Studies into the synthesis of primary phosphines for the preparation of macrocycles by template methods.

by

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To the dreamers…

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To all of you, thank you very much

ABSTRACT

This thesis is focused in the synthesis of phosphine-based macrocycles by template methods. Furthermore, it explores some alternative methods for the synthesis of known and unknown polydentate primary phosphine compounds necessary for the preparation of new macrocycles.

Following this new procedure the novel tripodal primary phosphine *cis, cis*-1,3,5-triphosphinomethylcyclohexane (**2.15**) has been prepared in good yields as well as the reported bis(2-phosphinoethyl)amine (**PNP, 3.4**). Mono-alkylation of **3.4** allowed the preparation of the asymmetric 2-(allylphosphino)-N-(2-phosphinoethyl)ethanamine ligand (**3.16**) in low yields. Whilst ligands **2.15** and **3.16** failed to form well-defined facially coordinated molybdenum(0) and chromium(0) complexes respectively, **3.4** formed octahedral complexes with Cr(0) and Fe(II) metals, [{*fac*-$Cr(CO)_3$(PNP)}, **3.8**] and [[{η^5-$C_5H_4(SiMe_3)$}Fe(PNP)]PF_6, **3.10**]. Different attempts have been made to cyclise the facially coordinated chromium complex **3.8**, however all of them have failed. The synthesis of **3.8** and **3.10** has been confirmed by X-ray diffraction.

The synthesis of a new Mn(I) 9-membered tribenzanulated triphosphamacrocycle complex $[Mn(CO)_3\{(C_6H_4F)PC_6H_4PHC_6H_4PHC_6H_4\}]OTf$, **4.10** has been successfully synthesised by sequential introduction of 1,2-diphosphinobenzene and tris(2-fluorophenyl)phosphine on a manganese(I) complex and subsequent addition of *t*-BuOK. Alkylation of the two secondary phosphorus of **4.10** with MeI allowed the isolation of the more stable manganese complex $[Mn(CO)_3\{(C_6H_4F)PC_6H_4P(CH_3)C_6H_4P(CH_3)C_6H_4\}]OTf/I$ **4.12**. The liberation of the phosphine trioxide macrocycle, $\{(C_6H_4F)P(O)C_6H_4P(O)(CH_3)C_6H_4P(O)(CH_3)C_6H_4\}$ **4.14** from the metal has been achieved using 4-methylmorpholine N-oxide in excess. In addition, the X-ray crystal structures of the non cyclised precursor intermediate $[Mn(CO)_3\{(C_6H_4F)_3P\}\{C_6H_4(PH_2)_2\text{-}o\}]OTf$ **4.9** and the half cyclised intermediate $[Mn(CO)_3\{(C_6H_4F)_2PC_6H_4PHC_6H_4PH_2\}]OTf$ **4.11** as well as the final macrocycle **4.12** have also been established.

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Chapter 1:
INTRODUCTION

1.1. Phosphine ligands

The number of known transition metal complexes containing phosphine ligands is enormous.[1] Numerous examples with mono-, bi-dentate or polydentate chelating phosphine ligands are known and the diversity of the phosphorus substituents further increases the variety of these ligands and of their complexes.[1]

The representative examples displayed in Figure 1-1 exhibit different steric and electronic properties. For example PH_3 (**1.1**) is the smallest known phosphine whilst P(*t*-Bu)$_3$ (**1.4**) is one of the biggest as defined by Tolman's cone angle.[2] Due to the electron-withdrawing effects of the fluorine atoms, PF_3 (**1.2**) rivals CO as a π-acceptor ligand.[1] Water-soluble phosphines such as **1.6** have also been synthesised and used successfully in biphasic systems.[3] Numerous bidentate phosphines are also known (**1.5**) and important chiral bidentate ligands such as CHIRAPHOS or BINAP have been developed for asymmetric catalysis.

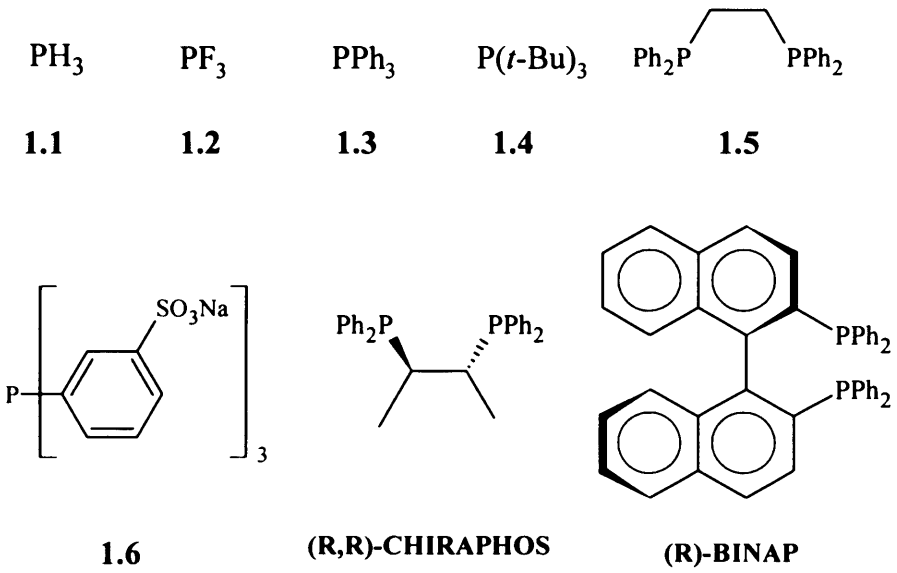


Figure 1-1

1.1.1. What is so special about phosphines?

Phosphines as well as other ligands containing group 15 donor atoms (oxidation state 3) have a lone pair of electrons and a pyramidal structure. By virtue of the lone pair on the phosphorus atom, phosphines can act as an electron pair donor (Lewis base) and coordinate to a metal center through a σ-bond (Figure 1-2).

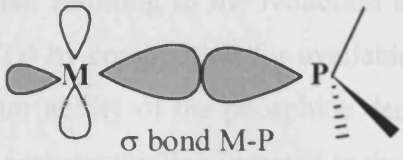


Figure 1-2

Unlike amines, phosphines have empty orbitals of π-symmetry with respect to the metal-ligand bond (Figure 1.3).[4] Consequently, phosphines can also be π-acceptor ligands.

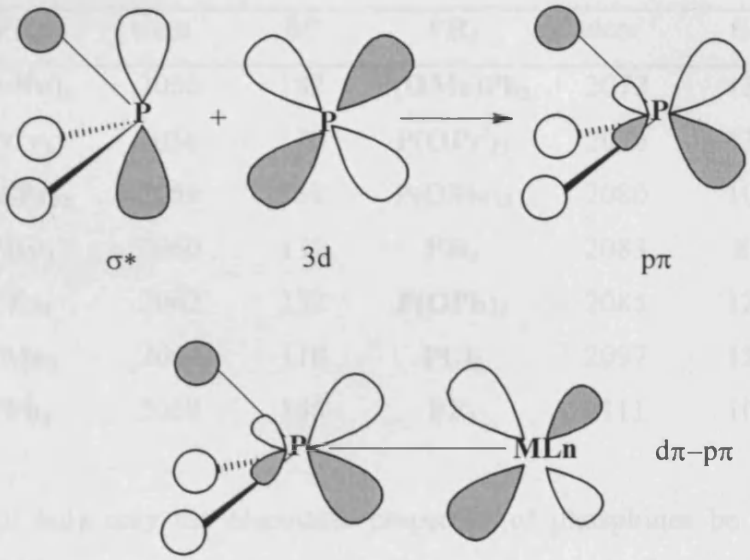


Figure 1-3

It is now commonly accepted that the M-P bonding acceptor orbital is a combination of a 3d orbital of the phosphorus (Figure 1-3) with a vacant σ^* (antibonding) orbital of the P-R bond (Figure 1-3).[5] Thus, the degree of the donor/acceptor capability of

the phosphine ligand is influenced by the nature of the R substituents on the phosphorus atoms. Consequently, alkyl phosphines are less π-acidic than aryl phosphines or phosphites with more electronegative substituents.[1, 4, 6]

The electronic properties of phosphine ligands were quantified by Tolman by comparing the carbonyl stretching bands in the IR spectra of a series of tricarbonyl phosphine nickel complexes, $LNi(CO)_3$.[2] π-Acidic phosphine ligands accept back-donation from the nickel metal, resulting in the reduction of the back-donation from the metal to the CO ligand (M-CO) by competition for available π-electron density on the Ni atom. Increasing the π-acceptor ability of the phosphine decreases back-bonding from Ni to π* on the CO ligands with a corresponding increase in the strength of the C-O bond and ν_{co}. The reverse is observed for pure σ-donor phosphine ligands (Table 1-1). The net effect of the substituents resulted in the determination of an electronic parameter, which allows the prediction of π-acceptor properties in tertiary phosphines.

Table 1-1: Electronic and steric parameters of phosphine ligands in $Ni(CO)_3(PR_3)$[4]

PR_3	ν/cm^{-1}	θ/°	PR_3	ν/cm^{-1}	θ/°
P(*t*-Bu)$_3$	2056	182	**P(OMe)Ph$_2$**	2072	132
PCy$_3$	2056	170	**P(OPr^i)$_3$**	2076	130
P(*i*-Pr)$_3$	2059	160	**P(OMe)$_3$**	2080	107
PBu$_3$	2060	132	**PH$_3$**	2083	87
PEt$_3$	2062	132	**P(OPh)$_3$**	2085	128
PMe$_3$	2064	118	**PCl$_3$**	2097	124
PPh$_3$	2069	145	**PF$_3$**	2111	104

Thus, not only may the electronic properties of phosphines be "fine tuned" by changing the substituents, but also the steric effects of the ligand. Tolman defined the **cone angle** to quantify the steric properties of phosphine and other ligands.[2] The cone angle, θ, is defined as the angle of the virtual cone defined by the van der Waals surface generated by a phosphine ligand bound to a metal (Table 1-1, Figure 1-4).

The understanding of the electronic and steric parameters of phosphine ligands has become a useful tool. Both factors affect the reactivity of the complexes formed with the

phosphine ligand. The quantification of these parameters has allowed alteration of the phosphine substituents in a systematic and predictable manner for the optimisation of catalytic reactions.

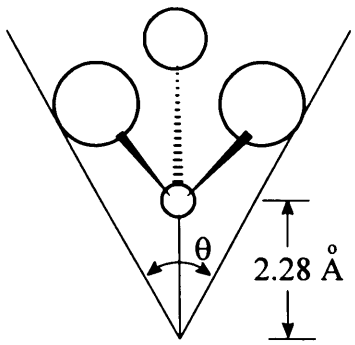


Figure 1-4: Definition of cone angle, θ

Finally, phosphine ligands, unlike amines, have large energetic barriers to pyramidal inversion (120-150 kJ/mol).[7] The resolved chiral phosphines retain their configuration at phosphorus atoms, and consequently the complexes formed exhibit selectivity towards one specific enantiomer in asymmetric catalysis.

1.2. Polydentate phosphines

A growing attention has been given to polydentate phosphine ligands since the advantages of polyphosphines over comparable monodentate phosphines became apparent.[8-10] The **chelate effect** is one of these observed advantages, where a complex formed with a polydentate ligand is kinetically more inert and thermodynamically more stable than the complex formed with analogous monodentate ligands. This effect is entropically favoured. It is more pronounced with five or six membered rings; with very large and flexible chains the effect becomes insignificant. The stabilisation properties arising from the chelate effect can be illustrated by the formation constants (or the logarithmic form) of the two pairs of equations shown in Scheme 1-1.

$Ni^{+2}(aq) + 6\ NH_3(aq) = [Ni(NH_3)_6]^{+2}(aq)$ $\log \beta = 8.61$

$Ni^{+2}(aq) + 3\ en(aq) = [Ni\ en_3]^{+2}(aq)$ $\log \beta = 18.28$

$Cd^{+2}(aq) + 4\ CH_3NH_2(aq) = [Cd(CH_3NH_2)_4]^{+2}(aq)$ $\log \beta = 6.52$

$Cd^{+2}(aq) + 2\ en(aq) = [Cd\ en_2]^{+2}(aq)$ $\log \beta = 10.6$

Scheme 1-1: Reaction illustrating the chelate effect[11]

However, complexes with polydentate ligands are also formed under restricted control of the co-ordination number, stoichiometry and stereochemistry; although they display a variety of metal oxidation states. The metal centres are affected by an increased nucleophilicity, which can be monitored together with other detailed structural and bonding information from $^{31}P\{^1H\}$ NMR spectroscopy. All these advantages have promoted the development of polydentate phosphines with several arrangements and donor atoms.[8-10] Examples of possible arrangements of tridentate phosphine ligands are depicted in Figure 1-5.

Most of the studies of polydentate phosphines have been concerned with bidentate, tridentate and tetradentate, although hexadentate and pentadentate phosphines are also known.[8]

Tridentate phosphines

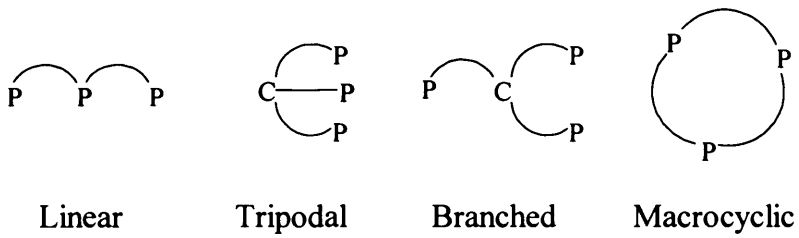


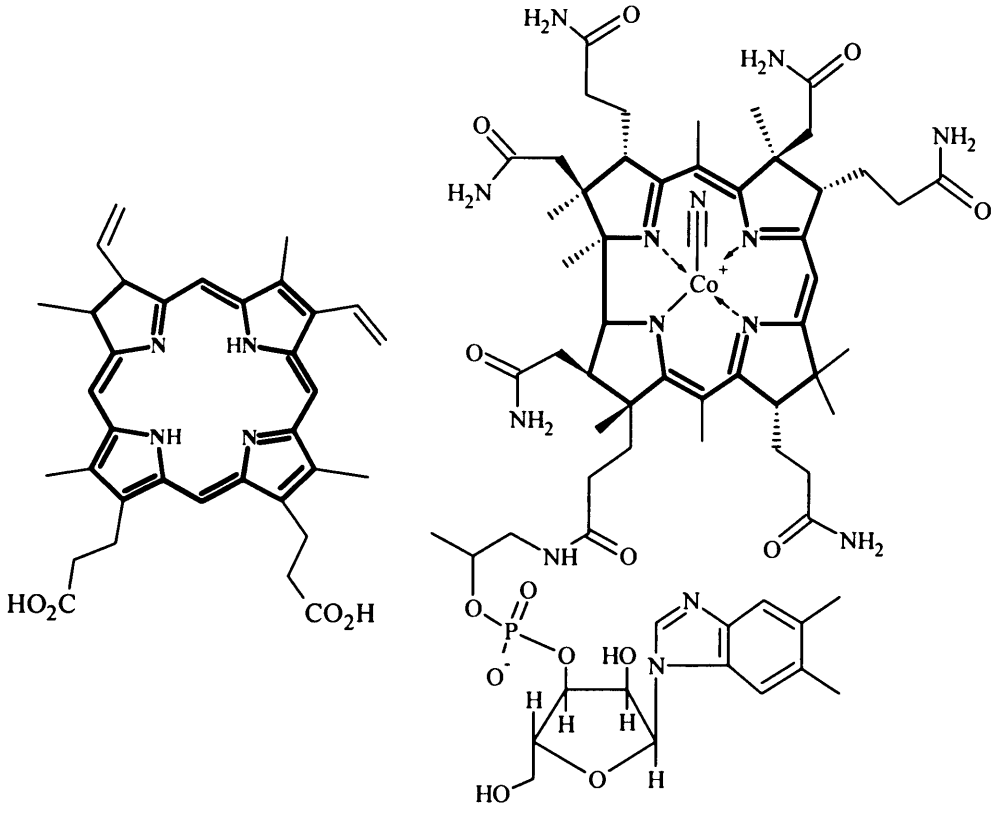
Figure 1-5

Our interest will focus on tridentate macrocyclic phosphines although tetradentate macrocyclic phosphines will also be mentioned.

1.2.1. Macrocycles: an extension of the chelate effect

A type of polydentate ligands is the macrocycles. The importance of macrocyclic ligands in biological processes such as photosynthesis or transport of oxygen stimulates their study.[12] Synthetic methods were developed to obtain macrocycles as valid models for studies of biochemical systems.[12] For example, the porphyrin and the corrin rings (Figure 1-6) have been studied as mimic systems of haem proteins and vitamin B_{12} respectively.[12] However, other applications were found to extend the use of macrocycles in other fields as for example the selective extraction of metals, or their use as chemotherapeutic or imaging agents, among others.[12]

For the purposes of this thesis, an accepted definition of macrocyclic ligands is adopted, i. e. that a macrocycle is a cyclic molecule with three or more potential donor atoms in a ring of at least nine atoms.[13]

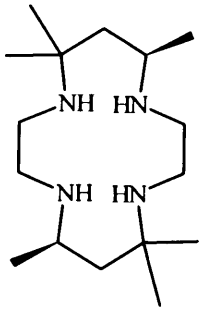


Protoporphyrin IX Vitamin B_{12}

Figure 1-6

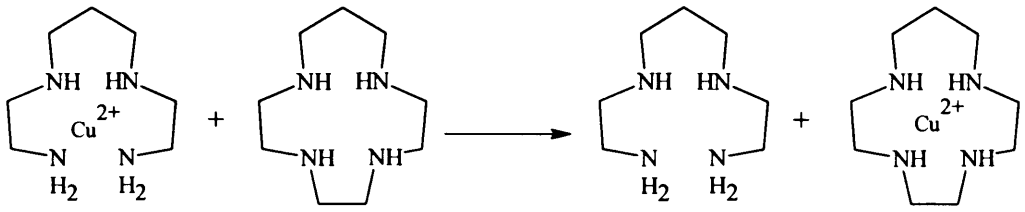
It has been observed that macrocyclic complexes exhibit extra kinetic and thermodynamic stability compared to the analogous open chain complexes with an equivalent number of donor atoms.[14] This is illustrated in Table 1-2 for a series of copper complexes with four nitrogen donor atoms.

Table 1-2: Formation constants for copper complexes[14]

ligand	logβ
$H_2N(CH_2)_2NH_2$	10.7
$H_2N(CH_2)_3NH_2$	9.8
$H_2N(CH_2)_2NH(CH_2)_2NH_2$	16.1
$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	20.1
$H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$	23.9
	28.0

$[Cu(L)(NH_3)_n]^{+2}$ n=1,2

However, unlike to chelate effect, the entropic effect is not the only factor contributing to the increased macrocyclic stability; thus changes in enthalpy, ring size and conformation are factors which favour the formation of macrocycle complexes. The sum of these factors has been defined as the **macrocyclic coordination effect**.[15] As Scheme 1-2 shows, there is a favourable thermodynamic change on passing from an open-chain ligand complex to a cyclic ligand complex.[15]



log K (27 °C)= 5.2

Scheme 1-2

The **ring size** of macrocycles also strongly influences the stability of the complexes formed.[15] Mismatch of the hole-size with the metal ion leads to different consequences either in template synthesis (*vide infra*) or in the coordination chemistry of the macrocycles as for example the formation of complexes where the macrocycle is partially bound to the metal centre.[14]

1.3. General Methods for the synthesis of phosphorus macrocycles

The synthesis of macrocyclic ligands has been mainly confined to N, S or O donor atoms.[15] The dearth of phosphorus macrocycles is due to the difficulties in handling many of the precursors, as primary or secondary phosphines, which are often volatile, toxic and air-sensitive. The development of preparative routes to phosphine macrocycles has represented a very significant synthetic challenge.

The reported methodologies for the synthesis phosphorus macrocycles can be divided in two major categories: cycloaddition reactions and template synthesis.[16]

1.3.1. Cycloaddition Reactions

The cyclisation step in cycloaddition reactions is purely a conventional organic reaction normally by nucleophilic substitution of an electrophile. Two ends of a chain, bearing the appropriate functionalities, react together forming a new bond and creating a ring (Figure 1-7).

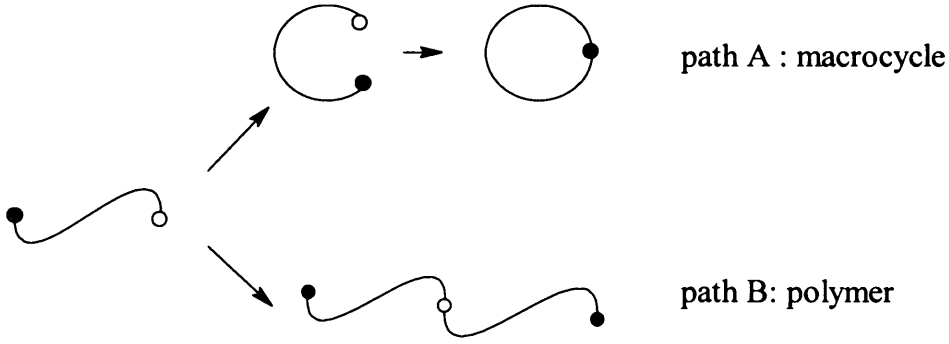
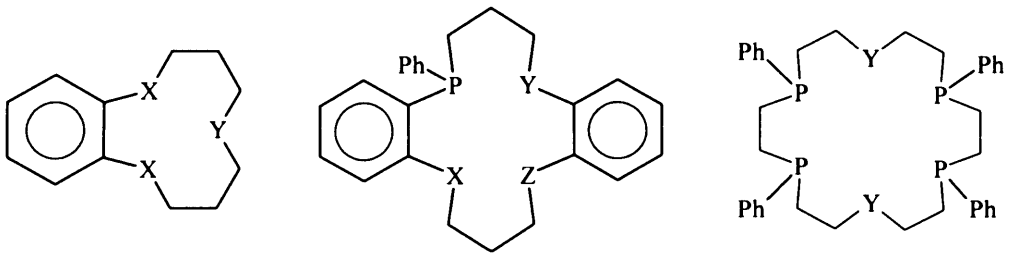


Figure 1-7

In order to cyclise, the two reactive groups must be brought closer to each other (Figure 1-7, path A). However, this process displays unfavourable entropy, and therefore intermolecular processes are favoured over intramolecular reactions leading to the formation of oligomers and polymers (Figure 1-7, path B). Nevertheless, intramolecular reactions can be favoured by performing the reactions under high dilution conditions and by slow addition of the reagents.

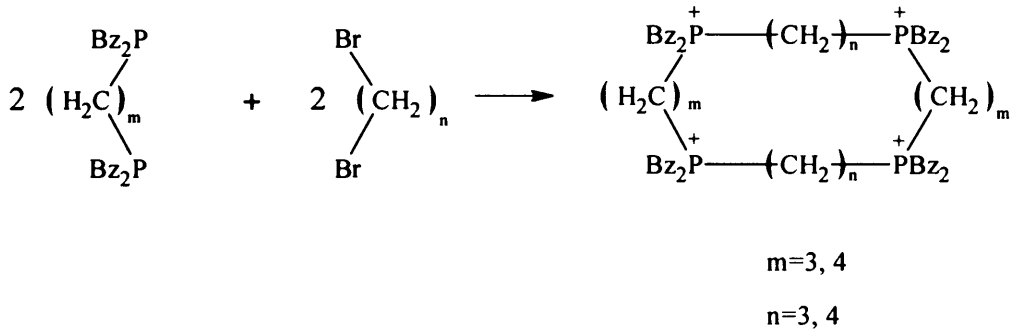
The groups of Kyba and Ciampolini have been the major earlier contributors to this field. Whilst Kyba synthesised various 11- and 14-membered macrocycles containing phosphorus donor atoms (Figure 1-8),[17-19] Ciampolini obtained 18-membered sexidentate macrocycles with four phosphorus atoms combined with two other donor atoms such as O, N and S (Figure 1-8).[20]



11[ane]X_2Y	14[ane]PXYZ	18[ane]P_4Y_2
X=P, S, As	X=P, S	Y=N, O, S
Y=N, O, S, P, As	Y=N, O, S, P, As	
	Z=N, O, S, P, As	

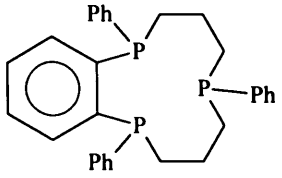
Figure 1-8

In those cases, the cycloaddition reactions involved lithium or potassium salts of diphosphines with bis-electrophiles with or without phosphino groups. However, there are also alternative approaches for the synthesis of macrocycles. For example, Horner and co-workers prepared macrocyclic phosphonium salts which were converted to phosphines by reduction with $LiAlH_4$ (Scheme 1-3).[21]

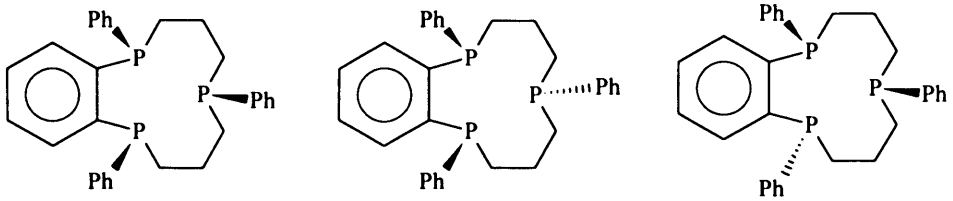


Scheme 1-3

Few reactions using cycloaddition processes have given high yields of the desired macrocycle, and these are exceptions rather than a rule. Furthermore, the lack of stereoselectivity in the reactions leads to the formation of various stereoisomers, reducing the yield of individual macrocycle isomer.



11[ane]P_3



meso-*cis* (syn, syn) | meso-*trans* (syn, anti) | *dl* (syn, anti)

Figure 1-9

Kyba's systems illustrate the lack of stereoselectivity in cycloaddition reactions. For example, the 11[ane]P_3 has three different stereoisomers (Figure 1-9): two meso forms and one *dl* pair although only the meso-*trans* isomer was isolated by crystallization in 5%.[17, 18] Clearly, the meso-*cis* (syn, syn) isomer is required for tridentate coordination to a single metal center.

Larger rings with an increased number of phosphorus atoms are even more complex due to the increase in the number of possible stereoisomers.

1.3.2. Template Methods

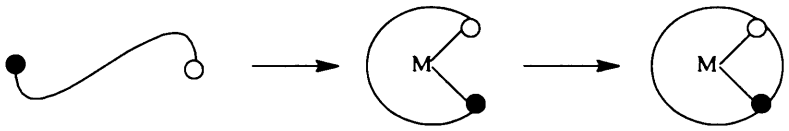
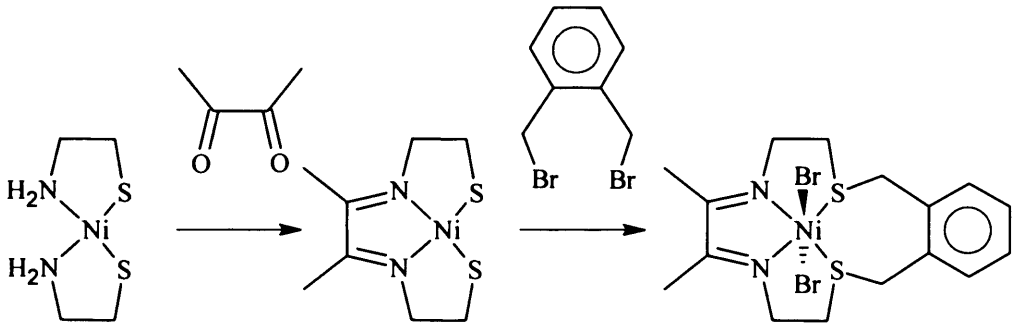


Figure 1-10

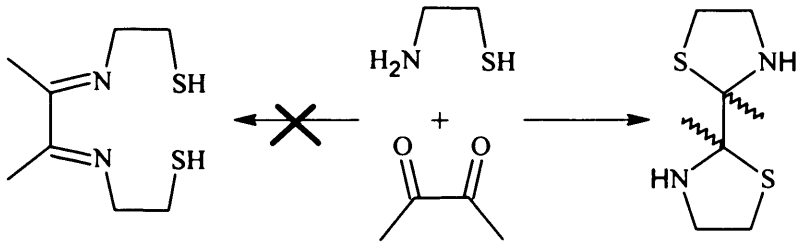
In a metal template assisted reaction, a metal center directs and controls the synthesis of a macrocycle by pre-organizing the acyclic intermediates prior the cyclisation reaction (Figure 1-10). Thus, the problems associated with the conformation of the acyclic intermediates are eliminated, and formation of polymers is inhibited by the proximity of pre-organised reagents. However, the role of the metal is not only conformational (in placing the reactants in the correct spatial arrangement for cyclisation) but may also function as a stabilising agent of otherwise unstable intermediates.[14] For example, the acyclic intermediate **1.8** (Scheme 1-4) necessary for the synthesis of the macrocycle **1.9** can only be prepared as a nickel complex.[13]



1.7 **1.8** **1.9**

Scheme 1-4

Attempts to obtain the demetallated analogue of **1.8** by reaction of (MeCOCOMe) with $H_2NCH_2CH_2SH$ did not yield to **1.11** but resulted in the formation of polymers and the cyclic product **1.10** (Figure 1-11).



1.11 **1.10**

Figure 1-11

The use of metal directed reactions can also induce more selectivity in the cyclisation due the reduction of reactivity of the functional groups involved in the cyclisation process. Electrophilic functional groups have their electrophilic abilities reduced by the back-bonding effect of the metal, whereas nucleophilic functional groups have their electron density reduced by the electrophilicity of cationic center.[13] In most cases, the cyclisation reactions involve the formation of heteroatom-carbon bonds by for example, nucleophilic substitutions, imine formation or hydrophosphination reactions.[22-24]

The advantages of template reactions can be listed, and it is worth to considering them together with the disadvantages.[14]

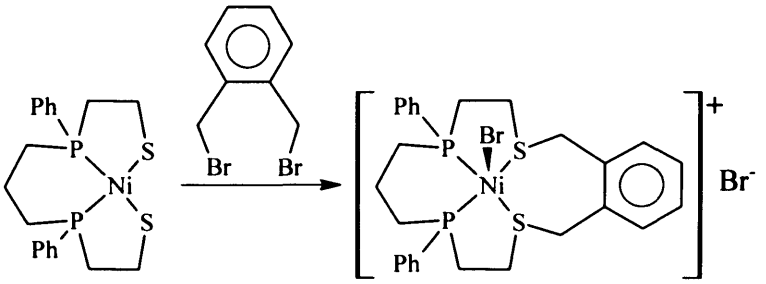
Advantages of template methods:

- Mild reaction conditions
- Good yields
- High dilution methods are not needed
- Metal complex of the macrocyclic ligand are obtained directly
- Synthesis of macrocyclic products derived from precursors which are not available metal-free
- In many cases high degree of stereo and conformational control of the reactions

Disadvantages of template methods:

- Not all metal ions can act as a template for a desired reaction
- A template reaction may not always gives the expected macrocycle but other products of other metal directed reactions
- It may be difficult to obtain the free macrocycle as a consequence of the strong coordination of the ligand to the metal resulting from the macrocyclic effect

Template methods have also been applied to the synthesis of phosphorus containing macrocycles. The first example dates from 1970, where a 15-membered mixed phosphorus thio macrocycle was prepared by using nickel(II) as a template metal (Scheme 1-5).[25] Since then, several other macrocycles have been prepared. Table 1-3 summarises some of these examples.

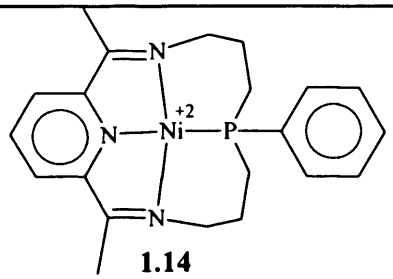
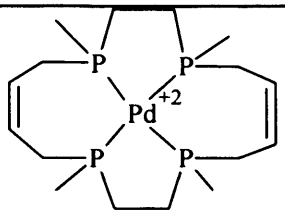
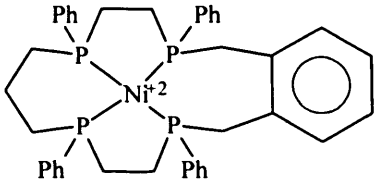
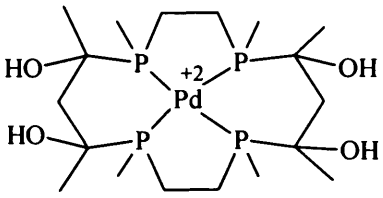
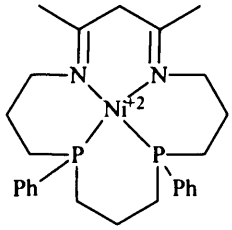
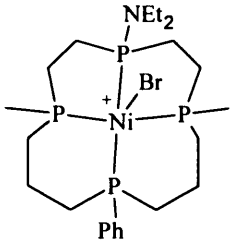


1.12 **1.13**

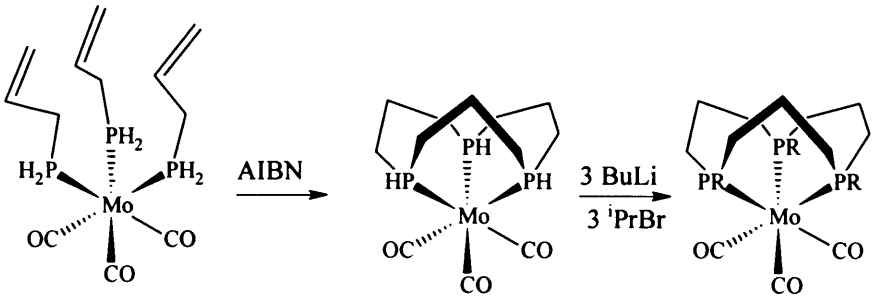
Scheme 1-5

Most of the phosphorus macrocyclic complexes previously known prepared by template methods (with all phosphorus donors) are tetradentate and have been prepared by using a square-planar metal like Ni(II) or Pd(II). These cyclisation reactions have not shown the desired stereoselectivity, and mixtures of stereoisomers have been obtained, although in some cases, stereo-discrimination has reduced enormously the number of compounds in those mixtures.

Table 1-3: Examples of complexes with phosphorus containing macrocycles

Complexes	ref	Complexes	ref
 **1.14**	[24]	 **1.15**	[26]
 **1.16**	[22]	 **1.17**	[27]
 **1.18**	[28]	 **1.20**	[23]

In 1982, Norman and co-workers prepared a novel tridentate secondary phosphorus macrocycle complex **1.22** by intramolecular hydrophosphination of tris(allyl)phosphine on a molybdenum centre (Scheme 1-6).[29] The addition of P-H to the carbon-carbon double bond, which was induced by a free radical initiator, was regio- and stereoselective and only one stereoisomer was obtained in very good yield (85%). The same reaction was performed using CH_2=$CHCH_2CH_2PH_2$ and the analoguous 15-membered triphosphorus macrocycle molybdenum complex was also obtained.[30]



1.21 **1.22** **1.23** R=^{i}Pr

Scheme 1-6

Norman was unable to liberate the macrocycle ligands from the metal centre however. The derivatisation of **1.22** to prepare the tertiary triphosphorus macrocycle **1.23** was performed later by Edwards and co-workers,[31, 32] who also achieved the liberation of 12-membered tertiary triphosphorus macrocycles in 1996 by treatment of the molybdenum complex **1.23** with bromine followed by strong base (NaOH) in ethanol.[7, 33] Edwards' group has also prepared various 9- and 10-membered triphosphorus macrocycles using different metals as template (*vide infra*).[34-38]

1.3.2.1. Liberation of the macrocycle from the metal

Once the macrocycle has been synthesised on a metal template, the liberation of the cycle from the metal ion, so called demetallation, will be desirable if studies of the reactivity of the macrocycle with different metals have to follow.

The methods reported to liberate the cycles are divided into three general categories.[12]

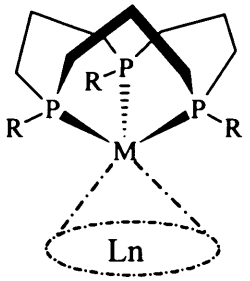
- Addition of a reagent to a solution of the macrocycle complex which modificates chemically the donor atoms and the cycle becomes labile. For example, the liberation of several nitrogen containing macrocycles (such as porphyrins) is achieved after addition of an excess of strong acid.[39]

- Addition of strongly competing ligands to a solution of the macrocycle complex can also induce demetallation such as CN^{-}, $EDTA^{4-}$, OH^{-} and S^{-2}. In phosphorus containing macrocycles, the agent most extensively used is the KCN,[22, 24] although less commonly, H_2S.[40]

- In macrocyclic systems where the metal ion is kinetically inert, it has been necessary to use oxidising or reducing agents in order to liberate the ligand. The lability of such ions is increased upon disrupting the metal ion's electronic configuration by changing the oxidation state. Examples found for phosphorus macrocyclic complexes use reagents such as Na, X_2 (X=halogens) or H_2O_2,[33, 41, 42] however, in some cases the liberation goes together with oxidation of the phosphine donors.[36, 42]

1.4. Aims of this thesis

Tridentate phosphorus macrocycles (9-12 membered rings) are very interesting ligands due to the potential advantages they present. Those compounds can behave as six electron donors upon coordination to a metal as a neutral analogue of the anionic η^5-Cp ligand but since they are neutral, access to complexes in lower oxidation states may be more feasible. Also, these tridentate triphosphorus macrocycle will coordinate to a metal in a facial fashion, forcing the remaining sites to be in *cis* positions, which may be useful for homogeneous catalysis (Figure 1-12). The extra stability in these complexes as a consequence of the macrocyclic coordination effect may be expected to inhibit decomposition of the catalyst in the catalytic cycle leading to more stable catalysis and higher product yields per mole of catalyst.



R= H, alkyl, aryl

Figure 1-12

However, as previously mentioned, the difficulty in obtaining suitable precursors reduces significantly the potential of template methods in the synthesis of triphosphorus macrocycles.

This thesis is focused on the investigation of new precursors for the synthesis of tridentate phosphorus macrocycles. The synthesis of a new 9-membered triphosphorus manganese(I) complex is described together with studies of liberation methods.

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Chapter 2:

SYNTHESIS OF TRIPODAL PHOSPHINES WITH A CYCLOHEXANE BACKBONE

2.1. Introduction

2.1.1. Tripodal tridentate phosphine ligands

The range of known tripodal ligands containing phosphorus donor atoms is far less abundant than their nitrogen, oxygen and sulphur donor atom counterparts (Figure 2-1). The poor availability of the appropriate phosphorus precursors as well as the sensitivity of many phosphorus compounds towards oxygen, are reasons that help to explain this lack of variety.

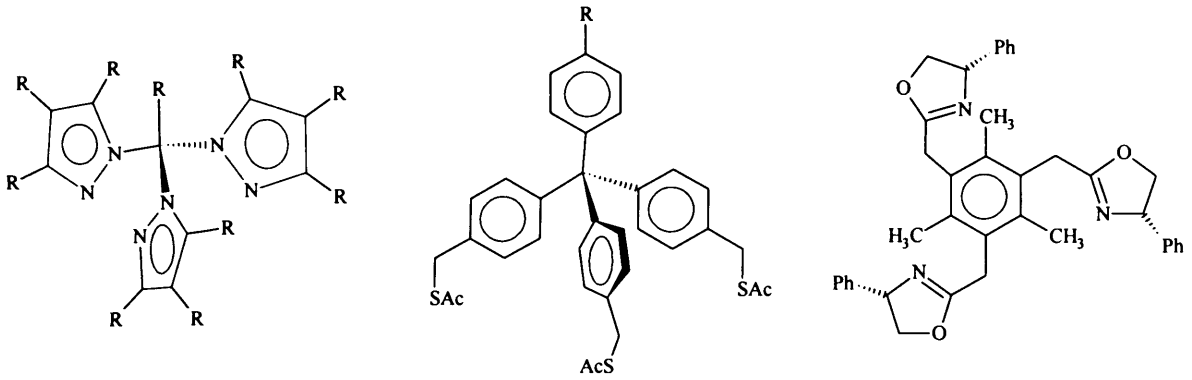


Figure 2-1: Examples of tripodal ligands with different donor atoms.[1-3]

Tripodal phosphine ligands have the same advantages as other polydentate ligands in acting as multidentate donors, but in addition, the stereochemistry and stoichiometry of the complexes formed can be better controlled due to the structural limitations of the backbone. Tripodal phosphine ligands can coordinate either in a chelating mode or in a bridging mode; they have formed stable complexes with most d-block metals, displaying different coordination modes and in a variety of stereochemistries.[4-7] However, the main factors controlling the complex's geometry are the nature of the metal and the ligand scaffolding design. For example, while Triphos (Figure 2-2) generally triligates to metal centers occupying a facial position in tetrahedral, square pyramidal, trigonal bipyramidal or octahedral geometries; Tripod may also favour a bridging mode facilitating formation of clusters.[6, 7]

Tripodal phosphine ligand complexes have been used as stoichiometric reagents for the synthesis of organic molecules and have showed high activity in homogeneous catalysis due to their adaptability to the different stereochemistries of the intermediates during the catalytic cycle. For example, the tripodal ligand Triphos, has been successfully used in hydrogenation and hydroformylation reactions.[5]

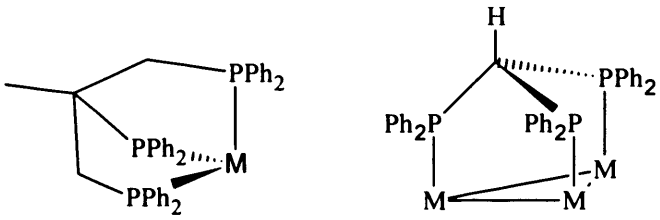
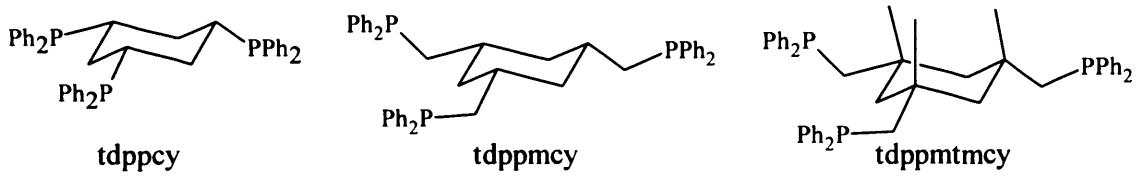


Figure 2-2:Triphos and Tripod complexes

A further class of structurally interesting tripodal phosphine ligands, are those prepared by Mayer and co-workers (Figure 2-3).[8-10] In these ligands, the three phosphine groups are bound to the 1,3,5 position of a cyclohexane ring in a *cis*, *cis* disposition.

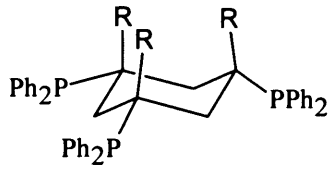


tdppcy **2.1** tdppmcy **2.2** tdppmtmcy **2.3**

Figure 2-3: Ligands synthesised with a cyclohexane backbone

Tdppcy (**2.1**), tdppmcy (**2.2**) and tdppmtmcy (**2.3**) were initially synthesised stereoselectively with yields of 20, 66 and 60 % respectively. The yield of analogues of **2.1** was enhanced by the stereoselective introduction of an electron-withdrawing group, COOMe, in the 1,3,5 positions of the cyclohexane ring (Figure 2-4). This method opened up a new route to this type of ligand in reasonable yield.[11,12] The use of the $Mo(CO)_3$ fragment both as a protector of the phosphine and as an activator of the ester group, allowed further modification.[13] The behaviour of the complexes of these ligands,

including solubility, would be expected to show some dependence on the nature of the substituent.



2.1R

R= COOMe, CN, CH_2OCH_3, $CH_2OCH_2OCH_3$,
$CH_2(OCH_2CH_2)_xOCH_3$, $CH_2OCH_2CHCH_2$,

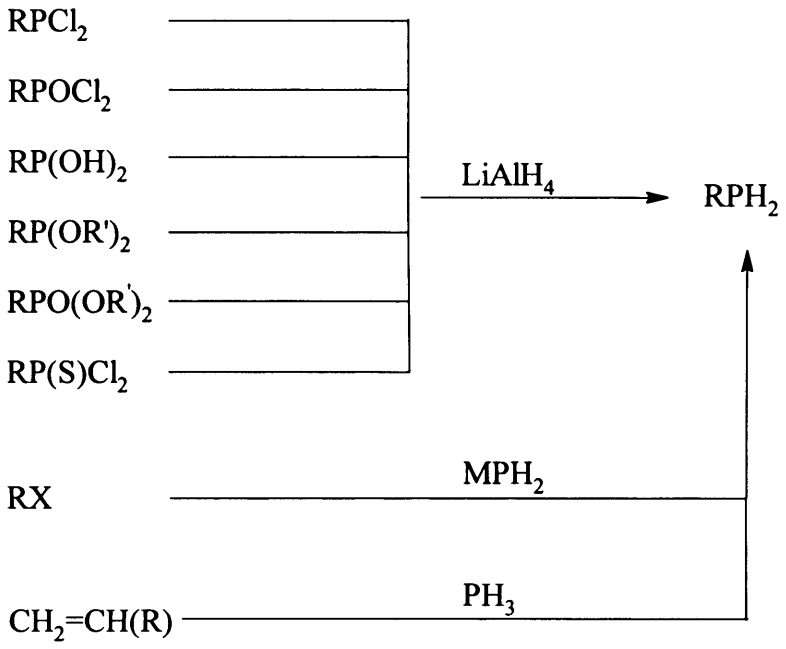
Figure 2-4

Facial coordination was not observed for rhodium and iridium complexes of **2.2** and **2.3**.[8, 9, 14] This is likely a consequence of the inherent instability of the large ring size of the 8-membered chelates. In contrast, **2.1** is able to form more stable 6-membered chelates and adopts facial coordination modes when coordinated to a trigonal-bipyramidal or octahedral metal center.[11, 12, 15] With Ni, Pd, and Pt, **2.1** and its derivatives (**2.1R**) behave as bidentate ligands in square-planar or pseudo-tetrahedral arrangements.[16] In addition, a water-soluble rhodium derivative of **2.1** is an active hydroformylation catalyst in biphasic systems.[15]

2.1.1. General synthetic methods for primary phosphines

Primary phosphines are mainly obtained by reduction of phosphonous or phosphonic derivatives with $LiAlH_4$ (Scheme 2-1). In some cases, auxiliary agents such as $AlCl_3$ or Me_3SiCl are needed to optimise yields. Na, Li, H_2S and LiH have also been used as reducing agents, and $LiBH_4$ has substituted $LiAlH_4$ as a milder reducing agent in reactions where other functionalities are present.[17] The disadvantages of reduction methods are that they often involve convoluted procedures and commonly give poor yields. This method also fails for some phosphines or leads to unexpected products. Other

methods which lead to primary phosphines are the direct reaction of metal phosphides (MPH_2) with alkylating agents (Scheme 2-1).



Scheme 2-1: General synthetic methods for the preparation of primary phosphines

The metal phosphide can be obtained either by reaction of phosphine, PH_3, with a metal (Na, K, Ca) in liquid ammonia (Scheme 2-2, eq. 2.1) or by deprotonation of PH_3 in a super basic medium of DMSO/*t*-BuOK, DMSO/KOH or organolithium compounds (Scheme 2-2, eq. 2.2).[18-20] Addition of phosphine to alkenes under the influence of non-oxidizing acids, strong bases or free radical initiators, also leads to primary phosphines (Scheme 2-1).[21] The disadvantages of these methods arise from the experimental problems presented by the manipulation of phosphine gas.

$$PH_3 + M \longrightarrow M(PH_2)_n + H_2 \quad M= Na, K, Ca \qquad (2.1)$$

$$PH_3 + Base \longrightarrow MPH_2 \quad M= K, Li \qquad (2.2)$$

$$P + 3\,Na + 2\,t\text{-BuOH} \longrightarrow NaPH_2 + 2\,t\text{-BuONa} \qquad (2.3)$$

Scheme 2-2: Different synthetic methods to obtain MPH_2

Brandsma and co-workers developed a new method to obtain MPH_2 without the involvement of phosphine gas (Scheme 2-2, eq. 2.3).[22] Phosphorus with either lithium or sodium was reacted in liquid ammonia to form M_3P. Further protonation of the later by *t*-butyl alcohol afforded the metal phosphide in a one-pot reaction. This method was improved by isolation of Na_3P by changing liquid ammonia for an inert solvent such as THF.[23] Subsequent protonolysis of Na_3P in THF provided a more controlled method in the formation of MPH_2. However, the use of *t*-butyl alcohol as a proton source leads to the formation of *t*-butyl alkoxide, which can further react with the acidic primary phosphines formed and lead to undesired products.

2.1.2. Aims

Although tridentate phosphine ligands based on a cyclohexane frame have showed interesting coordination chemistry with great potential to be used in homogeneous catalysis, to date only arylphosphine derivatives have been synthesised. In view of the wealth of chemistry surrounding *cis,cis*-1,3,5-triaminocyclohexane and its derivatives,[24] it is surprising that related primary phosphines remain unknown and synthetic routes to such compounds will be of value. Primary phosphines are good potential precursors for the synthesis of a range of substituted phosphines, including macrocycles.[25, 26] Therefore, the primary phosphine analogues of Mayer's cyclohexane ligands were sought. These ligands would have different steric and electronic properties from the ones synthesised by Mayer, and the complexes formed with these ligands could allow further modification at the phosphorus atoms, yielding a new range of tripodal tridentate phosphine ligands. In addition, the use of olefinic alkylating agents such as allyl or vinyl halide could open routes to the formation of precursors for the synthesis of cage compounds (Figure 2-5).

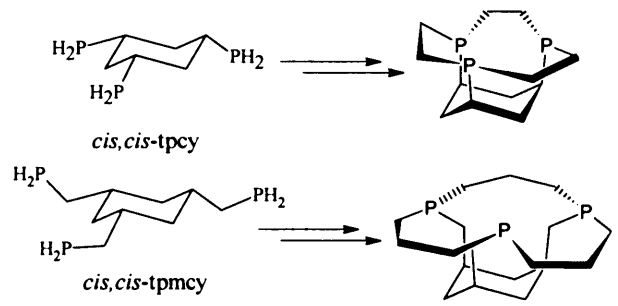
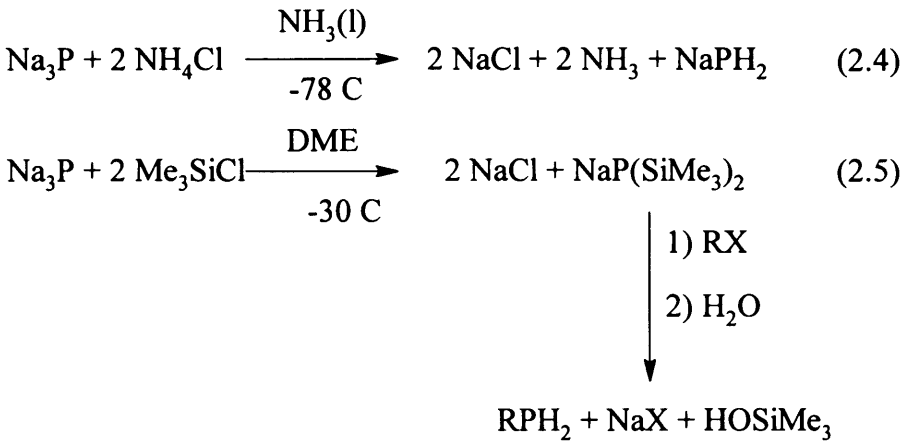


Figure 2-5

2.2. Results and discussion

2.2.1. Synthesis of $NaPH_2$ and $NaP[Si(Me_3)]_2$ by new methods. An alternative for the synthesis of primary phosphines.



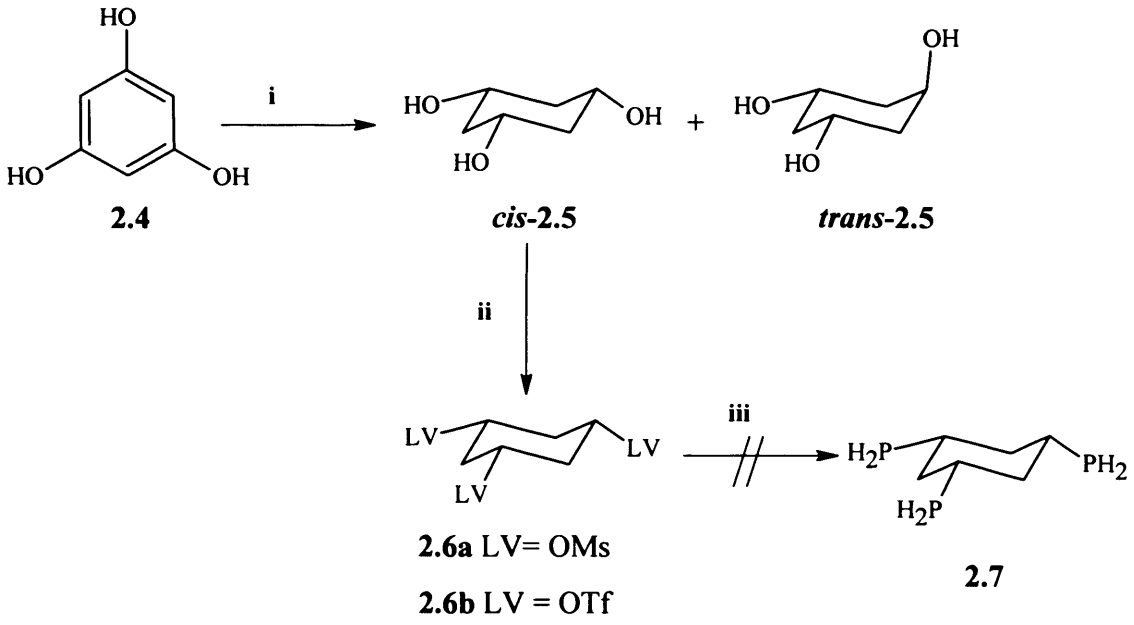
Scheme 2-3: New methods developed to synthesise primary phosphines

Our group has developed new methods to synthesise primary phosphines (Scheme 2-3). $NaPH_2$ was prepared by modifying the procedure reported by Brandsma,[22] whereby trisodium phosphide (Na_3P) is protonated in liquid ammonia using NH_4Cl instead of *t*-butyl alcohol (Scheme 2-3, eq. 2.4). A stoichiometric amount of NH_4Cl was slowly added to a suspension of Na_3P in liquid ammonia at -78°C and the mixture was stirred at this temperature for one hour to form $NaPH_2$. $NaPH_2$ was characterized in solution by $^{31}P\{^1H\}$NMR spectroscopy. A singlet at δ_P -297 ppm was observed which is consistent with the literature value.[27] Once the $NaPH_2$ has been formed, alkylating reagents can be added under suitable conditions to form primary phosphines.

Otherwise, slow addition of a stoichiometric amount of Me_3SiCl in DME into a suspension of Na_3P in DME at low temperature (-30°C) afforded sodium bis(trimethylsilyl)phosphide (Scheme 2-3, eq. 2.5). $NaP[Si(Me_3)]_2$ was characterized in solution by $^{31}P\{^1H\}$ NMR spectroscopy. A singlet at δ_P -302 ppm is consistent with the values reported in the literature.[28] $NaP[Si(Me_3)]_2$ also reacts with alkylating agents as a masked but less basic form of $NaPH_2$, with the primary phosphine being formed on protonolysis.

These methods offer the advantages of using metal phosphides but avoiding the disadvantages of phosphine gas or formation of reactive by-products. They also allow isolation of $NaPH_2$ or $NaP[Si(Me_3)]_2$ which enables choice of the most suitable conditions for the synthesis of individual phosphines. The advantage of using the $NaP[Si(Me_3)]_2$ modification is that the lower basicity and nucleophilicity of the phosphine avoids unwanted side reactions and gives good yields of new phosphines that have proved difficult to obtain by other means.

2.2.2. Attempts to synthesise *cis, cis*-1,3,5-triphosphinocyclohexane (2.7)



i) H_2, EtOH, Raney-Ni, 50°C; ii)**2.6a**: MsCl, pyridine, CH_2Cl_2. **2.6b:** $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2.
iii) $NaPH_2$ or $Na(BH_3)PH_2$, CF_3COOH

Scheme 2-4: Proposed synthetic route to 2.7

The Scheme 2-4 shows various attempted routes designed for the synthesis of **2.7** from the commercially available phoroglucinol (**2.4**). Compound **2.5** was first prepared by Stetter and co-workers by hydrogenation of **2.4** in ethanol.[29] The ***cis*-2.5** isomer was separated from the racemic mixture of 1,3,5-cyclohexane-triol by crystallization. **2.6a** and **2.6b** compounds were synthesised from ***cis*-2.5** as suitable precursors for the attempted

synthesis of **2.7**. $NaPH_2$ and $Na(BH_3)PH_2$ were used as nucleophiles under a range of different conditions. It was expected that $^-PH_2$ or $[(BH_3)PH_2]^-$ anions would displace the mesylate or the triflate groups in nucleophilic substitution reactions with inversion of configuration that would lead to the desired compound **2.7**. The different attempts are explained in more detail below.

2.2.2.1. Synthesis of *cis, cis*-1,3,5-tris(methanosulphonate)cyclohexane (2.6a).

Although the tosylate derivative of **2.6** has been described,[29] the mesylate derivative **2.6a** is new but is synthesised in a similar manner. Treatment of ***cis*-2.5** with excess of methanosulphonate chloride in pyridine results in the isolation of **2.6a** as a white solid in 62 % yield. The solubility of **2.6a** is very low in most organic solvents except DMSO. The ^1H and $^{13}C\{^1H\}$NMR spectra of **2.6a** confirm the C_{3v} symmetry of the compound with the mesylate groups in a *cis*, *cis*-disposition on the cyclohexane ring. The ^1H NMR spectrum shows four signals in the alkane region. Two multiplets at δ_H 1.79 and 2.40 ppm are assigned to the non-equivalent methylene protons. A singlet at δ_H 3.25 ppm is assigned to the methyl protons of the mesylate group, whilst the multiplet at δ_H 4.72 ppm is assigned to the methine proton. The $^{13}C\{^1H\}$NMR spectrum shows three resonances at 37.26, 37.85 and 73.14 ppm for the three different carbons of **2.6a**.

2.2.2.2. Synthesis of *cis, cis*-1,3,5-tris(trifluoromethanosulphonate)cyclohexane (2.6b)

Compound **2.6b** was synthesised following similar methods to those described in the literature.[30] The synthesis and stereochemistry of the compound was confirmed by ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectroscopies. The ^1H NMR spectrum of **2.6b** shows three multiplets at δ_H 2.26, 2.61 and 4.97 ppm from the non-equivalent methylene protons and the methine proton respectively. The protons of compound **2.6b** are deshielded compared to those of compound **2.6a** due to the higher electron-withdrawing properties of the triflate group. The $^{13}C\{^1H\}$ NMR spectrum displays two resonances at δ_C 36.5 and 77.5 ppm for the two types of carbons of the cyclohexane ring, and a quartet at δ_C 118.3 ppm ($J_{C\text{-}F}$=

319.8) for the carbon of the triflate groups. In addition, the ^{19}F NMR spectrum shows a singlet at δ_F -74.9 ppm. All these data are consistent with the C_{3v} symmetry of compound **2.6b.** Due to the instability of the compound, **2.6b** was used immediately for further reactions.

2.2.2.3. Attempted synthesis of 2.7 by reaction of $NaPH_2$ with 2.6

A suspension of **2.6a** in Et_2O was added to a cooled solution (-78°C) of $NaPH_2$ (synthesised *in situ*) in liquid ammonia. After addition, the reaction was stirred at this temperature for 5 hrs, after which time, the solution was allowed to warm to room temperature with evaporation of the liquid ammonia. The solid was extracted with Et_2O. The $^{31}P\{^1H\}$ NMR spectrum of the solution (Figure 2-6) showed predominantly resonances between -100 and -130 ppm. The ^{31}P-^1H coupled NMR spectrum showed these signals split into triplets with P-H coupling constants between 180-199 Hz. The pattern of the signals and the coupling constants are consistent with the formation of primary phosphines. The chemical shifts values also confirm the formation of primary phosphines bearing a cyclohexane ring.[31] These compounds are likely to be the mono, and di-substituted phosphines as well as elimination products and the desired compound. Other attempts were made to synthesise **2.7** as a single major product, such as increasing the ratio of $NaPH_2$, and/or the use of different solvents, or perform the reaction at different temperatures. All attempts to obtain **2.7** from **2.6a** however, led inevitably to similar mixtures of phosphorus-containing compounds which could not be separated.

The insolubility of **2.6a** in appropriate solvents may contribute to the observed poor selectivity and the triflate analogue, **2.6b**, was used in an attempt to minimise this problem. The reaction between **2.6b** and $NaPH_2$ under various conditions was unsuccessful. The crude products of the reaction were mixtures similar to those observed in reactions of **2.6a**.

Analysis of the ^1H NMR spectra of all these trials showed a common feature, a group of multiplets between 5-6 ppm which are attributed to olefinic protons (figure 2-7), this was also confirmed by $^{13}C\{^1H\}$ NMR spectroscopy. These olefinic compounds are likely to be formed by competing base mediated elimination reactions promoted by basic $^-PH_2$. In all cases, these mixtures could not be successfully separated.

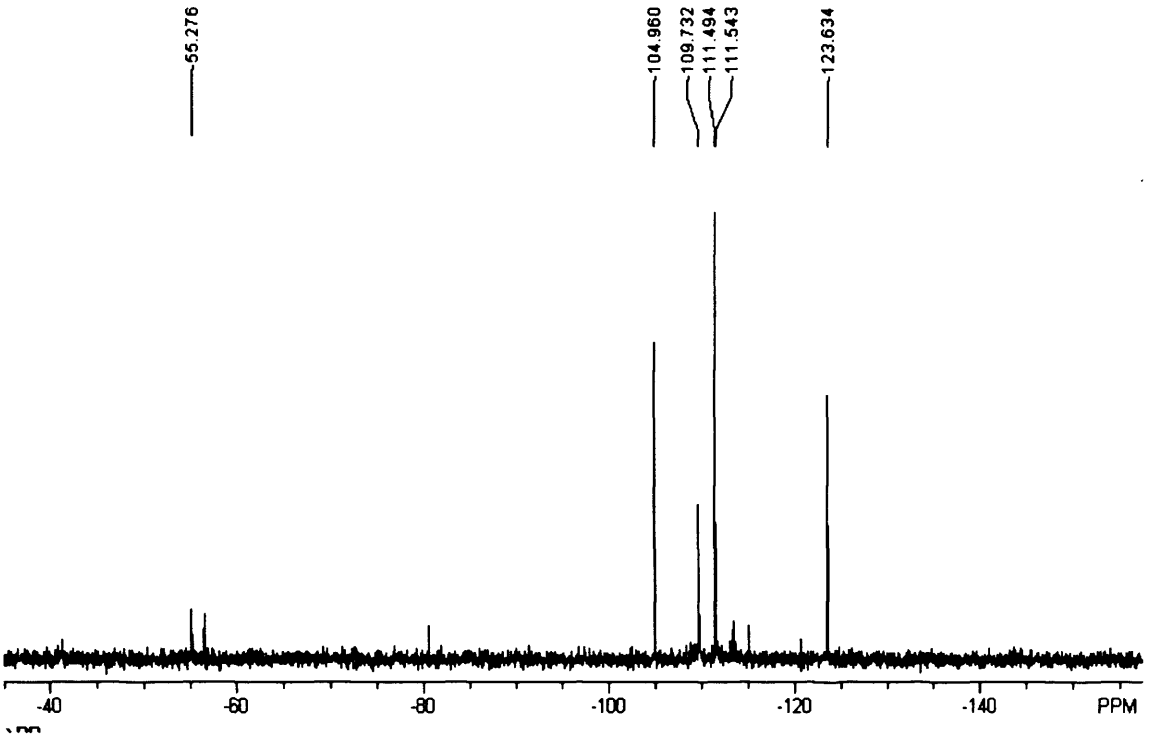


Figure 2-6: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between 2.6a and $NaPH_2$

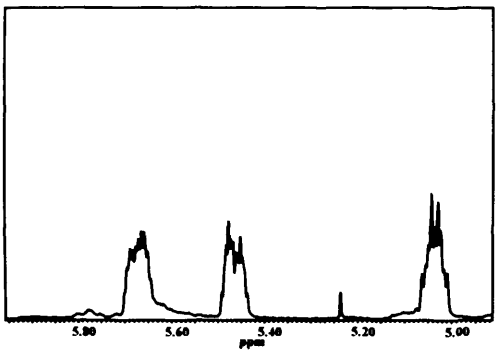


Figure 2-7: ^{1}H NMR spectrum of reaction between 2.6 and $NaPH_2$

2.2.2.4. Protection of $NaPH_2$ with boranes and attempted alkylation

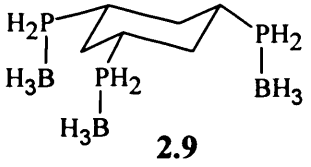
Organophosphine-borane anions have been used mainly in reactions with different electrophiles to form phosphorus derivatives with specific stereochemistry.[32] Nevertheless, previously inaccessible phosphines have also been synthesised by using dialkylphosphine-borane anions due to the reduced basicity compared to the non-borane

protected derivatives.[33] Deprotection is easily achieved with retention of configuration on treatment with a large excess of an amine or an acid.

Efforts were made to synthesise $Na(BH_3)PH_2$ (**2.8**) which would be expected to be less basic than $^-PH_2$, thus reducing base-promoted side reactions when reacting with **2.6** to obtain **2.9** (Scheme 2-5, eq. 2.7). $Na(BH_3)PH_2$ has been synthesised previously by reaction of PH_3BH_3 and sodium metal in liquid ammonia.[34] However there are no reported studies of its reactivity with electrophiles.

$$NaPH_2 + BH_3.OC_4H_8 \longrightarrow [H_2P\text{-}BH_3]^-Na^+ \quad (2.6)$$

2.8

2.8 + **2.6** ⟶//  (2.7)

2.9

Scheme 2-5: Proposed pathway to 2.9

To synthesise **2.8**, $NaPH_2$ was prepared in liquid ammonia by the usual procedure (see experimental) and after evaporation of ammonia, $NaPH_2$ was dissolved in THF and filtered from the reaction mixture. Compound **2.8** was then obtained by addition of an excess of BH_3.THF to a cooled solution (0°C) of $NaPH_2$ in THF (Scheme 2-5, eq. 2.6).

The phosphine-borane anion **2.8** was not isolated but was characterized *in situ* by $^{31}P\{^1H\}$ NMR spectroscopy. PH_3BH_3 was also formed as a by-product in the reaction mixture indicating some degree of over-protonolysis of the Na_3P. $^{31}P\{^1H\}$ NMR data for $NaPH_2.BH_3$ and PH_3BH_3 have been collected in Table 2-1. No $^{31}P\{^1H\}$ NMR data is available in the literature for $NaPH_2.BH_3$, but the chemical shift observed for PH_3BH_3 agrees with the published value.[35] A comparison of the $^{31}P\{^1H\}$ chemical shifts of free phosphines with those corresponding to the borane-adduct, show a pronounced deshielding of phosphorus upon adduct formation due to the lewis acidic character of the boron atom. The co-ordination chemical shift (defined as $\Delta^{31}P = \delta_{\text{co-ordinated P}} - \delta_{\text{unco-ordinated P}}$), is 134 ppm for $PH_3.BH_3$ and 177 ppm for $NaPH_2.BH_3$. The chemical shift of $NaPH_2BH_3$ is upfield of

that of $PH_3.BH_3$ as a consequence of higher electronic density on the phosphorus atom. Phosphorus-boron coupling constants could not be determinated from the $^{31}P\{^1H\}$ NMR spectra due to the broadness of the peaks, which is a consequence of the quadrupolar character of the boron atom.

Table 2-1: ^{31}P Chemical shift data for phosphines and phosphine-borane complexes

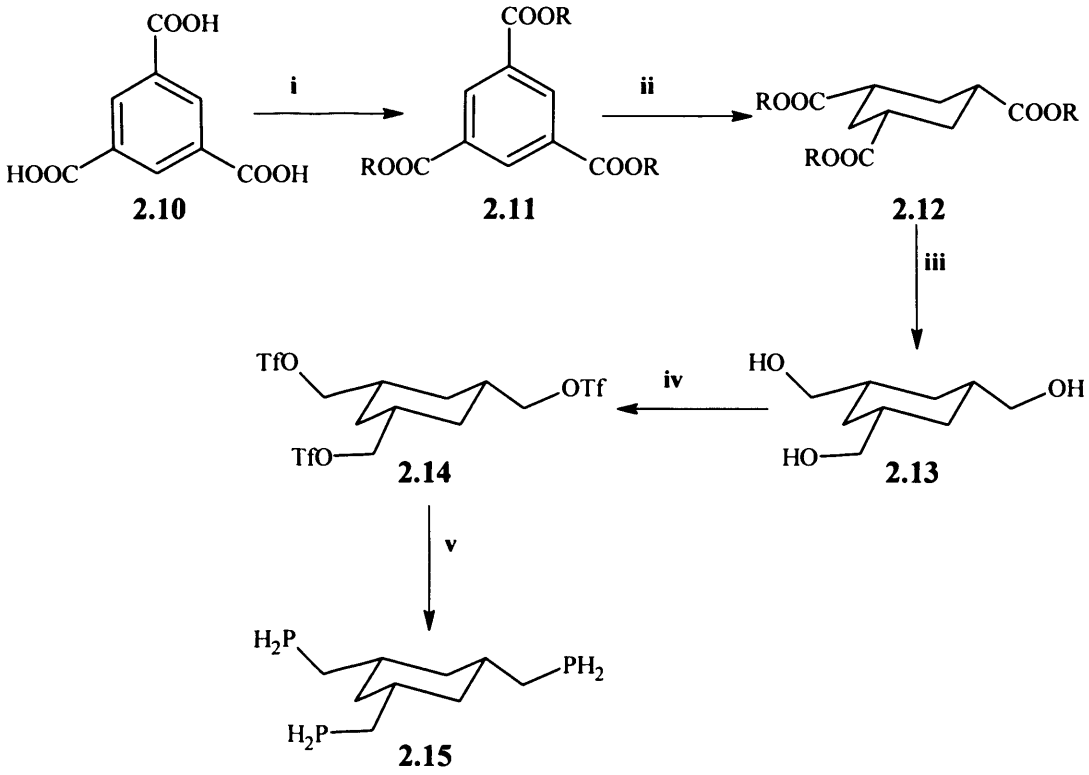
	$^{31}P\{^1H\}$		
Complex	δ_{free}	$\delta_{complex}$	$\Delta\delta$
$PH_3.BH_3$	-244.6	-110.2 (m)	-134
$NaPH_2.BH_3$	-297.1	-119.8 (m)	-177

Once the $NaPH_2.BH_3$ had been identified, the reaction between **2.6** and **2.8** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2-5, eq. 2.7). Several attempts to synthesise **2.9** were made. **2.6a** was initially used as the electrophile in DMSO as solvent. The reaction between **2.6a** and **2.8** yielded a mixture of compounds with chemicals shifts between -100 and -130 ppm. The sharpness of the peaks in the $^{31}P\{^1H\}$ NMR spectrum and the chemical shifts values as well as the absence of any ^{31}P-^{11}B coupling suggested that DMSO has deprotected the adducts.[36] Therefore, **2.6b** was reacted with **2.8** in THF at room temperature. The $^{31}P\{^1H\}$ NMR spectra of the reaction did not show any change, product **2.8** remained even after one week of stirring. Consequently, in order to force **2.8** to react, the reaction mixture was refluxed for 1 hour, after which a new broad peak at δ_P -56.40 ppm was seen in the $^{31}P\{^1H\}$ NMR spectrum. Compound **2.9** would be expected to have a downfield chemical shift characteristic of primary phosphine borane adducts. So, this was a positive result but polymerization of THF had also occurred in this reaction and no attempt was made to work-up the reaction. To avoid polymerization, DME was tried as solvent. Reaction of **2.6b** and **2.8** in DME was initially carried out at room temperature without showing any change in the $^{31}P\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of the reaction after refluxing for one hour did show formation of new compounds, as well as the continued presence of **2.8**. In addition, there was an encouraging resonance at δ_P -68.96 ppm, but longer refluxing time lead to decomposition of **2.8** with no formation of the

desired compound **2.9**. In summary, these results suggest that complexation of $NaPH_2$ with BH_3 decreases severely both the basicity and the nucleophilicity of the phosphide borane anion such that primary phosphine borane adducts are not readily formed.

2.2.3. Synthesis of *cis, cis*-1,3,5-triphosphinemethylcyclohexane (2.15)

Cis, cis-1,3,5-triphosphinomethylcyclohexane **2.15** has been prepared from trimesic acid by the 5 step-synthesis summarized in Scheme 2-6. The intermediates **2.10-2.13** have been described by others, but it has been necessary to adjust some steps of this synthesis to our conditions (see experimental).[37]



i) EtOH, H_2SO_4; ii) H_2, AcOH, PtO_2, 50°C; iii) $LiAlH_4$, Et_2O; iv) $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2; v) $NaPH_2$

Scheme 2-6: Synthetic pathway to 2.15

2.14 was synthesised by reaction of **2.13** with three equivalents of trifluoromethanesulfonic anhydride and pyridine in dichloromethane in 40 % yield. **2.14,** which decomposes within days at room temperature, was characterized by ^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectroscopy. The ^{1}H NMR spectrum shows four groups of multiplets corresponding to the four different types of hydrogen atoms. As well as in its precursors, the methylene protons of the cyclohexane ring are non-equivalent and give rise to different signals. The $^{13}C\{^{1}H\}$NMR spectrum displays three peaks in the alkane region and a quartet at δ_C 118.55 ppm with J_{C-F}= 319 Hz characteristic of the carbon of a triflate group. The ^{19}F NMR spectrum shows a singlet at -74.3 ppm. All these data agree with the C_{3v} symmetry of compound **2.14**.

The nucleophilic substitution reaction of **2.14** with an excess of $NaPH_2$ (generated *in situ*) was performed at -78°C. **2.14** was added as an ethereal solution to the $NaPH_2$ in liquid ammonia, the mixture stirred for 5 hours at this temperature, then for a further 12 hours at room temperature. **2.15** was isolated from the reaction as an air-sensitive colourless liquid in 77 % yield.

The number of resonances in the ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$NMR spectra of the compound **2.15** are in agreement with a C_{3v} symmetry which suggest that the cyclohexane ring prefers the chair conformation. Thus, the $^{31}P\{^{1}H\}$NMR spectrum displays a singlet at δ_H -149.14 ppm which appears as a triplet in the ^{1}H-coupled ^{31}P NMR spectrum ($^{1}J_{P-H}$=196 Hz). The ^{1}H NMR spectrum of **2.15** (Figure 2-8) shows four multiplets at δ_H 1.41, 0.6, 1.98 and 1.53 ppm assigned to the methine protons, the methylene protons of the cyclohexane ring, which are again non-equivalent, and the methylene protons of the arm, respectively. The protons of the PH_2 appear as doublets of triplets at δ_H 2.70 ppm. The chemical shifts of all the protons of the cyclohexane are displaced upfield compared with the precursor **2.14**. From the values of H-H coupling constants between the methine and the ring methylene protons it can be deduced that the phosphinomethyl group is situated in the equatorial position of the cyclohexane ring.[38]

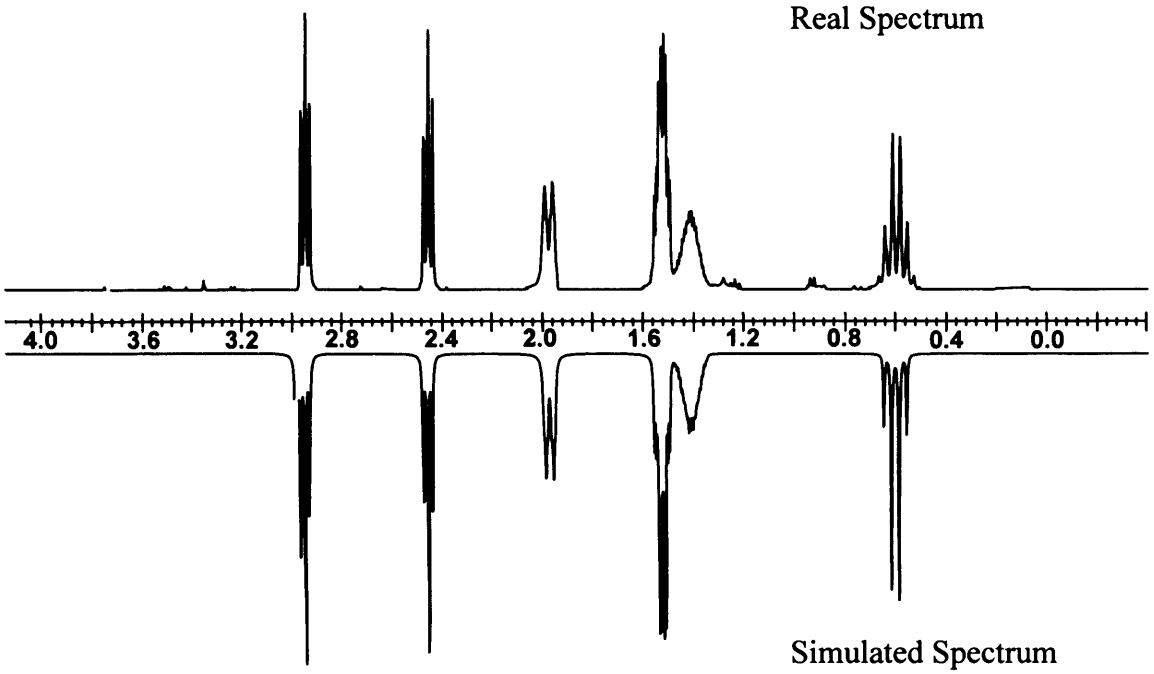


Figure 2-8: Real spectrum of 2.15 and simulated spectrum

The simulation of the ^{1}H NMR spectrum of compound **2.15** has been performed with gNMR Simulation Program (Figure 2-8).[39] This simulation has permitted the coupling between the phosphorus nuclei and some of the protons of the cyclohexane ring to be deduced (see experimental).

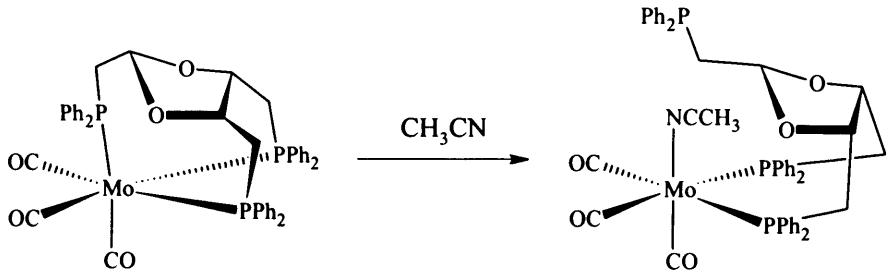
The $^{13}C\{^{1}H\}$ NMR spectrum of **2.15** shows three doublets in the alkane region at δ_C 20.8, 39.2 and 40.6 ppm corresponding to the carbons of the methylene arm, the methine and the methylene of the cyclohexane, respectively. The IR spectrum shows, among others, a band at 2289 cm^{-1} characteristic of P-H stretches. In addition, the nature of **2.15** was confirmed by mass spectroscopy in which the molecular ion was observed.

2.2.4. Attempts at complexation of *cis, cis*-1,3,5-triphosphinomethylcyclohexane to molybdenum(0)

Most of the attempts to coordinate **2.2** and **2.3** to rhodium(I) or iridium(I) in a facial fashion have failed, yielding complexes with two coordinated phosphine groups with the third phosphine group being uncoordinated, or coordinated to another metal center forming

oligomers.[8,9,14] The conformation of the cyclohexane ring restricting the phosphine groups to the equatorial positions in the **2.2** and **2.3** is believed to be the cause of the restriction to bidentate coordination in the complexes. In addition, in order to achieve the formation of the desired complexes it is necessary for the conformation of the cyclohexane ring to flip, with an interchange of equatorial-axial group positions. In this new conformation, where the methylenephosphine moieties are placed in the axial positions, and steric hindrance between the axial groups could destabilise this conformation.

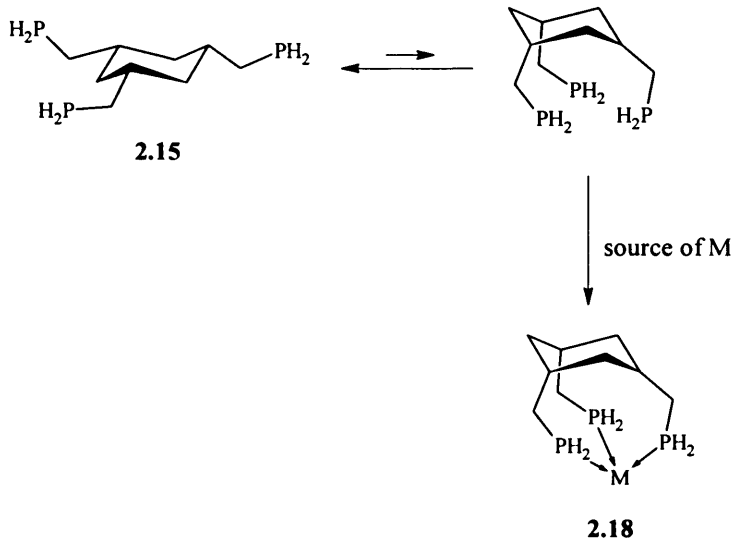
Börner and co-workers synthesised a tripodal phosphine ligand based on a 1,3-dioxolane ring which coordinates facially in the molybdenum complex **2.16** (Scheme 2-7).[40] The dioxolane ring adopts an envelope disposition upon coordination, with one methylenephosphino moiety placed in the equatorial position, and the other two placed in a pseudo-axial position. The η^3 coordination mode of the complex can be easily converted to a bidentate coordination mode by addition of acetonitrile, yielding complex **2.17** with an uncoordinated phosphine group, and presumably due to steric strain imposed by the backbone conformation since tertiary phosphines normally are not readily displaced by acetonitrile in molybdenum carbonyl complexes.



2.16 **2.17**

Scheme 2-7: Displacement of a phosphine group of 2.16 by acetonitrile

With the aim of showing which factors control the formation of facially coordinated complexes, the ligand **2.15** was reacted with molybdenum(0) precursors. It was expected that **2.15** would coordinate facially to the metal center if the cyclohexane ring was able to flip to the conformer with the methylenephosphino groups in the axial position (Scheme 2-8).



Scheme 2-8

The reaction of **2.15** with an equimolar amount of $Mo(CH_3CN)_3(CO)_3$ in toluene afforded a yellow solution. The $^{31}P\{^1H\}$ NMR spectrum of the solution showed a group of signals around δ_P -80 ppm and a singlet at δ_P -149.14 ppm (Figure 2-9). These data reveal that a mixture of molybdenum complexes have been formed as indicated by the downfield signals at δ_P -80 ppm. The singlet at δ_P -149.1 ppm is consistent with an uncoordinated phosphine group. This is a clear indication that different bridging and chelating modes of coordination occurred. Repeating the reaction in boiling toluene did not afford the coordination of the third arm and mixtures of products were formed. All attempts to crystallize single discrete complexes from various solvents failed.

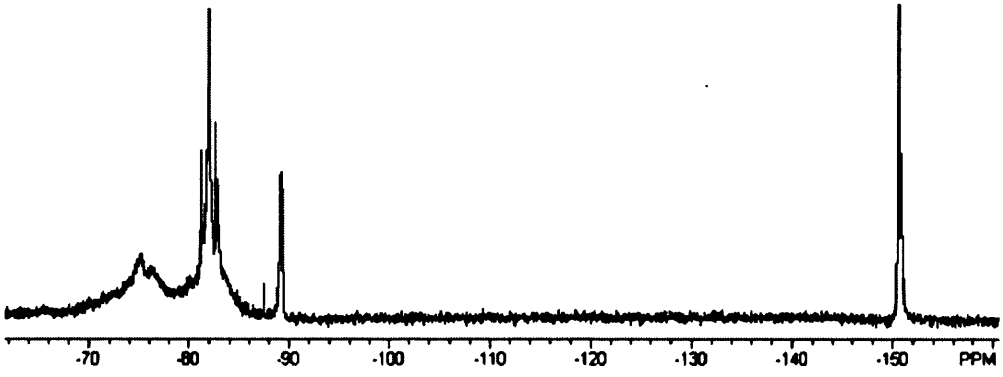


Figure 2-9: $^{31}P\{^1H\}$ NMR spectrum of the reaction of 2.15 and $Mo(CH_3CN)_3(CO)_3$

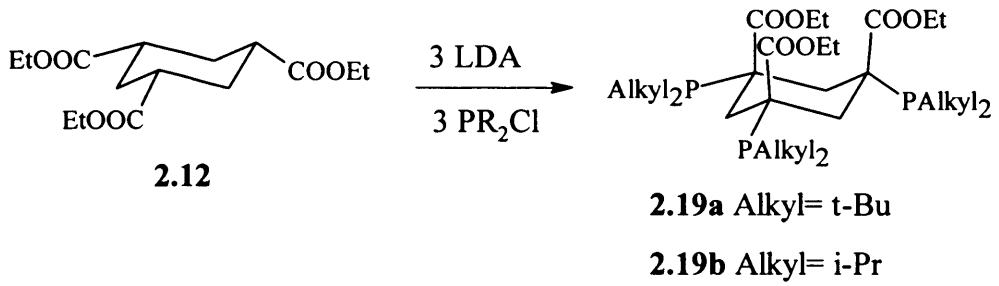
When **2.15** was treated with an equimolar amount of $Mo(C_7H_8)(CO)_3$ in toluene, an off-white precipitate was formed instantly. No signal was observed in the $^{31}P\{^1H\}$ NMR spectrum of the solution, indicating that no species containing phosphorus were present. The white solid was not soluble in any of the common solvents, and the IR spectrum (nujol) showed two bands (ν_{CO}) at 1942 and 1842 cm^{-1} which are characteristic of the presence of the $Mo(CO)_3$ moiety in a compound with approximate C_{3v} symmetry, and a band at assigned to the phosphine group (ν_{PH} 2320 cm^{-1}). These observations are consistent with the ligand **2.15** being coordinated to the molybdenum center but forming polymeric species by bridging molybdenum centres. The IR spectroscopy indicates the complete substitution of the cycloheptatriene ligand but it cannot distinguish whether the three primary phosphine groups coordinated to the metal belong to the same or to different molecules. From these attempts, it appears that **2.15** is not well suited to forming facially capped monomeric $Mo(CO)_3$ complexes.

2.2.5. Attempts to synthesise *cis, cis*-1,3,5-tris(dialkylphosphino)-1,3,5-tris(ethoxycarbonyl)cyclohexane (2.19)

The failure of the synthesis of the tripodal primary phosphine ligand **2.7**, prompted attempts to synthesise dialkylphosphino derivatives of **2.1** by a different approach. The direct reaction of dialkylphosphide anions with a suitable precursor such as **2.6** will likely encounter side reactions (elimination) due to the basic character of the nucleophile. As Mayer has observed for the diarylphosphide, the yield of dialkylphosphino derivatives of **2.1** will be affected, and the purification process can present some problems.[10] In an attempt to avoid competition between the undesirable elimination reaction and nucleophilic substitution, **2.12** was used (Scheme 2-9). Another benefit of using **2.12** is that further modifications can be made to the ester group, allowing access to ligands with different properties.

According to Scheme 2-9, the deprotonation of the triester **2.12** with a sterically hindered base such as LDA, and the subsequent treatment of the trianion with an electrophile such as dialkylchlorophosphine would lead to the desired product. This procedure has already been used to synthesise different compounds with the cyclohexane-

1,3,5-tricarboxylate ester as a scaffold.[11,41] We have attempted these substitutions using different chlorodialkylphosphines as detailed below.



2.12

2.19a Alkyl= t-Bu

2.19b Alkyl= i-Pr

Scheme 2-9: Proposed synthesis of dialkylphosphinocyclohexane derivatives

2.2.5.1. Attempts to synthesise *cis, cis*-1,3,5-tris(di-tert-butylphosphino)-1,3,5-tris(ethoxycarbonyl)cyclohexane (2.19a)

Di-tert-butylchlorophosphine was initially used as the electrophile. According to the literature,[11] the trianion of **2.12** was generated in ether after addition of **2.12** to a cooled solution of LDA (-10°C) which had been prepared *in situ*. After stirring the solution for 2 hours at this temperature, the electrophile was added. The mixture was stirred for a further 2 hours at this temperature, and then was allowed to warm to room temperature and stirred for a further 12 hours. Careful control of the temperature was essential to retain the configuration of the α-carbon atoms.

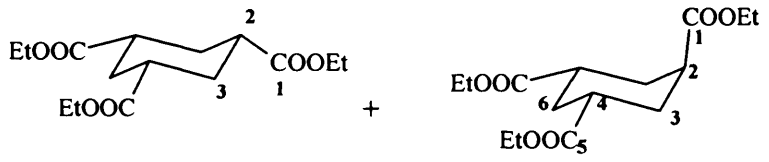
The reaction perfomed with di-tert-butylchlorophosphine was monitored by $^{31}P\{^{1}H\}$NMR spectroscopy. After stirring for 12 hours, only the signal for the di-tert-butylchlorophosphine at δ_P 147.28 ppm was observed in the $^{31}P\{^{1}H\}$NMR spectrum. Longer reaction times did not yield the desired compound.

The reaction was then repeated using THF as the solvent. After the addition of the electrophile, the reaction was refluxed for 48 hours and the $^{31}P\{^{1}H\}$NMR spectrum recorded. The spectrum showed resonances at δ_P 159.14, 151.92, 94,38, 66.54 and 66.93 ppm with a main peak at δ_P -57.8 ppm. It has been reported that **2.1R** compounds resonate downfield with typical values between δ_P 20-31 ppm due to the deshielding influence of the electro-withdrawing group on the phosphorus atom.[13] Therefore, the signal at δ_P -57.8 ppm, cannot be assigned to the compound **2.19a**. Also, the $^{13}C\{^{1}H\}$NMR spectrum of the

crude product showed that predominantly the starting material **2.12** remained, plus other signals which were assigned to the *cis, trans*-triethyl-1,3,5-cyclohexanetricarboxylate **2.20**, formed during the hydrolysis of the trianion of **2.12** (Figure 2-10, Table 2-2). It can be concluded that the sterically hindered *t*-butyl groups are probably too bulky for the incoming nucleophile to approach retarding or completely preventing nucleophilic attack.

Table 2-2: Selected $^{13}C\{^1H\}$ Chemical Shifts of carbons of 2.12 and 2.20

	$^{13}C\{^1H\}$	
	2.12	**2.20**
1	174.55	173.95
2	42.25	37.93
3	30.81	28.71
4		38.6
5		174.57
6		30.86



2.12 **2.20**

Figure 2-10: Mixture of isomers formed after hydrolysis of trianion of 2.12

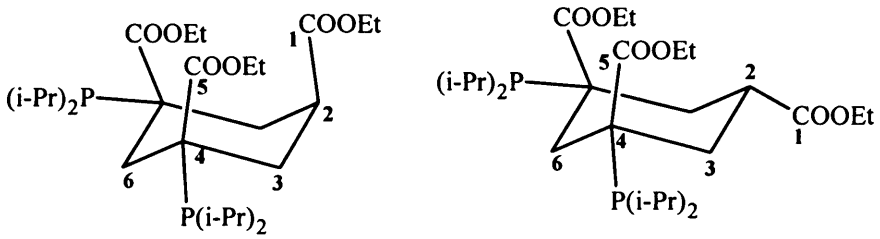
2.2.5.2. Attempts to synthesise *cis, cis*-1,3,5-tris(diisopropylphosphino)-1,3,5-tris(ethoxycarbonyl)cyclohexane (2.19b).

The less sterically hindered chlorodiisopropylphosphine was chosen as an alternative electrophile for synthesis of the tris(dialkylphosphino)cyclohexane derivatives. The procedure starting from **2.12** was as outlined above (section 2.2.7.1, Scheme 2-9). The $^{31}P\{^1H\}$ NMR spectrum of the resulting reaction mixture indicated the formation of

predominantly a compound with a chemical shift at δ_P 38.72 ppm, in addition to other phosphorus containing by-products. However, the $^{13}C\{^1H\}$ NMR spectrum of the mixture did not accord with the pattern expected for the C_{3v} symmetrical compound **2.19b**. The pattern of some of the resonances (a doublet, two triplets and a doublet of doublets at δ_C 30. 81, 35.56, 38.7 and 43.8 ppm; Table 2-3) suggest the formation of the disubstituted bis(diisopropylphosphino)cyclohexane **2.21** with C_S symmetry among other compounds. Two isomers of the di-substituted product **2.21** are possible after hydrolysis step (*cis*-, and *trans*- **2.21**, Figure 2-11), however the spectrum did not allow identification of which were formed.

Table 2-3: Selected $^{13}C\{^1H\}$ Chemical Shifts of carbons of 2.21

	$^{13}C\{^1H\}$	
	δ (ppm)	J (Hz)
2	35.53	t, 9.9
3	30.81	d, 17.2
4	43.8	dd, 30.8, 8
6	38.7	t, 21.8



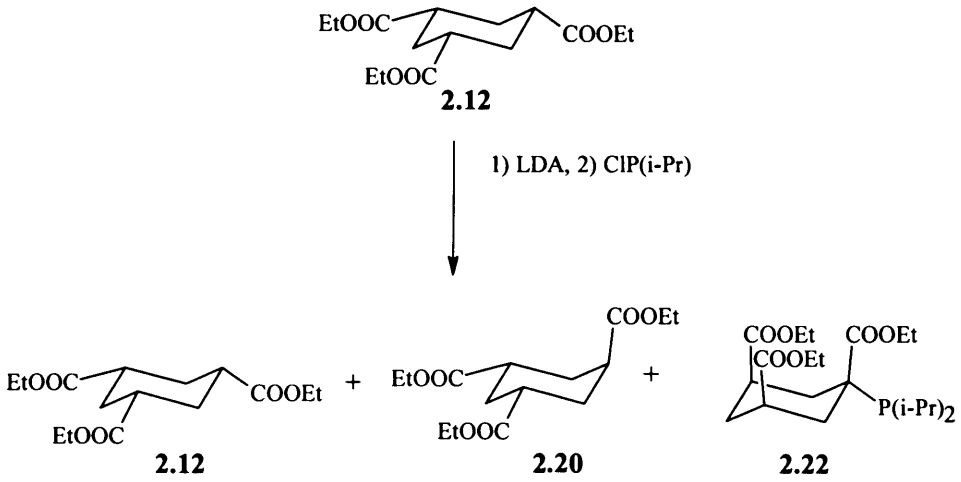
2.21
***cis*-meso**

2.21
***trans*-meso**

Figure 2-11: Possible stereoisomers formed during nucleophilic reaction

The conditions of the reaction were changed to induce the formation of **2.19b**. In order to understand this reaction in more detail, the reaction was performed stepwise and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. **2.12** was treated with one equivalent of LDA at low temperature (-10°C) in diethyl ether and, after formation of the mono-anion, one

equivalent of chlorodiisopropylphosphine was added at this temperature. The $^{31}P\{^{1}H\}$ NMR spectrum of the mixture during the reaction showed two signals at δ_P 150.51 and 44.83 ppm respectively. After hydrolysis, the $^{31}P\{^{1}H\}$ NMR spectrum showed only one signal at δ_P 44.83 ppm. In the $^{13}C\{^{1}H\}$ NMR spectrum of the crude product, three different compounds were observed: the starting material **2.12**, the isomer of the starting material **2.20** and the 1-diisopropylphosphino-1,3,5-tris(ethoxycarbonyl)cyclohexane **2.22** (Scheme 2-10). The presence of compound **2.22** was confirmed by mass spectroscopy. All attempts to separate this mixture by crystallization and/or chromatography failed.

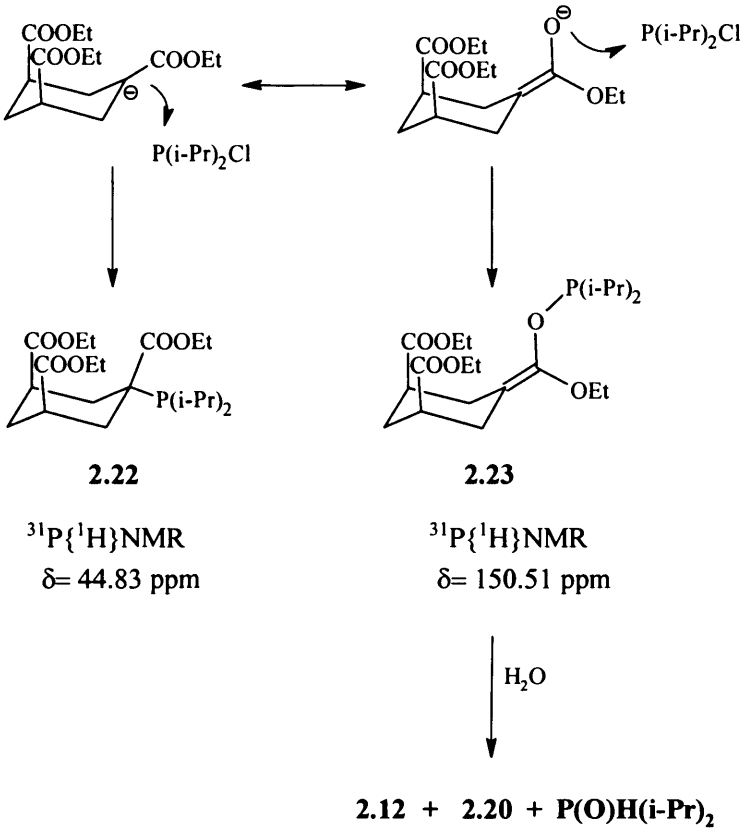


Scheme 2-10: Products obtained during reaction of 2.12 and ClP(i-Pr)$_2$

The data suggest that the compound producing the resonance at δ_P 150.51 ppm is a stable intermediate which competes with the desired reaction, and decomposes during the hydrolysis step leading to the recovery of the starting material **2.12**, the isomerized starting material **2.20**, and di-isopropylphosphineoxide which was detected by $^{31}P\{^{1}H\}$ NMR spectroscopy of the water used in the hydrolysis step.

It has been reported that the reaction of lithio ester enolates in nucleophilic substitution reactions at heteroatoms yield mixtures of C- and O-derivatives.[42] Thus, it is proposed that the intermediate at δ_P 150.51 ppm is the product of O-phosphination of the ester enolate **2.23** (Scheme 2-11). The proposed mechanism of the reaction is outlined in Scheme 2-11. The two resonance forms of the lithium ester enolate lead to the desired product **2.22** and **2.23**. The chemical shift of **2.23** at δ_P 150.51 ppm is consistent with

related phosphinite compounds.[43] The decomposition of the intermediate in the hydrolysis step also explains the formation of **2.23**.



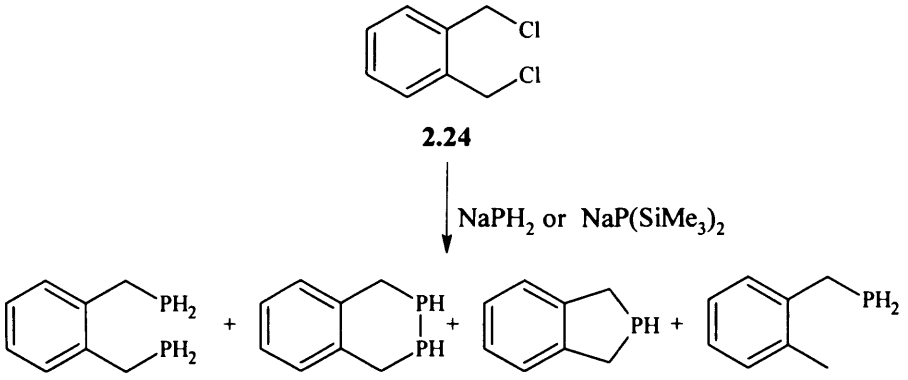
Scheme 2-11: C-Phosphination vs O-Phosphination of the ester enolate

The O-phosphination reaction was not reported by Mayer in the synthesis of the analoguos arylphosphine ligands **2.1R**. Other attempts (i.e refluxing the mixture, or preparing a *tert*-butyldimethyl silane derivative) were made to promote the formation of the C-phosphination compound **2.19b** but none of them lead to a successful result.

It can be summarized that for alkylphosphine derivatives, the synthesis of *cis, cis*-1,3,5-tris(dialkylphosphino)-1,3,5-tris(ethoxycarbonyl)cyclohexane derivatives **2.19** is not feasible using procedures known to be appropriate for R=Ph, presumably because of the steric hindrance of the substitution, electronic features and O-phosphination.

2.2.6. New compounds arising from the use of $NaPH_2$/ $NaP[Si(Me_3)]_2$ in the synthesis of primary phosphines.

Investigation of the potential of $NaPH_2/NaP[Si(Me_3)]_2$ as nucleophilic reagents in the synthesis of primary phosphines as an alternative methodology to the standard methods is of interest. Different substrates were tested with both $NaPH_2/NaP[Si(Me_3)]_2$ reagents. One of the precursors used in these studies was *α,α*-dichloro-*o*-xylene (**2.24**), from which the currently unknown diprimary phosphine 1,2-bis(phosphinomethyl)benzene **2.25** was obtained (Scheme 2-12).[44] By-products were also formed during the reaction, independently of the nucleophile used. Some of these compounds (Scheme 2-12) were isolated and identified as 1,2,3,4-tetrahydro-2,3-benzodiphosphinine (**2.26**), 2,3-dihydro-1H-isophosphindole (**2.27**) and 2-methylbenzylphosphine (**2.28**).

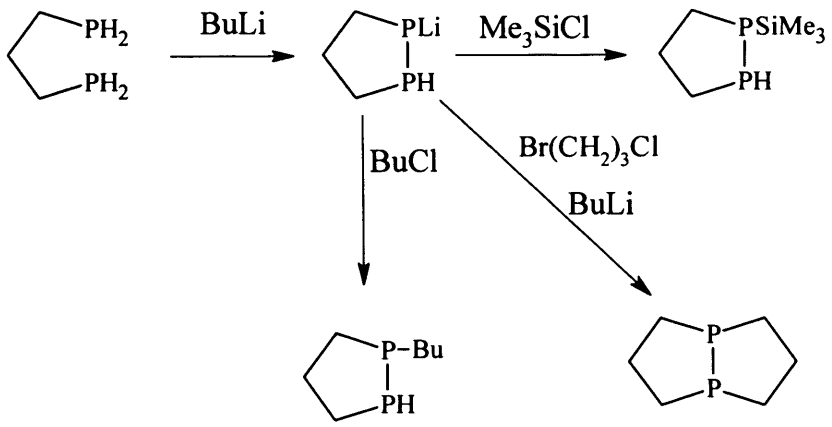


	2.25	**2.26**	**2.27**	**2.28**
$NaPH_2$	20 %	10 %	2 %	5 %
$NaP(SiMe_3)_2$	60 %	10 %	5 %	trace
$^{31}P\{^1H\}$ NMR	-123 ppm	-105 ppm	-59 ppm	-128 ppm

Scheme 2-12

The second major product of the reaction, **2.26**, is also unknown in the literature. Lithium salts of compounds related to **2.26** were initially prepared by Issleib and Thorausch,[45] although they were not isolated (Scheme 2-13). The route, used in those cases, involved the cyclisation of diphosphinopropane with butyllithium at -78°C with evolution of hydrogen. The mono-lithiated diphosphacyclopropane intermediate was

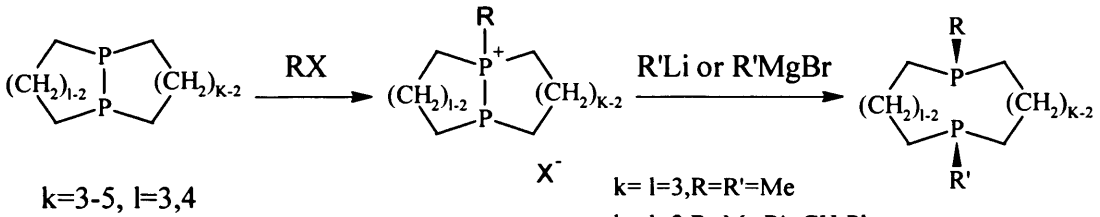
treated *in situ* with alkylating agents leading to new alkylated diphospholan compounds.[45, 46] When 1-bromo-3-chloropropane was used, followed by a further equivalent of butyllithium, the bicyclic diphosphine, *cis*-1,5-diphosphabicyclo[3.3.0]octane, was also obtained.



Scheme 2-13

Alder and co-workers expanded this chemistry effectively to diphosphinobutane and also synthesised several bicyclic diphosphines with various ring sizes (Scheme 2-14).[47-49] The subsequent treatment of the bicyclic diphosphines with haloalkanes allowed the preparation of the mono-quaternised salt which reacted with alkyllithium or Grignard reagents leading to the cleavage of the P-P bond and alkylation of the second phosphorus atom (Scheme 2-14). The resulting products are cyclic 8-, 9- and 10- membered diphosphines with *cis* stereochemistry at the phosphorus atoms. It is known that diphosphine ligands play an important role as chelating ligands in catalysis; however, despite the *cis*- stereochemistry of Alder's compounds, their coordination chemistry remains unexplored.

Although, the fortuitous formation of **2.26** could allow the possibility to expand studies to bicyclic diphosphine compounds and cyclic diphosphines, **2.26** was obtained in low yield. Consequently, the synthesis of **2.26** in higher yields by reaction of $NaP[Si(Me_3)]_2$ with **2.24** was investigated.



k=3-5, l=3,4

k= l=3,R=R'=Me
k= l=3,R=Me R'=CH_2Ph
k= l=3,R=Bz, R'=Ph
k= l=3,R=R'=Bz
k=4 l=3,R=R'=Me
k= l=4,R=R'=Me
k= l=4,R=R'=Bz

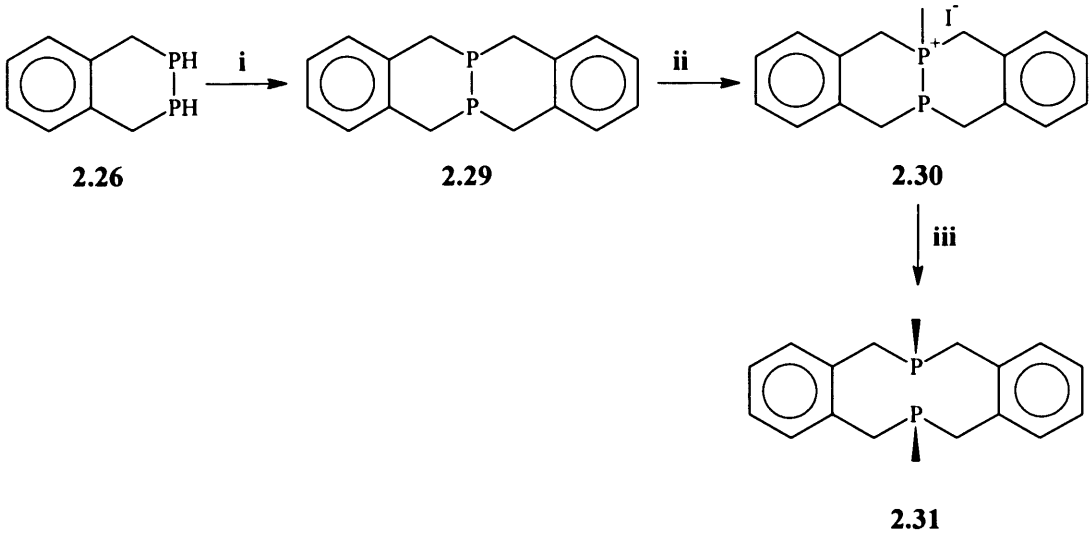
Scheme 2-14

2.2.6.1. Improvements in the synthesis of 1,2,3,4-tetrahydro-2,3-benzodiphosphinine (2.26)

In order to obtain **2.26** selectively, the reaction conditions used to synthesise **2.25** were modified. It was thought that by reversing the order of the addition of the reagents used in the synthesis of **2.25**, **2.26** might be preferentially formed. Therefore, a THF solution of **2.24** was added dropwise to a DME solution of $NaP[Si(Me_3)]_2$ at low temperature (-15°C). After work-up, **2.26** precipitated as a white solid from the crude oil after standing for two days at -35°C. **2.26** was obtained in 31 % yield.

The $^{31}P\{^1H\}$NMR spectrum of **2.26** displays a singlet at δ_P at -106 ppm, however the ^{31}P-^1H coupled NMR spectrum displays a second order pattern and the phosphorus-hydrogen coupling constants could not be determined. The ^1H NMR spectrum of **2.26** displays a broad multiplet between δ_H 2.44-2.91 ppm and an AA'BB' pattern between δ_H 6.97-7.08 ppm for the methylene and aromatic protons respectively. The $^{13}C\{^1H\}$NMR spectrum of **2.26** shows a virtual triplet at δ_C 21.01 ppm ($^1J_{C\text{-}P}$= 10 Hz) for the methylene carbon and three singlets at δ_C 126.64, 127.72 and 137.91 ppm for the aromatic protons. The identity of **2.26** is also confirmed by mass spectroscopy.

2.2.6.2. Medium ring diphosphines from 1,2,3,4-tetrahydro-2,3-benzodiphosphinine



2.26 **2.29** **2.30** **2.31**

i) 1.-*n*-BuLi, α,α'-dichloro-*o*-xylene, THF 2.-*n*-BuLi, ii) MeI, THF, iii) MeLi, Et_2O

Scheme 2-15

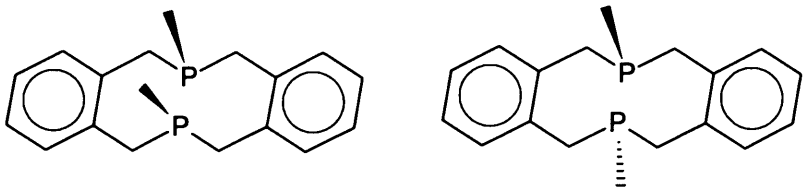
Following the literature procedure,[45,49] **2.26** was treated in THF with one equivalent of butyllithium at low temperature (-78°C). The yellow solution was added dropwise to a cooled solution of α, α'-dichloro-*o*-xylene (**2.24**) in THF. The $^{31}P\{^1H\}$ NMR spectrum of this solution showed two peaks at δ_P -106 and -65.27 ppm indicating the presence of the cyclic mono-alkylated compound. A further equivalent of butyllithium was added at room temperature to promote cyclisation (Scheme 2-15). The bicylic diphosphine **2.29** was then obtained as an air-sensitive white solid in 73 % yield. **2.29** has been characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$NMR spectroscopies. **2.29** displays a singlet at δ_P -65.27 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum of **2.29** shows a multiplet at δ_H 2.56 ppm assigned to the methylene protons and an AA'BB' system at δ_H 6.99-7.12 is attributed to the aromatic protons of **2.29**. The $^{13}C\{^1H\}$NMR spectrum of **2.29** shows a virtual triplet at δ_C 25.33 ppm ($^1J_{C\text{-}P}$= 16 Hz) for the methylene carbons and three singlets at δ_C 126.73, 129.40 and 134.39 ppm for the aromatic carbons.

The stereochemistry of the phosphorus atoms in **2.29** has not been determined since both the *cis*- and *trans*- isomers contain symmetry elements (C_2 axis and mirror plane) which make the phosphorus atoms and the methylene groups indistinguishable and all

attempts to obtain crystals of **2.29** failed. We believe, however, that **2.29** is probably the *cis*- isomer as has been reported for 1,6-diphosphabicyclo[4.4.0]nonane (Scheme 2-14, k=l=4) and related compounds prepared by the same method.[47-49]

The bicyclic diphosphine **2.29** underwent monoquaternisation in quantitative yield with iodomethane in THF (Scheme 2-15). The product, **2.30** precipitated from the THF solution as an air-sensitive white solid. The $^{31}P\{^{1}H\}$ NMR spectrum of **2.30** displays two doublets at δ_P 31.57 and -66.81 ppm with a coupling constant of 292 Hz. The former chemical shift is assigned to the quaternised phosphorus atom whilst the latter is attributed to the tertiary phosphine. Mass spectroscopy also confirms the synthesis of **2.30** with a molecular ion peak at 285 m/z (100%).

2.30 was treated with an excess of MeLi in Et_2O at low temperature. The methyl group is added to the non-quaternised phosphorus in **2.30** and the P-P bond was cleaved yielding a 10-membered cyclic diphosphine **2.31**. **2.31** was obtained after work-up as an air-sensitive white solid in 46 % yield. The $^{31}P\{^{1}H\}$ NMR spectrum of **2.31** shows a singlet at δ_P -22.31 ppm. The ^{1}H NMR spectrum of **2.31** displays a doublet at δ_H 1.35 ppm assigned to the methyl groups ($^{2}J_{H-P}$= 4.4 Hz), and two doublets of doublets at δ_H 2.75 ppm ($^{2}J_{Ha-Ha'}$= 14 Hz, $^{2}J_{Ha-P}$= 4.8 Hz) and 3.15 ppm ($^{2}J_{Ha'-P}$= 6.4 Hz) which are assigned to the diastereotopic methylene protons. The aromatic protons are observed as an AA'BB' system in the aromatic region (δ_H 6.80 and 7.18 ppm). The $^{13}C\{^{1}H\}$ NMR spectrum is also consistent with the formulation of **2.31**, two doublets at δ_C 13.83 ppm ($^{1}J_{C-P}$= 15 Hz) and δ_C 33.61 ppm ($^{1}J_{C-P}$= 17 Hz) are assigned to the methyl and the methylene groups respectively. The three different carbons of the aromatic ring display resonances at δ_C 125.28, 129.95 and 135.25 ppm. In addition, the mass spectrum of **2.31** displays the molecular ion peak at 301m/z (100%). The two possible isomers of **2.31** (Figure 2-12) contain symmetric elements which relate the phosphorus atoms, the methyl group and the methylene groups, therefore the stereochemistry at the phosphorus atoms could not be established by spectroscopic techniques. Attempts to obtain crystals of **2.31** suitable for crystallography failed.



cis-**2.31** *trans*-**2.31**

C_{2v} C_{2h}

Figure 2-12

2.2.6.3. Attempts at complexation of 2,11-dimethyl-2,11-diphospha [3.3]*ortho*cyclophane (2.31)

Studies of complexation were undertaken in order to both establish the stereochemistry of the phosphorus atoms and study the co-ordination chemistry of **2.31**. However, from reactions of **2.31** with $NiCl_2$ in ethanol and $PdCl_2$(COD) in DCM, a red and a yellow precipitate were obtained respectively. No signals were observed in the $^{31}P\{^1H\}$ NMR spectrum of the solution, indicating that no species containing phosphorus were present in solution. The red and yellow precipitates were insoluble in all common organic solvents presumably due to the formation of polymeric species.

It has not been possible to establish the stereochemistry of **2.31**. The conformation of cyclophanes may require changes in order to coordinate a metal[50] and similarly the formation of polymeric species does not necessarily mean a *trans*- configuration in the ligand **2.31**. The ligands may present different conformations if they are co-ordinated or unco-ordinated. It is possible that ligand **2.31** may not have the right conformation for the co-ordination to a mononuclear metallic center. No further studies of co-ordination were performed.

2.3. Conclusion

All attempts to synthesise the tripodal *cis,cis*-1,3,5-triphosphinocyclohexane (**2.7**) have failed. The basicity of the nucleophile ($NaPH_2$) is presumably the reason. Detection of by-products in the olefin region on ^1H NMR spectrum permits to suppose that elimination reactions occur. The use of the presumably less basic $Na(BH_3)PH_2$ did not lead to isolation of the desired product **2.7**.

The tripodal primary phosphine *cis,cis*-1,3,5-tris(phosphinomethyl)cyclohexane (**2.15**) was successfully synthesised by a nucleophilic substitution reaction with $NaPH_2$. Attempts to coordinate **2.15** in a facial disposition to a molybdenum(0) center failed.

The synthesis of various tripodal tertiary phosphine ligands, *cis,cis*-1,3,5-tris(dialkylphosphino)-1,3,5-tris(ethoxycarbonyl)cyclohexane (alkyl= ^{t}Bu, ^{i}Pr) was unsuccessful by procedures known to be approapiate for R=Ph.

A new 10-membered cyclic diphosphine (**2.31**) has been synthesised from the previously unknown 1,2,3,4-tetrahydro-2,3-benzodiphosphinine (**2.26**) following a similar procedure reported by Alder. The co-ordination of **2.26** with Ni(II) and Pd(II) has lead to polymeric species which have not been fully characterized.

2.4. Experimental

2.4.1. General procedures

Unless otherwise stated all manipulations were carried out using standard Schlenck techniques under an atmosphere of dry nitrogen. All solvents were dried and degassed by boiling under reflux over standard drying agents under a nitrogen atmosphere. Where appropriate, deuterated solvents were dried over molecular sieves and freeze-thaw degassed. NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^{1}H) and 125.75 MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz (^{1}H) and 100 MHz (^{13}C), Jeol Lamda Eclipse 300 at 121.65 MHz (^{31}P), 75.57 MHz (^{13}C), 282.78 MHz (^{19}F). ^{1}H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P chemical shifts are quoted in ppm relative to external 85% H_3PO_4. ^{19}F chemical shifts are quoted in ppm relative to external $CFCl_3$. Infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under N_2 as a KBr disk or in solution. Mass spectra of all the samples have been measured by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with a ESCI source. Elemental Analysis was performed by Warwick Analytical Services, University of Warwick.

2.4.2. Synthesis of trisodium phosphide (Na_3P)[51]

Red phosphorus (23.5 g, 0.76 mol) and DME (400 mL) were added to a 1L three necked round bottomed flask under N_2. The mixture was heated without stirring to ca. 60°C. Stirring was commenced and naphthalene (1 g, 8 mmol) and Na (52.3 g, 2.27 mol) (in small pieces) were added over 90 min whereupon a black precipitate slowly developed. The suspension was gently refluxed for 48 h, cooled at room temperature and filtered. The solid was dried under reduced pressure and stored under N_2. The reaction is quantitative.

2.4.3. Synthesis of sodium bis(trimethylsilyl)phosphide [$NaP(SiMe_3)_2$]

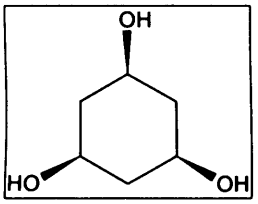
Na_3P (20.93 g, 0.21 mol) and DME (60 mL) were added to a 500 mL three necked round bottomed flask under N_2. The suspension was cooled (-30°C) and Me_3SiCl (53.50 mL, 0.42 mol) in DME (40 mL) was added dropwise. The suspension was allowed to

warm slowly to room temperature yielding a grey coloured suspension. The product was not isolated but analysed by $^{31}P\{^{1}H\}$NMR spectroscopy: -302 ppm ($LiP(SiMe_3)_2$, lit. $^{31}P\{^{1}H\}$NMR: -302 ppm).[28]

2.4.4. Synthesis of sodium phosphide ($NaPH_2$)

Na_3P (12.09 g, 0.12 mol) was added to a 500 mL three necked round bottomed flask fitted with a solid addition flask and a cold-finger condenser under N_2. The flask was cooled to -78°C and ca. 150 ml of NH_3(l) was condensed. NH_4Cl (12.92g, 0.2 mol) contained in a solid addition flask was added slowly to the suspension with efficient stirring. Once the Na_3P and NH_4Cl had started to react, the solution became thicker and the colour changed to reddish finally yielding a green-yellowish solution. The reaction was stirred for a minimum of 1 hr before the alkylating agent was added. The product was characterised in situ by $^{31}P\{^{1}H\}$NMR spectroscopy [$^{31}P\{^{1}H\}$NMR (D_2O external reference): -297 ppm ($NaPH_2$, lit.[27] $^{31}P\{^{1}H\}$NMR: -302 ppm).

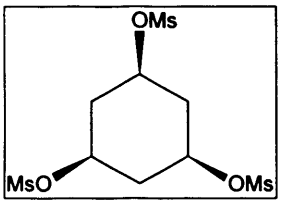
2.4.5. Synthesis of *cis*-phloroglucit (*cis*-2.5)



This compound was prepared by a modification of the procedure reported in the literature.[29] A suspension of phloroglucinol-dihydrate (15 g, 0.11 mol) in absolute ethanol (100 mL) was hydrogenated by using Raney-Ni (3.5 g) as catalyst. The hydrogenation was performed at 375 psi in an autoclave held at 50°C and with stirring. After 24 hrs, the pressure had decreased by ~270 psi. The catalyst was filtered from the otherwise homogeneous solution, and the solution kept in the freezer overnight to precipitate *cis*-phloroglucit. Recrystallization of *cis*-cyclohexane-1,3,5-triol from dioxane gave white crystals (5.326 g, 43%). Spectroscopic and physical properties agree with those reported.

^{1}H NMR δ ppm (MeOD): 1.15 (q, 3H, $^{2}J_{HaHe}$= 11.6, $^{3}J_{HaHx}$= 11.6 Hz, C**H**$_a$H$_e$), 2.17 (dt, 3H, $^{3}J_{CHe-CH}$= 4 Hz, CH$_a$**H**$_e$), 3.54 (tt, 3H, CH), 4.90 (s br, 3H, OH). $^{13}C\{^{1}H\}$ NMR δ ppm (MeOD): 44.86 (**C**H$_2$), 66.51 (**C**H).

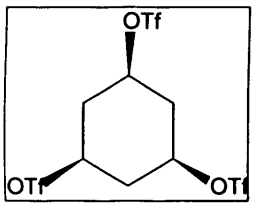
2.4.6. Synthesis of *cis, cis*-1,3,5-tris(methanosulphonate)cyclohexane (2.6a)



A suspension of *cis*-cyclohexane-1,3,5-triol (2.4g, 0.018 mol) in pyridine (75 mL) was cooled (0°C) in an ice-water bath. Methanosulphonate chloride (6.35 mL, 0.082 mol) was then added slowly. The solution was stirred for 15 hrs at room temperature, after which time it was added to ice. Once the ice had melted, the precipitate was filtered and **2.6a** was obtained as a white solid (4.09g, 62%).

^{1}H NMR δ ppm (DMSO): 1.79 (q, 3H, $^2J_{Ha\text{-}He}$= 11.2 Hz, $^3J_{CHa\text{-}CH}$= 11.2 Hz, C**H$_a$**H$_e$), 2.40 (dt, 3H, $^3J_{CHe\text{-}CH}$= 4.4 Hz, CH$_a$**H$_e$**), 3.25(s, 9H, CH_3), 4.72 (tt, 3H, C**H**). ^{13}C {^{1}H} NMR δ ppm (DMSO): 37.26 (**C**H$_2$), 37.85 (**C**H$_3$), 73.14 (**C**H). IR (KBr): ν(C-H)$_{st}$ 2945 s cm^{-1} ν(S=O)$_{st}$ 1363 s, 1332 s, 1172 s cm^{-1}. Anal Calc. for $C_9H_{18}O_9S_3$ (366.42): C, 29.49; H, 4.95. Found: C, 29.44; H, 4.89 %.

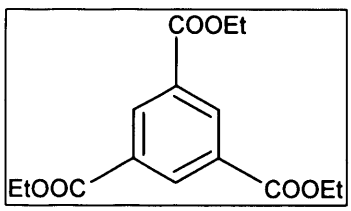
2.4.7. Synthesis of *cis, cis*-1,3,5-tris(trifluorosulphonate)cyclohexane (2.6b)



A solution of triflic anhydride (4.6 mL, 27.39mmol) in CH_2Cl_2 (15 mL) was added slowly to a suspension of *cis*-cyclohexane-1,3,5-triol (1 g, 7.57mmol) and pyridine (1.9 mL, 23.95 mmol) in CH_2Cl_2 (15 mL) at 0°C. After stirring the solution for 1.5 hrs at 0°C, the precipitate was filtered, and the solution passed through a column of silica gel. Removal of the solvent under reduced pressure afforded *cis, cis*-1,3,5-tris(triflate)cyclohexane as a white solid (2.7 g, 85 %) which decomposes within days at room temperature.

^{1}H NMR δ ppm ($CDCl_3$): 2.26 (d t, 3H, $^2J_{HaHe}$= 13.2 Hz, $^3J_{CHa\text{-}CH}$= 9.6 Hz, C**H$_a$**H$_e$), 2.61 (dt, 3H, $^3J_{CHe\text{-}CH}$= 4.4 Hz, CH$_a$**H$_e$**), 4.97 (tt, 3H, C**H**). ^{13}C{^{1}H} NMR δ ppm ($CDCl_3$): 36.5 (**C**H$_2$), 77.5 (**C**H), 118.3 (q, $J_{C\text{-}F}$= 319.8 Hz, **C**F$_3$). ^{19}F NMR δ ppm ($CDCl_3$): -74.9 (s, CF_3). Anal Calc. for $C_9H_9F_9O_9S_3$ (528.34): C, 20.46; H, 1.72. Found: C, 20.29; H, 1.57 %.

2.4.8. Synthesis of triethyl benzene-1,3,5-tricarboxylate (2.11)

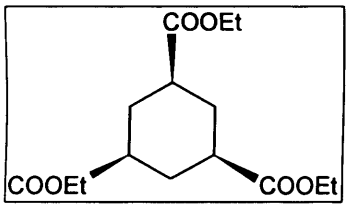


This compound was prepared in a manner similar to that reported in the literature.[37] A mixture of trimesic acid (30 g,

0.143 mol), absolute ethanol (600 mL) and sulphuric acid (120 mL) were refluxed for 12 hrs. Addition of water (600 mL) yielded a white precipitate which was filtered. The solid was dissolved in CH_2Cl_2 (250 mL), and the solution washed with a saturated solution of $NaHCO_3$ (2 x 150 ml) and subsequently washed with water (2 x 100 ml). The organic solution was then dried over $MgSO_4$, filtered and evaporated to yield a white solid. (34.45g, 82 %).

^{1}H NMR δ ppm ($CDCl_3$): 1.43 (t, 9H, $^3J_{CH3\text{-}CH2}$= 7.2 Hz, C**H**$_3$), 4.43 (q, 6H, C**H**$_2$), 8.84 (s, 3H, C**H**). $^{13}C\{^1H\}$ NMR δ ppm ($CDCl_3$): 14.70 (**C**H_3), 62.11 (**C**H_2), 134.68 (**C**H), 131.79(**C**), 165.46 (**C**O).

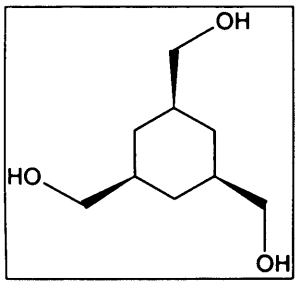
2.4.9. Synthesis of *cis, cis*-triethyl 1,3,5-cyclohexanetricarboxylate (2.12)



This compound was prepared by a modification of the procedure reported in the literature.[37] A suspension of triethyl trimesate (8.06 g, 0.027 mol) in acetic (80 mL) acid was hydrogenated by using PtO_2 (0.397 g) as catalyst. The hydrogenation was performed at 375 psi in an autoclave with heating at 50°C and stirring. After 24 hrs, the pressure had decreased to ~ 65 psi. Filtration of the catalyst through celite, followed by concentration to remove volatiles gave a yellow oil which was dissolved in CH_2Cl_2 (50 mL), and washed with a saturated solution of $NaHCO_3$ (2 x 50 ml) and followed by water (2 x 50 ml). The organic solution was dried over $MgSO_4$, filtered and evaporated yielding a white solid (8.05 g, 98 %).

^{1}H NMR δ ppm ($CDCl_3$): 1.24 (t, 9H, $^3J_{CH3\text{-}CH2}$= 6.8 Hz, C**H**$_3$), 1.52 (q, 3H, $^2J_{CHa\text{-}He}$= 12.8 Hz, $^3J_{CHa\text{-}CH}$= 12.8 Hz, C**H**$_a$H$_e$), 2.24 (dt, 3H, $^3J_{CHe\text{-}CH}$=3.2 Hz, CH$_a$**H**$_e$), 2.36 (tt, 3H, C**H**), 4.12 (q, 6H, C**H**$_2$). $^{13}C\{^1H\}$ NMR δ ppm ($CDCl_3$): 14.54 (s, **C**H_3), 61.02 (**C**H_2CH$_3$), 30.81 (Cy-**C**H_2), 42.25(**C**H), 174.55 (**C**O).

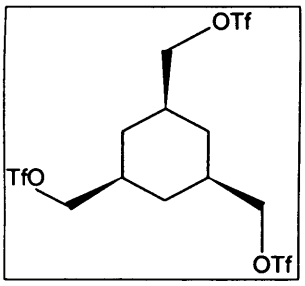
2.4.10. Synthesis of *cis, cis*-1,3,5-tris(hydroxymethyl)cyclohexane (2.13)



A solution of *cis,cis*-triethyl-1,3,5-cyclohexanetricarboxylate (7.78 g, 0.026 mol) in diethyl ether (50 mL) was added dropwise with stirring to a suspension of lithium aluminium hydride (4.49 g, 0.118 mol) in diethyl ether (175 mL) at 0°C.[37] After the addition was complete, the mixture was heated under reflux for 20 hrs. The mixture was cooled to 0°C and water (40 mL) was added dropwise, followed by the dropwise addition of EtOH (100 mL). The mixture was filtered, and the solid was washed with ethanol. The solid was extracted with boiling ethanol (2 x 50 mL). The filtrate and the combined extracts were concentrated leaving a white solid that was extracted with boiling dioxane (2 x 100 mL). The combined extracts were concentrated to a volume of 20 ml and cooled to give a white solid (3.6 g, 80 %).

^{1}H NMR δ ppm (d_4-MeOD): 0.57 (q, 3H, $^2J_{CHaHe}$=12.4 Hz, $^3J_{CHaCH}$=12.4 Hz, C**H$_a$**H$_e$), 1.51 (m, 3H, $^3J_{CH\text{-}CH2}$=6.4 Hz, C**H**), 1,87 (d, 3H, CH$_a$**H$_e$**), 3.40 (d, 6H, CH_2), 4.9 (s, 3H, OH) – ^{13}C{^{1}H} NMR δ ppm (d_4-MeOD): 34.29 (Cy-**C**H$_2$), 41.30 (**C**H), 69.15 (**C**H$_2$).

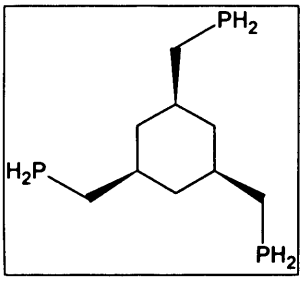
2.4.11. Synthesis of *cis, cis*-1,3,5-tris[(trifluorometahanosulphonate)methyl] cyclohexane (2.14)



Triflic anhydride (3.4 mL, 20.1 mmol) was slowly added to a cooled suspension of *cis,cis*-1,3,5-tris(hydroxymethyl)-cyclohexane (1.0 g, 5.74 mmol) and 1.4 ml of pyridine (17.22 mmol) in DCM (40 mL) at 0°C. The mixture was stirred for 3 hrs. Subsequently the mixture was passed through a silica column and the solvent removed yielding a white solid (1.3 g, 40 %).

^{1}H NMR δ ppm ($CDCl_3$): 0.95 (q, $^2J_{HaHe}$=12.4 Hz, $^3J_{CHaCH}$=12.4 Hz, 3H, C**H$_a$**H$_e$), 1.96 (d, 3H, CH$_a$**H$_e$**), 2.03 (m, 3H, C**H**CH$_2$), 4.40 (d, 6H, $^3J_{CH2\text{-}CH}$=5.6 Hz, C**H$_2$**OTf). ^{13}C{^{1}H} NMR δ ppm ($CDCl_3$): 30.1 (s, Cy-**C**H$_2$), 36.1 (s, **C**H), 79.7 (s, **C**H$_2$OTf), 118.55 (q, $^1J_{C\text{-}F}$=319.5 Hz, **C**F$_3$)). ^{19}F NMR δ ppm ($CDCl_3$): -74.3 (s, **C**F$_3$)

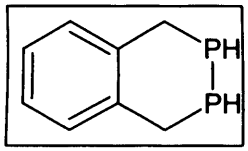
2.4.12. Synthesis of *cis, cis*-1,3,5-tris(phosphinomethyl)cyclohexane (2.15)



A solution of *cis, cis*-1,3,5-tris[(trifluorosulphonate)methyl]cyclohexane (1.299 g, 2.28 mmol) in diethyl ether (20 mL) was added slowly to a cooled solution (-78°C) of $NaPH_2$ prepared *in situ* [NH_4Cl (0.95 g, 17.8 mmol), Na_3P (0.88 g, 8.8 mmol), liquid NH_3 (60 mL)]. The mixture was stirred for 5 hrs at -78°C, then at room temperature for 12 hrs. The solution was filtered, and the solvent evaporated yielding a colourless liquid (0.39 g, 77 %).

^1H NMR δ ppm ($CDCl_3$): 0.60 (q, 3H, $^2J_{HaHe}$=12 Hz, $^3J_{CHa-CH}$=12 Hz, C**H**$_a$H$_e$), 1.41 (m, 3H, $^3J_{CH-CH2}$=7.2 Hz, $^3J_{CH-CHe}$=3 Hz, $^3J_{CH-P}$=-6.3 Hz, C**H**), 1.53 (m, 6H, $^2J_{CH2-P}$=3.2 Hz, $^3J_{CH2-PH2}$=7.2 Hz, C**H**$_2$), 1.98 (d, 3H, CH$_a$**H**$_e$), 2.70 (dt, 3H, $^1J_{H-P}$=196 Hz, P**H**$_2$). $^{13}C\{^1H\}$ NMR δ ppm ($CDCl_3$): 20.8 (d, $^1J_{C-P}$=8.7 Hz, **C**H$_2$PH$_2$), 39.2 (d, $^2J_{C-P}$=4.9 Hz, **C**H), 40.6 (t, $^3J_{C-P}$=5.4 Hz, Cy-**C**H$_2$). $^{31}P\{^1H\}$ NMR δ ppm ($CDCl_3$): -149.14 (**P**H$_2$). IR (film): ν(P-H) 2289 s cm^{-1}. MS (APCI): m/z 223 (100 %, $[M+1]^+$).

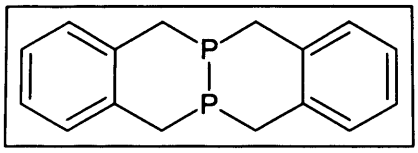
2.4.13. Synthesis of 1,2,3,4-tetrahydro-2,3-benzodiphosphinine (2.26)



A solution of *α,α'*-dichloro-*o*-xylene (14.20 g, 0.08 mol) in DME (40 mL) was added to a cooled solution (-15°C) of $NaP(SiMe_3)_2$ prepared *in situ* [Na_3P (23.22 g, 0.23 mol), Me_3SiCl (59.37 mL, 0.46 mol) see 2.4.3 section]. The reaction mixture was stirred at this temperature for 1 hour, then the bath was removed and the reaction was allowed to stir for one day. It was then cooled again in iced water and hydrolysed by careful addition of water (20 mL), the solution was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to leave an oily residue. A white solid precipitated after holding the oil at -35°C for 2 days. The solid was filtered while cold, washed with cold petroleum ether (2 x 10 mL), and cold methanol (2 x 10 mL). Petroleum ether (10 mL) was added to the oily residue and the solution kept to -35°C and more solid precipitated and the same procedure was repeated until all the product had precipitated. (combined yield; 4.3 g, 31 %).

^{1}H NMR δ ppm ($CDCl_3$): 2.44-2.91 (m, 6H, P**H**, C**H$_2$**), 6.97-7.08 (m, 4H, AA'BB' system, Aryl-C**H**). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): 21.01 (t, $^1J_{C-P}$= 10 Hz, **C**H$_2$), 126.64 (Aryl-**C**H), 127.72 (Aryl-**C**H), 137.91 (Aryl-**C**). ^{31}P{^{1}H}NMR δ ppm ($CDCl_3$): -106. IR (KBr): ν(ArC-H) 3056 w cm^{-1}, ν(P-H) 2271 s cm^{-1}, ν(ArC-C) 1471 s cm^{-1}, ν(P-C) 751 s cm^{-1}. MS (ES): m/z 169 (100 %, [M+1]$^+$).

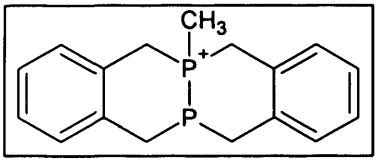
2.4.14. Synthesis of [c,h]-dibenzo-1,6-diphosphabicyclo[4.4.0]decane (2.29)



A solution of **2.26** (0.512 g, 3 mmol) in THF (30 mL), cooled to -78°C, was treated with a solution of *n*-butyllithium in hexanes (2.04 M, 1.5 mL, 3 mmol). The golden coloured reaction mixture was stirred for 5 minutes at this temperature, followed by a further 5 minutes at room temperature. The resultant mixture was slowly transferred to a Schlenck flask containing a stirred solution of *α,α'*-dichloro-*o*-xylene (0.537 g, 3 mmol) in THF (30 mL), cooled to -78°C. After warming to room temperature, the resulting colourless solution was treated with a solution of *n*-butyllithium in hexanes (2.04 M, 1.5 mL, 3 mmol). The solution was stirred (10 minutes) and then all the volatile materials were removed *in vacuo* to leave a white solid residue. DCM (60 mL) was added and the solution filtered. The solvent was removed and the white solid remaining was washed with cold petroleum ether (10 mL) and cold methanol (10 mL). **2.29** was obtained as an air-sensitive white solid (0.601g, 73%).

^{1}H NMR δ ppm ($CDCl_3$): 2.56 (m, 8H, C**H$_2$**), 6.99-7.12 (m, 8H, AA'BB' system, Aryl-C**H**). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): 25.33 (t, $^1J_{C-P}$= 16 Hz, **C**H$_2$), 126.73 (s, Aryl-**C**H), 129.40 (s, Aryl-**C**H), 134.39 (s, Aryl-**C**). ^{31}P{^{1}H}NMR δ ppm ($CDCl_3$): -65.27. IR (KBr): ν(ArC-H) 3060 w cm^{-1}, ν(ArC-C) 1483 s cm^{-1}, ν(P-C) 751 s cm^{-1}. MS (APCl): m/z 327 (100%, [M+CH_3CN+O]$^+$), 271 (15%, [M+1]$^+$].

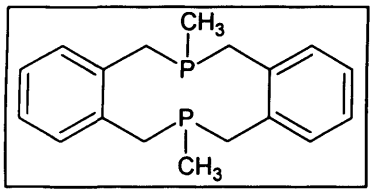
2.4.15. Synthesis of [c,h]-dibenzo-1-methyl-1-phosphonia-6-phosphabicyclo-[4.4.0]decane iodide (2.30)



A solution of **2.29** (0.6 g, 3 mmol) in THF (80 mL) was treated with methyl iodide (1mL, 16 mmol). The reaction mixture was stirred for 12 hr., during which time a white precipitate formed. All volatile materials were removed *in vacuo* to leave a white solid in nearly quantitative yield which was used without further purification.

$^{31}P\{^{1}H\}$NMR δ ppm ($CDCl_3$): -66.81 (d, $^{1}J_{P1\text{-}P2}$=292 Hz, **P**), 31.57 (d, **P**Me). MS (ES+): m/z 285 (100%, $[M]^+$).

2.4.16. Synthesis of 2,11-dimethyl-2,11-diphospha [3.3]*ortho*cyclophane (2.31)



A suspension of **2.30** (0.915, 2 mmol) in Et_2O (20 mL) cooled to -78 °C was treated with an excess of a solution of methyllithium in Et_2O (1.6 M, 3 mL, 5 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 hr. to leave a golden coloured solution, which was hydrolysed with degassed water (1 mL). The solution was then dried with $MgSO_4$ and filtered. All the volatile materials were removed *in vacuo* yielding a white solid (0.306 g, 46%).

^{1}H NMR δ ppm ($CDCl_3$): 1.35 (d, 6H, $^{2}J_{H\text{-}P}$= 4.4 Hz, C**H**$_3$), 2.75 (dd, 4H, $^{2}J_{Ha\text{-}Ha'}$= 14 Hz, $^{2}J_{Ha\text{-}P}$= 4.8 Hz, C**H**$_a$H$_{a'}$), 3.15 (dd, 4H, $^{2}J_{Ha'\text{-}P}$= 6.4 Hz, CH$_a$**H**$_{a'}$), 6.80 (m, 4H, Aryl-C**H**), 7.18 (m, 4H, Aryl-C**H**). $^{13}C\{^{1}H\}$NMR δ ppm ($CDCl_3$): 13.83 (d, $^{1}J_{C\text{-}P}$= 15 Hz, **C**H$_3$), 33.61 (d, $^{1}J_{C\text{-}P}$= 17 Hz, **C**H$_2$), 125.28 (s, Aryl-**C**H), 129.95 (d, $J_{C\text{-}P}$= 13 Hz, Aryl-**C**H), 135.25 (s, Aryl-**C**). $^{31}P\{^{1}H\}$NMR δ ppm ($CDCl_3$): -22.31. IR (KBr): ν(ArC-H) 3056 w cm^{-1}, ν(ArC-C) 1488 s cm^{-1}. MS (APCl): m/z 301 (100%, $[M+1]^+$).

2.5. References

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Chapter 3:

SYNTHESIS OF LINEAR P,N MIXED TRIDENATE LIGANDS AND COORDINATION CHEMISTRY

3.1. Introduction

3.1.1. Hybrid ligands

Hybrid ligands are interesting polydentate ligands which have been extensively studied.[1-3] By definition, these ligands contain at least two different types of donor atom capable of binding to one or more metal centers. These functionalities are often chosen to be very different to each other in order to combine different properties within the same molecule which will impact on the properties of the resulting complexes. Hybrid ligands with hard and soft donor atoms combined in the same molecule can give rise to the so called hemilabile ligands. An important feature of hemilabile ligands (and the meaning of the term) is that while one donor atom remains coordinated to a metal, the other donor atom can reversibly dissociate from the metal center creating a vacant site on the metal coordination sphere (Figure 3-1). This reversible association-dissociation reaction has made hemilabile ligands of interest in catalysis. In principle, a hemilabile ligand may support a co-ordinatively saturated ground state complex whilst allowing formation of unsaturated intermediates or activated complexes required during catalysis by reversible dissociation of only one part of the ligand. The proximity of the resultant pendant donor favours re-formation of the ground state chelate, rather than complete loss of a monodentate ligand (and further dissociation of other monodentate spectator ligands). Thus, it is conceived that hemilabile ligands may stabilise catalytic systems whilst supporting the reaction steps and activated complexes required in catalysis. This would be expected to result in benefits of greater catalyst activity (longevity) and possibly selectivity. The potential of hemilabile ligands has been exploited giving excellent results in catalytic reactions including hydrogenation, carbonylation, hydroformylation, olefin copolymerization and others.[1]

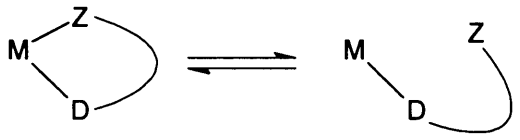
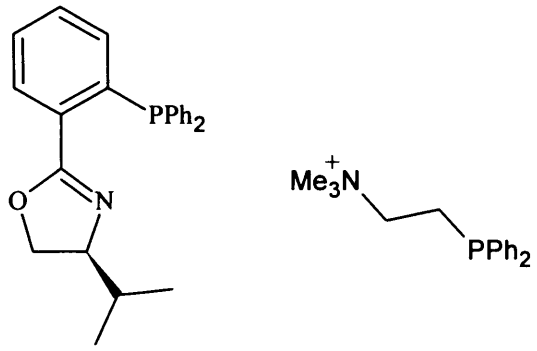


Figure 3-1: Hemilabile behaviour of a hybrid ligand

3.1.2. P, N-mixed ligands

Ligands containing both phosphorus and nitrogen atoms are one of the most commonly studied hybrid ligands systems.[3] Amines, pyridines and oxazolines are some of the functional groups which provide the nitrogen donor, whilst the phosphorus donor is generally provided by phosphine groups, most typically as aryl phosphine functions (PAr_2). P, N-mixed ligands have also found multiple applications in catalysis, for example a ruthenium complex of the chiral phosphinooxazoline ligand (**3.1**) (Figure 3-2) has been used as a catalyst in transfer hydrogenation with notable results for aliphatic ketones.[4]



3.1 **3.2**

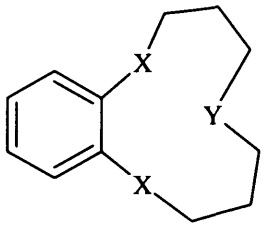
Figure 3-2

Another benefit of P,N-mixed ligands is that, by quaternization of the nitrogen donor, these ligands possess water-soluble properties and their catalytic applications can be extended to biphasic systems.[5-7] For instance, the Amphos ligand **3.2,** has been used with rhodium(I) in olefin hydrogenation and hydroformylation reactions in biphasic systems.[8] Quaternization of the nitrogen functionality results in loss of the hemilabile behaviour of the ligand, but allows manipulations and enhancement of solubility in polar solvents. Another potentially important benefit of ligands bearing different donors is that different electronic effects of the different donors may be exploited. For example, the ability to vary trans effects of the two ends of a chelate donor may influence reactivity and selectivity of the resulting complexes. This approach may be tested with P-N chelates since phosphines are known to have a high trans effect whilst amines have a low trans effect. In this context,

relatively non-labile ligands would be an advantage although this is diametrically opposed to the common principles of hemi-lability. An approach to minimising hemi-lability would be to incorporate the various donors into a macrocycle, thus maximising the robustness of the metal-ligand interaction.

3.1.3. Macrocyclic ligands containing phosphorus and other donors

Macrocyclic chemistry has also contributed in the hybrid ligand field by through the development of cycles containing different functionalities. Tridentate 11-membered macrocycles containing a combination of phosphorus atoms with other donors such sulphur, nitrogen, oxygen, and arsenic have been developed mostly by Kyba by cycloaddition reactions under high dilution conditions (Figure 3-3).[9]



entry	X	Y
1	PPh	S
2	PPh	O
3	PPh	NMe
4	PPh	NPh
5	S	PPh

Figure 3-3: Tridentate 11-membered rings containing phosphorus synthesised by Kyba.

In contrast, Edwards' group have employed template methods for the synthesis of various phosphorus and arsenic mixed tridentate macrocycles mostly containing tribenzannulated backbone function on a CpFe(II) fragment (Figure 3-4).[10-12]

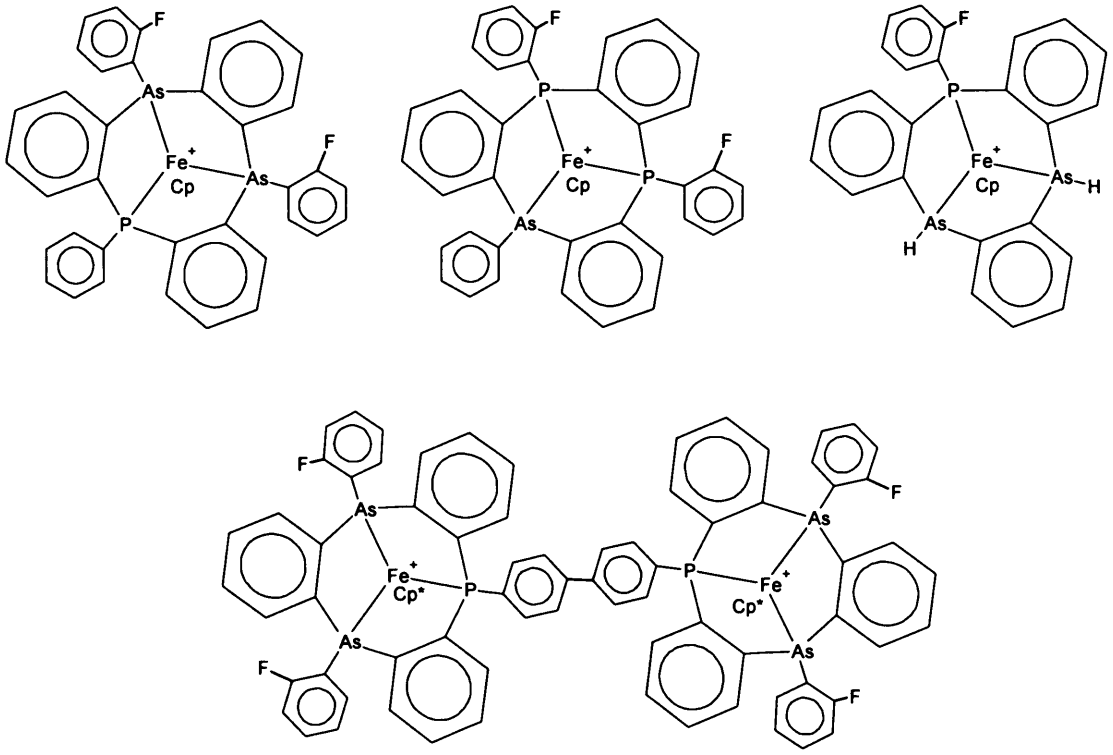


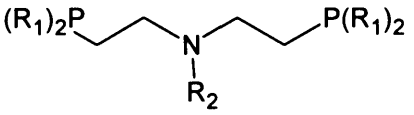
Figure 3-4: Phosphorus and arsenic mixed macrocycles

3.1.4. Aims

For all the large number of application of P, N mixed donor acyclic ligands to date, only two P, N-mixed tridentate macrocycles have been reported in the literature (Figure 3-3, entry 3 and 4).[9] Which from studies with different metals, the resulting complexes display bidentate and tridentate coordination modes in octahedral and square-pyramidal geometries.[13-15] However, no studies of reactivity with small molecules have been performed to evaluate any potential hemilabile behaviour of the P, N-mixed macrocycles.

Template methods have been used to synthesise P, N-mixed tetradentate macrocycles,[16] although this procedure has not been attempted for tridentate macrocycles. An additional benefit of using nitrogen donors in the template macrocyclic backbone may be that demetallation of the macrocycle can be facilitated by both the possible hemilabile behaviour and by quaternization of the nitrogen with acid,[17] the latter method having been used for demetallation of several nitrogen containing macrocycles from their templates.[18, 19]

Since the first synthesis of bis(2-diphenylphosphinoethyl)amine by Sacconi and co-workers,[20] several derivatives of PNP-type ligands have been synthesised using similar routes (Figure 3-5).[21, 22] PNP-type ligands form complexes with most of the d-block metals and hemilabile behaviour has been observed in some of these complexes.[17, 21, 23-28] In addition, chromium complexes of PNP-type ligands synthesised in our group have manifested high selectivity and activity for ethylene trimerization reactions.[29]



PNP ligands

Figure 3-5: General skeleton for PNP-type ligands

With this in mind, it was proposed to synthesise by template methods a P,N,P-mixed macrocycle from the primary phosphine analogue of Sacconi's compound. The pre-organization of the ligand on the metal coordination sphere would help the cyclisation reaction by bonding the two terminal phosphines with a linker, providing a perfect strategy for the synthesis of different macrocycles with both different ring sizes and backbone structures.

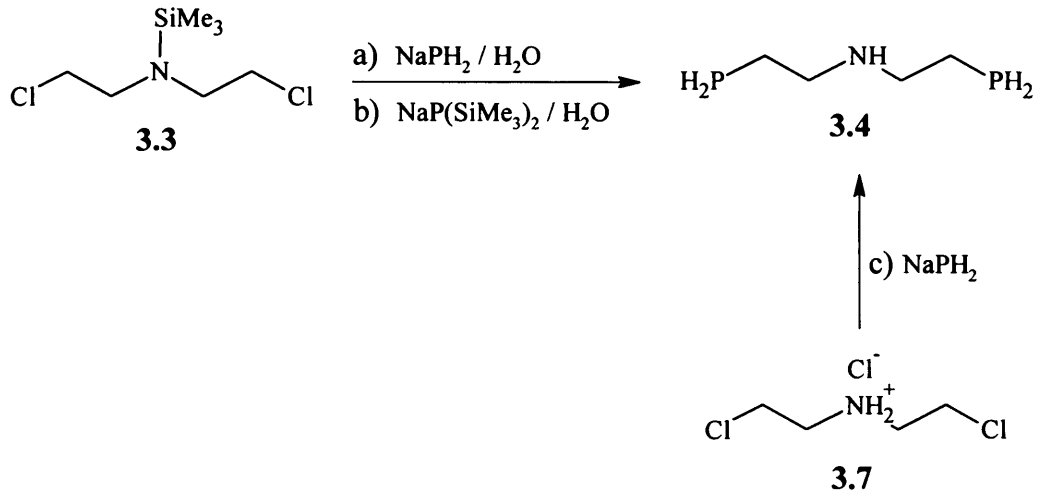
3.2. Results and discussion

3.2.1. Synthesis of bis(2-phosphinoethyl)amine (PNP) (3.4)

In order to study the template synthesis of macrocycles by cyclisation of linear phosphorus-nitrogen mixed tridentate ligands, the compound bis(2-phosphinoethyl)amine (**3.4**) was required. Stelzer and co-workers have already synthesised **3.4** as well as other N-alkyl substituted bis(2-phosphinoethyl)alkylamine derivatives.[6] Their synthesis involves the generation of potassium phosphide by the adsorption of phosphine gas into a superbasic medium of DMSO/KOH followed by treatment with the respective bis(2-chloroethyl)amine derivative giving reasonable to good yields. However, the very

demanding set-up and use of phosphine are inconvenient and restrict the availability of this compound.

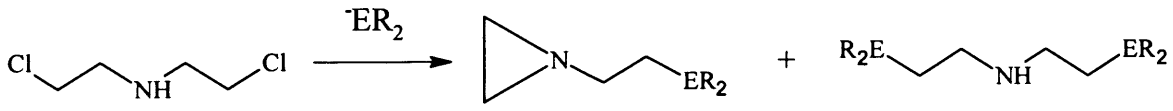
Therefore, studies of the synthesis of primary phosphines have continued to explore different approaches to the synthesis of **3.4** that avoid the use of phosphine gas. These methods, outlined in Scheme 3-1, involve the use of bis(2-chloroethyl)trimethylsilylamine (**3.3**) or the hydrochloride derivative of bis(2-chloroethyl)amine (**3.7**) as electrophiles, together with sodium phosphide or sodium bis(trimethylsilyl)phosphide as nucleophiles.



Scheme 3-1: Different methods attempted for the synthesis of 3.4

3.2.1.1. Synthesis of 3.4 with bis(2-chloroethyl)trimethylsilylamine as electrophile (methods a and b)

Previous studies in our group have shown that the reaction of bis-(2-haloalkyl)amines with alkylphosphido or arsenido anions lead to the formation of the desired disubstituted compound as well as the phosphino- or arsenido- aziridines as by-products with yields dependent on the nucleophilicity of the anion used (Scheme 3-2).[30]

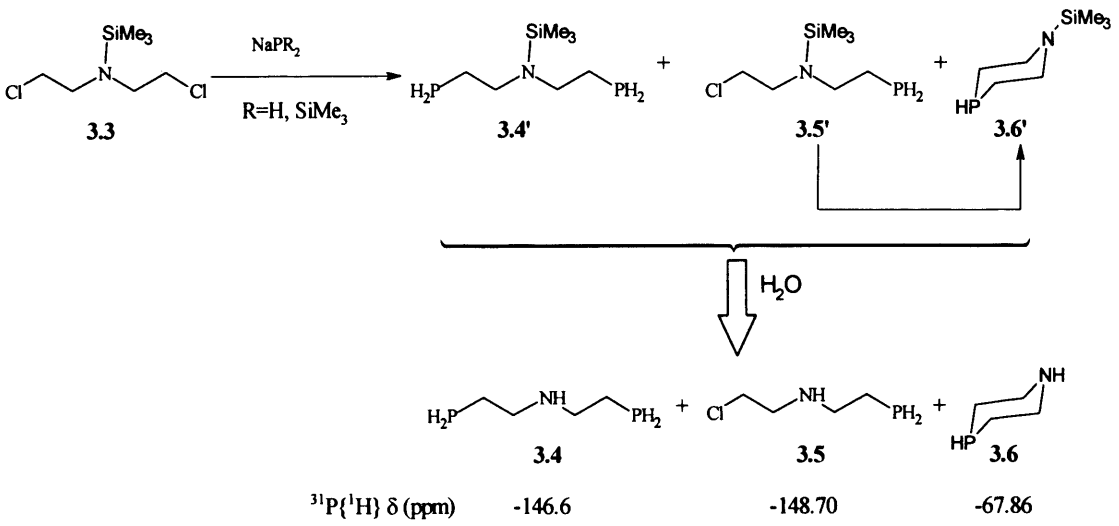


$^{-}ER_2$= $^{i}Pr_2P$, Et_2P, Et_2 As

Scheme 3-2: Mixture of aziridine and aminodipnictanes derivatives

This side reaction, which is initiated by proton abstraction of the amino group, can be avoided by protection of the nitrogen function with the trimethylsilyl group. To avoid competition between basicity and nucleophilicity of sodium phosphide or sodium bis(trimethylsilyl)phosphide, bis(2-chloroethyl)trimethylsilylamine (**3.3**) was initially prepared for the synthesis of **3.4**.[30] The reaction of **3.3** with either $NaPH_2$ or $NaP(SiMe_3)_2$ was performed using different reaction conditions. In all the trials, $NaPH_2$ or $NaP(SiMe_3)_2$ were both synthesised *in situ* in liquid ammonia or DME respectively (Chapter 2). When $NaPH_2$ was used, the liquid ammonia was allowed to evaporate, and the solvent chosen for the substitution reaction was added. To the solution of $NaPH_2$ was then added slowly a solution of **3.3**.

The ^{1}H, ^{13}C and $^{31}P\{^{1}H\}$NMR spectra of the mixture arising from these trials were recorded. The $^{31}P\{^{1}H\}$NMR spectra of the resulting oils after hydrolysis showed a mixture of three phosphorus-containing compounds (Scheme 3-3). Two resonances at δ_P -148.70 and -146.6 ppm ($^{1}J_{P\text{-}H}$= 196 Hz, triplet) were assigned to the mono- and di- substituted phosphine compounds **3.4** and **3.5** respectively with coupling constants P-H of 196 Hz. As expected, no aziridine compound was found; but instead a peak at δ_P -67.86 ppm ($J_{P\text{-}H}$= 187 Hz, doublet) attributed to 1,4-azaphosphorinane (**3.6**) was observed. Formation of **3.6** probably arises from an intramolecular nucleophilic substitution reaction of the monosubstituted primary phosphine **3.5'**.[6] In addition, the ^{1}H and $^{13}C\{^{1}H\}$NMR spectra show the presence of starting material **3.3** which indicates that the conversion of **3.3** into the products is not complete.



Scheme 3-3: Mixture of products of reaction of 3.3 and $NaPH_2$ or $NaP[Si(Me)_3]_2$

Another important aspect of these reactions is that the ratio of the compounds **3.3-3.6** depends strongly on the temperature of the reaction and the solvent used. Therefore, at low temperature (-40 °C) **3.6** is not formed, or, when using more polar solvents such as DMSO, the ratio of compound **3.4** increased.

It is possible that the difficulty of the nucleophilic substitution of Cl^- by $^-PH_2$ may be due to the inductive effect of the trimethylsilyl group on the alkyl chain which results in a decrease of the electrophilicity of the methylene group directly bound to the leaving chloro group. On the other hand, the formation of **3.6** by cyclisation of **3.5'** may be induced by the steric influence of the silicon atom which pushes the alkyl chains together in the pyramidal trigonal environment as well as the deprotonation (by $NaPH_2$) of the primary phosphine group inserted in the alkyl chain.

Compounds **3.5** and **3.6** have not been isolated from the reaction mixture.

Due to the difficulty of synthesising compound **3.4** in moderate yields, and the purification procedures needed; another strategy was adopted.

3.2.1.2. Synthesis of 3.4 with bis(2-chloroethyl)amine hydrochloride as electrophile (method c)

For the synthesis of **3.4,** bis(2-chloroethyl)amine hydrochloride **3.7** was added as a solid to a liquid ammonia solution of $NaPH_2$ at -45°C. The ratio of **3.7** and $NaPH_2$ based on Na_3P is 1:4.4. $NaPH_2$ is used in excess to insure the di-substitution of chloride groups and for the deprotonation of the quaternary amino group. The reaction was stirred at this temperature for 12 hours, after which it was left to reach room temperature to allow the evaporation of liquid ammonia. **3.4** was extracted from the resulting solid with petroleum ether. Evaporation of the solvent leads to the isolation of an air-sensitive, malodorous, colourless liquid which is identified as **3.4** in 55% yield. Compound **3.4** has been fully characterized by ^1H, $^{13}C\{^1H\}$and $^{31}P\{^1H\}$NMR and IR spectroscopy. The $^{31}P\{^1H\}$NMR spectrum of **3.4** exhibits one signal at δ_P -146.6 ppm ($^1J_{P-H}$= 196 Hz, triplet). The ^1H NMR spectrum of **3.4** shows a broad singlet at δ_H 1.10 ppm assigned to the amine proton, two multiplets at δ_H 1.60 and 2.69 ppm for the methylene groups of the alkyl chain and a doublet of virtual triplets at δ_H 2.57 ppm for the primary phosphine protons. ^1H NMR spectroscopy reflects the electron donating property of the phosphorus nuclei with chemical shifts of the methylene groups shifted upfield from the starting material **3.5**. The $^{13}C\{^1H\}$NMR spectrum displays two signals for the two methylene groups at δ_C 14.44 ppm ($^1J_{C-P}$=8.7 Hz) and 51.66 ppm ($^1J_{C-P}$=2.2 Hz), with both signals split into doublets due to coupling with the phosphorus nuclei. The IR spectrum of **3.4** shows, amongst others, two important stretching absorptions at 3295 and 2284 cm^{-1} assigned to N-H and P-H bonds respectively.

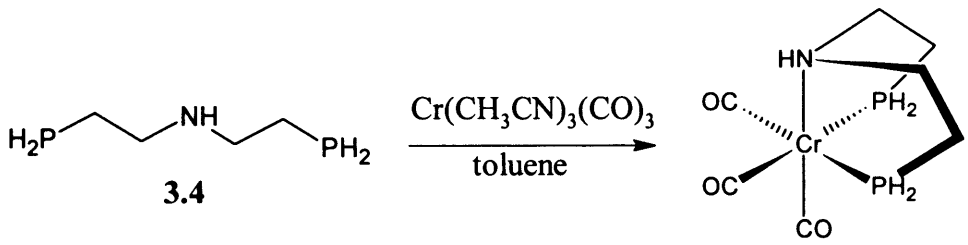
In conclusion, the synthesis of compound **3.4** has been obtained from **3.7** as electrophile and $NaPH_2$ as nucleophile, in a reasonable yield, and without the use of convoluted experimental procedures. Compound **3.4** is isolated pure after simple workup.

3.2.2. Coordination chemistry of bis(2-phosphinoethyl)amine.

In spite of the multiple ways that PNP-type ligands can co-ordinate to metal centers by using two or three donor atoms,[26, 31, 32] only the facially substituted mononuclear geometry, *fac*-$ML_3L'_3$, where the phosphino groups are in a cis-configuration, may allow

the synthesis of macrocycles by cyclisation of the tridentate linear ligand. Thus, the choice of suitable metal precursors is esential to avoid mixtures of facial and meridional isomers as well as other undesirable complexes. Following this premise, *fac*-$Cr(CH_3CN)_3(CO)_3$ and $[\eta^5$-$Cp(SiMe_3)Fe(CO)_2(CH_3CN)]PF_6$ were used as precursors to synthesise the facially substituted Cr and Fe complexes of the ligand **3.4**.

3.2.2.1. Synthesis of *fac*-$Cr(PNP)(CO)_3$ (3.8)



Scheme 3-4: Synthesis of 3.8

Under argon atmosphere, a stoichiometric amount of **3.4** was added to *fac*-$Cr(CH_3CN)_3(CO)_3$ in toluene at room temperature (Scheme 3-4); the colour of solution changed from yellow to orange. The reaction was monitored by $^{31}P\{^1H\}$NMR spectroscopy until no more free **3.4** ligand was observed. The solution was then evaporated to dryness, and washed with petroleum ether to afford **3.8** in 60 % yield. Compound **3.8** was isolated as an air and moisture sensitive orange solid soluble in most organic solvents.

The dilution is an important factor in this reaction, thus formation of discrete species with two different phosphorus atoms in the same complex has been observed by using more concentrated solutions of **3.4** and *fac*-$Cr(CH_3CN)_3(CO)_3$.

The $^{31}P\{^1H\}$NMR and ^{31}P NMR spectra of **3.8** clearly indicate the formation of a primary phosphine complex with a downfield resonance at δ_P -37.88 ppm due to the strong σ-donor bond from the phosphorus to the metal atoms ($^1J_{P\text{-}H}$= 322 Hz, triplet). The co-ordination chemical shift ($\Delta^{31}P = \delta_{\text{co-ordinated P}} - \delta_{\text{unco-ordinated P}}$) relative to the free phosphine ligand is *ca.* 109 ppm and $^1J_{P\text{-}H}$ increases by *ca.* 126 Hz. As is expected for first row metal complexes,[31] $\Delta^{31}P$ value of **3.8** has increased with respect to the molybdenum analogue

prepared by Heβler (δ_P -73.08 ppm, $^1J_{P-H}$= 308, $\Delta^{31}P$= 73.2).[6] In contrast, the coupling constants $^1J_{P-H}$ of **3.8** and the Mo complex have similar values.

The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **3.8** are in agreement with C_s symmetry, with the ligand **3.4** occupying a facial position of the coordination polyhedron. The ^1H NMR spectrum shows the non identical nature of the protons of the methylene groups of the CH_2CH_2 bridge. Four sets of broad multiplets at δ_H 1.84, 1.95 ppm and at δ_H 2.35, 2.77 ppm are assigned to the non-equivalent protons of the methylene groups directly linked to the phosphorus center and attached to the amine center, respectively. The two protons of the primary phosphine group are also diastereotopic and appear as two sets of doublets of multiplets at δ_H 4.02 and 4.22 ppm due to coupling with the phosphorus nuclei. A broad singlet at δ_H 5.15 ppm is assigned to the proton attached to the amine center. The $^{13}C\{^1H\}$ NMR spectrum of **3.8** exhibits four different signals for the four different carbon atoms. All the carbon resonances are split by the interaction with the phosphorus nuclei. Two virtual triplets at δ_C 15.26 ppm ($^1J_{C-P}$= 10 Hz) and 49.72 ppm ($^1J_{C-P}$= 7 Hz) are observed for the methylene carbons α and β to phosphorus, indicating the presence of two equivalent phosphorus nuclei. These chemical shifts are affected little upon co-ordination of the ligand to the metal center. A doublet and a triplet at δ_C 229.73 ppm ($^2J_{C-P}$= 6.9 Hz) and 233.97 ppm ($^2J_{C-P}$= 10.9 Hz) are assigned to the carbonyl ligands in the equatorial and axial position respectively. In the IR spectrum, three intense bands in the carbonyl region (1915, 1822, 1755 cm^{-1}) confirm the *fac*-octahedral geometry of the $Cr(CO)_3$ moiety and the C_s symmetry of the **3.8** complex.[32, 33] The characteristic P-H stretching absorption (2319 cm^{-1}) is also observed. The absence of the acetonitrile C-N absorption band in the IR indicates the complete substitution of the acetonitrile groups by the ligand **3.4**. No useful data was detected in the mass spectra of **3.8**.

The solid-state structure of **3.8** was determined by X-ray diffraction. An ORTEP diagram of **3.8** is shown in Figure 3-7 and selected bond distances and angles are presented in Table 3-1. As demonstrated by NMR spectroscopy, the X-ray analysis confirms the facial coordination of the ligand **3.4** in the complex **3.8**. The complex **3.8** shows a distorted octahedral geometry around the chromium(0) center. The two phosphorus and nitrogen atoms of ligand **3.4** plus three carbonyl groups complete the coordination sphere around the metal. The ligand forms two fused 5-membered rings defined by P(1)-Cr-N-C(4)-C(3).

The average Cr-P distance [2.3370(8) Å] is similar to that observed in other chromium carbonyl PNP-type ligand complexes {e.g. 2.381(5) Å in *fac*-$Cr(CO)_3[EtN(CH_2CH_2PPh_2)_2]$,[34] and is 0.17 Å shorter than that observed in the $\{Mo(CO)_4[\eta^2$-P, P-$(PH_2CH_2CH_2)_2NBu]\}$complex[6] as is expected for the smaller Cr nucleus.[35] The Cr-N distance [2.209(3)Å] also compares favourably with that in $[Cr(CO)_3dien]$ [2.185(4) Å],[36] but is shorter that that observed in the complex *fac*-$Cr(CO)_3[EtN(CH_2CH_2PPh_2)_2]$ [2.310(6) Å]. The average Cr-C distances [1.828 Å] are in the range observed for other $Cr(CO)_3$ complexes. The N-Cr-P bond angle [80.53(6) Å] is compressed compared with the idealized octahedral geometry but is in normal ranges if it is compared with that in *fac*-$Cr(CO)_3[EtN(CH_2CH_2PPh_2)_2]$ [average 81.85 Å].[34] The distance between the non-bonded P...P atoms of complex **3.8** (3.321 Å) is slightly longer than that observed for the secondary phosphine complex $[Cr(CO)_3\{H_2PC(Me)CH_2\}_3]$ (3.297(4) Å),[35] however it compares favourably to that observed for the $Cr(CO)_3\{cyclo$-$(HPC_3H_6)_3\}$ macrocycle (3.321(4) Å),[35] and it indicates that **3.8** match with the requirements (template size and stereochemistry, P-P distances, etc.) for a possible cyclisation in which a 3-carbon bridge is formed.

Table 3-1: Selected Bonds Lengths (Å) and Angles (deg) for 3.8

Cr-N	2.209(3)	C(1)-Cr-C(2)	89.26(12)
Cr-P	2.3370(8)	C(2)-Cr-C(2')	87.19(17)
Cr-C(1)	1.815 (4)	C(1)-Cr(1)-N(1)	177.49(15)
Cr-C(2)	1.841(3)	C(2)-Cr(1)-N(1)	92.55(10)
P-C(3)	1.836(3)	C(1)-Cr(1)-P(1)	97.73(9)
N-C(4)	1.488(4)	C(2)-Cr(1)-P(1)	172.67(9)
C(1)-O(1)	1.176(5)	C(2')-Cr(1)-P(1)	90.68(9)
C(2)-O(2)	1.158(3)	N(1)-Cr(1)-P(1)	80.53(6)
		P(1)-Cr(1)-P(1')	90.56(5)

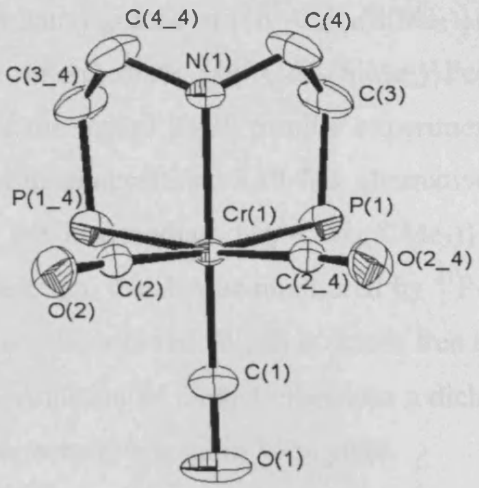
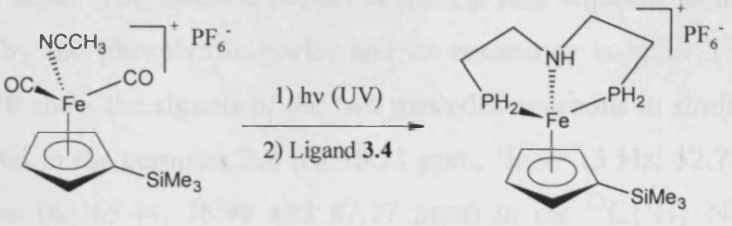


Figure 3-6: Molecular structure of 3.8, 50% probability Ellipsoids, H atoms omitted for clarity.

Attempts to synthesise the tungsten analogue of **3.8** by reaction of either tris(acetonitrile)tricarbonyltungsten(0) or tricarbonyl(η^6-mesitylene)tungsten(0) with **3.4** have not been successful. The conditions required to ligate **3.4** with this metal cause formation of mixtures of compounds signifying the presence of several different coordination modes of the PNP ligand. No further studies have been done with this metal.

3.2.2.2. Synthesis of [{η^5-$C_5H_4(SiMe_3)$}Fe(PNP)]PF_6 (3.10)



3.9 **3.10**

Scheme 3-5: Síntesis of 3.10

In previous studies involving tridentate and bidentate phosphine ligands,[11, 37] the photolytic cleavage of the carbonyl groups in $[\{\eta^5\text{-}C_5H_4(SiMe_3)\}Fe(CO)_2(CH_3CN)]^+$ (**3.9**) in acetonitrile to form the intermediate $[\{\eta^5\text{-}C_5H_4(SiMe_3)\}Fe(CH_3CN)_3]^+$, have been performed in the presence of the ligand itself. Similar experiments with ligand **3.4** have however resulted only in its decomposition. **3.10** has alternatively been synthesised by addition of ligand **3.4** after the intermediate $[\{\eta^5\text{-}C_5H_4(SiMe_3)\}Fe(CH_3CN)_3]^+$ has been formed (Scheme 3-5). The reaction, which was monitored by $^{31}P\{^1H\}$NMR spectroscopy, showed a colour change from yellow to red. When no more free ligand **3.4** was observed, the solution was evaporated. Addition of diethyl ether into a dichloromethane solution of **3.10** afforded **3.10** as a red, air-sensitive solid in 34 % yield.

The $^{31}P\{^1H\}$and ^{31}P NMR spectra of **3.10** are in agreement with the formation of a primary phosphine complex with a signal at δ_P -7.71 ppm (average $^1J_{P\text{-}H}$= 350 Hz, triplet). The signal for the counter anion PF_6 is observed at -143.75 ppm ($^1J_{P\text{-}F}$= 711 Hz, septet). The co-ordination chemical shift ($\Delta^{31}P$=138.89) has increased with respect to the chromium analogue indicating deshielding on the phosphine group as result of the electron-withdrawing nature of the cationic iron center.[38] The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **3.10** confirm the C_s symmetry of complex. The lack of acetonitrile ligand resonance signals in the ^1H NMR spectrum suggests the tridentate co-ordination of the ligand PNP. The protons of the methylene carbons of the PNP ligand are non-equivalent, and the multiplets at δ_H 1.92, 2.15 ppm and 1.99, 2.67 ppm are assigned to CH_2PH_2 and CH_2NH groups respectively. The primary phosphine protons again appear as two sets of doublets of triplets at δ_H 4.38 and 6.72 ppm. The protons of the Cp ligand are shifted to higher field with respect to the starting material **3.9** due to the electron-donating effect of the phosphorus atom. The methine proton of the Cp ring adjacent to the $SiMe_3$ group is more affected by the phosphorus nuclei and its resonance is split. The $^{13}C\{^1H\}$ NMR spectrum of **3.10** show the signals of the two methylene carbons in similar chemical shifts to those observed in the complex **3.8** (δ_C 18.21 ppm, $^1J_{C\text{-}P}$= 13 Hz; 52.75 ppm). The three other resonances (δ_C 65.44, 78.98 and 87.17 ppm) in the $^{13}C\{^1H\}$ NMR spectrum are assigned to the carbons of the Cp ligand. In the IR spectrum, the P-H stretch is observed at 2358 cm^{-1}. The mass spectrum of **3.10** exhibits the molecular ion of the cation $[\{\eta^5\text{-}C_5H_4(SiMe_3)\}Fe(PNP)]^+$, with the expected isotopic distribution.

The solid-state structure of **3.10** was determined by X-ray diffraction. An ORTEP diagram of **3.10** is shown in Figure 3-8.[39] The quality of the crystal was poor, although adequate to confirm the structure of complex **3.10** and the coordination of the ligand PNP to the metal center. Significant bond distances and angles are summarized in Table 3-2. The coordination of the iron atom is distorted pseudo-octahedral, with one face occupied by the η^5-{$C_5H_4(SiMe_3)$} group and the other face by two phosphorus and nitrogen donor atoms from the ligand **3.4**. The ligand conformation of **3.10** consists of two fused five-membered chelate rings defined by P(1)-Fe-N-C(3)-C(4) and P(2)-Fe-N-C(2)-C(1). Whilst the Fe-P distances of **3.10** (average Fe-P=2.168 Å) are shorter than those of similar compounds {$[(C_5H_5)Fe(CO)I$-μ-P-NP_2-$Fe(C_5H_5)]^+$,[40] P-NP_2= tris(2-diphenylphosphino-ethyl)amine, average Fe-P= 2.216 Å; $(C_5H_5)Fe[N(SiMe_2CH_2PPh_2)_2]$,[41] average Fe-P= 2.249 Å}, the Fe-N distance of **3.10** (Fe-N=2.024 Å) is in the normal range with compared to related compounds {$[(C_5H_5)Fe(CO)I$-μ-P-NP_2-$Fe(C_5H_5)]^+$,[40] Fe-N= 2.216 Å; $(C_5H_5)Fe[N(SiMe_2CH_2PPh_2)_2]$,[41] Fe-N= 2.086(3) Å}. The P(1)-C(4), P(2)-C(1) distances (1.695 Å, 1.673 Å) are 0.1 Å shorter than those of reported tertiary *o*-phenylenebisphosphino ligands co-ordinated to a CpFe(II) fragment ($[Cp\{1,2\text{-}C_6H_4\text{-}(PMePh)_2\}Fe(NCMe)]PF_6$,[42] 1.81-1.83 Å). It is likely that the relatively short Fe-P distances reflect the lower steric demands of the PH_2 donor function in comparison to the PPh_2 functions in the literature examples. The P-Fe-N angles (average 83.21°) and P(1)-Fe-P(2) (97.01°) have similar values to those of related compounds {$[(C_5H_5)Fe(CO)I$-μ-P-NP_2-$Fe(C_5H_5)]^+$,[40] average P-Fe-N=84.7°; P(1)-Fe-P(2)=96.1°}. As might be expected, the 5-membered chelate bite angles (P-Fe-N) are considerably compressed in comparison to the non-chelate angle P(1)-Fe-P(2). It is of interest to note that the distance between non-bonded P...P atoms of **3.10** (3.248 Å) is larger than that observed for related CpFe(II) templates with 9-membered macrocycles 9[ane]P_3R_3 (average 2.948 Å),[43, 44] and 12-membered macrocycles 12[ane]P_3R_3 (average 3.120 Å).[45]

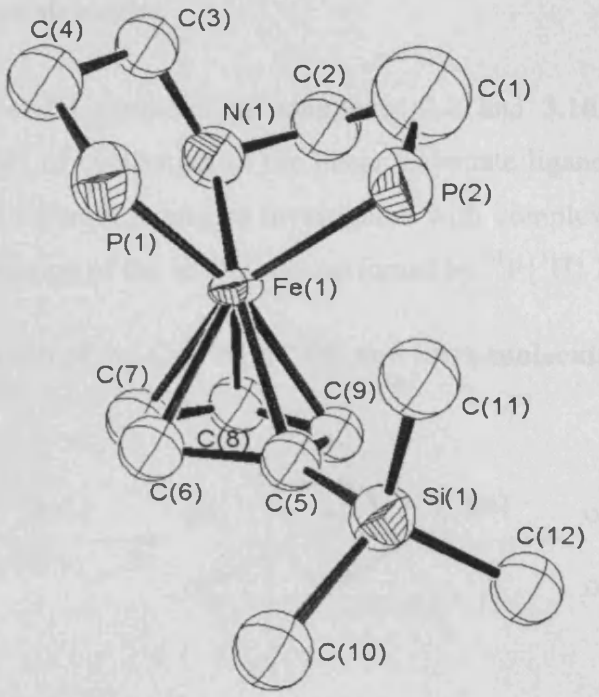


Figure 3-7: Molecular structure of 3.10, 50 % probability ellipsoids, H atoms omitted for clarity.

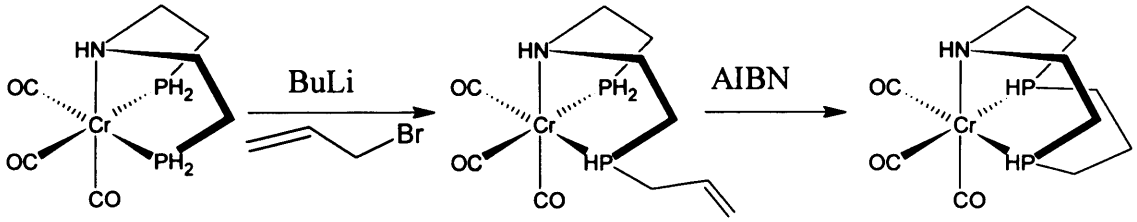
Table 3-2: Selected Bonds Lengths (Å) and Angles (deg) for 3.10

Fe-P(1)	2.167	P(1)-Fe-P(2)	97.01
Fe-P(2)	2.169	P(1)-Fe-N	83.48
Fe-N	2.024	P(2)-Fe-N	82.94
P(1)-C(4)	1.695	Fe-P(2)-C(1)	107.76
C(4)-C(3)	1.633	Fe-P(1)-C(4)	106.30
N-C(3)	1.518	Fe-N-C(3)	121.58
P(2)-C(1)	1.673	Fe-N-C(2)	110.61
C(1)-C(2)	1.623	N-Fe-C(8)	91.61
N-C(2)	1.514	P(2)-Fe- C(5)	98.50
Fe-C(5)	2.108	P(1)-Fe- C(6)	90.77
Fe-C(6)	2.062	Fe-C(5)-Si	131.90
Fe-C(7)	2.092		
Fe-C(8)	2.036		
Fe-C(19)	2.096		
C(5)-Si	1.827		

3.2.3. Cyclisation strategies.

After the successful synthesis of complexes **3.8** and **3.10**, different studies to determine the feasibility of cyclisation of the linear tridentate ligand by template method were undertaken. The different strategies investigated with complex **3.8** are described in the next sections. Evaluation of the results was perfomed by $^{31}P\{^{1}H\}$ NMR spectroscopy.

3.2.3.1. Alkylation of *fac*-Cr(PNP)(CO)$_3$ and intra-molecular cyclisation



3.8 **3.11** **3.12**

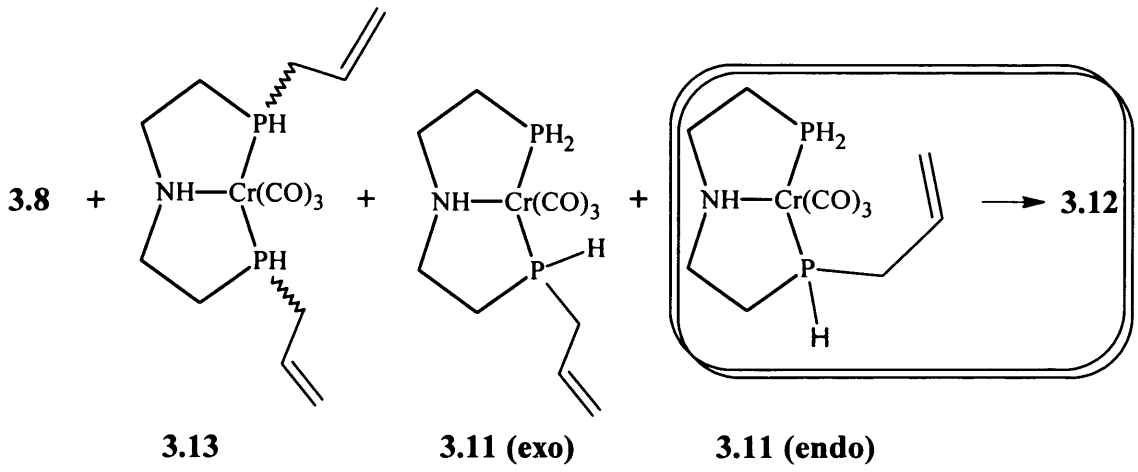
Scheme 3-6: Proposed strategy for the synthesis of 3.12

The strategy of cyclisation, summarized in Scheme 3-6, was based on previous studies reported by Treichel where intramolecular cyclisation of *cis*-$M(CO)_4(PPh_2H)(PPh_2(CH_2)_nCH{=}CH_2)$ compounds (M=Cr, Mo; n=0,1) was achieved successfully by both base and radical promoted reactions.[46] The strategy presented here involved the deprotonation of one of the PH_2 groups of **3.8** followed by alkylation with allyl bromide forming **3.11**. The subsequent ring closure reaction of **3.11** achieved by the known radical-promoted addition of P-H into the alkene bond would lead to the desired product **3.12**.[47]

Compound **3.8** was treated in THF at low temperature (-78°C) with one equivalent of BuLi and one equivalent of allylbromide following reported procedures.[48] The $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra of the solution showed a mixture of compounds. Examination of the $^{31}P\{^{1}H\}$ NMR spectrum revealed the mono-substituted **3.11** in two diastereoisomeric forms **endo** and **exo** (Scheme 3-7). Each diastereoisomer has two different phosphorus atoms which are coupled in the $^{31}P\{^{1}H\}$ NMR spectrum (diastereoisomer 1: δ_P -42.45 ppm (PH_2), 26.83 ppm (PH), $^{2}J_{P\text{-}P}$ = 38.7 Hz; diastereoisomer 2: δ_P -37.97 ppm (PH_2), 33.34 ppm (PH), $^{2}J_{P\text{-}P}$ = 32.7 Hz). The starting material **3.8** was also observed as well as other

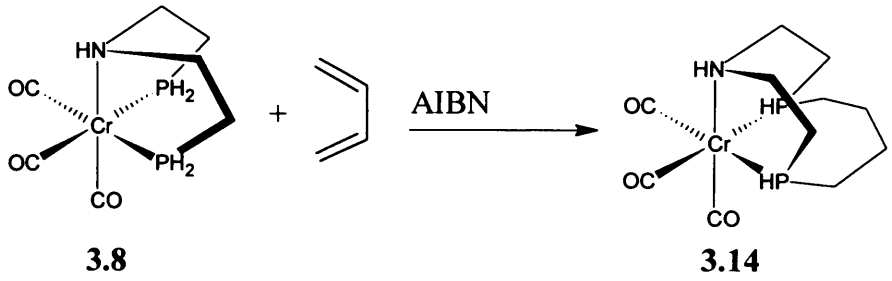
resonances which may be assigned to different diastereotopic forms of a bis-allyl-substituted compound **3.13** (Scheme 3-7). From all these compounds formed, only **3.11 (endo)** would afford the desired macrocycle. Attempts to separate the mixture by crystallisation or chromatography have failed. Other attempts were made by using two and three equivalents of BuLi and allyl bromide, other bases (MeLi) or electrophiles (*i*-PrCl). All these attempts resulted in mixtures of compounds which indicate that the deprotonation/alkylation step is not selective and does not form a single major compound.

Attempts to obtain **3.12** by cyclisation of compound **3.11 (endo)** included heating (90°C) a solution containing the mixture of compounds in toluene in the presence of catalytic amounts AIBN.[35] The $^{31}P\{^{1}H\}$ NMR spectra of the solution, recorded at various times, showed the disappearance of the signals of **3.11** as well as that of the other compounds. After 12 hours, a black precipitate was observed and no signal was observed in the $^{31}P\{^{1}H\}$ NMR spectrum. It is likely that **3.11**, as well as the other compounds, polymerize during the reaction. These inseparable mixtures of compounds restricted further studies of the cyclisation reaction of the linear tridentate PNP ligand by using this strategy.



Scheme 3-7: Compounds formed during the alkylation of 3.8 with allyl bromide

3.2.3.2. Radical initiated cyclisation with butadiene



3.8 **3.14**

Scheme 3-8: Proposed strategy for synthesis of 3.14

A new approach was designed making use again of the known radical promoted coupling reactions of co-ordinated primary phosphines with alkenes. The strategy outlined in Scheme 3-8 involved the double hydrophosphination reaction of complex **3.8** with a suitable diene such as *cis*-1,3-butadiene in the aim of forming the 4-aza-1,7-diphosphacycloundecane chromium tricarbonyl complex **3.14**.

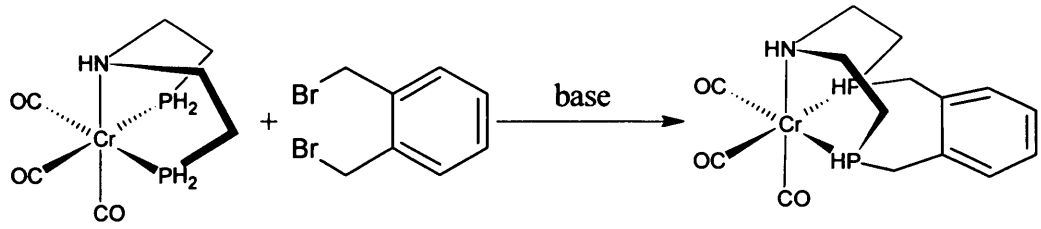
The reaction was carried out in a glass pressure reactor. A toluene solution of **3.8**, pressurized with four bar of *cis*-1,3-butadiene in the presence of catalytic quantities of aibn, was heated to 90°C. After three hours of reaction, the starting material **3.8** was the main product as observed by $^{31}P\{^{1}H\}$ NMR spectroscopy. Further hours of reaction lead to a colour change of the solution from yellow to dark brown with formation of a precipitate. The $^{31}P\{^{1}H\}$ NMR spectrum of the toluene solution did not show any resonances. The precipitate was insoluble in organic solvents and no further data could be recorded.

Therefore, the coupling reaction by radical promotion appears to go via uncontrolled pathways and is not selective for the cyclised product. It is assumed that the reaction of **3.8** with 1,3-butadiene caused precipitation of intractable, presumably polymeric materials. No further studies were carried out following this strategy.

3.2.3.3. Phosphide formation and reaction with di-haloalkanes

Another method explored in order to synthesise phosphorus nitrogen mixed macrocycles from the linear tridentate ligand by template methods was the cycloaddition of a dihalide with complex **3.8**. This method has been widely used to synthesise tetradentate

macrocycles in square-planar geometry complexes,[49-51] and involves the bis-deprotonation of secondary phosphines followed by di-alkylation with a dihaloalkane. The template effect assists the intra-molecular cyclisation over intermolecular reactions.



3.8 **3.15**

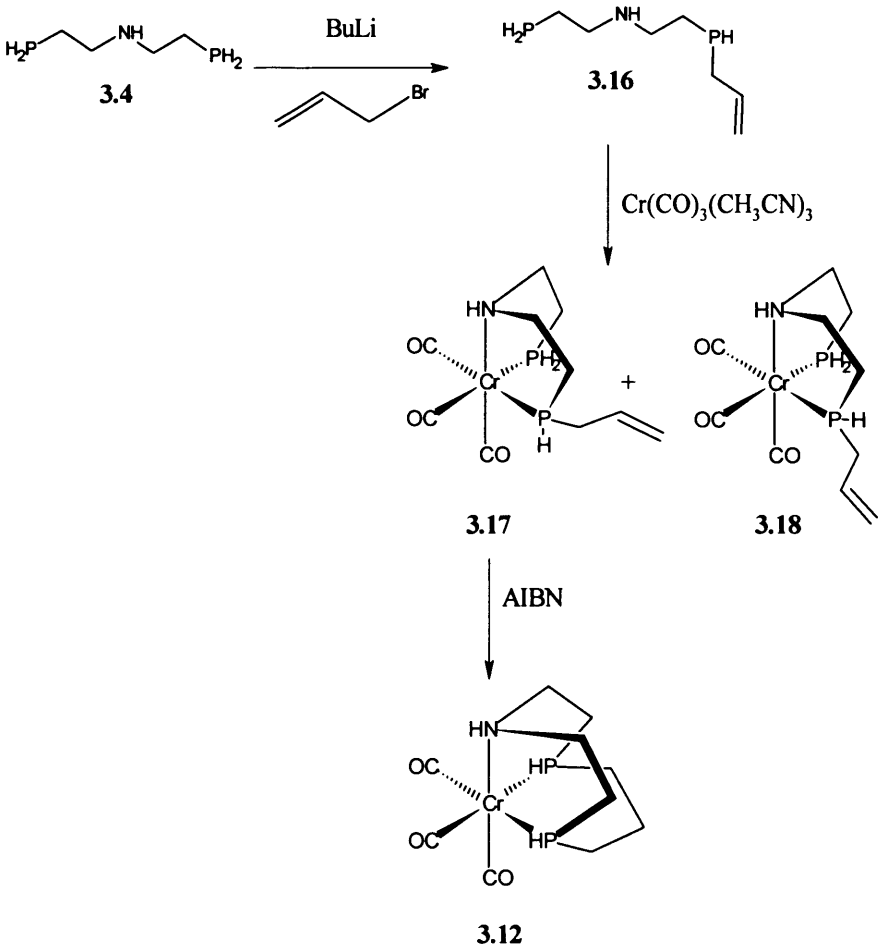
Scheme 3-9: Proposed strategy for synthesis of 3.15

Different attempts were performed using complex **3.8** and α,α'-dichloro-*o*-xylene as α-ω dihalide (Scheme 3-9). The use of excess of K_2CO_3 as base in ethanolic media is a procedure used in the literature to deprotonate the co-ordinated phosphines.[51] This same procedure could solve the problems derived from the non selective formation of the phosphide anions seen in section 3.2.3.1 by complete deprotonation of the phosphine groups. But it did not give good results in our case. The starting material **3.8** and α,α'-dichloro-*o*-xylene did not react in the desired manner, but insoluble materials were formed during the reaction. No better results were obtained upon changing some of the reaction parameters. The use of *t*-BuOK as base with complex **3.8** in the stoichiometric ratio 2:1 in cold THF (-78°) to form the di-phosphide followed by addition of the bis-electrophile did not yield the cyclised product, but again insoluble materials were obtained. Therefore, this approach also fails in forming the macrocycle from linear tridentate ligands.

3.2.4. An alternative for the synthesis of PNP-macrocycles. Synthesis of 2-(allylphosphino)-N-(2-phosphinoethyl)ethanamine (3.16).

After the discouraging results in attempted cyclisations of the linear tridentate ligand complexes **3.8**, a different approach was attempted. Efforts were made to synthesise a ligand derived from **3.4** which could undergo intramolecular cyclisation after coordination to a metal. Treichel's work inspired us to synthesise 2-(allylphosphino)-N-(2-

phosphinoethyl)ethanamine (**3.16**) by mono-alkylation of ligand **3.4** with allylbromide (Scheme 3-10).[46] Due to the relatively large barrier to pyramidal inversion at the phosphorus atom,[52] the non asymmetric synthesis of compound **3.16** would lead to a racemic mixture of R and S enantiomers. If, upon coordination with the chromium metal, the diastereoisomers formed **3.17** and **3.18** would be easy to separate, or further cyclisation of the mixture of diastereoisomers lead selectively to the formation of the cyclised compound as succeed in other examples,[45] the synthesis of the macrocycle **3.12** could be achieved.



Scheme 3-10

3.2.4.1. Ligand synthesis

Treatment of **3.4** in THF with stoichiometric amounts of BuLi at low temperature (-98°C), and subsequent addition of the stoichiometric amount of allylbromide afforded **3.16** as a malodorous, air-sensitive and colourless liquid in 10 % yield (Scheme 3-10). **3.16** has been fully characterized as a racemic mixture by ^{1}H, $^{13}C\{^{1}H\}$and $^{31}P\{^{1}H\}$NMR, IR and Mass spectroscopy. The $^{31}P\{^{1}H\}$NMR spectrum of **3.16** exhibits two resonances for the primary (δ_P -149.11 ppm, $^{1}J_{P-H}$= 195 Hz, triplet) and secondary phosphine groups (δ_P - 74.15 ppm, $^{1}J_{P-H}$= 201 Hz, doublet). Due to the decrease of the symmetry of **3.16** in respect to **3.4**, the ^{1}H NMR spectrum of **3.16** shows a more complicated pattern than in **3.4**, although, there are some common features. All the protons of the phosphinoethyleneamine arm ($PH_2CH_2CH_2NH$) corresponding to **3.16** appear at the same chemical shift as for compound **3.4**. The methylene protons directly attached to the amine function from the asymmetric arm appear at δ_H 2.70 ppm overlapping with the signals arising from the N-CH_2 protons in the arm connected to the PH_2 group. Two sets of broad multiplets at δ_H 1.66 and 1.83 ppm are assigned to the diastereotopic methylene protons directly linked to the secondary phosphorus center from the ethylene arm. The proton of the secondary phosphine arises as a doublet of quintuplets (δ_H, 3.08 $^{1}J_{P-H}$= 201 Hz, $^{3}J_{P-H}$= 6.8 Hz) by the interaction with the phosphorus nuclei and the four surrounding protons. The methylene protons of the allyl dangling arm appear as non-equivalent multiplets at δ_H 2.29 and 2.34 ppm. The three vinylic protons are also slightly shifted upfield. While one of the CH_2=CHR protons appear at δ_H 4.94 ppm as a singlet, the other (presumably *trans*) is a doublet at δ_H 4.97 ($^{3}J_{H-H}$= 9.5 Hz) due to the vicinal coupling. No geminal coupling is observed between the vinylic protons. The methine proton is assigned to a multiplet at δ_H 5.74 ppm. The acidic amino proton is not observed in the ^{1}H NMR spectrum. The $^{13}C\{^{1}H\}$NMR spectrum of **3.16** shows seven signals for the seven different carbons. All signals, except one, are split by coupling with the phosphorus nuclei. As in the ^{1}H NMR spectrum, similar resonances to compound **3.4** are found for the ethylene carbons of the primary phosphine arm (δ_C CH_2PH_2 14.26, CH_2NH 51.80 ppm). In contrast, the methylene carbon of the asymmetric arm directly linked to the amine function is shifted up-field and interacts with the two different phosphorus atoms, giving a doublet of doublets at δ_C 47.63

ppm ($^3J_{C\text{-}PH}$=22, $^4J_{C\text{-}PH2}$= 14 Hz). The remaining methylene carbon of the asymmetric arm is deshielded by the olefin group and resonates at δ_C 19.62 ppm. The other three resonances at δ_C 25.44, 115.49 and 135.22 ppm belong to the allyl group and are assigned to the allylic methylene groups, vinylic CH_2 and methine carbon, respectively. These signals have been shifted upfield with respect to the allylbromide by the electron donation of the phosphorus atom. The IR spectrum shows characteristic bands of compound **3.16**. Intense peaks at 3257 and 2280 cm^{-1} are assigned to the N-H and P-H stretching bands, whilst a weak peak at 1635 cm^{-1} is assigned to the carbon-carbon double bond stretch. In addition, the composition of compound **3.16** has been also verified by mass spectroscopy.

3.2.4.2. Attempts at complexation of 2-(allylphosphino)-N-(2-phosphinoethyl) ethanamine

An equimolar amount of **3.16** was added to a solution of $Cr(CO)_3(CH_3CN)_3$ in toluene at room temperature. The orange colour of the solution became darker and a yellow precipitate was formed within minutes. The $^{31}P\{^1H\}$NMR spectrum of the solution did not show any phosphorus containing compounds. The solid, isolated by filtration, was not soluble in any common organic solvents. The IR spectrum of the solid in nujol showed two bands in the carbonyl region (1914, 1810 cm^{-1}) indicating the presence of the $Cr(CO)_3$ moiety in the solid, in contrast no distinctive bands could be assigned to the co-ordinated olefin C=C stretching frequency. Due to the potential tetradenticiy of ligand **3.16**, it is likely that the ligand has coordinated by different modes to the metal center yielding polymeric species. No further attempts were made to isolate metal complexes of the ligand.

3.3. Conclusion

The diprimary phosphine bis(2-phosphinoethyl)amine (**3.4**) has been successfully synthesised in reasonable yield. The straightforward method uses $NaPH_2$ as the nucleophile and does not need further purification procedures to obtain the product. The potentially tetradentate ligand **3.16** has been prepared by derivatization of ligand **3.4** with allyl bromide. Ligand **3.4** coordinates through its three donor atoms to chromium(0) and iron(II) metals forming the diamagnetic complexes **3.8** and **3.10** with pseudo-octahedral geometry

and are both diamagnetic. All attempts to synthesise phosphorus nitrogen mixed macrocycles through template methods using **3.8** failed, presumably due to the formation of intractable polymeric compounds.

Table 3-3: Summary of Cristallographic Data for 3.8

	3.8
empirical formula	$C_7 H_{13} Cr N O_3 P_2$
fw	273.12
crystal syst	Monoclinic
space group	P 21/m
a, Å	6.8490(2)
b, Å	12.3780(2)
c, Å	7.4640(5)
α, deg	90
β, deg	114.841(1)
γ, deg	90
V, $Å^3$	574.23(4)
Z	2
δ_{calcd}, Mg/m^3	1.580
F_{000}	280
μ (Mo Kα), mm^{-1}	1.256
temp, K	150(2)
n. of meads rflns	10639
n. of unique rflns	1722 (R_{int} = 0.0882)

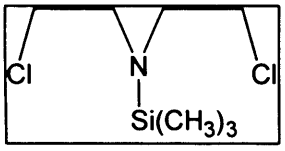
3.4. Experimental

3.4.1. General procedures

Unless otherwise stated all manipulations were carried out using standard Schlenck techniques under an atmosphere of dry nitrogen. All solvents were dried and degassed by boiling under reflux over standard drying agents under a nitrogen atmosphere. The compounds Na_3P, *fac*-$W(CO)_3(CH_3CN)_3$, *fac*-$Cr(CO)_3(CH_3CN)_3$, and $\{Fe\{\eta^5\text{-}C_5H_4[Si(CH_3)_3]\}(CO)_2(CH_3CN)\}PF_6$ were prepared by literature methods.[53, 54] All other chemicals were obtained from Aldrich Chemical Company or alternative commercial

sources. UV photolyses was carried out using a Hanovia 125 W mercury discharge lamp (254 nm).Where appropriate, chemicals were dried over molecular sieves and freeze-thaw degassed. NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^{1}H) and 125.75 MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz (^{1}H) and 100 MHz (^{13}C), and a Jeol Lamda Eclipse 300 at 121.65 MHz (^{31}P), 75.57 MHz (^{13}C). ^{1}H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P chemical shifts are quoted in ppm relative to external 85% H_3PO_4. Infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under N_2 as films, KBr disc or nujol mulls. Mass Spectra of all the samples have been collected by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with an ESCI source. Elemental Analyses were performed by Warwick Analytical Services, University of Warwick. X-ray diffraction data collection was carried out on a Bruker Kappa CCD diffractometer at 150 K for complex **3.8** in Cardiff and a Nonius Kappa CCD diffractometer for the complex **3.10** in Bath University.

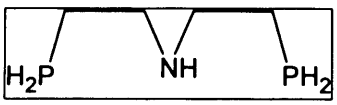
3.4.2. Synthesis of bis(2-chloroethyl)trimethylsilylamine[30] (3.3)



A suspension of $(ClCH_2CH_2)_2NH.HCl$ **3.7** (10g, 0.056 mol), NEt_3 (100 mL), Me_3SiCl (40 mL) and DMSO (0.25 mL) was refluxed for 16 h under N_2. After cooling to room temperature, the solution was filtered and the volatiles were removed *in vacuo*. The yellow oil was identified as **3.3** and used without further purification. The spectroscopy data was in agreement with the literature.

^{1}H NMR δ ppm ($CDCl_3$): 0.04 (s, 9H, Si(C**H**$_3$)), 2.82 (t, 4H, NHC**H**$_2$), 3.12 (t, 4H, C**H**$_2$Cl). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): -0.11 [Si(**C**H_3)$_3$], 42.84 (**C**H_2Cl), 49.77 (**C**H_2N).

3.4.3. Synthesis of bis(2-phosphinoethyl)amine (3.4)

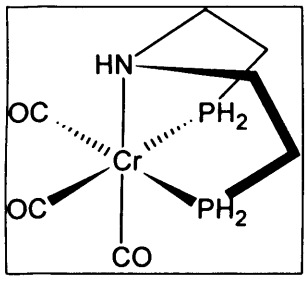


Into a 1 L three necked flask equipped with two N_2 inlets, and a solid addition funnel, was placed Na_3P (19.76 g, 0.19 mol). Ammonia (300 mL) was then condensed at -78 °C into the flask, and NH_4Cl (21.13g, 0.39 mol) was slowly added to the suspension at this temperature

through the solid addition funnel. After the addition, the solution was stirred at this temperature for 45 minutes. The resulting yellow solution was allowed to warm to -45 °C, and then bis(2-chloroethyl)amine hydrochloride (7.77g, 0.043 mol) was slowly added through the solid addition funnel. The solution was stirred at this temperature for 12 hours during which time a grey precipitate formed. The ammonia was then allowed to evaporate. The residual solid was washed with petroleum ether (50 ml x 2) and filtered. The organic solvent was removed *in vacuo*, and the remaining colourless oil was identified as **3.4** (3.24 g, 55 %). The spectroscopy data was in agreement with the literature.

^{1}H NMR δ ppm ($CDCl_3$): 1.10 (s br, N**H**), 1.60 (m, 4H, C**H**$_2$PH$_2$), 2.57 (d t, 4H, $^1J_{H\text{-}P}$=196 Hz, $^3J_{H\text{-}H}$=8 Hz, P**H**$_2$), 2.69 (q, 4H, $^3J_{H\text{-}H}$=6.9 Hz, $^3J_{H\text{-}P}$=6.9 Hz, C**H**$_2$NH). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): 14.44 (d, $^1J_{C\text{-}P}$=8.7 Hz, **C**H$_2$PH$_2$), 51.66 (d, $^2J_{C\text{-}P}$=2.2, **C**H$_2$NH). ^{31}P{^{1}H}NMR δ ppm ($CDCl_3$): -146.6. IR (film): ν(N-H) 3295 s br, ν(P-H) 2284 s br cm^{-1}.

3.4.4. Synthesis of triscarbonyl-bis(2-phosphinoethyl)amine chromium (3.8)

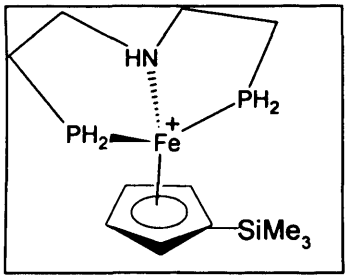


This reaction was carried out under an argon atmosphere. A solution of **3.4** (0.323 g, 2.3 mmol) in toluene (10 mL) was added to a suspension of ($Cr(CO)_3(CH_3CN)_3$) (0.610 g, 2.3 mmol) in toluene (110 mL) forming an orange solution which was stirred overnight. The solvent was removed *in vacuo*, and the residue washed with petroleum ether. The resultant solid was dried *in vacuo* to afford **3.8** as an orange powder (0.383 g, 60 %). Single crystals of **3.8** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **3.8** at room temperature.

^{1}H NMR δ ppm ($CDCl_3$): 1.84 (m, 2H, C**H**$_a$H$_{a'}$PH2), 1.95 (m, 2H, CH$_a$**H**$_{a'}$PH$_2$), 2.35 (m, 2H, NH$_2$C**H**$_b$H$_{b'}$), 2.77 (m, 2H, NH$_2$CH$_b$**H**$_{b'}$), 4.02 (d m, 2H, P**H**$_c$H$_{c'}$), 4.22 (d m, 2H, PH$_c$**H**$_{c'}$), 5.15 (s, 1H, N**H**). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): 15.26 (t, $^1J_{C\text{-}P}$= 10 Hz, **C**H$_2$PH$_2$), 49.72 (t, $^2J_{C\text{-}P}$= 7 Hz, **C**H$_2$NH), 229.73 (d, $^2J_{C\text{-}P}$= 6.9 Hz, **C**O$_{eq}$), 233.97 (t, $^2J_{C\text{-}P}$=

10.97Hz, CO_{ax}). $^{31}P\{^1H\}$NMR δ ppm ($CDCl_3$): -37.88 (t, J_{P-H}= 322 Hz, PH_2). IR (nujol): ν(P-H) 2319 s cm^{-1} ν(CO) 1915 s, 1822 s, 1755 s cm^{-1}. Anal Calc. for $C_7H_{13}CrNO_3P_2$(0.5 CH_2Cl_2) (312.95): C, 28.54; H, 4.47; N, 4.44. Found: C, 28.29; H, 4.77; N, 4.84 %.

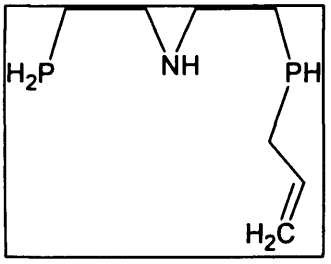
3.4.5. Synthesis of trimethylsilylcyclopentadienyl-bis(2-phosphinoethyl)amine iron (II) hexafluorophosphate (3.10)



{Fe{η^5-C_5H_4[$Si(CH_3)_3$]}$(CO)_2(CH_3CN)$}PF_6 (0.244 g, 5.6 mmol) was placed into a 100 mL UV reactor connected to a N_2 line. Acetonitrile (90 mL) was then added and the solution was irradiated for 1 hour resulting in a colour change from yellow to dark red. A solution of **3.4** (77 mg, 5.6 mmol) in acetonitrile (2 mL) was then added to the reaction mixture and stirred for 1 hour. The solvent was removed and the residue washed with petroleum ether (10 mL). The crude solid was dissolved in dichloromethane (10 mL), filtered and the solvent evaporated. The resultant solid was dried *in vacuo* to afford **3.10** as a red powder (91 mg, 34 %). Single crystals of **3.10** were obtained by slow diffusion of hexane into a dichloromethane solution of **3.10** at room temperature.

^1H NMR δ ppm ($CDCl_3$): 0.0 (s, 9H, $Si(CH_3)_3$ 1.92 (m, 2H, CH_aH_a·PH_2), 1.99 (m, 2H, CH_bH_b·NH), 2.15 (m, 2H, CH_aH_a·PH_2), 2.67 (m, 2H, CH_bH_b·NH), 4.38 (d m, 2H, $^1J_{P-H}$= 344 Hz, PH_cH_c·), 4.51 (d, $^3J_{H-P}$= 6 Hz, 2H, Cp-CH), 4.9 (s, 2H, Cp-CH), 5.21 (br s, 1H, NH), 6.72 (d m, 2H, $^1J_{P-H}$= 356 Hz, PH_cH_c·). $^{13}C\{^1H\}$NMR δ ppm (CD_2Cl_2): -0.23 [$Si(CH_3)_3$], 18.21 (t, $^1J_{C-P}$=13 Hz, CH_2PH_2), 52.75 (s, CH_2NH), 65.44 [Cp-C], 78.98 (Cp-CH), 87.17 (Cp-CH); $^{31}P\{^1H\}$NMR δ ppm ($CDCl_3$): -7.71 (PH_2), -143.75 (h, J_{P-F}= 711 Hz, PF_6). IR (nujol): ν(P-H) 2358 s cm^{-1}. MS (ES): m/z 330 (100 %, [M^+]). Anal Calc. for $C_{12}H_{26}F_6FeNP_3Si$ (475.18): C, 30.33; H, 5.51; N, 2.94. Found: C, 29.53; H, 5.32; N, 2.77 %.

3.4.6. Synthesis of 2-(allylphosphino)-N-(2-phosphinoethyl)ethanamine (3.16)



A solution of **3.4** (1.005 g, 7.3 mmol) in THF (40 mL) cooled to -98 °C with a methanol/N_2 slush, was treated with a solution of *n*-butyllithium in hexanes (1.64 M, 4.5 mL, 7.3 mmol), the resulting yellow solution was stirred at this temperature for 10 minutes. Allyl bromide (0.638 mL, 7.3mmol) was then added, and the reaction mixture was allowed to stir overnight. The solvent was removed *in vacuo*, and the residue was dissolved in petroleum ether (10 mL). The solution was filtered, and the solvent evaporated yielding a colourless, air-sensitive liquid identified as **3.16** (0.131 g, 10 %).

^{1}H NMR δ ppm ($CDCl_3$): 1.66 (m, 2H, C**H**$_2$PH$_2$), 1.66 (m, 1H, $CH_2CH_aH_{a'}PH$), 1.83 (m, 1H, CH_2CH_a**H**$_{a'}$PH), 2.29 (m, 1H, CHC**H**$_b$H$_{b'}$PH), 2.34 (m, 1H, $CHCH_b$**H**$_{b'}$PH), 2.606 (doublet of triplet, 2H, $^1J_{P-H}$= 195 Hz, $^3J_{P-H}$= 7.6 Hz, P**H**$_2$), 2.74 (m, 4H, C**H**$_2$NH), 3.08 (doublet of quintuplet, 1H, $^1J_{P-H}$= 201 Hz, $^3J_{P-H}$= 6.8 Hz, P**H**), 4.94 ppm (s, 1H, C**H**$_c$H$_{c'}$=CH), 4.97 (d, 1H, $^3J_{H-H}$= 9.5 Hz, CH_c**H**$_{c'}$=CH), 5.74 (m, 1H, C**H**). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): 14.26 (d, $^1J_{C-P}$= 10 Hz, **C**H$_2$PH$_2$), 19.62 (d, $^1J_{C-P}$= 12 Hz, **C**H$_2$PH), 25.44 (d, $^1J_{C-H}$=15 Hz, CH**C**H$_2$PH), 47.63 (dd, $^3J_{C-PH}$=22, $^4J_{C-PH2}$= 14 Hz, PHCH$_2$**C**H$_2$NH), 51.80 (d, $^3J_{C-P}$= 24 Hz, (PH$_2$)-**C**H$_2$NH), 115.49 (d, $^3J_{C-P}$= 6 Hz, **C**H$_2$=CH), 135.22 (s, CH$_2$=**C**H). ^{31}P{^{1}H}NMR δ ppm ($CDCl_3$): -149.11 (**P**H$_2$), -74.15 (**P**H). IR (film): ν(N-H) 3257 s br, ν(P-H) 2280 s br, ν(C=C) 1635 w, ν(P-C) 800 s cm^{-1}. MS (APCl): m/z 194 (70 %, $[M+O+1]^+$), 178 (30 %, $[M+1]^+$).

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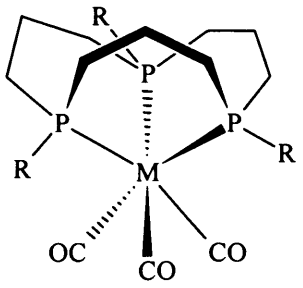
Chapter 4:

TRICARBONYL MANGANESE TRIBENZANNULATED MACROCYCLE COMPLEXES

4.1. Introduction

4.1.1. Synthesis of tridentate macrocycles by template methods.

Following Norman's elegant synthesis of 1,5,9-triphosphacyclododecane macrocycle (12[ane]P_3H_3) by a metal template synthesis using the tricarbonylmolybdenum(0) fragment as template,[1] Edwards and co-workers developed the further derivatization and demetallation of this type of macrocycle (Figure 4-1).[2-6] The co-ordination abilities of the 12[ane]P_3R_3 ligands were also tested with a range of transition metals.[7-11] Attempts to synthesise smaller ring triphosphorus macrocycles by using vinylphosphines on $M(CO)_3$ (M=Cr, Mo) templates were unsuccessful.[6] It was proposed that the lack of steric compression of the carbonyl ligands to reduce the distance between the three phosphorus atoms was one of the reasons for which the cyclisation process did not proceed.[6]



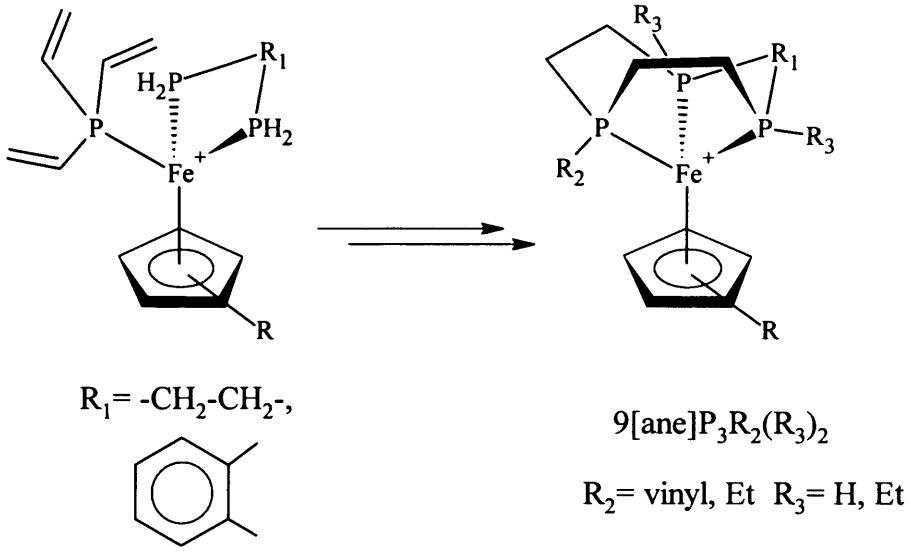
M= Cr, Mo

12[ane]P_3R_3

Figure 4-1

Later investigations using cationic RFe(II) (R= Cp, Cp^*, $CpSiMe_3$) fragments as template allowed to access to small ring-size triphosphorus macrocycles.[12-15] Using this approach, 9-membered triphosphorus macrocycles were synthesised by a Michael-type addition between a primary diphosphine with tris(alkenyl)phosphine both coordinated to a CpFe(II) fragment (Scheme 4-1). The presence of the Cp^- spectator ligand in these systems assists in compressing the non-bonded P-P distances in the precursor complexes and the manipulation of substituents on the Cp^- ligand introduces a degree of control of these steric

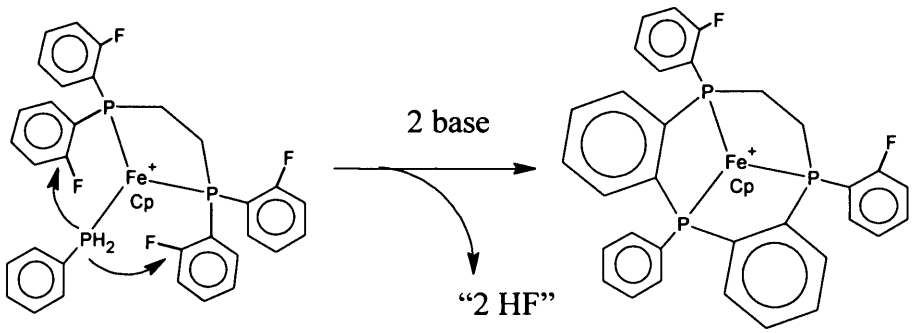
properties facilitating cyclisation. The rates of cyclisation as well as the solubility of the complexes were also dependent upon the substituents of the Cp group. The base catalysed reaction also allowed the synthesis of macrocycles with asymmetric backbones unachievable by the pre-existing group 6 $M(CO)_3$ template methods.



Scheme 4-1

It has been previously noted that fluoro aryl substituents are susceptible to nucleophilic displacement when situated *ortho* to an electron withdrawing group.

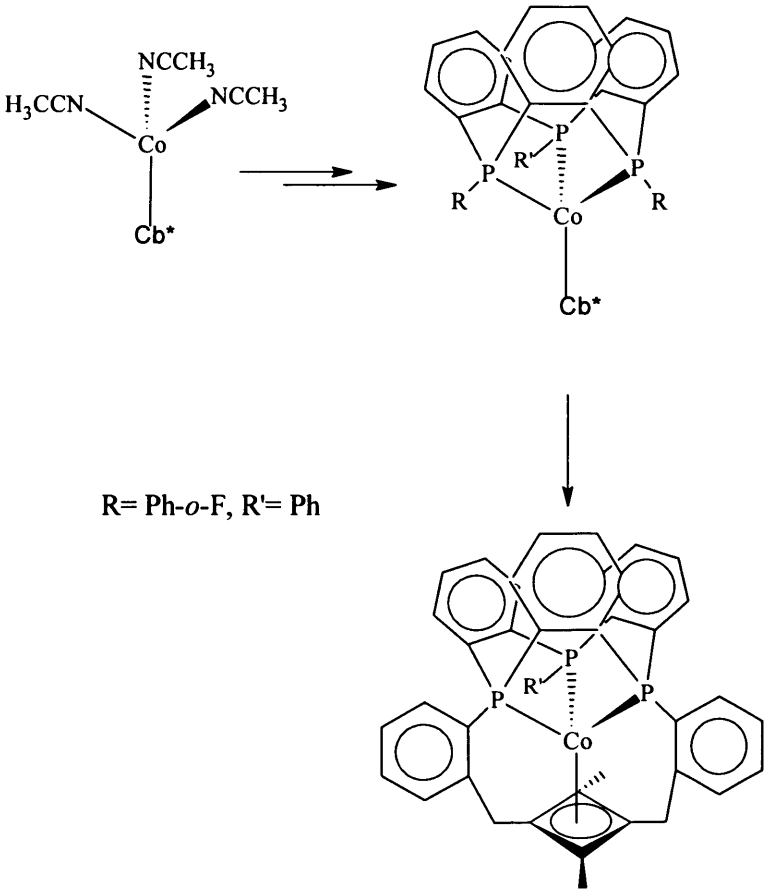
This property was successfully exploited in the base activated template cyclisation of *o*-fluoro arylphosphines with primary phosphines (Scheme 4-2) resulting in rigid *o*-phenylene bridged 9-membered P_3 macrocycles, again on the CpFe(II) template. [16]



Scheme 4-2

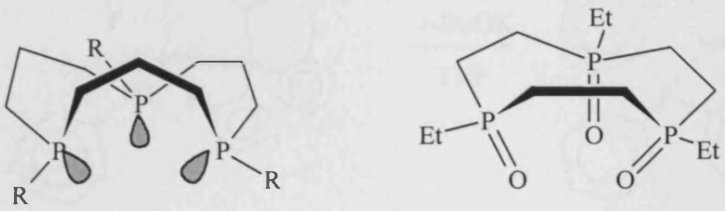
In general, these types of macrocycles are more rigid than macrocycles synthesised by other means due to the inherent rigidity of the di- and tribenzannulated backbones functions.

In all cases, removal of the macrocycle from the CpFe(II) template was unsuccessful and the method was successfully transferred to a tetra(methyl)cyclobutadienyl cobalt(I) template (Cb^*Co) (Scheme 4-3).[17] A subsequent side reaction also occurred whereby remaining *o*-fluorophenyl substituents in the macrocycle underwent substitution resulting in C-C bond formation to the methyl groups in Cb^* (Scheme 4-3).[17] This type of reaction is precedented by observations of Saunders and co-workers who found C-C bond formation between penta(fluoro)phenylphosphine and Cp* ligands coordinated to Ir(I) and Rh(I) complexes.[18]



Scheme 4-3

Unfortunately, the ligand liberation of most of the macrocycle complexes prepared remains a significant problem. To date, only 1,5,9-triphosphacyclododecane ligands, 12[ane]P_3R_3, have been successfully liberated in reasonable yield from Cr(0) and Mo(0) templates by oxidation of the metal with halogens followed by digestion with NaOH in ethanol.[4, 19] The ligand liberation also proceeds for 12[ane]P_3R_3 ligand in CpFe(II) templates with sodium metal in liquid ammonia (Figure 4-2).[20] However, only one 9-membered phosphine macrocycle has been liberated as its phosphine trioxide using either aqueous hydrogen peroxide under acidic conditions or bromine in dichloromethane followed by digestion with sodium hydroxide (Figure 4-2).[15] Efforts to reduce the trioxide phosphine using different reducing agents such as $LiAlH_4$ or $PhSiH_3$ have failed, possibly due to the poor solubility of the oxide in appropriate solvents.[15]



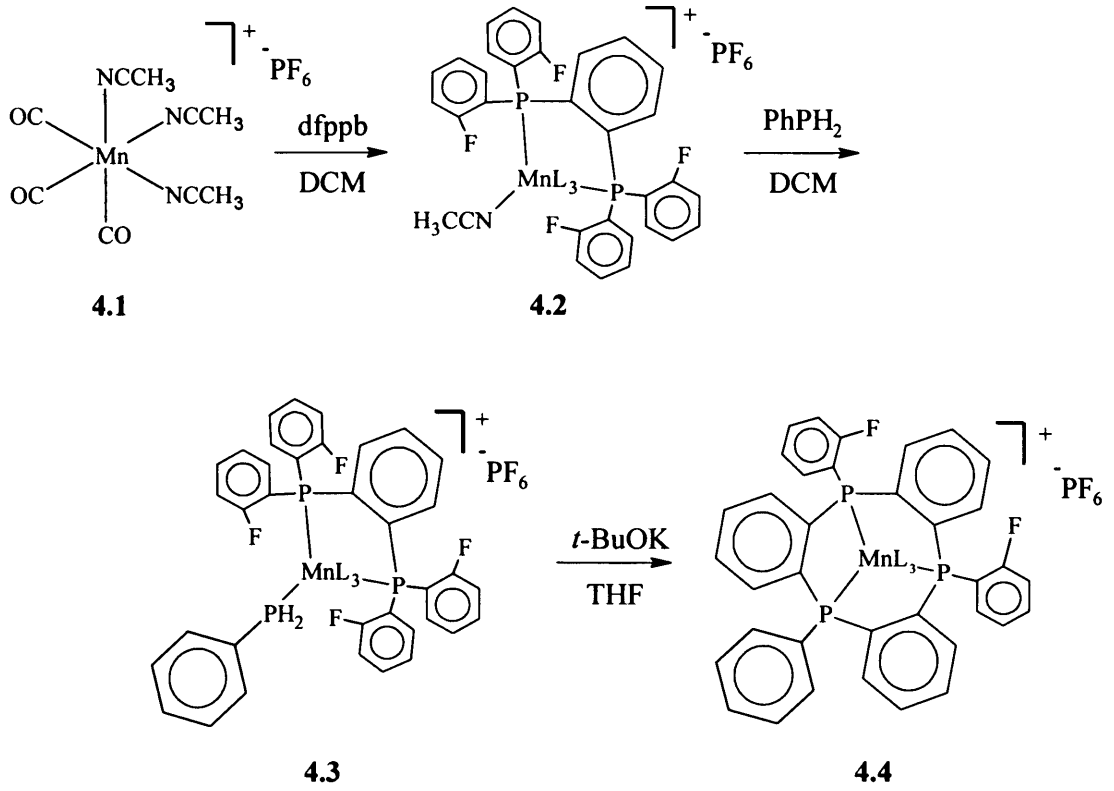
12-[ane]P_3R_3 9-[ane]P_3Et_3

Figure 4-2: Liberated 12- and 9- membered triphosphorus macrocycles

In a recent study,[17] the fragment $Mn^I(CO)_3$ was used as template to synthesise a 9-membered triphosphorus macrocycle. The synthetic route involves the sequential substitution of acetonitrile ligands in the $[Mn(CH_3CN)_3(CO)_3]PF_6$ precursor (**4.1**) by successive introduction of 1,2-bis(di-2-fluorophenylphosphino)benzene and phenylphosphine ligands (Scheme 4-4). It has been suggested that by using the $Mn^I(CO)_3^+$ template, the formation of the macrocycle **4.4** was possible in contrast to group 6 metal carbonyls $M(CO)_3$ due to the intrinsically smaller radius of the cationic Mn(I) center compared to that of neutral metal in the group 6 metal carbonyls (covalent radii: 1.34 Å for Mn, 1.37 Å for Cr, 1.51 Å for Mo).[21]

Liberation studies with **4.4** reported the formation of a new complex **4.5** by ultaviolet irradiation of **4.4** in benzonitrile at high temperature (Figure 4-3).[17] The formation of **4.5** suggests that the macrocycle is initially released from the metal and

oxidised before reco-ordinating to form **4.5**. Complex **4.5** was obtained using harsh conditions and in very low yield.



dfppb= 1,2-bis(di-2-fluorophenyl)phosphinobenzene
L= CO

Scheme 4-4: Synthetic route to 4.4

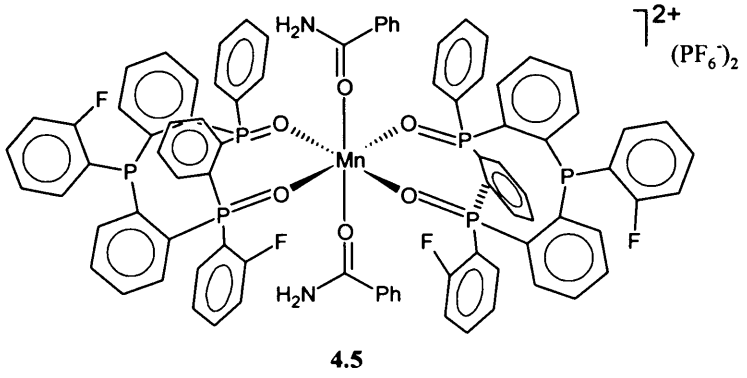


Figure 4-3: Compound 4.5 obtained from photolysis of 4.4 in benzonitrile

4.1.2. Aims

The promising results obtained with the Mn(I) macrocycle complex **4.4** indicate the possibility of demetallation of the 9-membered triphosphorus macrocycles from the manganese(I) center. However, problems associated with the synthesis of **4.4** lie in the difficulty to access to one of its precursors 1,2-bis(di-2-fluorophenyl)phosphinobenzene (32 % yield) as well as the presence of two additional C-F bonds susceptible of nucleophilic reactions in the product. The lack of opportunity to functionalise the phosphorus atoms is also an inconvenience of this system. Therefore, it was desirable to find an alternative synthetic route to 9-membered triphosphorus macrocycles which does not present these disadvantages.

9-Membered macrocycles formed by a double dehydrofluorination reaction in the cyclisation step, can be prepared by two different manners. The first reaction, already seen in the synthesis of **4.4**, comprises the coupling of a monodentate primary phosphine with a bidentate phosphine bearing *o*-fluorophenyl groups on the phosphorus atom (disconnection **d1** in Figure 4-4).

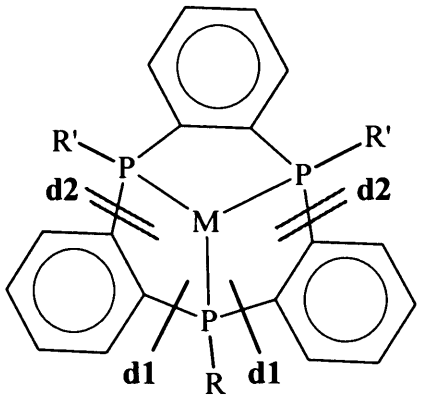


Figure 4-4: Possible disconnections for the retro-synthesis of 9-membered triphosphorus macrocycles (d1, d2)

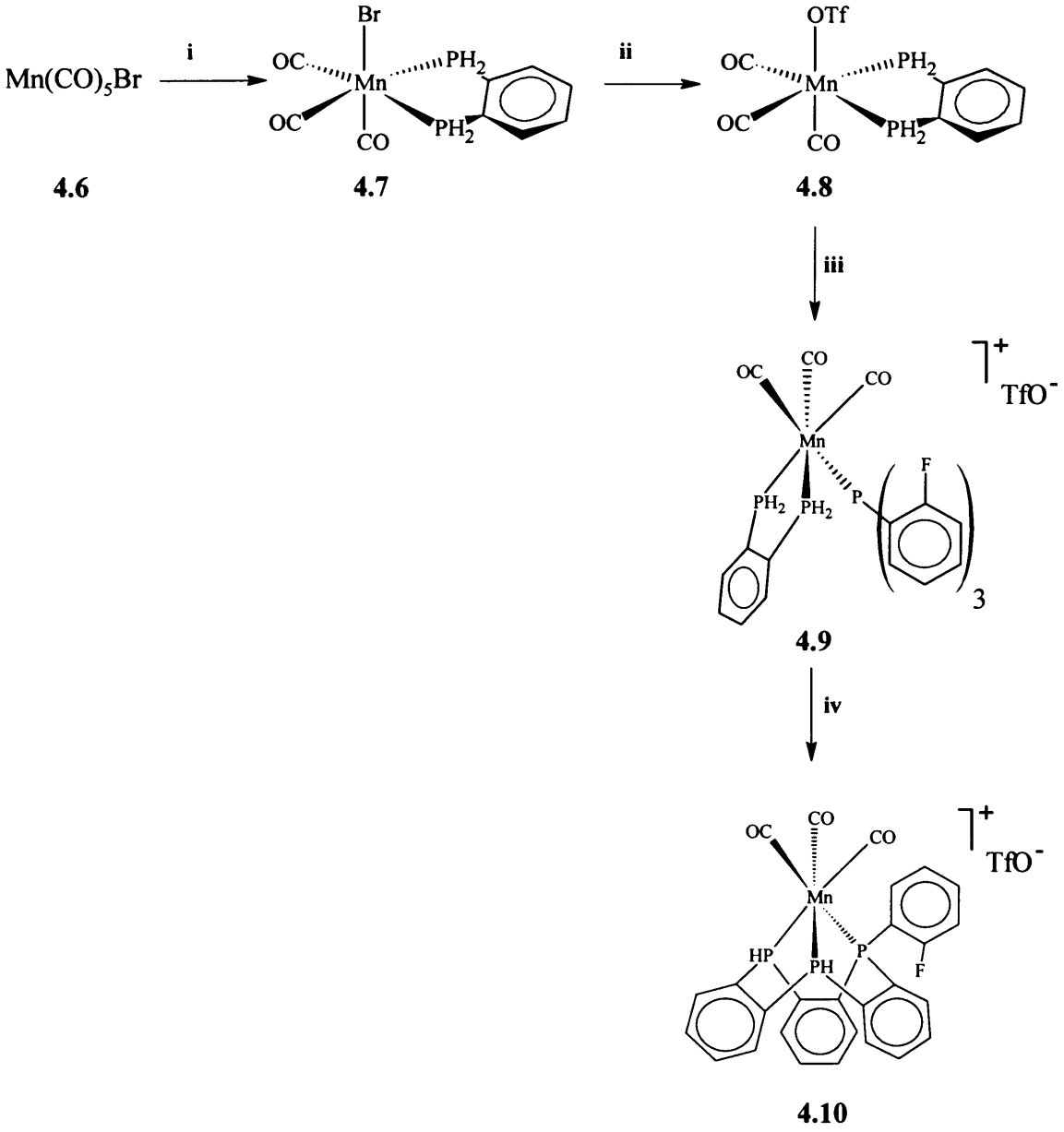
The second method comprises the coupling of a bidentate primary diphosphine with a monodentate *o*-fluorophenyl phosphine (disconnection **d2** in Figure 4-4). This second method was therefore investigated as an alternative way to obtain a 9-membered

triphosphorus macrocycle on a $Mn^{I}(CO)_3$ fragment without the disadvantages observed in the synthesis of **4.4**.

The study of different liberation methods was also investigated in order to achieve the demetallation of the macrocycle without oxidation of the phosphorus atoms.

4.2. Results and discussion

4.2.1. Alternative route to tribenzannulated 9-membered triphospha-macrocycles based on the $Mn^{I}(CO)_3$ fragment



4.6 **4.7** **4.8** **4.9** **4.10**

i) 1,2-bisphosphinobenzene, $CHCl_3$; ii) TfOAg, DCM; iii) tris-(2-fluorophenyl)-phosphine, DCM; iv) *t*-BuOK, THF

Scheme 4-5: Synthetic route to 4.10

The tribenzannulated 9-membered triphosphorus macrocycle **4.10** was synthesised in good yield from $Mn(CO)_5Br$ in a 4-step reaction (Scheme 4-5). The synthesis strategy involved substitution, by 1,2-bis(phosphine)benzene, of two carbonyls in **4.6** which lead to the known compound **4.7**.[22] The bromide was then substituted by the weakly coordinating triflate group leading to the diphosphine-triflate **4.8**. The triflate group was readily displaced by tris(2-fluorophenyl)phosphine, resulting in the formation of the bisphosphine-monophosphine complex **4.9**. The cyclisation of **4.9** by double dehydrofluorination gave rise to the secondary phosphine 9-membered macrocycle **4.10**. The followed synthetic route is going to be explained in more detail in the next section.

4.2.1.1. Synthesis of tricarbonyl-{1-(2-fluorophenyl)-[b,e,h]-tribenzo-1,4,7-triphosphacyclononane}manganese(I) triflate (4.10)

As has been previously reported,[22] the reaction of **4.6** with 1,2-diphosphinobenzene in refluxing chloroform gave rise to compound **4.7**. The reaction, followed by $^{31}P\{^1H\}$ NMR spectroscopy, showed complete consumption of 1,2-diphosphinobenzene after 1 hour of reaction. Compound **4.7** was isolated in good yields as an orange, air-sensitive solid.

4.8 was prepared following a procedure reported for similar phosphine chelate complexes.[23] The treatment of **4.7** with an equimolar amount of silver triflate in dichloromethane at room temperature afforded the neutral triflate complex **4.8** which was readily isolated. The reaction was followed in solution by IR spectroscopy. The three initial carbonyl bands of the facial compound **4.7** (2039, 1976, 1931 cm^{-1}) were shifted to higher frequencies during the formation of **4.8** (2057, 1994, 1944 cm^{-1}). This shift is attributed to the increased electron-withdrawing properties of the triflate group compared to bromide group resulting in weaker π- bonding in the metal-carbonyl bond. **4.8** has been characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopies. The $^{31}P\{^1H\}$NMR spectrum of **4.8** shows a singlet at δ_P -3.25 ppm (triplet, $^1J_{P\text{-}H}$= 341 Hz) confirming the facial disposition of the ligands in **4.8**. Since a meridional isomer would give rise to an AB ^{31}P NMR pattern. The resonance is slightly shifted to high-field compared to its precursor **4.7** (δ_P -1.00 ppm, triplet, $^1J_{P\text{-}H}$= 380 Hz) due to the electronegativity of the triflate ligand. The ^1H NMR spectrum shows a doublet at δ_H 5.97 ppm assigned to the protons of the

primary phosphine, and two broad singlets at δ_H 7.65 and 8.01 ppm assigned to the aromatic protons. The $^{13}C\{^1H\}$NMR spectrum also confirms the synthesis of **4.8**, a quartet at δ_C 118.90 ppm ($^1J_{C\text{-}F}$= 321 Hz) is assigned to the quaternary carbon of the triflate group, whilst the virtual triple at δ_C 131.04 ppm (triplet, $^1J_{C\text{-}P}$= 45 Hz) is assigned to the quaternary aromatic carbon. The signals of the two other aromatic carbons are observed at δ_C 132.27 and 135.44 ppm. The two different carbonyl carbons of **4.8** appear at δ_C 213.65 and 218.09 as broad singlets in a 2:1 ratio, and are assigned to the equatorial and axial carbonyls, respectively. The broadness of the signal precludes resolution of J_{PC} and is caused by the ^{55}Mn quadrupole.[24] The ^{19}F NMR spectrum shows a singlet at δ_F -77.59 ppm from the triflate group. Complex **4.8** was normally generated *in situ*, as its isolation it is not necessary for the next step.

The weakly coordinating triflate group of **4.8** is readily labile and was displaced in dichloromethane by the neutral tris(2-fluorophenyl)phosphine ligand under mild conditions to yield **4.9**. The reaction was followed by $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopies. The $^{31}P\{^1H\}$NMR spectrum showed the growth of two new signals at δ_P -1.86 and 39.69 ppm whilst the resonance at δ_P -3.25 ppm decreased. The ^{19}F NMR spectrum also showed the formation of a new specie at δ_F -93.15 ppm. The rate of the reaction was shown to be dependent upon the incoming-ligand concentration, reactions with a large excess of tris(2-fluorophenyl)phosphine (**4.8**:PR_3=1:10) occurred smoothly at room temperature, whereas reactions with small excess (**4.8**:PR_3=1:1.6 ratio) required further heating. The use of tris(2-fluorophenyl)phosphine in large excess however, induced apparently side-reactions (*vide supra*).

Compound **4.9** was isolated as an off-white and air-sensitive solid in 59 % yield. The facial geometry of the complex **4.9** is confirmed by the $^{31}P\{^1H\}$NMR spectrum of **4.9** which shows two broad peaks assigned to two different types of phosphorus atoms at δ_P -1.86 and 39.69 ppm. The former resonance, assigned to the coordinated bidentate primary phosphine, is little affected by the displacement of the triflate group by the tris(2-fluorophenyl)phosphine ligand as compared to **4.8**. The latter resonance is assigned to the phosphorus of the tris(2-fluorophenyl)phosphine ligand. This resonance is considerably shifted downfield ($\Delta\delta$= 81.79 ppm) upon co-ordination to the manganese centre in comparison to free tris(2-fluorophenyl)phosphine (δ_P= -42.6 ppm, q, $^3J_{P\text{-}F}$=59 Hz).[25] The

broadness of the signals in the $^{31}P\{^{1}H\}$NMR spectrum is again due to the coupling between the ^{31}P and the quadrupolar ^{55}Mn atoms, and does not permit resolution of coupling constants between the nucleii.[24] The ^{19}F NMR spectrum of **4.9** also reflects the effect of the co-ordination of the tris(2-fluorophenyl)phosphine ligand to the manganese centre with a singlet at δ_F -93.15 ppm shifted by $\Delta\delta$= 11.13 ppm compared to the free ligand (doublet, δ_F= -104.28 ppm, $^{3}J_{F\text{-}P}$=59 Hz). The $^{3}J_{F\text{-}P}$ coupling constant is no longer visible in the ^{19}F NMR spectrum. The other resonance observed at δ_F -77.73 ppm in the ^{19}F NMR spectrum is assigned to the triflate counter-anion.

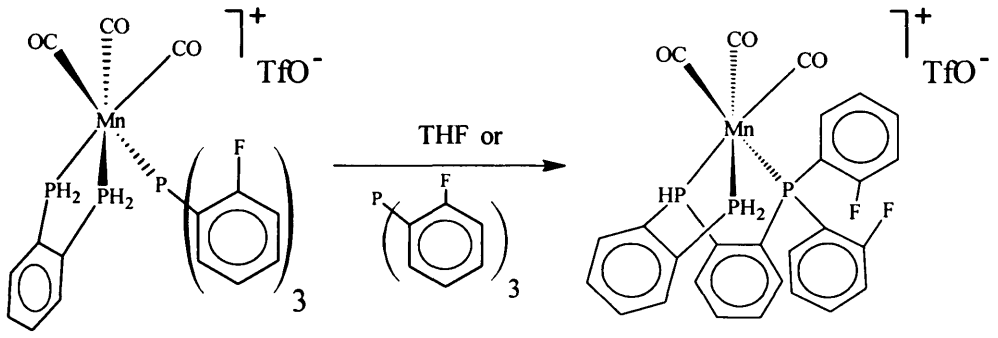
The ^{1}H NMR spectrum of **4.9** displays two sets of doublets of doublets at δ_H 5.37 and 6.13 ppm which are assigned to the non-equivalent primary phosphine protons. These protons are coupled to the phosphorus atom to which they are directly attached ($^{1}J_{H1\text{-}P1}$=380 Hz, $^{1}J_{H2\text{-}P1}$=386 Hz), and also to the phosphorus atom of the co-ordinated tris(2-fluorophenyl)phosphine ligand ($^{3}J_{H1\text{-}P2}$= 14.4 Hz, $^{3}J_{H2\text{-}P2}$= 9 Hz). Six multiplets between δ_H 7.05-8.02 ppm complete the spectrum, and are assigned to the aromatic protons of **4.9**. The $^{13}C\{^{1}H\}$NMR spectrum of **4.9** also confirms the C_s symmetry of the complex. Nine different carbons from the co-ordinated 1,2-bis(phosphine)benzene and tris(2-fluorophenyl)phosphine ligands are observed (see experimental). In some cases, these signals show coupling with the phosphorus or the fluorine atoms, or both. A broad resonance at δ_C 214 ppm is assigned to the carbonyl groups, however, signals due to the axial and equatorial carbonyls are coincident within the linewidth of the resonance.

The IR spectrum of **4.9** shows two intense bands (2053 and 1983 cm^{-1}) and a weak band (2383 cm^{-1}) assigned to the carbonyl and the P-H stretching bonds respectively. The number of bands in the carbonyl region is consistent with a facial coordination of the ligands in the co-ordination sphere of the manganese. **4.9** has also been characterised by X-ray diffraction (*vida supra*).

Facial tricarbonylmanganese(I) complexes with phosphine donor ligands are known to isomerise from the facial to the meridional isomer at room temperature or by boiling in different solvents.[26, 27] No evidence (NMR) of isomerisation of **4.9** to the meridional isomer was observed under the conditions used (see experimental).

4.2.1.1.1. Partial cyclisation of 4.9

Although isomerization of **4.9** was not observed, the dissolution of a small amount of **4.9** in THF resulted in a rapid colour change from colourless to pale yellow. The $^{31}P\{^{1}H\}$NMR and ^{19}F NMR spectra of the solution indicated the formation of a new compound as the major component of the solution. Spectroscopic data revealed the formation of **4.11**, the product of the partial cyclisation of **4.9** (Scheme 4-6). The spectroscopic data for **4.11** is identical to that recorded for the by-product formed in reaction of **4.8** with an excess of the tris(2-fluorophenyl)phosphine ligand. The partial cyclisation of **4.9** is presumably activated by the THF solvent or the excess of tris(2-fluorophenyl)phosphine ligand both acting as base to yield complex **4.11**. It is of interest to note that only partial cyclisation of **4.9** was obtained. The complete cyclisation of **4.9** requires stronger bases (*vide supra*).



4.9 **4.11**

Scheme 4-6: Partial cyclisation of 4.9

Complex **4.11** was isolated as a pale yellow air-sensitive solid. **4.11** is the first example of a linear intermediate isolated in macrocyclisations of this type. It is also the first complex which contains primary, secondary and tertiary phosphine groups in the coordination sphere. **4.11** has been fully characterized by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{19}F NMR and IR spectroscopy. **4.11** has also been characterised by X-ray diffraction. The $^{31}P\{^{1}H\}$NMR spectrum of **4.11** displays a signal at δ_P -1.69 ppm assigned to the phosphorus of the primary phosphine (triplet, $^{1}J_{H\text{-}P1}$= 374 Hz), whilst the secondary phosphorus ($^{1}J_{H\text{-}P}$= 404 Hz) and the tertiary phosphorus atoms have overlapping signals

centred at δ_P 71.90 ppm. The ^{19}F NMR spectrum of **4.11** shows two signals for the non-equivalent fluorine atoms of the co-ordinated tris(2-fluorophenyl)phosphine ligand at δ_F -95.85 and -96.78 ppm. The resonance of the triflate counter-anion is seen at δ_F -78.79 ppm. In the ^1H NMR spectrum of **4.11**, two sets of doublets of multiplets at δ_H 4.56 and 5.82 ppm are attributed to the two non-equivalent protons of the primary phosphine. The resonance peaks at δ_H 5.52, 6.62, 8.47 and 8.84 ppm are assigned to the new benzannulated ring formed. The rest of the protons are observed as multiplets between 7.02-7.89 ppm. The $^{13}C\{^1H\}$NMR spectrum of **4.11** shows a complicated pattern resulting from the C_1 symmetry of **4.11**. A broad multiplet at δ_C 214.22 ppm is assigned to the carbonyl groups. The IR spectrum of **4.11** shows the P-H stretching band at 2367 cm^{-1} and two bands at 2045, 1957 cm^{-1} characteristic of the presence of the $Mn(CO)_3$ moiety. In addition, the molecular ion of **4.11** is observed in the mass spectrum at m/z = 577 (100 %).

4.2.1.1.2. Complete cyclisation of 4.9

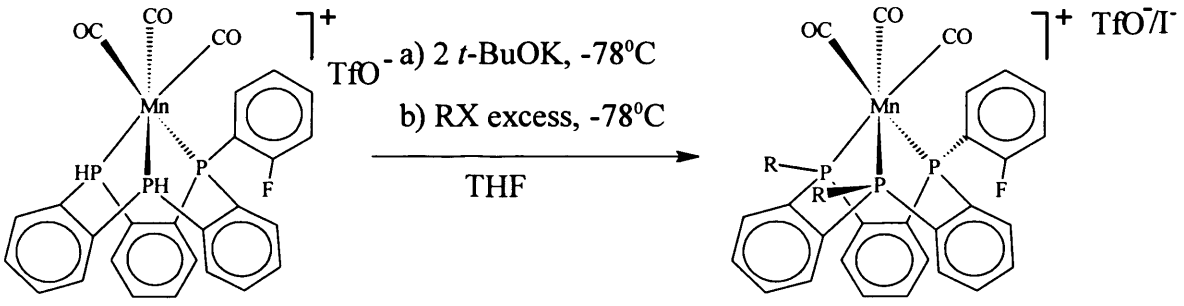
Intramolecular coupling of **4.9** was carried out at low temperature (-78°C) to avoid partial cyclisation (Scheme 4-5). After the addition of two equivalents of *t*-BuOK to a THF solution of **4.9**, the colourless solution changed immediately to yellow. The $^{31}P\{^1H\}$ NMR spectrum of the solution showed the rapid formation of the new compound **4.10**. Presumably due to the acidic protons of the secondary phosphine groups, complex **4.10** has shown instability in solution, especially in chlorinated solvents and therefore has been prepared for subsequent reactions normally without isolation.

The $^{31}P\{^1H\}$ NMR spectrum of **4.10** displays two broad signals at δ_P 74.42 and 110.47 ppm. The former is assigned to the secondary phosphine whilst the latter is attributed to the tertiary phosphine. The broadness of the signals, again due to the quadrupolar ^{55}Mn nuclei, does not allow the resolution of the P-H coupling constant. The ^{19}F NMR spectrum of **4.10** displays two peaks at δ_F -79.34 and -96.87 ppm from the triflate counter-anion and the fluorine of the aryl group respectively. The IR spectrum of **4.10** is consistent with the facial geometry of **4.10**, with only two bands in the carbonyl region (2044 and 1970 cm^{-1}). These two carbonyl bands have lower frequencies than in complex **4.9** indicating stronger σ-donor properties of the macrocycle **4.10** as compared to its

precursor. The mass spectrum of **4.10** also confirms its composition and the molecular ion is observed at m/z =557 (100 %).

4.2.1.2. Secondary Phosphine Functionalisation

The reactivity of the phosphorus-hydrogen bond of the secondary phosphines offers great synthetic potential for further derivatization of **4.10**. The previously mentioned 12-membered macrocycle was functionalised through the secondary phosphine atom by hydrophosphination and alkylation reactions.[2, 28] We decided to alkylate the secondary phosphine groups of complex **4.10**, preventing in this manner undesirable reactions resulting from its instability in solution. The procedure proceeds by an initial deprotonation of the secondary phosphine groups with a base, followed by alkylation with a haloalkane (Scheme 4-7).



4.10 R=Me, **4.12**

Scheme 4-7: Alkylation of secondary phosphines in complex 4.10

Methyl iodide was initially used as an alkylating agent according to the following.

The treatment (at -78°C) of **4.10** with two equivalents of *t*-BuOK in THF produce a colour change from yellow to brown indicating the formation of the di-phosphide anions. The addition of excess of methyl iodide at -78°C, causes the slow precipitation of a white solid identified as the tri-tertiary macrocycle complex, **4.12,** in good yield (65 % based on **4.9**). Compound **4.12** has been isolated as a mixture of a triflate and iodide salt. The $^{31}P\{^{1}H\}$ NMR spectrum of **4.12** displays a broad resonance from δ_P 95.44 to 107.09 ppm. The broadness of this resonance signal is due to the quadrupolar ^{55}Mn nuclei, the signals corresponding to the two different types of phosphorus in **4.12** overlap. The ^{19}F NMR

spectrum of **4.12** shows two signals at δ_F -76.85 and -94.34 ppm corresponding to the triflate of the counter-anion and the aryl group, respectively. Integration of the triflate/fluorine signal is not consistent with a 3:1 ratio, and varies depending upon conditions and between samples. The crystal structure of **4.12** shows, however, iodide as counter-anion. The ^{1}H NMR spectrum of **4.12** displays a virtual triplet at δ_H 2.57 ppm ($^2J_{H-P}$= 4.8 Hz) assigned to the protons of the methyl groups. Three multiplets between the ranges 7.24-7.38, 7.57-7.76 and 8.23-8.30 ppm correspond to the aromatic protons. The $^{13}C\{^1H\}$NMR spectrum of **4.12** shows a doublet of doublets at δ_C 13.91 ppm for the carbon of the methyl group coupled to the two phosphorus atoms with a similar coupling constant ($^1J_{C-P}$= 18.7 Hz, $^3J_{C-P}$= 19 Hz). It has not been possible to assign all the aromatic carbons, however the resonances observed at δ_C 117.44, 125.33, 132.61, 134.97 and 163.15 ppm are assigned to the carbons of the 2-fluorophenylphosphine group. The resonances of the carbonyl groups were not detected, even by increasing the relaxation time and presumably due to broadening by the manganese nucleus. The IR spectrum of **4.12** confirms the presence of the carbonyl groups with two stretching bands at 2025 and 1965 cm^{-1}. These bands appear at lower frequencies of **4.10** reflecting the increase of the σ-donation abilities of the macrocycle ligand after the introduction of the methyl groups on the phosphorus atoms. The mass spectrum also confirms the formation of **4.12** (m/z=585, 100 %, [M$^+$]). Table 4-1 summaries the spectroscopic data collected for the complexes **4.7-4.12**.

Table 4-1: $^{31}P\{^1H\}$, ^{19}F and IR data of complexes 4.7-4.12

Complex	δ (^{31}P) ppm	δ (^{19}F) ppm	ν(CO) cm^{-1}
4.7	-1.00	-	2039, 1976, 1931
4.8	-3.25	-77.59	2057, 1994, 1944
4.9	-1.86	-77.73	2053, 1983
	39.69	-93.15	
4.10	74.42	-79.34	2044, 1970
	110.47	-96.87	
4.11	-1.69	-78.79	2045, 1957
	71.90	-95.85	
	71.90	-96.78	
4.12	95.44-107.09	-76.85	2025, 1965
		-94.34	

In order to explore other alkyl derivatives, *i*-PrCl was also used as an alkylating agent in the substitution reaction of **4.10**. The procedure followed was identical to that followed for the synthesis of **4.12**; however the synthesis of the bis-isopropyl-substituted macrocycle resulted in the recovery of **4.10**. This failure is probably due to the steric bulkiness of the alkylating agent, hindering the formation of the phosphorus carbon bond. Further studies will be needed in order to find suitable conditions for the introduction of bulkier alkyl groups, by either alkylation or hydrophosphination reactions.

4.2.2. Structural Studies

X-Ray diffraction structural analyses were carried out on complexes **4.9**, **4.11** and **4.12** (Figures 4-5, 4-6 and 4-7 respectively). The crystals of complex **4.9** and **4.11** were obtained by slow diffusion of hexane into a dichloromethane solution of the compound; however crystals of **4.12** were grown by standing a saturated $CDCl_3$ solution of **4.12** at room temperature. In order to compare the crystal data of the three structures, selected bonds length and angles have been compiled in Table 4-2. Complexes **4.9** and **4.11** crystallized as triflate salts whilst **4.12** crystallized as a mixture of iodide/triflate salt confirmed by both NMR spectroscopy and X-ray difraction. The three crystal structures show a distorted octahedral arrangement of the ligands around the Mn centre as predicted from the spectroscopic studies, with three CO ligands occupying *fac* co-ordination sites.

The structure of the cation **4.9** (Figure 4.5) shows a 5-membered ring formed by the chelating 1,2-bisphosphinobenzene ligand in the pseudo-equatorial plane, whilst the tris(2-fluorophenyl)phosphine ligand coordinates in the axial position. The Mn-P(3) distance [2.3749(5) Å] is longer than that of the chelating 1,2-bisphosphinobenzene ligand [Mn-P(1)= 2.3068(5), Mn-P(2)= 2.2927(5) Å], probably reflecting the greater steric demand of the tris(2-fluorophenyl)phosphine ligand; the primary phosphine donors might also be expected to be effective π-acceptors. In contrast, complex **4.3** presents the Mn-P bond lengths similar to each other [e. g. 2.332(1) Å for the dfppb ligand and 2.322(1) Å for the $PPhH_2$ ligand].[17]

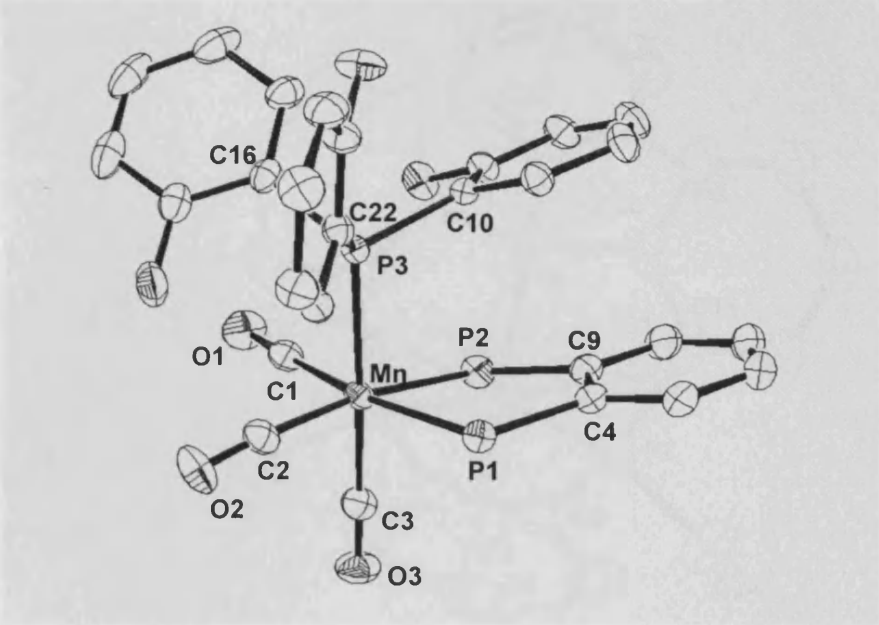


Figure 4-5: Molecular structure of 4.9, 50% probability Ellipsoids, H atoms omitted for clarity.

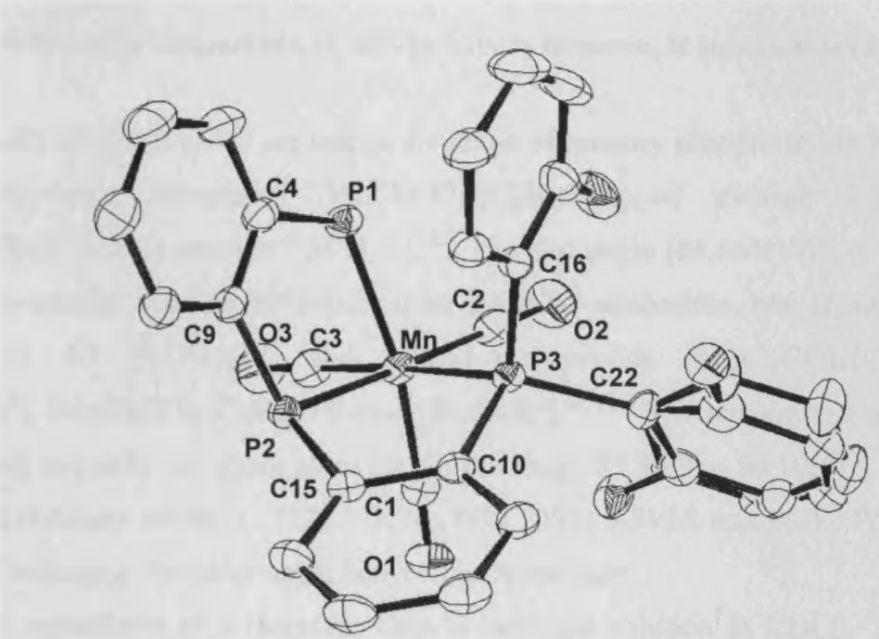


Figure 4-6: Molecular structure of 4.11, 50% probability Ellipsoids, H atoms omitted for clarity.

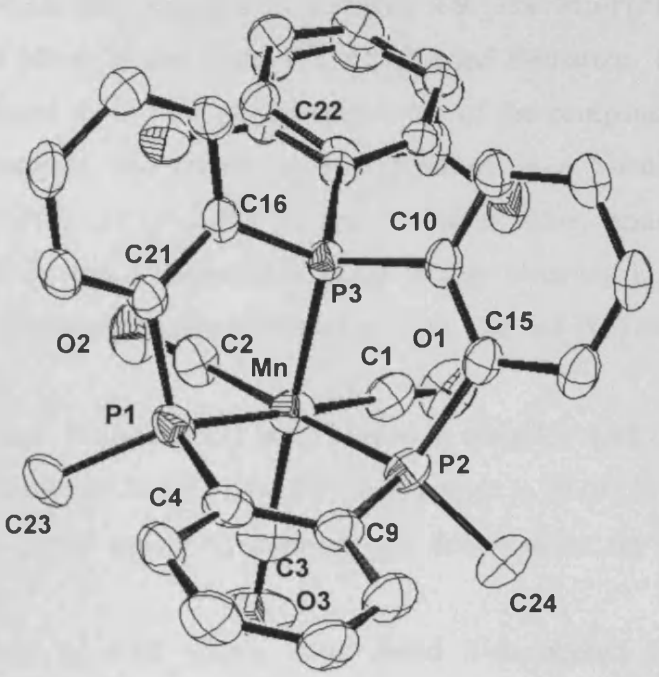


Figure 4-7: Molecular structure of 4.12, 50% probability Ellipsoids, H atoms omitted for clarity.

The Mn-P1/P2 distances of **4.9** are within the range of primary phosphine-Mn bond length observed in other complexes $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}$ average 2.281 Å],[22] $[\{MnBr(CO)_3(PPhH_2)_2\}$ average 2.3135 Å].[22] The bite angle [81.664(19)°] of the chelate ring in **4.9** is smaller than the 90° expected for a regular octahedron, but is similar to that observed in **4.3** [83.61(4)°], and related compounds $[MnCl(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}$[83.06(6)°], $[MnCl(CO)_3\{C_6H_4(PPh_2)_2\text{-}o\}$[81.97(6)°].[17, 22] The remaining angles around Mn involving mutually *cis* donor atoms lie in the range 85.95(9) - 96.10(6) °. The P....P non-bonded distances are P(1)...P(2) 3.007Å, P(1)...P(3) 3.317Å and P(2)...P(3) 3.480Å; the last two reflecting the wider angle between both nucleus.

4.11 crystallised as a racemate from a saturated solution in $CDCl_3$. The X-Ray diffraction of **4.11** (Figure 4.6) shows two fused 5-membered rings comprising the P(1)-Mn-P(2)-C(9)-C(4) atoms of the 1,2-bisphosphinobenzene chelating ligand and the P(2)-Mn-P(3)-C(10)-C(15) atoms of the new ring resulting from the dehydrofluorination reaction. The Mn-P(1)/P(2)/P(3) distances [2.2817(6), 2.2657(6) and 2.3373(6) Å,

respectively] are shorter than that observed in complex **4.9**. The Mn-P(2) distance is slightly shorter than that of Mn-P(1) due to the P(2)-C(15) bond formation. The Mn-P(3) distance has also been reduced due to the partial cyclisation of the compound. The non-bonded P...P distances between phosphorus atoms contained in a 5-membered ring [P(1)...P(2)= 3.0039 Å, P(2)...P(3)= 2.974 Å] are of similar value, whilst the length between P(1)...P(3) [3.395 Å] has a comparable value to that observed in **4.9**. The 2-fluorophenyl group perpendicular to the plane defined by P(1), Mn and P(2) atoms exhibits positional disorder.

The P(1)-Mn-P(2) and P(2)-Mn-P(3) bond angles in complex **4.11** are 83.86(2)° and 80.49(2)° respectively, however the P(1)-Mn-P(3) bond angle is 94.59(2)°. The rest of the angles around the Mn centre involving mutually *cis* donor atoms lie in the range 85.85(8) - 94.58(11)°.

The crystal structure of **4.12** shows three fused 5-membered rings of the triphosphorus 9-membered macrocycle coordinating in a facial mode to the Mn centre (Figure 4.7). The Mn-P distances (average 2.255 Å) are significantly shorter than those observed for **4.9** and **4.11**. However these values are similar to those reported for **4.3** (average 2.259 Å).[17] The P...P non-bonded distances for both macrocycle complexes **4.11** and **4.3** have the same average (3.023 Å). The residual 2-fluorophenyl group also exhibits a positional disorder. The average P-Mn-P angles (84.19°) also compare favourably with those reported for **4.3** (average 83.99°).[17]

Table 4-2: Selected bonds lengths (Å) and angles (°) for complexes 4.9, 4.11 and 4.12

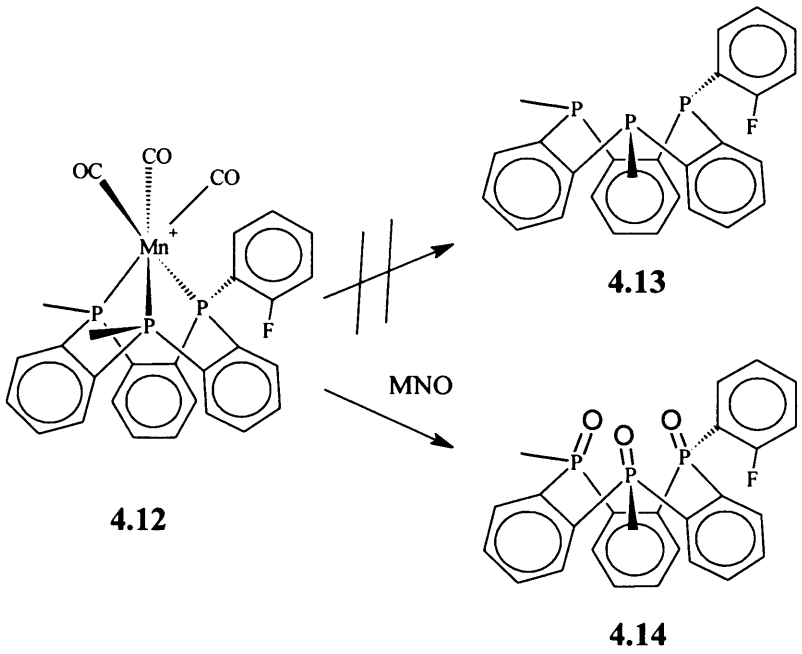
	4.9	4.11	4.12
Mn-P(1)	2.3068(5)	2.2817(6)	2.257
Mn-P(2)	2.2927(5)	2.2657(6)	2.258
Mn-P(3)	2.3749(5)	2.3373(6)	2.250
Mn-C(1)	1.8181(19)	1.826(2)	1.837
Mn-C(2)	1.839(2)	1.830(2)	1.824
Mn-C(3)	1.8354(19)	1.808(2)	1.814
C(1)-O(1)	1.142(2)	1.138(3)	1.130
C(2)-O(2)	1.138(2)	1.138(3)	1.143
C(3)-O(3)	1.133(2)	1.144(3)	1.143
P(1)-C(4)	1.8229(19)	1.812(2)	1.823
P(2)-C(9)	1.811(2)	1.822(2)	1.828
P(3)-C(10)	1.8238(17)	1.824(2)	1.823
P(3)-C(16)	1.8433(18)	1.822(2)	1.832
P(3)-C(22)	1.8350(18)	1.828(2)	1.857
P(2)-C(15)	-	1.807(2)	1.823
P(1)-C(21)	-	-	1.825
P(1)-C(23)	-	-	1.804
P(2)-C(24)	-	-	1.809
P(1)-Mn-P(2)	81.664(19)	83.86(2)	84.39
P(1)-Mn-P(3)	90.198(18)	94.59(2)	83.95
P(2)-Mn-P(3)	96.398(18)	80.49(2)	84.23
P(1)-Mn-C(3)	91.24(6)	85.85(8)	92.13
P(1)-Mn-C(2)	96.10(6)	92.77(8)	89.55
P(2)-Mn-C(3)	84.58(6)	93.67(8)	90.32
P(2)-Mn-C(1)	89.92(6)	90.55(7)	90.53
P(3)-Mn-C(1)	86.99(6)	91.82(7)	91.72
P(3)-Mn-C(2)	93.13(6)	91.32(7)	91.51
P(3)-Mn-C(3)	178.37(6)	174.05(8)	173.72
C(1)-Mn-C(2)	92.83(9)	93.84(10)	95.25
C(1)-Mn-C(3)	91.71(8)	87.09(10)	91.76
C(2)-Mn-C(3)	85.95(9)	94.58(11)	93.57

4.2.3. Studies of macrocyclic liberation reactions

An extensive study into potential alternative liberation methods of the macrocyclic ligand was performed. The complex **4.12** was treated with several reagents in order to release the free 9-membered triphosphorus macrocycle ligand; so far, none of these methods resulted in the isolation of **4.13**. The only compound obtained was the triphosphine oxide macrocycle, **4.14**, in very low yields (< 5%) (Scheme 4-8).

Nevertheless, this is an encouraging result as it confirms the possibility of demetallation of the macrocycle. Further studies will be required in order to find a milder method to obtain either **4.13** or **4.14** in reasonable yields.

All the experiments attempted with the complex **4.12** are discussed below.



4.12

4.13

4.14

MNO=4-methylmorpholine N-oxide

Scheme 4-8

4.2.3.1. Reactivity versus oxidants

4.2.3.1.1. Halogens

Attempts to liberate the 9-membered macrocycle from its cationic Mn(I) template based on the reported liberation of 12[ane]P_3R_3 by halogens failed.[4, 19] The stoichiometric reaction of **4.12** with Br_2 at room temperature in DCM did not give rise to the oxidative addition of the halogen to the Mn center or to oxidative decarbonylation of **4.12**. The use of an excess either of the Br_2 or a stronger oxidant like Cl_2 gas, led only to the recovery of the starting material **4.12**.

The inertness of **4.12** with respect to halogens is quite surprising, although similar behaviour has already been reported for the analogous $[Mn(CO)_3$(1,4,7-trithiacyclononane]X (X= halogen) complex.[29]

4.2.3.1.2. Oxidation by $NOBF_4$

$NOBF_4$ has been used as single electron oxidant for transition metal systems. Manganese(I) tricarbonyl complexes have also shown reactivity towards this agent forming stable manganese(II) complexes, which in some cases have involved dissociation of a CO group and co-ordination of NO.[30, 31]

The same procedure was followed for **4.12** expecting the formation of a stable oxidised complex. The treatment of **4.12** with an excess of $NOBF_4$ in DCM produced an immediate colour change of the solution from colourless to purple. This colour-change is indicative of the formation of an oxidised Mn^{II} complex,[32] however all attempts to isolate the new compound ended in failure. In addition, the purple colour of the solution was shown to be dependent upon the concentration of $NOBF_4$, disappearing after long stirring times following consumption of $NOBF_4$, and allowing recovery of the starting material, **4.12**. The instability of the presumably Mn^{II} complex may be due to its oxidising capability, as it has been seen in other analogous complexes such *fac*-$[Mn(CO)_3L_2Br]PF_6$ {L=1,2-bis[di(phenyl)phosphino]ethane, bis[di(phenyl)phosphino]methane}, where the oxidising salts were found to react with the solvent to return to the initial Mn^{I} complex.[30]

The reaction was repeated, but after the formation of the purple solution, an aqueous solution of NaOH was added. The purple colour of the solution changed to green. After work-up, the $^{31}P\{^{1}H\}$ NMR spectrum of the solution showed mainly the presence of the starting material **4.12** but other signals between 29.34-39.35 ppm were also observed. These latter signals may be assigned to the free triphosphine oxide macrocycle **4.14**, but no further attempts were made to isolate the compound due to the low conversion of the reaction.

4.2.3.1.3. Amine N-oxides.

Trimethylamine oxide (Me_3NO) has been used as a versatile decarbonylating agent in organometallic chemistry. Me_3NO either oxidise the CO ligand, thus generating unsaturated species or the metal center.[33]

Therefore, Me_3NO was used in attempts to liberate the ligand **4.13** from the $Mn^{I}(CO)_3$ fragment. Following a reported procedure,[31] **4.12** was treated with Me_3NO in excess in toluene at room temperature. The initially pale solution turned slowly to orange after 12 hr. of stirring. The $^{31}P\{^{1}H\}$ NMR spectrum of the solution showed the disappearance of the broad resonance assigned to **4.12**, however four new broad resonances at δ_P 88.76, 99.65, 119.30 and 133.18 ppm were observed. The ^{19}F NMR spectrum of the solution displayed two signals at δ_F -96.16 and -97.62 ppm. The signals of the counter-anion and the compound **4.12** were no longer observed. The IR spectrum of the crude reaction mixture in DCM showed two carbonyl stretching bands at 1953 and 1898 cm^{-1} which are in lower frequencies than the starting material **4.12** (2039 and 1973 cm^{-1} in DCM solution). The mixture was stirred for extended periods, however, liberation of **5.13** did not occur. The data obtained suggests the formation of two new compounds, indicated by the two different signals in the ^{19}F NMR spectrum at δ_F -96.39 and 98.25 ppm (which indicates two types of 2-fluorophenyl moieties) and four signals in the $^{31}P\{^{1}H\}$ NMR spectrum at δ_P 88.2, 99.16, 118.99 and 132.33 ppm (each compound will have two type of phosphorus atoms). Unfortunately, the two compounds formed have not yet been identified.

It has been suggested that not all the carbonyl ligands can be attacked by Me_3NO,[33] however in some cases the combination of Me_3NO and irradiation with

ultraviolet light has solved this inconvenience.[34] Another experiment was designed in order to test the liberation of **4.13**. Thus, a DCM solution of **4.12** was treated with excess Me_3NO and irradiated for 12 hr. The $^{31}P\{^1H\}$ NMR spectrum showed a mixture of compounds with broad resonances between δ_P -45.61 and 32.69 ppm. No further attempts were made to separate the mixture.

The decarbonylating agent, 4-methylmorpholine N-oxide (MNO), was also investigated for liberation of the ligand **4.13**. A suspension **4.12** in toluene was treated with an excess of 4-methylmorpholine N-oxide. The reaction was refluxed for 12 hr. The yellow solution was filtered and the solvent removed *in vacuo*. The crude product was purified by chromatography on silica gel with dichloromethane, ethyl acetate and finally methanol as eluents. The methanol fraction contained a compound identified by mass spectroscopy as the trioxide **4.14** in a very low yield <5%. The mass spectrum showed a peak for $[2(9\text{-ane}P_3O_3)+Na]^+$ (m/z =1011, 100 %) indicating the affinity of the compound for hard metal ions. The $^{31}P\{^1H\}$NMR spectrum of **4.14** displayed two main peaks at δ_P 38.91 and 32.91 ppm assigned to the 2-fluoroarylphosphine and methylphosphine groups, respectively. The different phosphorus atoms of **4.14** are not coupled as has been reported for other trioxide macrocycles.[15] Other signals in a similar range were also observed (δ_P 39.81 and 31.98 ppm), which may belong to an isomer of **4.14**. The ^{19}F NMR spectrum shows a singlet at δ_F -93.63 assigned to the fluorine of the 2-fluorophenyl group. The liberation and identification of **4.14** is of interest, however the low yield of the reaction was a disadvantage for posterior studies of reduction of the oxide **4.14** and further investigations were carried out.

It has been reported that tripodal phosphine ligands were liberated from $Mo(CO)_3$ fragments by using pyridine N-oxide.[34] The reaction activated by irradiation, proceeded in good yields without oxidising the phosphorus atoms. Therefore, this procedure was also attempted in order to obtain the free 9-membered triphosphorus macrocycle **4.13**. Following the reported procedure,[34] the solution was then irradiated for 12 hr., however the $^{31}P\{^1H\}$ NMR spectrum of the solution showed that the starting material, **4.12**, remain intact.

4.2.3.2. Reactivity versus organolithiums

The reaction of nucleophiles with transition metal organometallic complexes can be divided in two different general types, those where the nucleophilic reagent attacks at the metal center itself replacing one of the ligands, or those where the nucleophile attacks at one of the ligands co-ordinated to the metal.[35]

The reactivity of complex **4.12** towards nucleophilic reagents is expected to fall in the second type. The carbonyl groups of **4.12** may be susceptible to nucleophiles as has been reported in other metal carbonyls;[36] also the C-F bond present in the 9-membered triphosphorus ligand of **4.12** can be activated by the acceptor abilities of the cationic metal center and be susceptible to nucleophilic attack.[37] Therefore, reactions of **4.12** towards nucleophiles can give rise to new interesting complexes which may be easier to liberate than **4.12**.

The reactivity of **4.12** was tested with organolithium reagents. A THF solution of **4.12** was treated with an equimolar amount of MeLi at low temperature (-78°C) however, no reaction was observed and the starting material was fully recovered.

4.2.3.3. Reactivity versus photolysis

As mentioned before, the complex **4.5** was obtained by photolysis of a solution of **4.4** in benzonitrile at high temperature with subsequent work-up in air.[17] The low yield, as well as the complexity of the mechanism operating in this reaction were reasons to examine the reaction again, but using milder conditions.

A DCM solution of **4.12** was irradiated for 12 hr at room temperature. The colourless solution became yellow and IR spectroscopy showed no trace of the carbonyl stretching bands of the starting material **4.12**. The $^{31}P\{^{1}H\}$ NMR spectrum of the solution showed a broad resonance in the same region as the phosphorus atoms of **4.12** (δ 99.53-105.36 ppm) but also a new broad resonance down-field (δ 123.44 ppm). The ^{19}F NMR spectrum of the solution showed a peak at δ_F 92.35 ppm which can be assigned to the fluorine of the fluoroaryl group of the macrocycle and there was no trace of the peak of the counter-anion. All these data suggest the formation of a new species, where the macrocycle is still co-ordinated to the manganese nuclei as indicated by the width of the resonances.

Further studies will be required to characterise the compound and fully understand the mechanism of the reaction.

4.3. Conclusion

A new 9-membered tribenzannulated triphosphorus macrocycle manganese(I) complex (**4.12**) has been succesfully synthesised by a 5-step synthesis in good yield. Crystal structures of different intermediates of the synthesis have been obtained (Table 4-3). The intermediates in the cyclisation can be readily identified. Liberation of the triphosphorus oxide macrocyclic ligand **4.14** has been achieved by boiling the manganese complex with MNO in toluene, although in very low yield.

Table 4-3: Summary of crystallographic data for 4.9 and 4.11

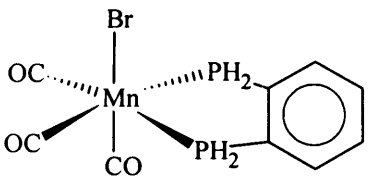
	4.9	**4.11**
empirical formula	$C_{28}H_{20}F_6MnO_6P_3S$	$C_{28}H_{19}F_5MnO_6P_3S$
fw	746.35	726.34
crystal syst	Monoclinic	Triclinic
space group	$P2_1/c$	P-1
a, Å	10.8280(1)	9.0220(1)
b, Å	14.9880(1)	13.4210(1)
c, Å	19.0140(2)	13.6260(2)
α, deg	90	69.978(1)
β, deg	100.439(1)	80.994(1)
γ, deg	90	76.824(1)
V, Å^3	3034.71(5)	1503.80(3)
Z	4	2
δ_{calcd}, Mg/m^3	1.634 Mg/m^3	1.604
F_{000}	1504	732
μ (Mo Kα), mm^{-1}	0.741 mm^{-1}	0.741
temp, K	150(2) K	150(2)
n. of meads rflns	43985	24905
n. of unique rflns	6913 (R_{int}= 0.0467)	8430 (R_{int} = 0.0485)

4.4. Experimental

4.4.1. General procedures

Unless otherwise stated all manipulations were carried out using standard Schlenck techniques, under an atmosphere of dry nitrogen. All solvents were dried and degassed by refluxing over standard drying agents under a nitrogen atmosphere. The compounds 1,2-bis(phosphino)benzene and tris-*o*-fluorophenylphosphine were prepared according to literature methods.[25, 38] *t*-BuOK was obtained from Aldrich Chemical Company and was purified by sublimation. $MnBr(CO)_5$, $AgOSO_2CF_3$, trimethylamine N-oxide, 4-methylmorpholine N-oxide, pyridine N-oxide and $NOBF_4$ were obtained from Aldrich Chemical Company and used without further purification. MeI, *i*-PrCl and deuterated solvents were dried over 3 or 4 Å molecular sieves and degassed by freeze-thaw methods. UV photolyses was carried out using a Hanovia 125 W lamp (254 nm). The NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz (^1H) and 125.75 MHz (^{13}C), Bruker DPX-400 instrument at 400 MHz (^1H) and 100 MHz (^{13}C), Jeol Lamda Eclipse 300 at 121.65 MHz (^{31}P), 75.57 MHz (^{13}C), 282.78 MHz (^{19}F). ^1H and ^{13}C chemical shifts are quoted in ppm relative to residual solvent peaks, and ^{31}P chemical shifts are quoted in ppm relative to external 85% H_3PO_4. ^{19}F chemical shifts are quoted in ppm relative to external $CFCl_3$. Infra-red spectra were recorded on a Nicolet 500 FT-IR spectrometer and the samples were prepared under N_2 as a KBr disk or as a solution. Mass Spectra of all the samples have been collected by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with a ESCI source. Elemental Analyses were performed by Warwick Analytical Services, University of Warwick. X-ray diffraction data collection was carried out on a Nonius Kappa CCD diffractometer in Bath University.

4.4.2. Synthesis of tricarbonyl-bis-(1,2-phosphino)benzene manganese(I) bromide (4.7)[22]

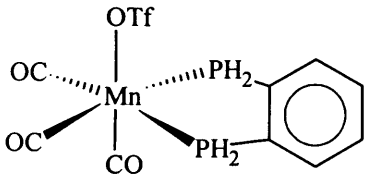


In absence of light, a solution of 1,2-bis(phosphino)benzene (1.29 g, 9 mmol) in $CHCl_3$ (10

mL) was added to a solution of $[MnBr(CO)_5]$ (2.49 g, 9 mmol) in $CHCl_3$ (60 mL). The reaction mixture was refluxed for 1 hour. The orange solution was filtered, and the solvent removed *in vacuo* leaving a yellow-orange solid. The solid was washed with cold Et_2O (3 x 30 mL), yielding a pale-yellow solid (2.25 g, 68%).

^1H NMR δ ppm ($CDCl_3$): 5.92 (d, 2H, $^1J_{P-H}$= 380 Hz, P**H**$_a$H$_{a'}$), 6.24 (d, 2H, $^1J_{P-H}$= 336 Hz, PH$_a$**H**$_{a'}$), 7.64 (s br, 2H, Ph), 7.97 (s br, 2H, Ph). $^{13}C\{^1H\}$NMR δ ppm ($CDCl_3$):131.38 (s, Ph), 132.11 (t, $^1J_{C-P}$= 44.2 Hz, $^2J_{C-P}$= 44.2 Hz Ph-**C**) 135.13 (d, $^2J_{C-P}$= 6.92 Hz, Ph), 214.92 (s br, **C**O eq), 217.92 (s br, **C**O ax). $^{31}P\{^1H\}$NMR δ ppm ($CDCl_3$): -1.00 (s br). IR ($CHCl_3$): ν(CO) 2039 s, 1976 s, 1931 s cm^{-1}.

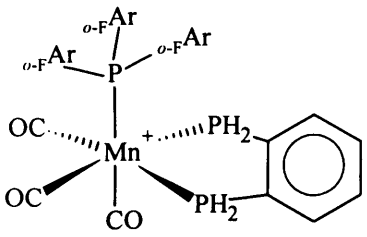
4.4.3. Synthesis of tricarbonyl-bis-(1,2-phosphino)benzene manganese(I) triflate (4.8)



In absence of light, to a solution of $[MnBr(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}]$ **4.7** (0.5 g, 1.38 mmol) in dichloromethane (15 mL) was added CF_3SO_3Ag (0.354 g, 1.38 mmol) in one portion. The reaction mixture was stirred for 2 hours during which time a grey precipitate formed. The solution was then filtered through Celite. All volatiles were removed *in vacuo* to leave a yellow solid in quantitative yield which was used without further purification. (Normally, this compound was synthesised *in situ* without isolation and used directly for the next step).

^1H NMR δ ppm ($CDCl_3$): 5.97 (d, 4H, $^1J_{P-H}$= 341 Hz, P**H$_2$**), 7.65 (m, 2H, Ph), 8.01 (m, 2H, Ph). $^{13}C\{^1H\}$NMR δ ppm ($CDCl_3$): 118.90 (q, $^1J_{C-F}$= 321 Hz, **C**F$_3$), 131.04 (t, $^1J_{C-P}$= 45 Hz, Ph-**C**), 132.27 (s, Ph), 135.44 (s, Ph), 213.65 (s br, **C**O eq), 218.09 (s br, **C**O ax). $^{31}P\{^1H\}$NMR δ ppm ($CDCl_3$): -3.25. ^{19}F NMR δ ppm ($CDCl_3$): -77.59. IR (CH_2Cl_2): ν(CO) 2057 s, 1994 s, 1944 s cm^{-1}. MS (ES): m/z 322 (70 %, $[Mn(CO)_3\{C_6H_4(PH_2)_2\text{-}o\}.MeCN]^+$).

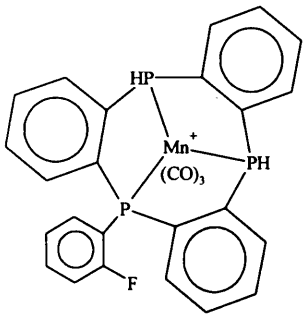
4.4.4. Synthesis of tricarbonyl-tris-(2-fluorophenyl)phosphine-bis-(1,2-phosphino)benzene manganese(I) triflate phosphino)benzene manganese(I) triflate (4.9)



$[Mn(CO)_3(OSO_2CF_3)\{C_6H_4(PH_2)_2\text{-}o\}]$ **4.8** (0.59 g, 1.38 mmol) was dissolved in DCM (20 mL) and a solution of tris(*o*-fluorophenyl)phosphine (0.7 g, 2.2 mmol) in dichloromethane (5 mL) was added. The reaction mixture was refluxed for 1 day in absence of light. The solvent was removed *in vacuo* and the remaining solid was washed with Et_2O (5 x 10 mL) leaving an off-white solid (0.609 g, 59 %). Single crystals of **4.9** were obtained by slow diffusion of hexane into a dichloromethane solution of **4.9** at room temperature.

^1H NMR δ ppm ($CDCl_3$): 5.37 (dd, 2H, $^1J_{H\text{-}P1}$= 380 Hz, $^3J_{H\text{-}P2}$= 14.4 Hz, $PH_aH_{a'}$), 6.13 (dd, 2H, $^1J_{P\text{-}H}$= 386 Hz, $^3J_{H\text{-}P2}$= 9 Hz, $PH_a\mathbf{H_{a'}}$), 7.05 (m, 3H, *o*-F-Aryl-**H**), 7.36 (m, 3H, *o*-F-Aryl-**H**), 7.47 (m, 3H, *o*-F-Aryl-**H**), 7.57 (m, 3H, *o*-F-Aryl-**H**), 7.63 (m, 2H, Ph), 8.02 (m, 2H, Ph). $^{13}C\{^1H\}$NMR δ ppm ($CDCl_3$): 115.22 (dd, $^1J_{C\text{-}P}$= 43 Hz, $^2J_{C\text{-}F}$= 16 Hz, *o*-F-Aryl-**C**), 116.86 (dd, $^2J_{C\text{-}F}$= 26 Hz, $^3J_{C\text{-}P}$= 2.5 Hz, *o*-F-Aryl-**C**H), 125.66 (d, $^3J_{C\text{-}P}$= 8.80 Hz, *o*-F-Aryl-**C**H), 130.08 (t, $^1J_{C\text{-}P}$= 45.3 Hz, Ph), 132.09 (s, Ph), 133.49 (d, $^3J_{C\text{-}F}$= 5.03 Hz, *o*-F-Aryl-**C**H), 134.70 (t, $^2J_{C\text{-}P}$= 6.3 Hz, $^3J_{C\text{-}F}$= 6.3 Hz, *o*-F-Aryl-**C**H), 135.06 (d, $^3J_{C\text{-}P}$= 8.80 Hz, Ph), 167.27 (dd, $^1J_{C\text{-}F}$= 246 Hz, $^2J_{C\text{-}P}$= 2.5 Hz, *o*-F-Aryl-**C**), 214 (br, **C**O). $^{31}P\{^1H\}$NMR δ ppm ($CDCl_3$): -1.86 (s br, PH_2), 39.69 (s br, **P**(*o*-F-Aryl)$_3$). ^{19}F NMR δ ppm ($CDCl_3$): -77.73 (s, CF_3), -93.15 (s, P(*o*-**F**-Aryl)$_3$)). IR (KBr): ν(P-H) 2383 s cm^{-1} ν(CO) 2053 s, 1983 s br cm^{-1}. MS (ES): m/z 577 (95 %, $[M\text{-}HF]^+$). Anal Calc. for $C_{28}H_{20}F_6MnO_6P_3S$ (745.95): C, 45.05; H, 2.70. Found: C, 45.24; H, 2.66%.

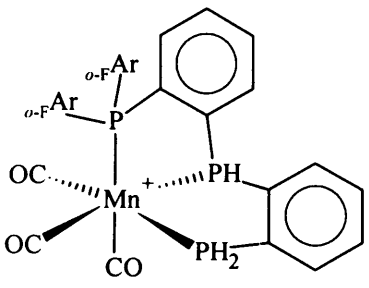
4.4.5. Synthesis of tricarbonyl-{1-(2-fluorophenyl)-[b,e,h]-tribenzo-1,4,7-triphosphacyclononane} manganese(I) triflate (4.10)



$[Mn(CO)_3\{P(o\text{-}F\text{-}C_6H_4)_3\}\{C_6H_4(PH_2)_2\text{-}o\}](OSO_2CF_3)$ **4.9** (0.175 g, 0.23 mmol) was dissolved in THF (10 mL) at -78 °C, immediately following a cooled solution of potassium terbutoxide in THF (0.142 M, 3.36 0.47mol) was added. The colourless solution instantly changed to yellow. The solution was then allowed to warm slowly to room temperature. The solvent was then removed *in vacuo*, and the residue triturated with degassed water (5mL). The solid was then dissolved in THF (25 mL) and dried with $MgSO_4$. The yellow solution was filtered and the solvent was removed *in vacuo* yielding a yellowish powder. (Due to its instability in solution, this compound was normally synthesised *in situ* without isolation and used directly for the next step).

^1H NMR δ ppm (d_4-MeOD): 7.34-7.44 (m, 4H, Ph), 7.63-7.78 (m, 8H, Ph), 8.01 (m, 2H, Ph), 8.31 (m, 4H, Ph). $^{13}C\{^1H\}$NMR δ ppm (d_4-MeOD): 118.52 (d, $^2J_{C\text{-}F}$= 22 Hz, *o*-F-Aryl-**C**H), 126.79 (d, $^3J_{C\text{-}P}$= 9.35 Hz, *o*-F-Aryl-**C**H), 132.27-140.88 (m, Ph, *o*-F-Aryl-**C**H), 164.70 (d, $^1J_{C\text{-}F}$= 251 Hz, *o*-F-Aryl-**C**). $^{31}P\{^1H\}$NMR δ ppm (d_4-MeOD): 74.42 (s br, **P**H), 110.47 (s br, **P**(*o*-F-Aryl)$_3$).^{19}F NMR δ ppm (MeOD-d_4): -79.34 (s, **CF$_3$**), -96.87 (s, P(*o*-**F**-Aryl)$_3$). IR (KBr): ν(CO) 2044s, 1970 s br cm^{-1}. MS (ES): m/z 557 (100 %, [M^+]).

4.4.6. Synthesis of triscarbonyl-bis(2-fluorophenyl){2-[(2-phosphinophenyl)phosphino]phenyl}phosphine manganese(I) triflate (4.11)

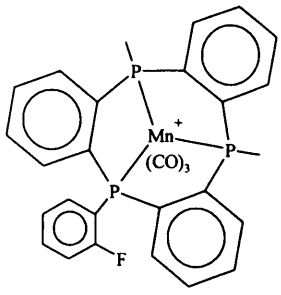


$[Mn(CO)_3\{P(o\text{-}F\text{-}C_6H_4)_3\}\{C_6H_4(PH_2)_2\text{-}o\}](OSO_2CF_3)$ **4.9** (0.1 g, 0.1 mmol) was dissolved in THF (2 mL), and the solution was allowed to stir for 7 days at room temperature. The solvent was then removed *in vacuo*, and no further purification was performed. Single

crystals of **4.11** were obtained by slow diffusion of hexane into a dichloromethane solution at room temperature.

^{1}H NMR δ ppm ($CDCl_3$): 4.56 (d, 1H, $^{1}J_{H\text{-}P1}$= 374 Hz, P**H$_a$**H$_{a'}$), 5.52 (m, 1H, Aryl-**H**), 5.82 (dd, 1H, $^{1}J_{H\text{-}P}$= 374 Hz, $^{3}J_{H\text{-}P2}$= 14.4 Hz, PH$_a$**H$_{a'}$**), 6.62 (m, 1H, Ph), 7.02-7.73 (m, 12H, Ph, P**H**), 7.89 (m, 1H, Ph), 8.47 (m, 1H, Ph), 8.84 (m, 1H, Ph). ^{13}C{^{1}H}NMR δ ppm ($CDCl_3$): 116.46 (d, $^{2}J_{C\text{-}F}$= 21.17 Hz, *o*-F-Aryl-**C**H), 117.59 (d, $^{2}J_{C\text{-}F}$= 22.42 Hz, *o*-F-Aryl-**C**H), 125.21 (s, *o*-F-Aryl-**C**H), 125.53 (s, *o*-F-Aryl-**C**H), 130.45-138.76 (m, *o*-F-Aryl-**C**H, Ph), 161.73 (d, $^{1}J_{C\text{-}F}$= 253 Hz, *o*-F-Aryl-**C**), 163.25 (d, $^{1}J_{C\text{-}F}$= 250 Hz, *o*-F-Aryl-**C**), 214.22 (m br, **C**O). ^{31}P{^{1}H}NMR δ ppm ($CDCl_3$): -1.69 (s br, **P**H$_2$), 71.90 (s br, $^{1}J_{H\text{-}P}$= 404 Hz, **P**H), 71.90 (s br, **P**(*o*-F-Aryl)$_3$). ^{19}F NMR δ ppm ($CDCl_3$): -78.79 (s, C**F$_3$**), -95.85 (s, P(*o*-**F$_1$**-Aryl)$_3$)), -96.78 (s, P(*o*-**F$_2$**-Aryl)$_3$)). IR (KBr): ν(P-H) 2367 s cm^{-1} ν(CO) 2045 s, 1957 s br cm^{-1}. MS (ES): m/z 577 (100 %, [M$^+$]). Anal Calc. for $C_{28}H_{19}F_5MnO_6P_3S$ (725.94): C, 46.30; H, 2.64. Found: C, 46.13; H, 2.57%.

4.4.7. Synthesis of tricarbonyl-1,4-dimethyl-7-(2-fluorophenyl)-[b,e,h]-tribenzo-1,4,7-triphosphacyclononane manganese(I) iodine/triflate (4.12)



A solution of potassium terbutoxide in THF (0.213 M, 1.25 mL, 0.26 mmol) was added to a solution of **4.10** (0.095 g, 0.13 mmol) in THF (20 mL) cooled to -78 °C. The colour of the solution changed from yellow to red-brownish. The reaction mixture was let to warm slowly to room temperature. The solution was then cooled again to -78 °C and an excess of MeI (0.05 ml, 0.8 mmol) was added, the solution was let to warm to room temperature and stirred overnight during which time a white solid precipitated. All the volatiles were then removed *in vacuo*, the crude material was dissolved in dichloromethane, filtered and the product **4.12** precipitated by adding cold Et_2O. **4.12** was isolated as a white

solid (64 mg, 65 % based in **4.9**). Single crystals of **4.12** were obtained from a saturated solution of $CDCl_3$.

^{1}H NMR δ ppm (CD_2Cl_2): 2.57 (t, 6H, $^2J_{H-P}$= 4.8 Hz, C**H$_3$**), 7.24-7.38 (m, 3H, Ph), 7.57-7.76 (m, 9H, Ph), 8.23-8.30 (m, 4H, Ph). ^{13}C{^{1}H}NMR (CD_2Cl_2): 13.91 (dd, $^1J_{C-P}$= 18.7 Hz, $^3J_{C-P}$= 19 Hz, **C**H$_3$), 117.44 (dd, $^2J_{C-F}$= 21.92 Hz, $^3J_{C-P}$= 4.62 Hz, *o*-F-Aryl-**C**H), 125.33 (dd, $^3J_{C-P}$= 9.22 Hz, $^4J_{C-F}$= 2.31 Hz, *o*-F-Aryl-**C**H), 129.75 (t, J_{C-P}= 9.08 Hz, Ph), 130.12 (s, Ph), 130.14 (d, J_{C-P}= 16 Hz, Ph), 132.61 (d, $^3J_{C-F}$= 6.92 Hz, *o*-F-Aryl-**C**H), 132.81 (d, $^1J_{C-P}$= 6.92 Hz, Ph), 133.07 (s, Ph), 133.20 (s, Ph), 134.97 (d, J_{C-P}= 9.23 Hz, *o*-F-Aryl-**C**H), 139.24 (t, $^1J_{C-P}$= 42 Hz, Ph), 163.15 (dd, $^1J_{C-F}$= 251 Hz, $^2J_{C-P}$= 2.3 Hz, *o*-F-Aryl-**C**). ^{31}P{^{1}H}NMR (CD_2Cl_2): 95.44-107.09 (m, **P**CH$_3$, **P**(*o*-F-Aryl)$_3$). ^{19}F NMR δ ppm (CD_2Cl_2): -76.85 (s, C**F$_3$**), -94.34 (s, P(*o*-**F**-Aryl)$_3$)). IR (KBr): ν(CO) 2025 s, 1965 s br cm^{-1}. MS (ES): m/z 585 (100 %, [M$^+$]).

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APPENDIX

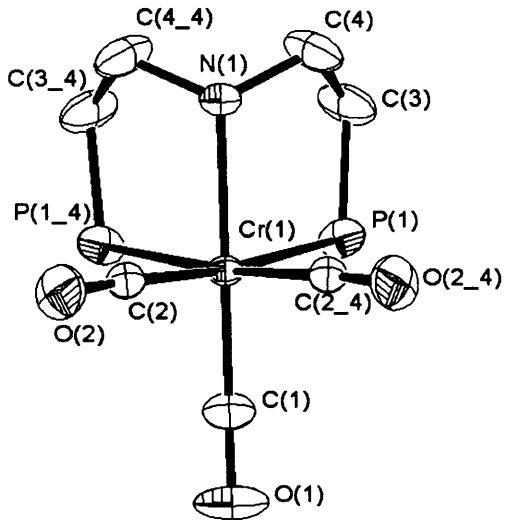

Figure 1: Molecular structure of 3.8

Table 1. Bond lengths [Å] and angles [°] for **3.8**.

C(1)-O(1)	1.176(5)		
C(1)-Cr(1)	1.815(4)		
C(2)-O(2)	1.158(3)		
C(2)-Cr(1)	1.841(3)		
C(3)-C(4)	1.498(5)		
C(3)-P(1)	1.836(3)		
C(3)-H(3A)	0.9900		
C(3)-H(3B)	0.9900		
C(4)-N(1)	1.488(4)		
C(4)-H(4A)	0.9900		
C(4)-H(4B)	0.9900		
N(1)-C(4)#1	1.488(4)		
N(1)-Cr(1)	2.209(3)		
N(1)-H(1)	0.9300		
P(1)-Cr(1)	2.3370(8)		
P(1)-H(1C)	0.9900		
P(1)-H(1D)	0.9900		
Cr(1)-C(2)#1	1.841(3)		
Cr(1)-P(1)#1	2.3370(8)		
O(1)-C(1)-Cr(1)	176.8(3)	Cr(1)-P(1)-H(1D)	110.7
O(2)-C(2)-Cr(1)	176.2(2)	H(1C)-P(1)-H(1D)	108.8
C(4)-C(3)-P(1)	109.2(2)	C(1)-Cr(1)-C(2)	89.26(12)
C(4)-C(3)-H(3A)	109.8	C(1)-Cr(1)-C(2)#1	89.26(12)

P(1)-C(3)-H(3A)	109.8	C(2)-Cr(1)-C(2)#1	87.19(17)
C(4)-C(3)-H(3B)	109.8	C(1)-Cr(1)-N(1)	177.49(15)
P(1)-C(3)-H(3B)	109.8	C(2)-Cr(1)-N(1)	92.55(10)
H(3A)-C(3)-H(3B)	108.3	C(2)#1-Cr(1)-N(1)	92.55(10)
N(1)-C(4)-C(3)	112.7(3)	C(1)-Cr(1)-P(1)	97.73(9)
N(1)-C(4)-H(4A)	109.0	C(2)-Cr(1)-P(1)	172.67(9)
C(3)-C(4)-H(4A)	109.0	C(2)#1-Cr(1)-P(1)	90.68(9)
N(1)-C(4)-H(4B)	109.0	N(1)-Cr(1)-P(1)	80.53(6)
C(3)-C(4)-H(4B)	109.0	C(1)-Cr(1)-P(1)#1	97.73(9)
H(4A)-C(4)-H(4B)	107.8	C(2)-Cr(1)-P(1)#1	90.68(9)
C(4)-N(1)-C(4)#1	116.8(4)	C(2)#1-Cr(1)-P(1)#1	172.67(9)
C(4)-N(1)-Cr(1)	114.76(19)	N(1)-Cr(1)-P(1)#1	80.53(6)
C(4)#1-N(1)-Cr(1)	114.76(19)	P(1)-Cr(1)-P(1)#1	90.56(5)
C(4)-N(1)-H(1)	102.5		
C(4)#1-N(1)-H(1)	102.5		
Cr(1)-N(1)-H(1)	102.5		
C(3)-P(1)-Cr(1)	105.12(11)		
C(3)-P(1)-H(1C)	110.7		
Cr(1)-P(1)-H(1C)	110.7		
C(3)-P(1)-H(1D)	110.7		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3.8**.U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	4886(6)	2500	6255(6)	30(1)
C(2)	8416(4)	3525(2)	7061(4)	24(1)
C(3)	7034(6)	1058(3)	1536(6)	48(1)
C(4)	9228(6)	1476(3)	2836(6)	47(1)
N(1)	9157(5)	2500	3852(5)	25(1)
O(1)	3685(5)	2500	7008(5)	51(1)
O(2)	9365(4)	4140(2)	8289(3)	42(1)
P(1)	5298(1)	1158(1)	2851(1)	33(1)
Cr(1)	6865(1)	2500	5230(1)	18(1)

Table 3. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3.8**. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

	U^{11}	U^{33}	U^{23}	U^{13}	U^{12}	
C(1)	18(2)	50(2)	22(2)	0	6(1)	0
C(2)	29(1)	24(1)	25(1)	0(1)	15(1)	0(1)
C(3)	39(2)	64(2)	47(2)	-32(2)	23(2)	-8(2)
C(4)	35(2)	61(2)	52(2)	-26(2)	24(2)	-2(2)

	U^{11}	U^{33}	U^{23}	U^{13}	U^{12}	
N(1)	20(2)	32(2)	24(2)	0	12(1)	0
O(1)	25(2)	103(3)	30(2)	0	16(1)	0
O(2)	54(2)	38(1)	37(1)	-15(1)	20(1)	-16(1)
P(1)	33(1)	42(1)	27(1)	-12(1)	14(1)	-15(1)
Cr(1)	17(1)	23(1)	15(1)	0	7(1)	0

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3.8**.

Atom	x	y	z	U(eq)
H(3A)	7133	295	1184	58
H(3B)	6413	1485	302	58
H(4A)	10007	922	3840	57
H(4B)	10040	1599	2027	57
H(1)	10482	2500	4941	30
H(1C)	5250	462	3482	40
H(1D)	3816	1363	1933	40

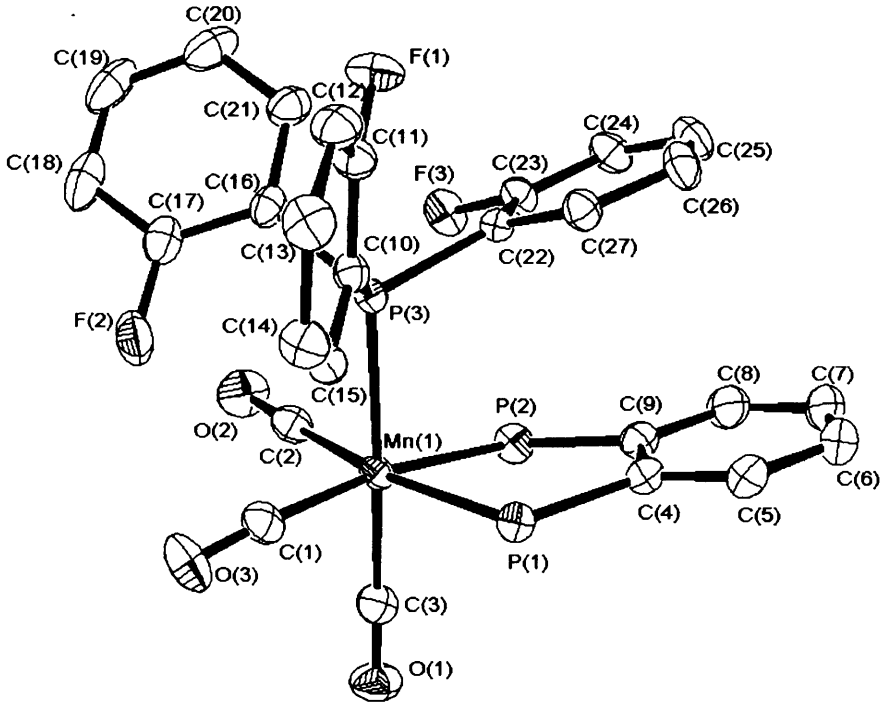

Figure 2: Molecular structure of 4.9, 50% probability Ellipsoids, H atoms omitted for clarity.

Table 5. Bond lengths [Å] and angles [°] for **4.9**.

Mn(1)-C(2)	1.8181(19)	Mn(1)-C(3)	1.8354(19)
Mn(1)-C(1)	1.839(2)	Mn(1)-P(2)	2.2927(5)
Mn(1)-P(1)	2.3068(5)	Mn(1)-P(3)	2.3749(5)
S(1)-O(6)	1.4339(15)	S(1)-O(25)	1.4387(15)
S(1)-O(47)	1.4394(16)	S(1)-C(28)	1.827(2)
P(1)-C(4)	1.8229(19)	P(2)-C(9)	1.811(2)
P(3)-C(22)	1.8238(17)	P(3)-C(10)	1.8350(18)
P(3)-C(16)	1.8433(18)	F(1)-C(11)	1.357(2)
F(2)-C(17)	1.358(2)	F(3)-C(23)	1.367(2)
F(4)-C(28)	1.326(2)	F(5)-C(28)	1.324(3)
F(6)-C(28)	1.321(2)	O(1)-C(3)	1.133(2)
O(2)-C(2)	1.142(2)	O(3)-C(1)	1.138(2)
C(4)-C(9)	1.390(3)	C(4)-C(5)	1.399(3)
C(5)-C(6)	1.388(3)	C(6)-C(7)	1.385(3)
C(7)-C(8)	1.378(3)	C(8)-C(9)	1.402(3)
C(10)-C(11)	1.395(2)	C(10)-C(15)	1.399(2)
C(11)-C(12)	1.373(3)	C(12)-C(13)	1.387(3)
C(13)-C(14)	1.382(3)	C(14)-C(15)	1.391(3)
C(16)-C(17)	1.387(3)	C(16)-C(21)	1.398(3)
C(17)-C(18)	1.379(3)	C(18)-C(19)	1.375(4)
C(19)-C(20)	1.384(4)	C(20)-C(21)	1.394(3)
C(22)-C(23)	1.380(2)	C(22)-C(27)	1.403(2)
C(23)-C(24)	1.377(3)	C(24)-C(25)	1.387(3)
C(25)-C(26)	1.380(3)	C(26)-C(27)	1.388(3)
C(2)-Mn(1)-C(3)	91.71(8)	C(2)-Mn(1)-C(1)	92.83(9)
C(3)-Mn(1)-C(1)	85.95(9)	C(2)-Mn(1)-P(2)	89.92(6)
C(3)-Mn(1)-P(2)	84.58(6)	C(1)-Mn(1)-P(2)	170.21(6)
C(2)-Mn(1)-P(1)	170.78(6)	C(3)-Mn(1)-P(1)	91.24(6)
C(1)-Mn(1)-P(1)	96.10(6)	P(2)-Mn(1)-P(1)	81.664(19)
C(2)-Mn(1)-P(3)	86.99(6)	C(3)-Mn(1)-P(3)	178.37(6)
C(1)-Mn(1)-P(3)	93.13(6)	P(2)-Mn(1)-P(3)	96.398(18)
P(1)-Mn(1)-P(3)	90.198(18)	O(6)-S(1)-O(25)	115.77(10)
O(6)-S(1)-O(47)	114.59(9)	O(25)-S(1)-O(47)	114.42(10)
O(6)-S(1)-C(28)	103.29(9)	O(25)-S(1)-C(28)	103.25(9)
O(47)-S(1)-C(28)	103.14(10)	C(4)-P(1)-Mn(1)	110.79(6)
C(9)-P(2)-Mn(1)	112.05(7)	C(22)-P(3)-C(10)	102.99(8)
C(22)-P(3)-C(16)	104.27(8)	C(10)-P(3)-C(16)	100.37(8)
C(22)-P(3)-Mn(1)	111.13(6)	C(10)-P(3)-Mn(1)	118.32(6)
C(16)-P(3)-Mn(1)	117.81(6)	O(3)-C(1)-Mn(1)	173.66(17)
O(2)-C(2)-Mn(1)	178.34(17)	O(1)-C(3)-Mn(1)	178.52(18)
C(9)-C(4)-C(5)	119.69(18)	C(9)-C(4)-P(1)	116.92(14)
C(5)-C(4)-P(1)	123.39(15)	C(6)-C(5)-C(4)	119.3(2)
C(7)-C(6)-C(5)	120.8(2)	C(8)-C(7)-C(6)	120.3(2)
C(7)-C(8)-C(9)	119.5(2)	C(4)-C(9)-C(8)	120.34(19)
C(4)-C(9)-P(2)	115.94(14)	C(8)-C(9)-P(2)	123.72(16)

C(11)-C(10)-C(15)	115.97(16)	C(11)-C(10)-P(3)	121.13(13)
C(15)-C(10)-P(3)	122.86(13)	F(1)-C(11)-C(12)	117.02(16)
F(1)-C(11)-C(10)	118.76(16)	C(12)-C(11)-C(10)	124.23(17)
C(11)-C(12)-C(13)	118.03(17)	C(14)-C(13)-C(12)	120.36(17)
C(13)-C(14)-C(15)	120.22(17)	C(14)-C(15)-C(10)	121.16(17)
C(17)-C(16)-C(21)	116.48(17)	C(17)-C(16)-P(3)	119.65(15)
C(21)-C(16)-P(3)	123.86(14)	F(2)-C(17)-C(18)	117.83(19)
F(2)-C(17)-C(16)	118.48(17)	C(18)-C(17)-C(16)	123.7(2)
C(19)-C(18)-C(17)	118.5(2)	C(18)-C(19)-C(20)	120.3(2)
C(19)-C(20)-C(21)	120.1(2)	C(20)-C(21)-C(16)	120.8(2)
C(23)-C(22)-C(27)	116.79(16)	C(23)-C(22)-P(3)	122.05(13)
C(27)-C(22)-P(3)	120.79(13)	F(3)-C(23)-C(24)	117.84(16)
F(3)-C(23)-C(22)	118.13(15)	C(24)-C(23)-C(22)	124.02(17)
C(23)-C(24)-C(25)	117.80(17)	C(26)-C(25)-C(24)	120.51(18)
C(25)-C(26)-C(27)	120.37(18)	C(26)-C(27)-C(22)	120.48(17)
F(6)-C(28)-F(5)	107.04(17)	F(6)-C(28)-F(4)	106.95(18)
F(5)-C(28)-F(4)	108.73(18)	F(6)-C(28)-S(1)	111.44(14)
F(5)-C(28)-S(1)	111.07(15)	F(4)-C(28)-S(1)	111.41(14)

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4.9**.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Mn(1)	8265(1)	3302(1)	3889(1)	20(1)
S(1)	13336(1)	2698(1)	5093(1)	25(1)
P(1)	9349(1)	2021(1)	4290(1)	22(1)
P(2)	6578(1)	2376(1)	3883(1)	26(1)
P(3)	8540(1)	2985(1)	2703(1)	18(1)
F(1)	9357(1)	2425(1)	1331(1)	33(1)
F(2)	9159(1)	4920(1)	2735(1)	39(1)
F(3)	5763(1)	2713(1)	2199(1)	31(1)
F(4)	13356(2)	4121(1)	4296(1)	57(1)
F(5)	15045(1)	3924(1)	5073(1)	59(1)
F(6)	13383(2)	4402(1)	5394(1)	54(1)
O(1)	7899(2)	3767(1)	5355(1)	39(1)
O(2)	6537(2)	4737(1)	3255(1)	41(1)
O(3)	10421(1)	4556(1)	4209(1)	42(1)
O(6)	13857(2)	2536(1)	5830(1)	37(1)
O(25)	13889(2)	2201(1)	4582(1)	43(1)
O(47)	11986(1)	2741(1)	4935(1)	42(1)
C(1)	9630(2)	4053(1)	4059(1)	27(1)
C(2)	7209(2)	4191(1)	3508(1)	27(1)
C(3)	8051(2)	3581(1)	4799(1)	28(1)
C(4)	8319(2)	1051(1)	4151(1)	25(1)

Atom	x	y	z	U(eq)
C(5)	8756(2)	171(1)	4224(1)	33(1)
C(6)	7900(2)	-526(1)	4120(1)	41(1)
C(7)	6623(2)	-361(2)	3936(1)	43(1)
C(8)	6184(2)	502(2)	3854(1)	36(1)
C(9)	7038(2)	1214(1)	3964(1)	27(1)
C(10)	10138(2)	2785(1)	2543(1)	20(1)
C(11)	10355(2)	2536(1)	1869(1)	25(1)
C(12)	11525(2)	2394(1)	1707(1)	29(1)
C(13)	12561(2)	2527(1)	2244(1)	31(1)
C(14)	12405(2)	2779(1)	2921(1)	28(1)
C(15)	11206(2)	2900(1)	3071(1)	22(1)
C(16)	7997(2)	3824(1)	2007(1)	24(1)
C(17)	8372(2)	4706(1)	2117(1)	30(1)
C(18)	7994(2)	5381(1)	1634(1)	41(1)
C(19)	7220(2)	5171(2)	999(1)	45(1)
C(20)	6841(2)	4298(2)	852(1)	42(1)
C(21)	7231(2)	3628(1)	1351(1)	32(1)
C(22)	7711(2)	1968(1)	2368(1)	19(1)
C(23)	6419(2)	1937(1)	2179(1)	23(1)
C(24)	5748(2)	1170(1)	1978(1)	29(1)
C(25)	6410(2)	377(1)	1989(1)	32(1)
C(26)	7701(2)	369(1)	2182(1)	30(1)
C(27)	8355(2)	1156(1)	2368(1)	24(1)
C(28)	13806(2)	3846(1)	4955(1)	32(1)

Table 7. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4.9**. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	19(1)	19(1)	21(1)	-4(1)	4(1)	1(1)
S(1)	28(1)	25(1)	23(1)	-1(1)	7(1)	-7(1)
P(1)	21(1)	23(1)	24(1)	0(1)	4(1)	1(1)
P(2)	20(1)	29(1)	29(1)	-2(1)	8(1)	-1(1)
P(3)	18(1)	16(1)	20(1)	-1(1)	3(1)	0(1)
F(1)	28(1)	49(1)	22(1)	-9(1)	3(1)	-1(1)
F(2)	42(1)	26(1)	49(1)	0(1)	7(1)	-11(1)
F(3)	22(1)	28(1)	40(1)	-4(1)	0(1)	5(1)
F(4)	96(1)	41(1)	32(1)	11(1)	6(1)	-12(1)
F(5)	38(1)	39(1)	99(1)	-1(1)	15(1)	-17(1)
F(6)	85(1)	31(1)	51(1)	-11(1)	20(1)	7(1)
O(1)	49(1)	44(1)	25(1)	-6(1)	8(1)	9(1)
O(2)	42(1)	38(1)	41(1)	1(1)	7(1)	21(1)
O(3)	35(1)	33(1)	55(1)	-14(1)	5(1)	-11(1)
O(6)	44(1)	37(1)	29(1)	7(1)	0(1)	-9(1)

Atom	U11	U22	U33	U23	U13	U12
O(25)	56(1)	32(1)	47(1)	-11(1)	26(1)	-8(1)
O(47)	28(1)	56(1)	40(1)	3(1)	3(1)	-13(1)
C(1)	29(1)	25(1)	29(1)	-6(1)	5(1)	4(1)
C(2)	29(1)	27(1)	27(1)	-6(1)	8(1)	3(1)
C(3)	27(1)	27(1)	28(1)	-2(1)	3(1)	5(1)
C(4)	31(1)	25(1)	20(1)	2(1)	6(1)	-1(1)
C(5)	44(1)	27(1)	27(1)	5(1)	3(1)	2(1)
C(6)	63(2)	23(1)	34(1)	4(1)	4(1)	-3(1)
C(7)	58(2)	31(1)	37(1)	5(1)	3(1)	-18(1)
C(8)	39(1)	37(1)	32(1)	3(1)	4(1)	-14(1)
C(9)	32(1)	28(1)	22(1)	1(1)	7(1)	-5(1)
C(10)	19(1)	18(1)	24(1)	-1(1)	6(1)	0(1)
C(11)	23(1)	28(1)	23(1)	-2(1)	4(1)	-1(1)
C(12)	30(1)	33(1)	26(1)	-3(1)	11(1)	1(1)
C(13)	22(1)	36(1)	37(1)	-2(1)	12(1)	0(1)
C(14)	20(1)	32(1)	31(1)	-2(1)	4(1)	-1(1)
C(15)	22(1)	22(1)	23(1)	-2(1)	5(1)	-1(1)
C(16)	26(1)	21(1)	27(1)	4(1)	9(1)	5(1)
C(17)	31(1)	26(1)	37(1)	4(1)	14(1)	2(1)
C(18)	48(1)	25(1)	55(1)	13(1)	26(1)	7(1)
C(19)	55(2)	40(1)	45(1)	23(1)	24(1)	22(1)
C(20)	49(1)	48(1)	29(1)	12(1)	11(1)	19(1)
C(21)	38(1)	31(1)	27(1)	4(1)	7(1)	9(1)
C(22)	22(1)	19(1)	17(1)	-1(1)	3(1)	0(1)
C(23)	23(1)	21(1)	25(1)	-3(1)	3(1)	1(1)
C(24)	23(1)	31(1)	32(1)	-7(1)	0(1)	-4(1)
C(25)	35(1)	26(1)	36(1)	-10(1)	8(1)	-9(1)
C(26)	34(1)	19(1)	38(1)	-6(1)	11(1)	1(1)
C(27)	23(1)	22(1)	27(1)	-2(1)	3(1)	2(1)
C(28)	39(1)	28(1)	28(1)	-2(1)	7(1)	-4(1)

Table 8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4.9**.

Atom	x	y	z	U(eq)
H(5)	9631	53	4344	40
H(6)	8192	-1124	4174	49
H(7)	6048	-845	3867	51
H(8)	5309	615	3722	44
H(12)	11622	2211	1242	35
H(13)	13382	2445	2144	37
H(14)	13120	2868	3286	33
H(15)	11111	3065	3541	27
H(18)	8261	5978	1737	49
H(19)	6945	5627	660	54

Atom	x	y	z	U(eq)
H(20)	6314	4156	410	50
H(21)	6974	3029	1244	38
H(24)	4861	1184	1837	35
H(25)	5971	-166	1863	38
H(26)	8146	-179	2188	36
H(27)	9245	1144	2495	29
H(2A)	6010(20)	2475(15)	4412(10)	39(6)
H(2B)	5601(18)	2374(15)	3384(10)	37(6)
H(1A)	9820(20)	1970(15)	4966(8)	33(6)
H(1B)	10279(18)	1742(15)	4012(11)	36(6)

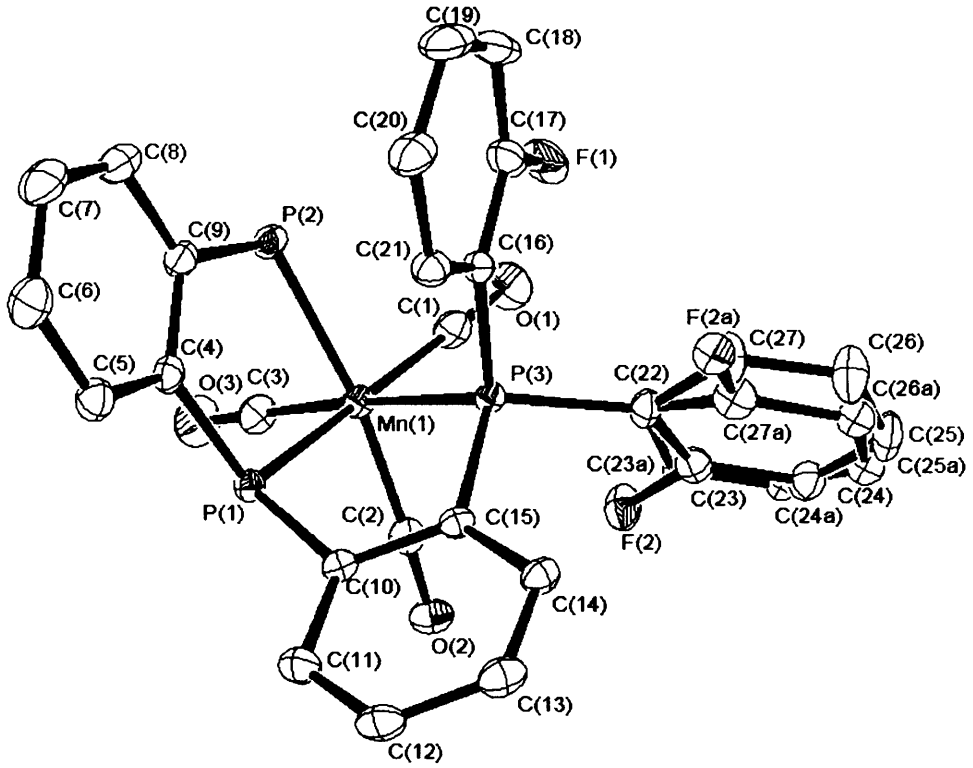

Figure 3: Molecular structure of 4.11, 35% probability Ellipsoids, H atoms omitted for clarity.

Table 9. Bond lengths [Å] and angles [°] for **4.11**.

Mn(1)-C(3)	1.808(2)	Mn(1)-C(2)	1.826(2)
Mn(1)-C(1)	1.830(2)	Mn(1)-P(1)	2.2657(6)
Mn(1)-P(2)	2.2817(6)	Mn(1)-P(3)	2.3373(6)
S(1)-O(4)	1.4055(19)	S(1)-O(6)	1.407(3)
S(1)-O(5)	1.423(3)	S(1)-C(28)	1.804(3)
P(1)-C(10)	1.807(2)	P(1)-C(4)	1.822(2)
P(2)-C(9)	1.812(2)	P(3)-C(16)	1.822(2)

P(3)-C(15)	1.824(2)	P(3)-C(22)	1.828(2)
F(1)-C(17)	1.363(3)	F(2)-C(23)	1.367(4)
F(3)-C(28)	1.308(4)	F(4)-C(28)	1.287(4)
F(5)-C(28)	1.333(4)	F(2A)-C(27A)	1.32(3)
O(1)-C(1)	1.138(3)	O(2)-C(2)	1.138(3)
O(3)-C(3)	1.144(3)	C(4)-C(5)	1.395(3)
C(4)-C(9)	1.395(3)	C(5)-C(6)	1.386(3)
C(6)-C(7)	1.389(4)	C(7)-C(8)	1.381(4)
C(8)-C(9)	1.399(3)	C(10)-C(11)	1.399(3)
C(10)-C(15)	1.401(3)	C(11)-C(12)	1.393(3)
C(12)-C(13)	1.379(4)	C(13)-C(14)	1.390(3)
C(14)-C(15)	1.400(3)	C(16)-C(17)	1.387(3)
C(16)-C(21)	1.396(3)	C(17)-C(18)	1.375(4)
C(18)-C(19)	1.380(4)	C(19)-C(20)	1.384(4)
C(20)-C(21)	1.395(3)	C(22)-C(27A)	1.26(3)
C(22)-C(23)	1.360(4)	C(22)-C(27)	1.426(4)
C(22)-C(23A)	1.575(16)	C(23)-C(24)	1.373(5)
C(24)-C(25)	1.381(5)	C(25)-C(26)	1.386(5)
C(26)-C(27)	1.378(5)	C(23A)-C(24A)	1.37(2)
C(24A)-C(25A)	1.29(3)	C(25A)-C(26A)	1.36(3)
C(26A)-C(27A)	1.44(3)		

C(3)-Mn(1)-C(2)	87.09(10)	C(3)-Mn(1)-C(1)	94.58(11)
C(2)-Mn(1)-C(1)	93.84(10)	C(3)-Mn(1)-P(1)	93.67(8)
C(2)-Mn(1)-P(1)	90.55(7)	C(1)-Mn(1)-P(1)	170.84(8)
C(3)-Mn(1)-P(2)	85.85(8)	C(2)-Mn(1)-P(2)	170.68(7)
C(1)-Mn(1)-P(2)	92.77(8)	P(1)-Mn(1)-P(2)	83.86(2)
C(3)-Mn(1)-P(3)	174.05(8)	C(2)-Mn(1)-P(3)	91.82(7)
C(1)-Mn(1)-P(3)	91.32(7)	P(1)-Mn(1)-P(3)	80.49(2)
P(2)-Mn(1)-P(3)	94.59(2)	O(4)-S(1)-O(6)	115.7(3)
O(4)-S(1)-O(5)	113.21(16)	O(6)-S(1)-O(5)	115.2(3)
O(4)-S(1)-C(28)	104.07(14)	O(6)-S(1)-C(28)	102.54(18)
O(5)-S(1)-C(28)	104.06(19)	C(10)-P(1)-C(4)	105.36(9)
C(10)-P(1)-Mn(1)	109.57(7)	C(4)-P(1)-Mn(1)	110.68(7)
C(9)-P(2)-Mn(1)	110.55(7)	C(16)-P(3)-C(15)	102.85(9)
C(16)-P(3)-C(22)	102.24(10)	C(15)-P(3)-C(22)	103.65(9)
C(16)-P(3)-Mn(1)	113.84(7)	C(15)-P(3)-Mn(1)	107.18(7)
C(22)-P(3)-Mn(1)	124.70(7)	O(1)-C(1)-Mn(1)	179.8(3)
O(2)-C(2)-Mn(1)	175.02(19)	O(3)-C(3)-Mn(1)	179.5(2)
C(5)-C(4)-C(9)	119.8(2)	C(5)-C(4)-P(1)	123.32(18)
C(9)-C(4)-P(1)	116.88(16)	C(6)-C(5)-C(4)	119.6(2)
C(5)-C(6)-C(7)	120.5(2)	C(8)-C(7)-C(6)	120.5(2)
C(7)-C(8)-C(9)	119.4(2)	C(4)-C(9)-C(8)	120.3(2)
C(4)-C(9)-P(2)	116.90(16)	C(8)-C(9)-P(2)	122.85(18)
C(11)-C(10)-C(15)	120.72(19)	C(11)-C(10)-P(1)	123.85(16)
C(15)-C(10)-P(1)	115.34(15)	C(12)-C(11)-C(10)	118.7(2)
C(13)-C(12)-C(11)	120.7(2)	C(12)-C(13)-C(14)	121.1(2)

C(13)-C(14)-C(15)	119.1(2)	C(14)-C(15)-C(10)	119.67(18)
C(14)-C(15)-P(3)	124.26(16)	C(10)-C(15)-P(3)	116.02(14)
C(17)-C(16)-C(21)	117.3(2)	C(17)-C(16)-P(3)	119.62(17)
C(21)-C(16)-P(3)	122.89(16)	F(1)-C(17)-C(18)	119.5(2)
F(1)-C(17)-C(16)	117.2(2)	C(18)-C(17)-C(16)	123.3(2)
C(17)-C(18)-C(19)	118.4(2)	C(18)-C(19)-C(20)	120.5(2)
C(19)-C(20)-C(21)	120.1(3)	C(20)-C(21)-C(16)	120.3(2)
C(27A)-C(22)-C(23)	100.7(11)	C(27A)-C(22)-C(27)	19.3(10)
C(23)-C(22)-C(27)	115.1(3)	C(27A)-C(22)-C(23A)	114.7(13)
C(23)-C(22)-C(23A)	14.1(6)	C(27)-C(22)-C(23A)	128.3(6)
C(27A)-C(22)-P(3)	130.5(12)	C(23)-C(22)-P(3)	125.9(2)
C(27)-C(22)-P(3)	118.9(2)	C(23A)-C(22)-P(3)	112.8(6)
C(22)-C(23)-F(2)	117.3(3)	C(22)-C(23)-C(24)	125.7(4)
F(2)-C(23)-C(24)	116.9(3)	C(23)-C(24)-C(25)	117.7(3)
C(24)-C(25)-C(26)	120.1(3)	C(27)-C(26)-C(25)	120.2(4)
C(26)-C(27)-C(22)	121.1(4)	F(4)-C(28)-F(3)	106.4(3)
F(4)-C(28)-F(5)	105.5(3)	F(3)-C(28)-F(5)	108.5(3)
F(4)-C(28)-S(1)	113.8(2)	F(3)-C(28)-S(1)	110.5(3)
F(5)-C(28)-S(1)	111.8(2)	C(24A)-C(23A)-C(22)	116.8(13)
C(25A)-C(24A)-C(23A)	121.5(18)	C(24A)-C(25A)-C(26A)	124(2)
C(25A)-C(26A)-C(27A)	116.2(19)	C(22)-C(27A)-F(2A)	115(2)
C(22)-C(27A)-C(26A)	125(2)	F(2A)-C(27A)-C(26A)	119(2)

Table 10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4.11**.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Mn(1)	4569(1)	2581(1)	8614(1)	21(1)
S(1)	2466(1)	1570(1)	12611(1)	42(1)
P(1)	2336(1)	2040(1)	9354(1)	21(1)
P(2)	4548(1)	1567(1)	7573(1)	26(1)
P(3)	2859(1)	4068(1)	7675(1)	18(1)
F(1)	4736(2)	4040(1)	5717(1)	43(1)
F(2)	4820(2)	5209(1)	8435(1)	38(1)
F(3)	3488(4)	713(3)	14433(2)	141(2)
F(4)	1128(3)	901(2)	14492(2)	88(1)
F(5)	2472(4)	-345(2)	13984(2)	108(1)
F(2A)	1331(10)	6145(7)	6144(7)	31(2)
O(1)	7220(2)	3497(2)	7344(2)	49(1)
O(2)	4610(2)	3515(2)	10288(1)	36(1)
O(3)	6460(2)	634(2)	9944(2)	50(1)
O(4)	2252(3)	2600(2)	12715(2)	49(1)
O(5)	3961(4)	1224(2)	12185(3)	121(2)
O(6)	1270(6)	1371(4)	12196(2)	148(2)

Atom	x	y	z	U(eq)
C(1)	6205(3)	3144(2)	7832(2)	31(1)
C(2)	4546(2)	3195(2)	9625(2)	26(1)
C(3)	5722(3)	1386(2)	9429(2)	32(1)
C(4)	1712(2)	1349(2)	8596(2)	24(1)
C(5)	287(3)	1047(2)	8789(2)	31(1)
C(6)	-95(3)	524(2)	8174(2)	41(1)
C(7)	923(3)	307(2)	7363(2)	46(1)
C(8)	2335(3)	605(2)	7161(2)	38(1)
C(9)	2730(3)	1136(2)	7777(2)	26(1)
C(10)	848(2)	3208(2)	9314(2)	21(1)
C(11)	-497(3)	3181(2)	9984(2)	28(1)
C(12)	-1615(3)	4114(2)	9826(2)	32(1)
C(13)	-1398(3)	5048(2)	9030(2)	31(1)
C(14)	-54(2)	5090(2)	8372(2)	25(1)
C(15)	1081(2)	4160(2)	8513(2)	19(1)
C(16)	2266(2)	3899(2)	6532(2)	22(1)
C(17)	3310(3)	3886(2)	5671(2)	32(1)
C(18)	2980(4)	3704(2)	4802(2)	45(1)
C(19)	1548(4)	3505(2)	4794(2)	47(1)
C(20)	470(3)	3501(2)	5637(2)	37(1)
C(21)	819(3)	3707(2)	6502(2)	26(1)
C(22)	3192(2)	5455(2)	7169(2)	25(1)
C(23)	4045(4)	5888(3)	7598(3)	27(1)
C(24)	4178(4)	6954(3)	7274(3)	32(1)
C(25)	3404(4)	7651(2)	6428(3)	38(1)
C(26)	2527(4)	7269(3)	5937(4)	44(1)
C(27)	2434(4)	6191(3)	6285(4)	35(1)
C(28)	2377(4)	674(2)	13943(2)	52(1)
C(23A)	4375(18)	5658(13)	7783(13)	7(3)
C(24A)	4620(20)	6696(15)	7501(14)	20(4)
C(25A)	3820(20)	7480(20)	6834(18)	29(4)
C(26A)	2730(20)	7369(16)	6313(14)	27(4)
C(27A)	2430(30)	6300(20)	6587(19)	36(7)

Table 11. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4.11**. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	17(1)	20(1)	26(1)	-8(1)	-3(1)	0(1)
S(1)	72(1)	33(1)	27(1)	-14(1)	6(1)	-25(1)
P(1)	22(1)	19(1)	21(1)	-6(1)	-3(1)	-2(1)
P(2)	25(1)	22(1)	30(1)	-12(1)	1(1)	0(1)
P(3)	16(1)	18(1)	21(1)	-7(1)	-1(1)	-3(1)

Atom	U11	U22	U33	U23	U13	U12
F(1)	34(1)	49(1)	38(1)	-10(1)	14(1)	-11(1)
F(2)	51(1)	31(1)	39(1)	-7(1)	-18(1)	-14(1)
F(3)	120(2)	180(3)	85(2)	39(2)	-69(2)	-37(2)
F(4)	110(2)	71(1)	54(1)	-10(1)	43(1)	-10(1)
F(5)	167(3)	30(1)	88(2)	1(1)	44(2)	-9(1)
O(1)	26(1)	62(1)	60(1)	-20(1)	10(1)	-16(1)
O(2)	34(1)	45(1)	33(1)	-20(1)	-5(1)	-5(1)
O(3)	46(1)	38(1)	56(1)	-8(1)	-22(1)	13(1)
O(4)	63(1)	29(1)	52(1)	-13(1)	-2(1)	-5(1)
O(5)	153(3)	41(1)	129(3)	-30(2)	98(3)	-12(2)
O(6)	253(5)	180(4)	54(2)	10(2)	-52(2)	-175(4)
C(1)	24(1)	31(1)	40(1)	-15(1)	-2(1)	0(1)
C(2)	17(1)	27(1)	31(1)	-9(1)	-4(1)	-1(1)
C(3)	27(1)	31(1)	38(1)	-12(1)	-7(1)	0(1)
C(4)	28(1)	18(1)	25(1)	-5(1)	-6(1)	-3(1)
C(5)	32(1)	29(1)	33(1)	-10(1)	-3(1)	-10(1)
C(6)	42(1)	41(1)	47(2)	-17(1)	-5(1)	-20(1)
C(7)	55(2)	49(2)	49(2)	-28(1)	-4(1)	-21(1)
C(9)	30(1)	21(1)	27(1)	-9(1)	-4(1)	-4(1)
C(10)	21(1)	23(1)	22(1)	-10(1)	-2(1)	-3(1)
C(11)	25(1)	35(1)	27(1)	-13(1)	2(1)	-7(1)
C(12)	22(1)	42(1)	34(1)	-20(1)	6(1)	-3(1)
C(13)	22(1)	34(1)	37(1)	-18(1)	-3(1)	5(1)
C(14)	24(1)	23(1)	27(1)	-10(1)	-5(1)	1(1)
C(15)	18(1)	22(1)	20(1)	-9(1)	-3(1)	-2(1)
C(16)	26(1)	19(1)	19(1)	-6(1)	-1(1)	-2(1)
C(17)	34(1)	31(1)	26(1)	-7(1)	5(1)	-2(1)
C(18)	58(2)	47(2)	20(1)	-12(1)	4(1)	7(1)
C(19)	69(2)	45(2)	28(1)	-21(1)	-17(1)	8(1)
C(20)	47(1)	36(1)	33(1)	-15(1)	-16(1)	-3(1)
C(21)	28(1)	27(1)	24(1)	-9(1)	-6(1)	-3(1)
C(22)	22(1)	20(1)	33(1)	-8(1)	2(1)	-5(1)
C(23)	25(2)	27(2)	27(2)	-8(1)	-1(1)	-4(1)
C(24)	35(2)	28(2)	37(2)	-13(2)	1(2)	-11(2)
C(25)	42(2)	19(1)	50(2)	-6(1)	-1(2)	-10(1)
C(26)	50(2)	26(2)	53(2)	-1(2)	-19(2)	-8(1)
C(27)	33(2)	24(2)	43(2)	-1(2)	-12(2)	-6(1)
C(28)	70(2)	40(2)	35(1)	-5(1)	-2(1)	-1(1)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4.11**.

Atom	x	y	z	U(eq)
H(5)	-416	1199	9339	37
H(6)	-1062	311	8307	49
H(7)	645	-49	6944	55
H(8)	3032	451	6609	45

Atom	x	y	z	U(eq)
H(11)	-645	2539	10535	34
H(12)	-2536	4107	10272	39
H(13)	-2180	5674	8929	38
H(14)	92	5742	7834	30
H(18)	3720	3716	4222	54
H(19)	1301	3369	4205	56
H(20)	-510	3357	5627	44
H(21)	69	3718	7073	31
H(24)	4781	7204	7620	39
H(25)	3473	8394	6182	45
H(26)	1989	7752	5359	53
H(27)	1854	5934	5929	42
H(23A)	4894	5090	8322	8
H(24A)	5396	6838	7804	24
H(25A)	4000	8191	6699	35
H(26A)	2210	7964	5797	33
H(1)	2180(30)	1420(19)	10340(15)	31(7)
H(2A)	4780(30)	1960(20)	6549(15)	36(7)
H(2B)	5530(30)	650(17)	7730(20)	40(8)

ABBREVIATIONS

AIBN		2,2'-Azabiisobutyronitrile
APCI		Atmospheric pressure chemical ionisation
Ar		Aryl group
n-Bu		*n*-Butyl
t-Bu		*t*-Butyl
Cb*		Tetramethylcyclobutadienyl
Cp		Cyclopentadienyl
Cp*		Pentamethylcyclopentadienyl
Cy		Cyclohexyl
DCM		Dichloromethane
dien		diethylenetriamine
DME		1,2-Dimethoxyethane
DMSO		Dimethylsulfoxide
en		Ethylenediamine
ESI		Electrospray ionisation
Et_2O		Diethyl ether
IR		Infra-red
	(s)	strong
	(m)	medium
	(w)	weak
L		generic ligand
LDA		Lithium diisopropylamide
Me		Methyl
MS		Mass spectrum
MNO		4-Methylmorpholine N-oxide
NMR		Nuclear Magnetic Resonance
	(s)	singlet
	(b)	broad

	(d)	doublet
	(t)	triplet
	(q)	quartet
	(m)	multiplet
Ph		Phenyl
Pr		Propyl
ppm		Parts per million
R		generic alkyl