244 | 0.801724  |
| 4                | 8                | 0              | 0.080478                | 1.353874  | -1.149062 |
| 5                | 8                | 0              | -0.878629               | -1.851521 | -0.346697 |
| 6                | 7                | 0              | -2.120415               | 2.123290  | 0.658938  |
| 7                | 7                | 0              | -3.165161               | -0.358986 | 0.714018  |
| 8                | 6                | 0              | -3.477697               | 2.005438  | 1.198811  |
| 9                | 1                | 0              | -4.248246               | 2.220873  | 0.438889  |
| 10               | 1                | 0              | -3.649508               | 2.706079  | 2.030401  |
| 11               | 6                | 0              | -3.691554               | 0.581145  | 1.711845  |
| 12               | 1                | 0              | -3.161985               | 0.467079  | 2.668449  |
| 13               | 1                | 0              | -4.768979               | 0.447078  | 1.907308  |
| 14               | 6                | 0              | -0.103351               | 3.670900  | -0.711336 |
| 15               | 6                | 0              | 0.590878                | 2.557380  | -1.260013 |
| 16               | 6                | 0              | 1.816538                | 2.843268  | -1.952410 |
| 17               | 6                | 0              | 2.316690                | 4.141850  | -1.880074 |
| 18               | 1                | 0              | 3.261230                | 4.344598  | -2.374766 |
| 19               | 6                | 0              | 1.685500                | 5.219852  | -1.231399 |
| 20               | 6                | 0              | 0.435591                | 4.963848  | -0.682993 |
| 21               | 1                | 0              | -0.140259               | 5.761688  | -0.226544 |
| 22               | 6                | 0              | -2.479987               | 4.948415  | 0.496461  |
| 23               | 6                | 0              | -3.415348               | 5.809951  | -0.085235 |
| 24               | 1                | 0              | -3.792518               | 5.614945  | -1.084623 |
| 25               | 6                | 0              | -3.878422               | 6.919581  | 0.622198  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 26 | 1 | 0 | -4.605682 | 7.584903  | 0.163534  |
| 27 | 6 | 0 | -3.414648 | 7.170086  | 1.912223  |
| 28 | 1 | 0 | -3.777355 | 8.035220  | 2.461970  |
| 29 | 6 | 0 | -2.493747 | 6.302967  | 2.501807  |
| 30 | 1 | 0 | -2.139849 | 6.484360  | 3.513286  |
| 31 | 6 | 0 | -2.028327 | 5.191495  | 1.803018  |
| 32 | 1 | 0 | -1.332428 | 4.505160  | 2.280975  |
| 33 | 6 | 0 | -2.684316 | 3.269547  | -1.953403 |
| 34 | 6 | 0 | -2.554709 | 4.266474  | -2.928771 |
| 35 | 1 | 0 | -1.976143 | 5.162876  | -2.718654 |
| 36 | 6 | 0 | -3.140035 | 4.100354  | -4.181994 |
| 37 | 1 | 0 | -3.034743 | 4.877453  | -4.934933 |
| 38 | 6 | 0 | -3.843800 | 2.931104  | -4.474753 |
| 39 | 1 | 0 | -4.293778 | 2.799249  | -5.455664 |
| 40 | 6 | 0 | -3.951584 | 1.925259  | -3.515883 |
| 41 | 1 | 0 | -4.476927 | 1.002519  | -3.749599 |
| 42 | 6 | 0 | -3.371974 | 2.090880  | -2.257429 |
| 43 | 1 | 0 | -3.426733 | 1.296108  | -1.516898 |
| 44 | 6 | 0 | -2.998315 | -2.914865 | -0.540060 |
| 45 | 6 | 0 | -1.628984 | -2.773285 | -0.898006 |
| 46 | 6 | 0 | -1.111753 | -3.705021 | -1.862770 |
| 47 | 6 | 0 | -1.983439 | -4.637667 | -2.414348 |
| 48 | 1 | 0 | -1.583451 | -5.326554 | -3.151151 |
| 49 | 6 | 0 | -3.346945 | -4.756597 | -2.089559 |
| 50 | 6 | 0 | -3.830505 | -3.879592 | -1.130175 |
| 51 | 1 | 0 | -4.869531 | -3.929616 | -0.824058 |
| 52 | 6 | 0 | -5.529356 | -1.966527 | 0.658648  |
| 53 | 6 | 0 | -6.142271 | -0.991038 | -0.136638 |
| 54 | 1 | 0 | -5.526737 | -0.231140 | -0.610669 |
| 55 | 6 | 0 | -7.524912 | -0.990999 | -0.307093 |
| 56 | 1 | 0 | -7.993602 | -0.226891 | -0.922025 |
| 57 | 6 | 0 | -8.304826 | -1.967577 | 0.312730  |
| 58 | 1 | 0 | -9.383804 | -1.967584 | 0.179926  |
| 59 | 6 | 0 | -7.700007 | -2.942207 | 1.105681  |
| 60 | 1 | 0 | -8.304983 | -3.703570 | 1.591416  |
| 61 | 6 | 0 | -6.316524 | -2.941281 | 1.282157  |
| 62 | 1 | 0 | -5.851113 | -3.698229 | 1.907370  |
| 63 | 6 | 0 | -3.332322 | -2.786184 | 2.393570  |
| 64 | 6 | 0 | -2.398476 | -3.826821 | 2.440234  |
| 65 | 1 | 0 | -1.917911 | -4.161574 | 1.525527  |
| 66 | 6 | 0 | -2.089052 | -4.437788 | 3.654764  |
| 67 | 1 | 0 | -1.366587 | -5.249811 | 3.679823  |
| 68 | 6 | 0 | -2.707945 | -4.014648 | 4.830129  |
| 69 | 1 | 0 | -2.468377 | -4.494411 | 5.775885  |
| 70 | 6 | 0 | -3.641064 | -2.978020 | 4.790193  |
| 71 | 1 | 0 | -4.129107 | -2.646422 | 5.703184  |
| 72 | 6 | 0 | -3.951815 | -2.364907 | 3.578500  |
| 73 | 1 | 0 | -4.686482 | -1.564361 | 3.557688  |
| 74 | 6 | 0 | 2.514683  | 1.778309  | -2.812945 |
| 75 | 6 | 0 | 2.354809  | 6.598861  | -1.195441 |
| 76 | 6 | 0 | -4.214682 | -5.815828 | -2.779075 |
| 77 | 6 | 0 | 0.368989  | -3.677627 | -2.268807 |
| 78 | 6 | 0 | 3.026043  | 0.616739  | -1.944925 |
| 79 | 6 | 0 | 1.509648  | 1.252076  | -3.857955 |
| 80 | 6 | 0 | 3.720138  | 2.341578  | -3.582153 |
| 81 | 6 | 0 | 2.578107  | 7.111016  | -2.632029 |
| 82 | 6 | 0 | 1.502123  | 7.633875  | -0.448819 |
| 83 | 6 | 0 | 3.714823  | 6.493528  | -0.477676 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 84  | 6 | 0 | -5.661304 | -5.800114 | -2.267102 |
| 85  | 6 | 0 | -4.241444 | -5.551969 | -4.297436 |
| 86  | 6 | 0 | -3.632091 | -7.218721 | -2.517342 |
| 87  | 6 | 0 | 0.694420  | -2.338762 | -2.954650 |
| 88  | 6 | 0 | 0.733015  | -4.797976 | -3.255800 |
| 89  | 6 | 0 | 1.250880  | -3.868470 | -1.018353 |
| 90  | 1 | 0 | -6.246043 | -6.570542 | -2.783697 |
| 91  | 1 | 0 | -5.714597 | -6.010310 | -1.192248 |
| 92  | 1 | 0 | -6.149324 | -4.835879 | -2.451056 |
| 93  | 1 | 0 | -4.241361 | -7.986745 | -3.011074 |
| 94  | 1 | 0 | -2.608893 | -7.313443 | -2.897330 |
| 95  | 1 | 0 | -3.610558 | -7.438590 | -1.443537 |
| 96  | 1 | 0 | -4.849666 | -6.308472 | -4.810046 |
| 97  | 1 | 0 | -4.668964 | -4.566025 | -4.514108 |
| 98  | 1 | 0 | -3.236486 | -5.581254 | -4.732793 |
| 99  | 1 | 0 | 2.024910  | 8.597502  | -0.424700 |
| 100 | 1 | 0 | 0.535169  | 7.796284  | -0.939637 |
| 101 | 1 | 0 | 1.311917  | 7.332126  | 0.587736  |
| 102 | 1 | 0 | 4.217042  | 7.469447  | -0.456040 |
| 103 | 1 | 0 | 3.583749  | 6.154600  | 0.556559  |
| 104 | 1 | 0 | 4.384165  | 5.785294  | -0.978653 |
| 105 | 1 | 0 | 3.062793  | 8.095976  | -2.619518 |
| 106 | 1 | 0 | 3.215592  | 6.434735  | -3.211976 |
| 107 | 1 | 0 | 1.624196  | 7.207218  | -3.163837 |
| 108 | 1 | 0 | 0.626286  | 0.829841  | -3.374932 |
| 109 | 1 | 0 | 1.977505  | 0.473490  | -4.474291 |
| 110 | 1 | 0 | 1.187143  | 2.062702  | -4.523036 |
| 111 | 1 | 0 | 2.211922  | 0.152759  | -1.388427 |
| 112 | 1 | 0 | 3.493684  | -0.147723 | -2.580455 |
| 113 | 1 | 0 | 3.781041  | 0.966116  | -1.230774 |
| 114 | 1 | 0 | 3.438430  | 3.168629  | -4.245078 |
| 115 | 1 | 0 | 4.516810  | 2.689601  | -2.913073 |
| 116 | 1 | 0 | 4.145436  | 1.548594  | -4.209243 |
| 117 | 1 | 0 | 1.075563  | -4.855017 | -0.570266 |
| 118 | 1 | 0 | 2.313223  | -3.804953 | -1.287390 |
| 119 | 1 | 0 | 1.029203  | -3.104036 | -0.270814 |
| 120 | 1 | 0 | 0.101064  | -2.222627 | -3.869763 |
| 121 | 1 | 0 | 0.483313  | -1.490959 | -2.301979 |
| 122 | 1 | 0 | 1.755249  | -2.302418 | -3.234059 |
| 123 | 1 | 0 | 0.191332  | -4.707204 | -4.204989 |
| 124 | 1 | 0 | 0.542242  | -5.795685 | -2.841701 |
| 125 | 1 | 0 | 1.803544  | -4.736919 | -3.485844 |
| 126 | 8 | 0 | 1.642231  | -0.048223 | 1.055566  |
| 127 | 6 | 0 | 2.394704  | 0.211728  | 1.974786  |
| 128 | 6 | 0 | 2.460869  | 1.532186  | 2.732003  |
| 129 | 8 | 0 | -0.651072 | -0.011952 | 2.635453  |
| 130 | 1 | 0 | 2.742964  | 1.308402  | 3.767397  |
| 131 | 8 | 0 | 1.249671  | 2.268484  | 2.693977  |
| 132 | 6 | 0 | 3.532351  | 2.412088  | 2.089770  |
| 133 | 6 | 0 | -0.069534 | 0.465238  | 3.789905  |
| 134 | 6 | 0 | 0.201296  | 1.955243  | 3.532866  |
| 135 | 1 | 0 | 3.644093  | 3.325050  | 2.681124  |
| 136 | 1 | 0 | 4.487509  | 1.881552  | 2.048416  |
| 137 | 1 | 0 | 3.228094  | 2.686985  | 1.075792  |
| 138 | 1 | 0 | 0.892964  | -0.049125 | 3.993723  |
| 139 | 6 | 0 | -0.949479 | 0.279722  | 5.021057  |
| 140 | 8 | 0 | -0.527023 | 2.855474  | 3.870372  |
| 141 | 1 | 0 | -1.201981 | -0.780400 | 5.117154  |

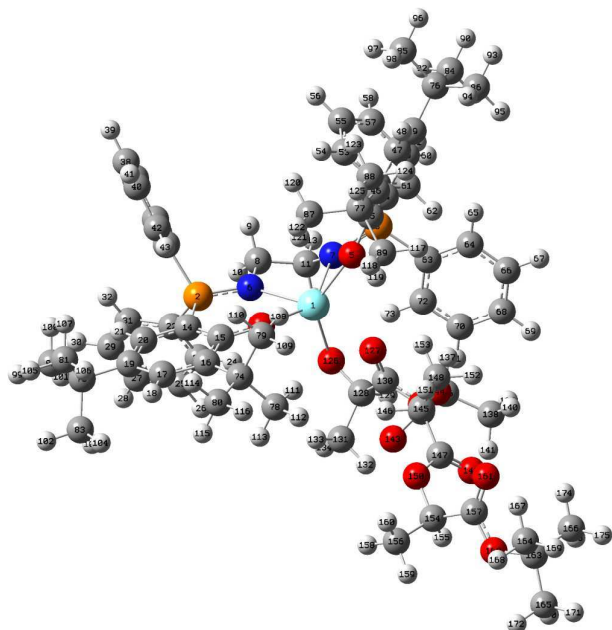
## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 142 | 1 | 0 | -0.437731 | 0.610378  | 5.933576  |
| 143 | 1 | 0 | -1.871400 | 0.857404  | 4.913590  |
| 144 | 8 | 0 | 3.335434  | -0.615693 | 2.433361  |
| 145 | 6 | 0 | 3.588738  | -1.836676 | 1.724612  |
| 146 | 1 | 0 | 2.720439  | -2.081319 | 1.106117  |
| 147 | 6 | 0 | 4.786274  | -1.587373 | 0.813751  |
| 148 | 6 | 0 | 3.855256  | -2.929663 | 2.748744  |
| 149 | 8 | 0 | 5.389175  | -0.545598 | 0.723008  |
| 150 | 8 | 0 | 5.070224  | -2.700431 | 0.115347  |
| 151 | 1 | 0 | 4.059333  | -3.872022 | 2.235381  |
| 152 | 1 | 0 | 4.720083  | -2.677500 | 3.368966  |
| 153 | 1 | 0 | 2.977073  | -3.054889 | 3.388772  |
| 154 | 6 | 0 | 6.246614  | -2.637436 | -0.695677 |
| 155 | 1 | 0 | 6.246625  | -1.699726 | -1.259248 |
| 156 | 6 | 0 | 6.217986  | -3.838913 | -1.627585 |
| 157 | 6 | 0 | 7.478278  | -2.650328 | 0.216831  |
| 158 | 1 | 0 | 5.321976  | -3.804394 | -2.253933 |
| 159 | 1 | 0 | 7.100369  | -3.827720 | -2.272713 |
| 160 | 1 | 0 | 6.207768  | -4.771471 | -1.054572 |
| 161 | 8 | 0 | 7.440148  | -2.909950 | 1.397627  |
| 162 | 8 | 0 | 8.559060  | -2.360487 | -0.510412 |
| 163 | 6 | 0 | 9.902285  | -2.301288 | 0.090904  |
| 164 | 6 | 0 | 10.281793 | -3.671350 | 0.648073  |
| 165 | 6 | 0 | 10.784324 | -1.933660 | -1.098189 |
| 166 | 6 | 0 | 9.940277  | -1.208326 | 1.156388  |
| 167 | 1 | 0 | 9.650036  | -3.944294 | 1.495587  |
| 168 | 1 | 0 | 10.189302 | -4.439502 | -0.127733 |
| 169 | 1 | 0 | 11.325243 | -3.652097 | 0.982031  |
| 170 | 1 | 0 | 10.477163 | -0.973625 | -1.525359 |
| 171 | 1 | 0 | 11.828606 | -1.853245 | -0.778949 |
| 172 | 1 | 0 | 10.719542 | -2.697205 | -1.880413 |
| 173 | 1 | 0 | 9.603008  | -0.254482 | 0.737020  |
| 174 | 1 | 0 | 9.306976  | -1.461989 | 2.008551  |
| 175 | 1 | 0 | 10.969702 | -1.080886 | 1.509703  |

-----  
Rotational constants (GHZ): 0.0230639 0.0178658  
0.0133744

Sum of electronic and zero-point Energies= -3706.934935  
Sum of electronic and thermal Energies= -3706.843165  
Sum of electronic and thermal Enthalpies= -3706.842221  
Sum of electronic and thermal Free Energies= -3707.072135

|                | 1      | 2      | 3 |
|----------------|--------|--------|---|
|                | A      | A      | A |
| Frequencies -- | 7.4230 | 9.2722 |   |
| 11.3924        |        |        |   |
| Red. masses -- | 5.2518 | 4.9772 |   |
| 4.4953         |        |        |   |
| Frc consts --  | 0.0002 | 0.0003 |   |
| 0.0003         |        |        |   |
| IR Inten --    | 0.2275 | 0.2148 |   |
| 0.0037         |        |        |   |

*Propagation : P'*

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 39               | 0              | 1.294758                | 0.046618  | -0.612627 |
| 2                | 15               | 0              | 3.783836                | 2.683492  | -0.305088 |
| 3                | 15               | 0              | 2.850383                | -3.106288 | -0.932561 |
| 4                | 8                | 0              | 0.826505                | 1.897140  | 0.434719  |
| 5                | 8                | 0              | 0.948813                | -1.577088 | 0.837541  |
| 6                | 7                | 0              | 3.385866                | 1.170495  | -0.793640 |
| 7                | 7                | 0              | 3.001882                | -1.499346 | -1.134590 |
| 8                | 6                | 0              | 4.519513                | 0.371159  | -1.277195 |
| 9                | 1                | 0              | 5.159592                | 0.045535  | -0.440543 |
| 10               | 1                | 0              | 5.161086                | 0.927029  | -1.983326 |
| 11               | 6                | 0              | 3.995219                | -0.872429 | -1.993573 |
| 12               | 1                | 0              | 3.545852                | -0.560170 | -2.950285 |
| 13               | 1                | 0              | 4.847993                | -1.527214 | -2.228437 |
| 14               | 6                | 0              | 2.406171                | 3.675034  | 0.334227  |
| 15               | 6                | 0              | 1.116911                | 3.154700  | 0.627378  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 16 | 6 | 0 | 0.144871  | 4.081628  | 1.149565  |
| 17 | 6 | 0 | 0.526848  | 5.402364  | 1.343136  |
| 18 | 1 | 0 | -0.214025 | 6.091427  | 1.734595  |
| 19 | 6 | 0 | 1.806108  | 5.920903  | 1.062265  |
| 20 | 6 | 0 | 2.729901  | 5.027281  | 0.550157  |
| 21 | 1 | 0 | 3.728925  | 5.371929  | 0.302808  |
| 22 | 6 | 0 | 4.507110  | 3.630838  | -1.725276 |
| 23 | 6 | 0 | 3.948782  | 3.374652  | -2.984380 |
| 24 | 1 | 0 | 3.169618  | 2.621182  | -3.079453 |
| 25 | 6 | 0 | 4.393626  | 4.078408  | -4.101415 |
| 26 | 1 | 0 | 3.955651  | 3.875122  | -5.075380 |
| 27 | 6 | 0 | 5.397190  | 5.039120  | -3.970970 |
| 28 | 1 | 0 | 5.743170  | 5.587022  | -4.843944 |
| 29 | 6 | 0 | 5.958179  | 5.294357  | -2.720522 |
| 30 | 1 | 0 | 6.742678  | 6.039596  | -2.615248 |
| 31 | 6 | 0 | 5.516284  | 4.591589  | -1.599475 |
| 32 | 1 | 0 | 5.964217  | 4.790788  | -0.629475 |
| 33 | 6 | 0 | 5.093087  | 2.678520  | 1.003762  |
| 34 | 6 | 0 | 6.427434  | 2.385590  | 0.689462  |
| 35 | 1 | 0 | 6.730613  | 2.267052  | -0.347482 |
| 36 | 6 | 0 | 7.377033  | 2.258636  | 1.702350  |
| 37 | 1 | 0 | 8.410232  | 2.035732  | 1.447915  |
| 38 | 6 | 0 | 7.002127  | 2.418519  | 3.035862  |
| 39 | 1 | 0 | 7.743459  | 2.320622  | 3.824982  |
| 40 | 6 | 0 | 5.675429  | 2.706705  | 3.355341  |
| 41 | 1 | 0 | 5.379035  | 2.834416  | 4.393294  |
| 42 | 6 | 0 | 4.723928  | 2.835204  | 2.345367  |
| 43 | 1 | 0 | 3.691534  | 3.063436  | 2.595905  |
| 44 | 6 | 0 | 2.285193  | -3.537708 | 0.734222  |
| 45 | 6 | 0 | 1.386931  | -2.665585 | 1.409420  |
| 46 | 6 | 0 | 0.985781  | -3.048037 | 2.736272  |
| 47 | 6 | 0 | 1.467860  | -4.246151 | 3.250885  |
| 48 | 1 | 0 | 1.154171  | -4.527781 | 4.250869  |
| 49 | 6 | 0 | 2.338837  | -5.123085 | 2.576223  |
| 50 | 6 | 0 | 2.741953  | -4.736683 | 1.306370  |
| 51 | 1 | 0 | 3.430530  | -5.357707 | 0.742329  |
| 52 | 6 | 0 | 4.462433  | -3.964750 | -1.191504 |
| 53 | 6 | 0 | 5.515591  | -3.645344 | -0.321972 |
| 54 | 1 | 0 | 5.345332  | -2.953434 | 0.498984  |
| 55 | 6 | 0 | 6.771883  | -4.216238 | -0.505517 |
| 56 | 1 | 0 | 7.582499  | -3.966533 | 0.174262  |
| 57 | 6 | 0 | 6.988329  | -5.107859 | -1.558027 |
| 58 | 1 | 0 | 7.969571  | -5.553886 | -1.699479 |
| 59 | 6 | 0 | 5.946231  | -5.425075 | -2.426421 |
| 60 | 1 | 0 | 6.110961  | -6.117910 | -3.247604 |
| 61 | 6 | 0 | 4.685492  | -4.854162 | -2.246342 |
| 62 | 1 | 0 | 3.877080  | -5.105489 | -2.926689 |
| 63 | 6 | 0 | 1.688088  | -3.882798 | -2.146575 |
| 64 | 6 | 0 | 1.115760  | -5.140493 | -1.920919 |
| 65 | 1 | 0 | 1.327893  | -5.676161 | -0.999116 |
| 66 | 6 | 0 | 0.259757  | -5.697726 | -2.868946 |
| 67 | 1 | 0 | -0.184729 | -6.673325 | -2.688312 |
| 68 | 6 | 0 | -0.030273 | -5.002313 | -4.044189 |
| 69 | 1 | 0 | -0.697313 | -5.439215 | -4.783335 |
| 70 | 6 | 0 | 0.528104  | -3.743821 | -4.265712 |
| 71 | 1 | 0 | 0.294569  | -3.195582 | -5.174903 |
| 72 | 6 | 0 | 1.382526  | -3.180139 | -3.317072 |
| 73 | 1 | 0 | 1.789390  | -2.183111 | -3.466665 |

## Appendix 2. Optimised Structures

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 74  | 6 | 0 | -1.288764 | 3.626106  | 1.466421  |
| 75  | 6 | 0 | 2.108667  | 7.402889  | 1.309404  |
| 76  | 6 | 0 | 2.809929  | -6.414584 | 3.255002  |
| 77  | 6 | 0 | 0.053866  | -2.149866 | 3.563834  |
| 78  | 6 | 0 | -1.969191 | 3.124761  | 0.178320  |
| 79  | 6 | 0 | -1.272079 | 2.508351  | 2.526806  |
| 80  | 6 | 0 | -2.155974 | 4.766601  | 2.023742  |
| 81  | 6 | 0 | 1.868831  | 7.742892  | 2.793678  |
| 82  | 6 | 0 | 3.561786  | 7.760995  | 0.969457  |
| 83  | 6 | 0 | 1.183838  | 8.270975  | 0.433348  |
| 84  | 6 | 0 | 3.745375  | -7.233334 | 2.354854  |
| 85  | 6 | 0 | 3.574534  | -6.070084 | 4.548752  |
| 86  | 6 | 0 | 1.593089  | -7.293796 | 3.604186  |
| 87  | 6 | 0 | 0.728646  | -0.783310 | 3.797137  |
| 88  | 6 | 0 | -0.258900 | -2.743776 | 4.946352  |
| 89  | 6 | 0 | -1.289825 | -1.962444 | 2.830641  |
| 90  | 1 | 0 | 4.059307  | -8.144934 | 2.877069  |
| 91  | 1 | 0 | 3.250750  | -7.539617 | 1.425184  |
| 92  | 1 | 0 | 4.651082  | -6.674403 | 2.091565  |
| 93  | 1 | 0 | 1.915137  | -8.219585 | 4.098476  |
| 94  | 1 | 0 | 0.900299  | -6.780298 | 4.279720  |
| 95  | 1 | 0 | 1.035905  | -7.565876 | 2.700039  |
| 96  | 1 | 0 | 3.914876  | -6.984507 | 5.051802  |
| 97  | 1 | 0 | 4.454152  | -5.453609 | 4.329403  |
| 98  | 1 | 0 | 2.947654  | -5.515197 | 5.255271  |
| 99  | 1 | 0 | 3.736365  | 8.825717  | 1.164483  |
| 100 | 1 | 0 | 4.273445  | 7.191901  | 1.579851  |
| 101 | 1 | 0 | 3.790421  | 7.577327  | -0.087020 |
| 102 | 1 | 0 | 1.377103  | 9.337524  | 0.607212  |
| 103 | 1 | 0 | 1.346867  | 8.062580  | -0.630411 |
| 104 | 1 | 0 | 0.126465  | 8.084291  | 0.650767  |
| 105 | 1 | 0 | 2.071393  | 8.804999  | 2.982475  |
| 106 | 1 | 0 | 0.834918  | 7.543963  | 3.096358  |
| 107 | 1 | 0 | 2.525385  | 7.150210  | 3.441466  |
| 108 | 1 | 0 | -0.701802 | 1.644555  | 2.183657  |
| 109 | 1 | 0 | -2.297923 | 2.183699  | 2.746234  |
| 110 | 1 | 0 | -0.826694 | 2.869336  | 3.462445  |
| 111 | 1 | 0 | -1.427982 | 2.283097  | -0.255374 |
| 112 | 1 | 0 | -2.994610 | 2.796899  | 0.388201  |
| 113 | 1 | 0 | -2.020025 | 3.926937  | -0.568331 |
| 114 | 1 | 0 | -1.758745 | 5.170936  | 2.962992  |
| 115 | 1 | 0 | -2.267039 | 5.591986  | 1.309981  |
| 116 | 1 | 0 | -3.160370 | 4.379742  | 2.232909  |
| 117 | 1 | 0 | -1.800914 | -2.926965 | 2.716655  |
| 118 | 1 | 0 | -1.944516 | -1.300056 | 3.412541  |
| 119 | 1 | 0 | -1.145276 | -1.528576 | 1.839857  |
| 120 | 1 | 0 | 1.663342  | -0.907191 | 4.358352  |
| 121 | 1 | 0 | 0.957398  | -0.285332 | 2.853250  |
| 122 | 1 | 0 | 0.067736  | -0.128775 | 4.379659  |
| 123 | 1 | 0 | 0.643076  | -2.869619 | 5.557751  |
| 124 | 1 | 0 | -0.767292 | -3.713207 | 4.876021  |
| 125 | 1 | 0 | -0.926778 | -2.061764 | 5.486010  |
| 126 | 8 | 0 | 0.779603  | 0.317580  | -2.686435 |
| 127 | 8 | 0 | -1.111670 | -0.558843 | -1.070465 |
| 128 | 6 | 0 | -0.430404 | 0.106008  | -3.287311 |
| 129 | 1 | 0 | -0.368366 | -0.634432 | -4.110583 |
| 130 | 6 | 0 | -1.386358 | -0.501421 | -2.265516 |
| 131 | 6 | 0 | -1.046870 | 1.388523  | -3.872692 |

## Appendix 2. Optimised Structures

|  |   |   |            |              |           |
|--|---|---|------------|--------------|-----------|
| 132  | 1 | 0 | -2.009106  | 1.195961     | -4.359390 |
| 133  | 1 | 0 | -1.188908  | 2.133260     | -3.082851 |
| 134  | 1 | 0 | -0.348458  | 1.799091     | -4.608710 |
| 135  | 8 | 0 | -2.515530  | -0.997292    | -2.769291 |
| 136  | 6 | 0 | -3.427117  | -1.612080    | -1.849272 |
| 137  | 1 | 0 | -2.865306  | -2.232888    | -1.145386 |
| 138  | 6 | 0 | -4.399150  | -2.447747    | -2.669539 |
| 139  | 1 | 0 | -3.853169  | -3.227129    | -3.209059 |
| 140  | 1 | 0 | -5.134514  | -2.913928    | -2.009093 |
| 141  | 1 | 0 | -4.929055  | -1.818452    | -3.390370 |
| 142  | 6 | 0 | -4.165606  | -0.534036    | -1.066705 |
| 143  | 8 | 0 | -4.241067  | 0.630325     | -1.372422 |
| 144  | 8 | 0 | -4.762776  | -1.088881    | 0.004523  |
| 145  | 6 | 0 | -5.618237  | -0.223378    | 0.753755  |
| 146  | 1 | 0 | -5.096664  | 0.716218     | 0.957945  |
| 147  | 6 | 0 | -6.863754  | 0.082179     | -0.070081 |
| 148  | 6 | 0 | -5.979360  | -0.945511    | 2.043271  |
| 149  | 8 | 0 | -7.246413  | -0.553475    | -1.022277 |
| 150  | 8 | 0 | -7.495163  | 1.154478     | 0.442317  |
| 151  | 1 | 0 | -6.657445  | -0.327438    | 2.637080  |
| 152  | 1 | 0 | -6.477630  | -1.893842    | 1.822286  |
| 153  | 1 | 0 | -5.072257  | -1.145613    | 2.620537  |
| 154  | 6 | 0 | -8.755233  | 1.472824     | -0.148986 |
| 155  | 1 | 0 | -8.669696  | 1.408955     | -1.237948 |
| 156  | 6 | 0 | -9.116841  | 2.883534     | 0.290784  |
| 157  | 6 | 0 | -9.795254  | 0.445730     | 0.309891  |
| 158  | 1 | 0 | -8.345896  | 3.584723     | -0.041512 |
| 159  | 1 | 0 | -10.074457 | 3.175365     | -0.148184 |
| 160  | 1 | 0 | -9.192914  | 2.940113     | 1.381332  |
| 161  | 8 | 0 | -9.612013  | -0.350055    | 1.202133  |
| 162  | 8 | 0 | -10.908447 | 0.603926     | -0.411420 |
| 163  | 6 | 0 | -12.098536 | -0.232642    | -0.188791 |
| 164  | 6 | 0 | -12.628058 | -0.015823    | 1.227051  |
| 165  | 6 | 0 | -13.082242 | 0.301673     | -1.225417 |
| 166  | 6 | 0 | -11.759424 | -1.695862    | -0.464433 |
| 167  | 1 | 0 | -11.922414 | -0.384673    | 1.973966  |
| 168  | 1 | 0 | -12.815001 | 1.048548     | 1.407988  |
| 169  | 1 | 0 | -13.576646 | -0.550966    | 1.347375  |
| 170  | 1 | 0 | -12.680223 | 0.184601     | -2.237025 |
| 171  | 1 | 0 | -14.027521 | -0.247359    | -1.161902 |
| 172  | 1 | 0 | -13.286730 | 1.363954     | -1.055436 |
| 173  | 1 | 0 | -11.323728 | -1.805115    | -1.463310 |
| 174  | 1 | 0 | -11.054001 | -2.085233    | 0.271977  |
| 175  | 1 | 0 | -12.676091 | -2.294935    | -0.424312 |
| -----  |   |   |            |              |           |
| Rotational constants (GHZ):                  |   |   | 0.0227976  | 0.0136529    |           |
| 0.0106176                                    |   |   |            |              |           |
| Sum of electronic and zero-point Energies=   |   |   |            |              |           |
|  |   |   |            | -3706.959836 |           |
| Sum of electronic and thermal Energies=      |   |   |            | -3706.867698 |           |
| Sum of electronic and thermal Enthalpies=    |   |   |            | -3706.866754 |           |
| Sum of electronic and thermal Free Energies= |   |   |            | -3707.101318 |           |
|  |   |   |            |              |           |
|  |   |   | 1          | 2            | 3         |
|  |   |   | A          | A            | A         |
| Frequencies --                               |   |   | 3.7920     | 6.2181       |           |
| 9.0497                                       |   |   |            |              |           |

## Appendix 2. Optimised Structures

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|                |        |        |
|----------------|--------|--------|
| Red. masses -- | 4.9559 | 5.0555 |
| 4.6139         |        |        |
| Frc consts --  | 0.0000 | 0.0001 |
| 0.0002         |        |        |
| IR Inten --    | 0.1983 | 0.2288 |
| 0.1065         |        |        |