Novel Approaches Towards Phosphorus Containing Macrocycles

A Thesis Submitted to Cardiff University by

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Abstract

The first chapter in this thesis discusses the general trends in group 15 donor ligands, in particularly nitrogen and phosphorus. The major advancements in phosphorus donor macrocyclic chemistry over the past two decades are documented, and the various synthetic strategies are described. The properties of triphosphorus macrocycles and ensuing complexes are discussed, and the aims of this thesis are summarised.

In chapter 2, the preparation of 1-trimethylsilylphosphirane, **2.3**, from chloroethylbis(trimethylsilyl)phosphine, **2.1,** is discussed. 1-trimethylsilylphosphirane may be converted to the parent phosphirane, **2.4**, by methanolysis, and the coordination chemistry of these phosphines to iron(II), manganese(I), cobalt(III) and Cr(0) centres is discussed. The coordination of the parent phosphirane, **2.4**, to the harder metal centres Fe(II) and Co(III) yields the bridging *phosphido*-phosphirane dimeric complexes, **2.13** and **2.14**, respectively. The reaction of phosphiranes with phosphides is also shown to yield 1,2-bis(phosphino)ethane

The manganese(I)-templated assembly of novel N_2P [9]ane macrocycles from coordinated *cis* and *trans* 1,2-diaminocyclohexane precursors is reported in chapter 3. The efficiency of macrocycle formation is shown to be effected greatly by the different chelate conformations adopted by *cis* and *trans* diaminocyclohexane. Thus, the assembly of [9]ane N_2P using the *trans* isomer is more efficient than the *cis* analogue. The reactivity of ([9]ane N_2P)$Mn(CO)_3$ towards the decarbonylating agent, 4-methylmorpholine-N-oxide is shown to be selective, with only the carbonyl group *trans* to the phosphorus being removed. Attempts to liberate the macrocycle from the manganese centre using hydrogen peroxide and bromine result in the recovery of the free macrocycle, however, oxidation of the phosphorus atom is always observed.

Chapter 4 reports the synthesis of seven and nine-membered triphosphines with two primary phosphines at each terminus is also reported. The coordination chemistry of these ligands to the d^6 centres Fe(II) and Mo(0) is discussed, as is their reactivity with ring-closing agents, vinyl bromide and 1-fluoro,2-iodobenzene.

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iii- Crystal structure data for $[Mn(CO)_3(PhP(allyl)_2(trans\text{-}CHXN)]PF_6$
iv- Publication in support of this thesis.
v- Pull-out summary card for use as a bookmark.

Chapter 1- Introduction

Huw Tallis
Cardiff University

1.1 A (Very) Brief History of Elemental Phosphorus

Figure 1.1. The Alchemist in Search of the Philosophers Stone (1771) by Joseph Wright

Hennig Brandt was the first person to isolate phosphorus in 1669. As an alchemist, his search eventually led him to isolate the element by heating urine and collecting the residue. The substance gave a pale-green glow so Brandt called it "phosphorus" from the Greek words "phos" meaning light and "phorus" meaning bearer. The painting above was Joseph Wright's depiction of Brand's discovery of phosphorus.

Elemental phosphorus exists as several allotropes, which are characterised by their physical appearance. White phosphorus consists of individual molecules of four atoms in a tetrahedral arrangement, resulting in high ring strain and instability. Red phosphorus may be formed by heating white phosphorus to 250 °C, or by exposing white phosphorus to sunlight. After this treatment, red phosphorus consists of an amorphous network of atoms. This conformation is less strained, and subsequently more stable. Red phosphorus becomes crystalline upon extensive heating. Red phosphorus does not catch fire in air at temperatures below 240 °C, whereas white phosphorus spontaneously ignites in air at ambient temperature. Black phosphorus is the thermodynamically most stable form of the element at

room temperature and pressure. It is obtained by heating white phosphorus under very high pressures (ca. 12,000 atmospheres). In appearance, properties and structure it is very similar to graphite, being black and flaky, a conductor of electricity and having puckered sheets of linked atoms. Black phosphorus has an orthorhombic structure and is the least reactive of all allotropes, as it consists of many interlinked six-membered rings. [1]

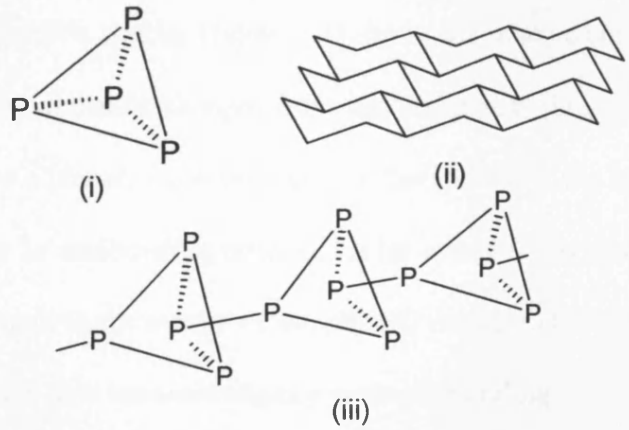


Figure 1.2. The molecular structure of the most common allotropes of phosphorus; white (i), black (ii) and red (iii).

1.2 Trends in Group 15 Donor Ligands

Group 15 donor ligands of the general formula R_3D are able to act as an electron pair donor (Lewis base) to transition metals, by virtue of the lone pair (figure 1.3) A general trend in group 15 coordination chemistry is that the σ-basicity of R_3D moieties (where D= group 15 atom) decrease upon descent of the group.

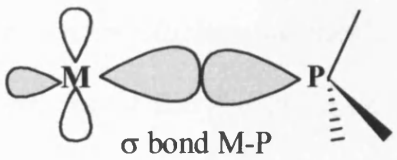


Figure 1.3

This phenomenon is accompanied by a decrease in R-D-R bond angle from nitrogen to stibine in the group, as shown by the bond angles in the group 15 hydrides (Table 1.1).

Compound	H-D-H angle (deg)
NH_3	107.5
PH_3	93.2
AsH_3	92.1
SbH_3	91.6

Table 1.1.[2]

The Walsh diagram for EH_3 species (figure 1.4) shows the relative change in orbital energies as the geometry of the molecule changes from trigonal planar (D_{3h} symmetry) to pyramidal (C_{3v} symmetry).[2] For a planar, 8 electron species the HOMO is the non-bonding a_2'' orbital, and the LUMO is the 2a' antibonding orbital. As the symmetry is changed to C_{3v}, these two sets of orbitals mix, causing the energy of the HOMO orbital to be lowered. Conversely, the LUMO energy is raised, as it becomes slightly more antibonding.

The degree of 'mixing' orbitals affects the ability of the lone pair to form σ-bonds in transition metal complexes (since the lone pair reside in the HOMO). In the planar species, the HOMO has entirely p-character, while in the pyramidal species, the HOMO has some s-character. The more pyramidal the geometry, the more s-character that will be in the HOMO. Therefore, in more pyramidal species (such as those of the heavier group 15 elements), the weaker the σ-component of any given metal-donor bond.

Compounds of group 15 elements display increasing pyramidality (and therefore decreasing σ-bonding abilities) down the group as the orbitals become more diffuse. Therefore the mixing of s and p orbitals becomes more efficient, and the C_{3v} conformation is favoured.

Another trend in group 15 elements, is that the inversion barriers progressively increase down the group. Therefore, amines are more readily inverted than phosphines and compounds of heavier group 15 elements (inversion barriers; 24.2 kJ/mol for NH_3 compared

to 132 KJ/mol for PH_3). Consequently resolved chiral phosphines retain their configuration at the phosphorus atom, and as a result the complexes formed exhibit selectivity towards one specific enantiomer in asymmetric catalysis, whereas the complexes of amines do not.[3]

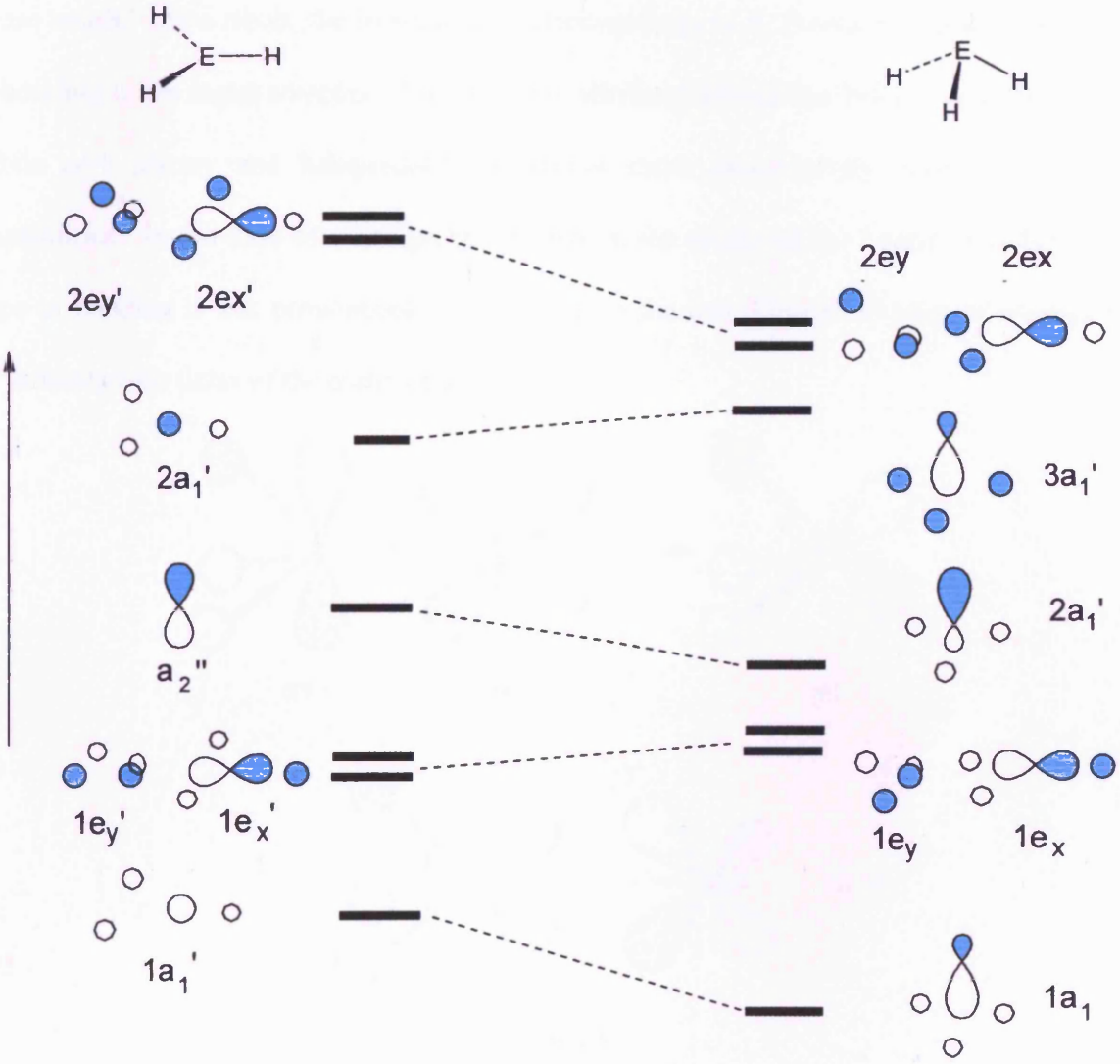


Figure 1.4. A Walsh diagram for EH_3 (where E = group 15 element).

1.3 Phosphine Donors

A second component of bonding between metal centres and ligands, in particularly phosphines, is π-bonding. Phosphines are known to behave as π-acid ligands, whereby electron density is 'back-donated' from the full or partially filled d-orbital of the metal centre

to the phosphine. It is now accepted that the vacant 3d orbital combined with the σ* orbital of the P-R bond accepts the electrons from electron rich metals, and therefore the electronic nature of the substituents, R, have a large influence on the capacity of the complex to form these bonds.[4] As a result, the increasing electronegativity of R, results in a greater degree of π-bonding in the metal complex. For example, alkylated phosphines behave as weak π-acids while aryl, alkoxy and halogenated phosphines show progressively stronger π-bonding capabilities.[5] In the case of other group 15 donors, the ability of the ligand to undergo this type of bonding is less pronounced. This is due to the less effective overlap of appropriate σ* orbitals with those of the metal centre.

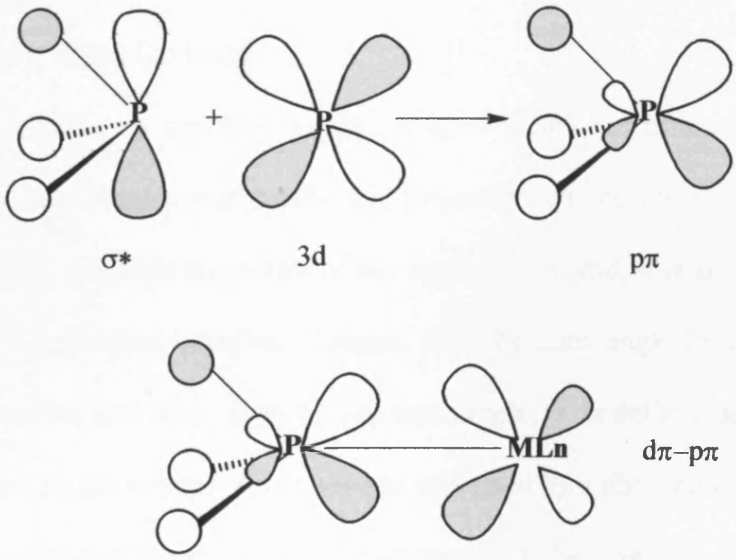


Figure 1.5

The π-acidity of various phosphines may be quantified by comparing the stretching frequency of carbonyl bands in a series of metal carbonyl complexes containing different phosphine donors. The most commonly used example is that compiled by Tolman, of Nickel tricarbonyl phosphine complexes shown in the table below.[6]

PR_3	$\upsilon(CO)/ cm^{-1}$	PR_3	$\upsilon(CO)/cm^{-1}$
$P(t\text{-}Bu)_3$	2056	$P(OMe)Ph_2$	2072
PCy_3	2056	$P(O\text{-}Pr^i)_3$	2076
$P(i\text{-}Pr)_3$	2059	$P(OMe)_3$	2080
PBu_3	2060	PH_3	2083
PEt_3	2062	$P(OPh)_3$	2085
PMe_3	2064	PCl_3	2097
PPh_3	2069	PF_3	2111

Table 1.2. Carbonyl stretching frequencies of complexes $Ni(CO)_3(PR_3)$.[6]

The information in Table 1.2 shows that the magnitude of the carbonyl stretching frequency increases as the electronegativity of R increases. This is due to less metal-carbonyl π-bonding due to competition from the increasingly π-acidic phosphine donors. Therefore, less electron density is back-donated to the vacant π* orbital of the CO ligand which results in an overall strengthening of the CO bond.

Therefore, it is possible to see that subtle changes in the electronic properties of the phosphine ligand may impart vastly different properties on the ensuing metal complex. However, by varying the steric properties of the phosphine ligand, it is also possible to alter the behaviour of the resultant complex. Tolman used the cone angle to quantify the steric properties of phosphine and other ligands. 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 (figure 1.6). Tolman has shown that by increasing θ, the lone pair gain more p-orbital character and are therefore more σ basic.[6] This observation is also accompanied by a downfield shift in the ^{31}P NMR signal. The understanding of the electronic and steric parameters of phosphine ligands can be useful to predict reactivity and behaviour of phosphine containing metal complexes.

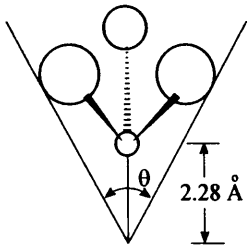


Figure 1.6 Definition of cone angle, θ

1.4 Synthetic Pathways to Phosphines

Although phosphine donors offer significant advantages in coordination chemistry, there are also disadvantages to their use. Often, the preparation of trivalent phosphines is hindered by the instability of the desired product, and many reactions are capricious and low yielding. Many phosphines react violently in air, often pyrophorically to form the pentavalent oxide species, and most are offensively odorous. Generally, phosphines are distillable oils, however, some tertiary phosphines with large substituents are isolated as crystalline solids (such as triphenylphosphine). As a general rule, phosphines become more stable with more bulky substituents. Consequently, trimethylphosphine is a pyrophoric, distillable oil, whereas triphenylphosphine may be stored in air for considerable time with no evidence of oxidation. Another complication with using phosphines is their toxicity. Phosphines are known to attack the central nervous system, cause severe liver damage, nausea and even death upon exposure. Generally trivalent phosphines exhibit greater toxicity, however sarin, a pentavalent odourless fluoronated phosphine is estimated to be ca. 500 times more potent than cyanide.[7]

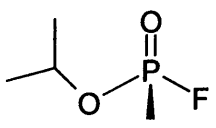
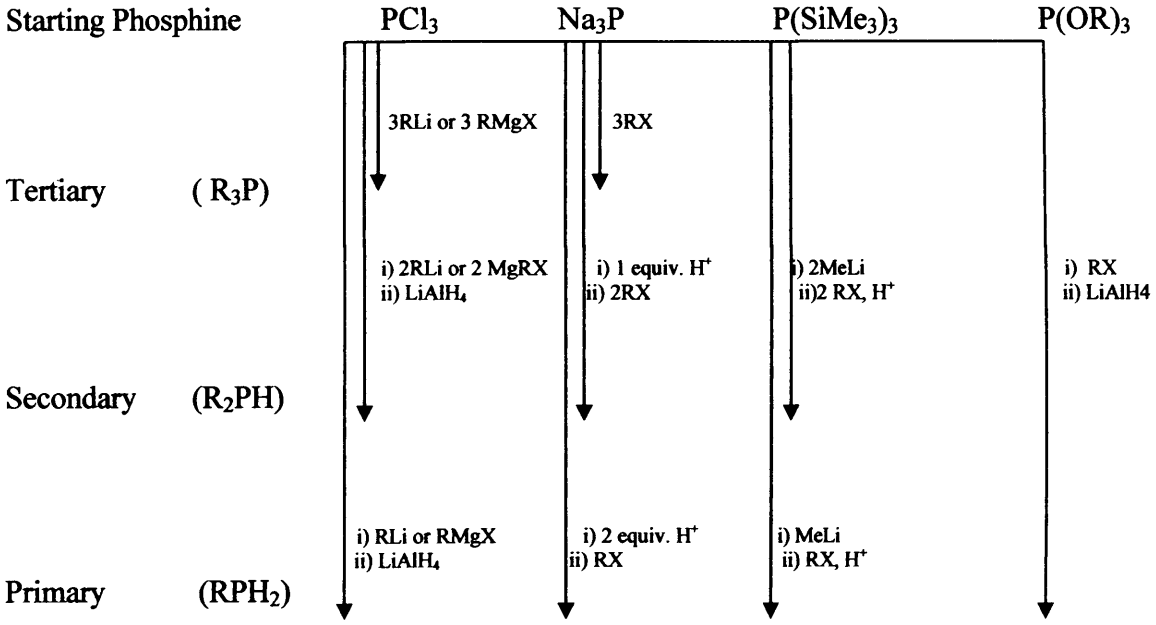


Figure 1.7. The structure of sarin

Synthetically, there are a number of routes to primary, secondary and tertiary phosphines. Usually, this involves substitution of a phosphide (P^-) species with a cationic function, or vice-versa. Reduction of chlorinated phosphines with $LiAlH_4$ result in de-chlorination, and the resultant P-H bond is formed.[8] Chlorinated phosphines may also undergo alkylation, using an appropriate Grignard reagent.[9] Scheme 1.1 (below) shows the most common synthetic routes to primary, secondary and tertiary phosphines.

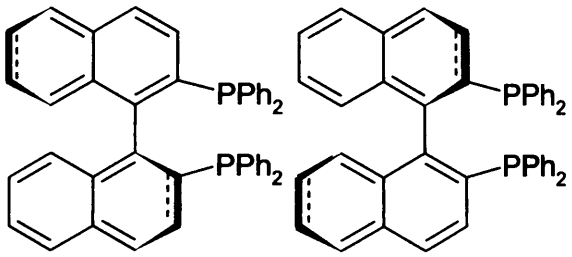


Scheme 1.1 Selected synthetic routes to primary, secondary and tertiary phosphines.

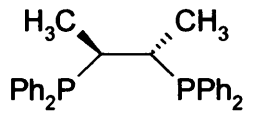
1.5 Application of Phosphine Ligands in Catalysis

Due to the ability of chiral phosphines to maintain their configuration, they are important ligands in asymmetric catalysis, because they impart stereospecificity on the ensuing products.[10] This is of great importance in the fine chemical industries especially in the pharmaceutical sector. Additionally, chiral ligands containing phosphines, such as BINAP

and CHIRAPHOS (shown below) are also widely used in many catalysed reactions to give a chiral product. For example, BINAP is employed as a ligand in the preparation of (1R,2S,5R)-menthol. This process (shown below) is employed to produce 3000 tonnes of menthol in a 94 % ee, and was developed by Nobel Laureate Ryoji Noyori.[11]

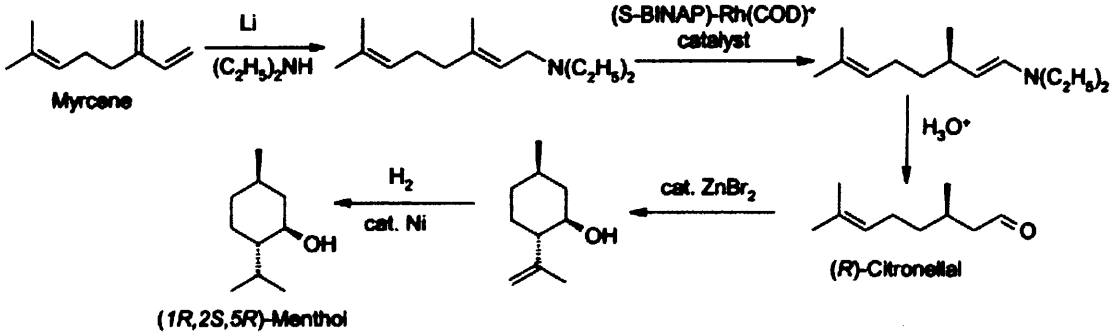


(S)-BINAP (R)-BINAP



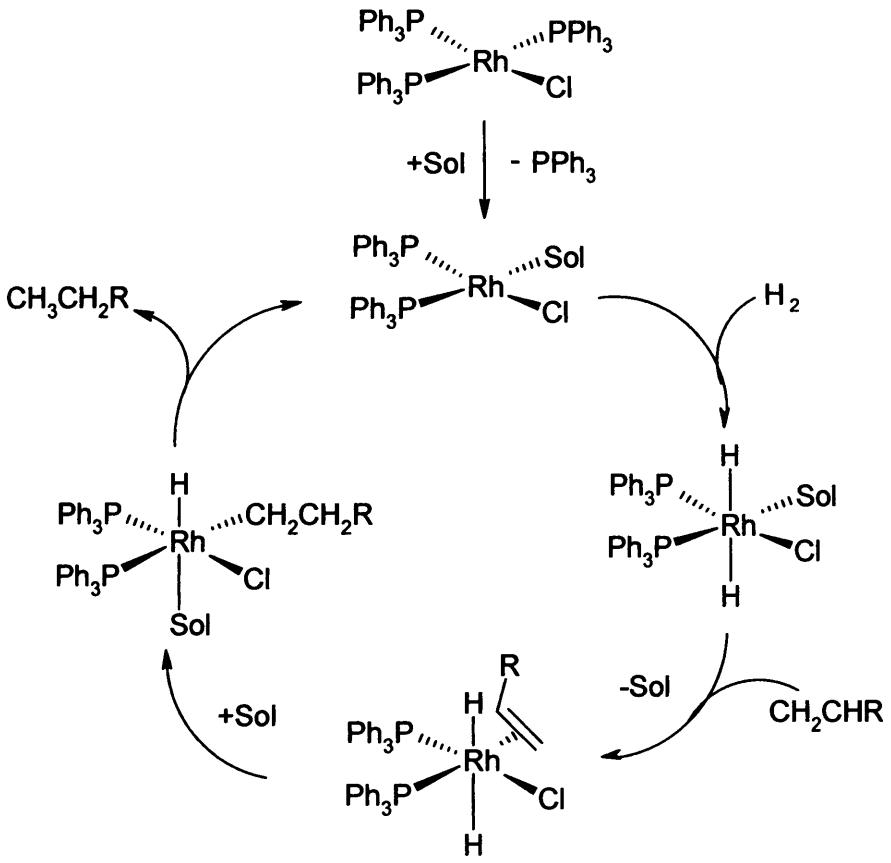
(S,S)-CHIRAPHOS

Figure 1.8



Scheme 1.2

Non-chiral phosphines are also important in catalysis. Firstly, due to the trans effect, they are effective ligands for labilising the ligands trans to the phosphine. Secondly, since bulky phosphines readily dissociate from metal centres under some conditions, they may be used to speed up catalytic cycles involving dissociative mechanisms. For example, Wilkinson's catalyst, $RhCl(PPh_3)_3$, is a widely used alkene hydrogenation catalyst (scheme 1.3).[12]



Scheme 1.3. Wilkinson`s catalytic cycle

The mechanism of this reaction involves the dissociation of the PPh_3 ligand (aided by the steric bulk at P). Subsequent studies have shown that replacing PPh_3 with the chiral phosphine, PhP(Pr)(Me) result in the isolation of enantiomerically enriched chiral products.[13]

1.6 Polydentate and Macrocyclic Ligands

Polydentate ligands are a popular class of compounds in coordination chemistry, and are able to form cyclometallated chelate rings with the metal centre. A major factor in the popularity and use of this class of ligands is the chelate effect. Due to this effect, complexes of polydentate ligands are kinetically more inert and thermodynamically more stable than their

monodentate, acyclic analogues. This effect is more evident with five or six membered chelates. Smaller chelates tend to be more strained and therefore less stable, while with very large and flexible chains the effect becomes insignificant. The formation of chelates in coordination compounds is entropically favoured, as this leads to greater dissorder (ie. more species) in the system. Since the Gibbs free energy value and the change in entropy for the formation of the compound are related ($\Delta G^{\Theta} = \Delta H^{\Theta} - T\Delta S^{\Theta}$), it is apparent that a more positive entropic contribution (ie. more disorder) will result in lower Gibbs free energy value. This consideration is illustrated in equations 1.1, 1.2 and 1.3 below, showing the reaction between Cd^{2+} ions and methylamine (*monodentate*) or ethylene diamine (*bidentate*) ligands.[14]

1.1 $$Cd^{2+}_{(aq)} + 4MeNH_{2(aq)} \leftrightarrow [Cd(MeNH_2)_4]^{2+}_{(aq)}$$

$\Delta G^{\Theta} = -37.2\ kJ.mol^{-1}$
$\Delta H^{\Theta} = -57.3\ kJ.mol^{-1}$
$-T\Delta S^{\Theta} = 20.1\ kJ.mol^{-1}$
$Log_{10}\beta_n = 6.52$

1.2 $$Cd^{2+}_{(aq)} + 2en_{(aq)} \leftrightarrow [Cd(en)_2]^{2+}_{(aq)}$$

$\Delta G^{\Theta} = -60.7\ kJ.mol^{-1}$
$\Delta H^{\Theta} = -56.5\ kJ.mol^{-1}$
$-T\Delta S^{\Theta} = -4.2\ kJ.mol^{-1}$
$Log_{10}\beta_n = 10.6$

1.3 $$[Cd(MeNH_2)_4]^{2+}_{(aq)} + 2en_{(aq)} \leftrightarrow [Cd(en)_2]^{2+}_{(aq)} + 4MeNH_{2(aq)}$$

$\Delta G^{\Theta} = -23.5\ kJ.mol^{-1}$
$\Delta H^{\Theta} = +0.8\ kJ.mol^{-1}$
$-T\Delta S^{\Theta} = -24.3\ kJ.mol^{-1}$
$Log_{10}\beta_n = 4.08$

Note: $Log_{10}\beta_n$ = stability constant.

From equations 1.1 and 1.2, it is clear that the stability constant for $[Cd(MeNH_2)_4]^{2+}$ is considerably lower than that of $[Cd(en)_2]^{2+}$ ($10^{6.52}$ compared to $10^{10.6}$, respectively). This observation is accompanied by a lower ΔG^{Θ} value for the chelating complex (eq. 1.1) over the monodentate complex in equation 1.2. However both reactions have similar ΔH^{Θ} values, which indicate that the difference in free energy comes mainly from the $-T\Delta S^{\Theta}$ component.

Equation 1.3 shows the direct replacement of four methylamine ligands by two en. The various parameters are extrapolated by deduction of the values of 1.1 from 1.2. The values for equation 1.3 show that the process of substituting $[Cd(MeNH_2)_4]^{2+}$ with two chelating en ligands is opposed enthalpically, as the $\Delta H^{\ominus}$ value is positive (+ 0.8 $kJ.mol^{-1}$). This reaction is therefore driven entirely by the entropic contribution. Whilst it is important not to overlook other factors such as the change in enthalpy for the formation of a given chelating complex, this example illustrates the important contribution of entropy in the stability of these complexes.

Macrocycles are a class of cyclic ligands containing three or more donor atoms within a ring of at least nine atoms. Each donor is separated by at least two heteronuclear atoms, usually carbon, from the adjacent donor atom. There are numerous examples of macrocycles in the literature with various donor functions with N, O and S donors being the most common (figure 1.9).[15,16,17]

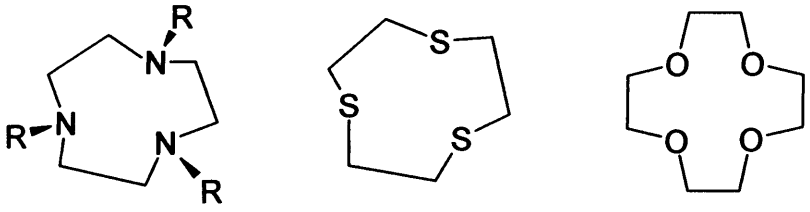


Figure 1.9. Selected examples of macrocycles of N, S and O donor atoms.

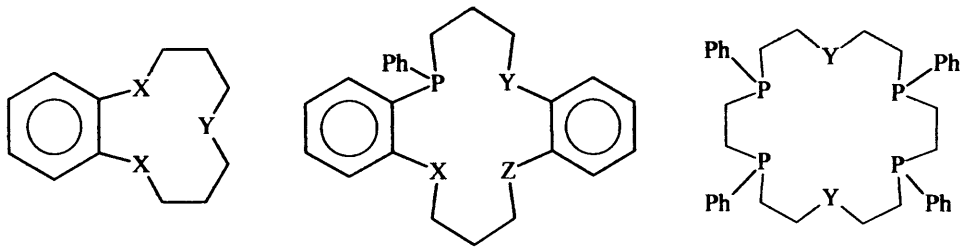
Macrocyclic complexes are intrinsically stable, primarily due to the macrocyclic effect.[18] The macrocyclic effect can be considered as an extension of the chelate effect; a proportion of stability is imparted on the metal complex by formation of chelates encompassing the metal centre. However, the macrocyclic effect is more difficult to rationalise than the chelate effect. If the size of the macrocyclic cavity closely matches that of the metal ion, the ligand is said to be 'preorganised', as the metal-macrocycle bonding is optimised. In these instances, a macrocyclic effect may be observed. However, in instances where the ligand is not

'preorganised' (ie. when the ligand is in its lowest energy conformation and the cavity size does not match that of the metal ion), the ligand may be required to reorganise itself, resulting in a reduction in the enthalpy change of macrocycle formation.[19]

Currently, there are relatively few phosphorus containing macrocycles, primarily due to the difficulties in preparing and handling the appropriate primary and secondary phosphines. The development of preparative routes to phosphine macrocycles has represented a very significant synthetic challenge. The synthesis of phosphorus containing macrocycles can be divided in two major categories: non-template reactions and template synthesis.[20]

In non-template reactions, the desired macrocycle is prepared by a reaction between a nucleophilic and an electrophilic terminus in the absence of a metal template. One main disadvantage of this approach is the capricious nature of the cyclisation. Often, intermolecular reactions result in the recovery of oligomeric species from the reaction mixture, due to entropically favoured polymerisation reactions. Nevertheless, the formation of macrocyclic species can be favoured by performing the reactions under high dilution conditions and by slow addition of the reagents.

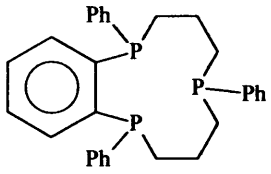
Whilst this approach is used more routinely for other donor macrocycles, non-template assemblies of phosphorus containing macrocycles are rare. Nevertheless, Kyba synthesised the 11- and 14-membered macrocycles containing phosphorus donor atoms, shown below.[21] Ciampolini obtained 18-membered mixed donor sexidentate macrocycles with four phosphorus atoms combined with two other donor atoms.[22] The macrocycles shown below were prepared by generation of a phosphide species (potassium or lithium salt), followed by controlled addition of the alkyl-halo electrophile.



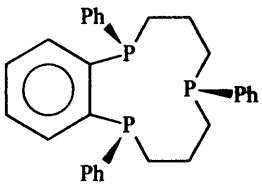
$11[ane]X_2Y$	$14[ane]PXYZ$	$18[ane]P_4Y_2$
X=P, S, As	X=P, S	Y=N, O, S
Y=N, O, S, P, As	Y=N, O, S, P, As	
	Z=N, O, S, P, As	

Figure 1.10. Various group 15 donor macrocycles prepared by high dilution reactions.

As well as being low yielding due to the unwanted formation of oligomeric species, non-templated reactions are also problematic, as there is no stereochemical control imposed on the phosphines. Therefore, in cases where there are more than one phosphorus donor atoms, the lone pair may be orientated away from each other (anti) or in the same direction (syn). This is illustrsted in Kyba's 11-membered macrocycle; the $11[ane]P_3$ has three possible stereoisomers (figure 1.11), containing a mixture of syn and anti configurations. The meso-*trans* isomer was isolated by crystallization in 5%.[23] From figure 1.11 it is evident that the syn, syn conformation is the favoured form to coordinate to a single metal centre.

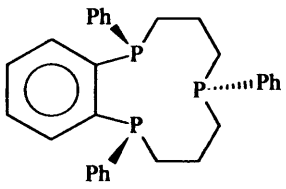


11[ane]P_3



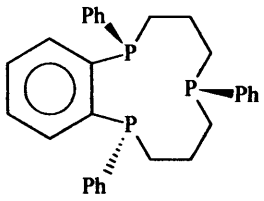
meso-*cis*

(syn, syn)



meso-*trans*

(syn, anti)

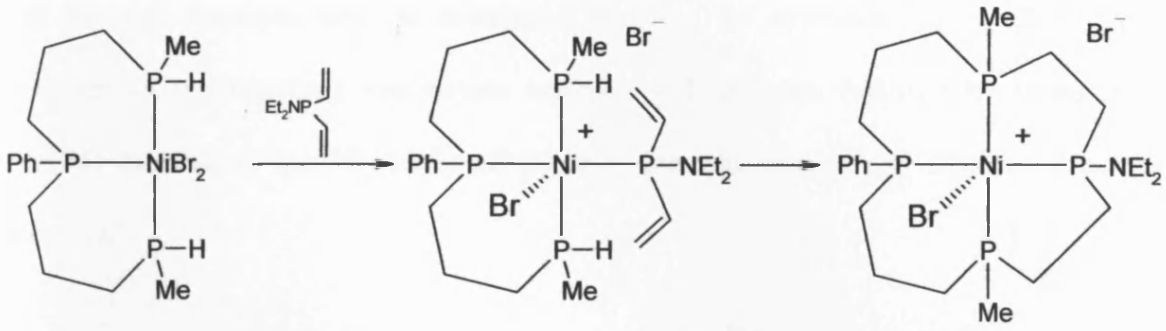


dl

(syn, anti)

Figure 1.11. Various conformations of Kyba's macrocycle.

In template assemblies, the phosphine donors are, by definition, coordinated to the metal centre and therefore are preorganised in the favoured stereoconformation. Metal templated cyclisations are favoured due to the increased stereochemical control that they offer. Also, due to 'activation' of various reactive functions once coordinated, new classes of phosphorus containing macrocycles have been isolated. For example, Stelzer has shown that coordinated vinylphosphines are capable of undergoing base initiated intramolecular cyclisation,[24] thus forming numerous four donor macrocyclic complexes, such as the tetraphospha macrocycle on a Ni (II) template, achieved by intramolecular hydrophosphination of the coordinated triphosphine with a divinyl phosphine species (scheme 1.4).[24]



Scheme 1.4. The preparation of P_4 macrocycles from intramolecular hydrophosphination of a coordinated linear P_3 unit with a divinyl phosphine on a nickel(II) template.

In octahedral metal complexes, so called facially capping, tri-donor macrocycles are of particular interest. This is due to the fact that the three remaining coordination sites are mutually cis, and therefore within close proximity to each other. The macrocycle-metal core remains stable, and, in the case of triphosphine macrocycles, the remaining reactive sites of the metal are labilised by the presence of high trans effect donors (figure 1.12). Therefore, triphosphine macrocyclic complexes are of particular interest in applications that rely on reactivity or exchangeable sites on a metal centre.

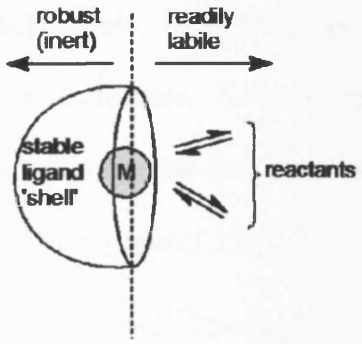
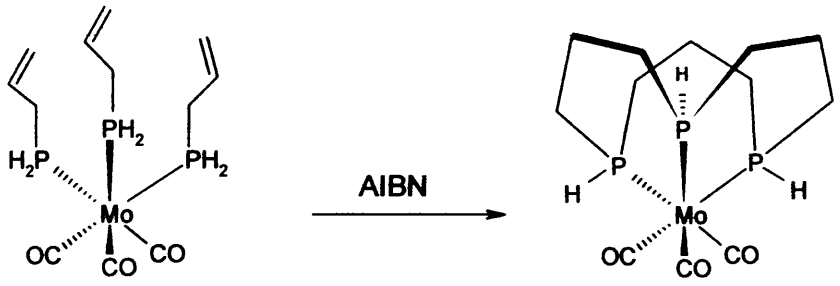


Figure 1.12

Perhaps the most pertinent of the early P_3 macrocycles, is that of Norman, the 12-membered triphosphine shown in scheme 1.5.[25] The macrocycle is formed by radical-initiated intramolecular hydrophosphination on a Mo template. Norman was unable to liberate the trisecondary macrocycle from its template. However, Edwards and co workers have shown

that the P-H functions may be substituted, yielding the tritertiary macrocycle.[26] Upon treatment of the tritertiary macrocycle complex with bromine followed by strong base (NaOH) in ethanol, the 12-membered triphosphine was successfully liberated from its template.[27]



Scheme 1.5

Using this methodology, Edwards has extended the pool of 12-membered triphosphorus macrocycles, incoorperating ethyl[28] and isopropyl[29] functions at the phosphorus. Furthermore, the liberation of the macrocycle from its molybdenum template has allowed explorations into its coordination to other metal centres.[30] In 2002 the catalytic properties of early transition metal complexes of the triethyl macrocycle were tested.[31] These complexes were shown to be moderately active as olefin polymerisation catalysts, upon addition of an alkylaluminium co-catalyst. Additionally, these catalysts displayed greater activity than other well known, acyclic catalytic complexes. Edwards was also able to demonstrate that incorporating pendant methoxypropyl functions onto the phosphorus donors directly affected the activity and selectivity of the system (figure1.13).[31]

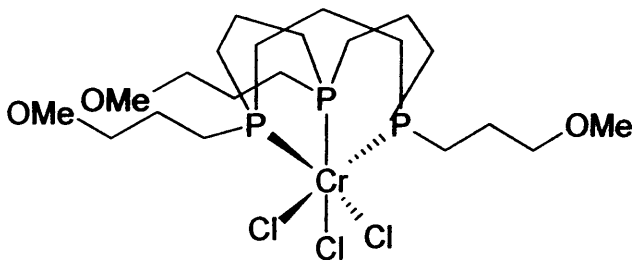
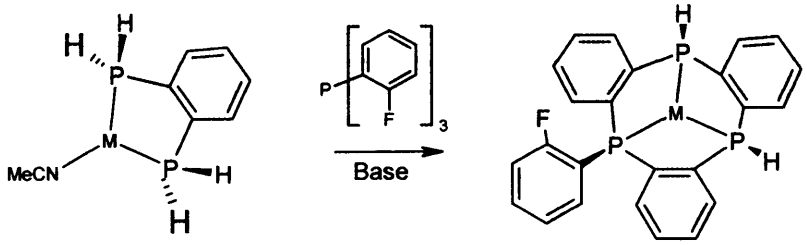


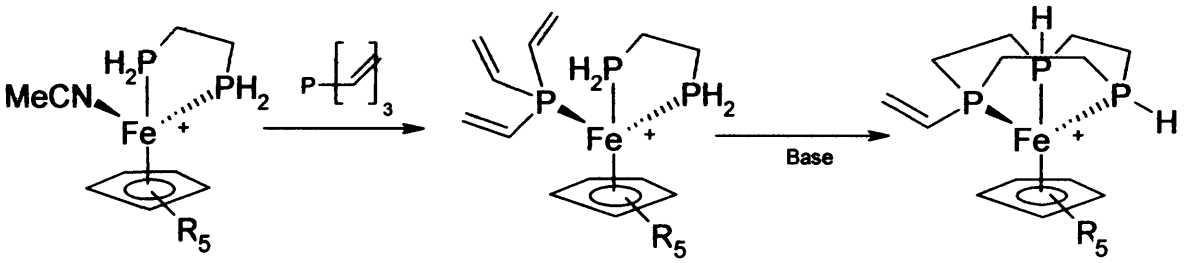
Figure 1.13

Given the rich coordination chemistry of the 12-membered systems, there is much interest in triphosphorus macrocycles with smaller ring sizes. Therefore, the last decade has seen a concerted effort by the Edwards group to develop novel, 9-membered triphosphorus macrocycles.[32] The smaller ring size is of considerable advantage, as the increased rigidity (over the 12-membered analogue) affords greater stability. Also, as the phosphorus donor atoms require a two-carbon bridge in between each other, there is a potential to incorporate benzannulated backbones into the macrocycle, further increasing the rigidity of the system. Saunders has made the observation that ortho-fluoroaryl functions are activated upon coordination to a metal centre.[33] Therefore coordinated orthofluorophenyl phosphines have been shown to act as electrophiles, and Edwards and Albers have developed a series of benzannulated [9]ane triphosphorus macrocycles using this approach (scheme1.6).[34]



Scheme 1.6. (where M = $Cp^{R}Fe^{+}$)

Similarly, vinyl phosphines are also known to be 'activated' upon coordination.[24] Vinyl functions are highly reactive, and the presence of other coordinated P-H functions is known to lead to hydrophosphination under basic conditions (scheme 1.7).[24] Therefore vinylphosphines are ideal synthons for the assembly of 5-membered chelates with aliphatic C_2 backbones. This approach has led to the publication of a substantial number of aliphatic [9]ane P_3R_3 macrocyclic complexes.[35]



Scheme 1.7.

Although there is a relatively large number of [9]aneP_3 macrocyclic complexes in the literature, the chemistry is limited to d_6 metal centres, mainly Fe(II).[36] This is due to the fact that the Edwards group has been unable to liberate the free macrocycle from its metal template. The metal templates are selected because of their stability and steric properties. Cp^RFe^+ complexes are ideal in both instances, as the Cp-Fe fragment is highly stable, and the complex is an 18-electron species. Given that the Cp ligand is a facial 'dust cap' ligand, auxiliary coordination sites are blocked and therefore unwanted coordination or reactivity is hindered. Furthermore the steric compression of the Cp ligand trans to the coordinated phosphines promote the ring closure to the macrocycle, by pushing the reactive sites closer together.

The macrocyclic complexes formed are extremely stable. Frustratingly, attempts to liberate the macrocycle led to the recovery of the trioxide alone.[32] Therefore, other metal templates have subsequently been sought. In recent years, manganese(I) and cobalt(III) centres have been used as templates, with the manganese systems showing particular promise with respect to liberation of the assembled macrocycle.[37,38]

1.7 Liberation of P-containing Macrocycles

The liberation of macrocycles from their metal templates can be divided into two main categories. Strong oxidants such as halogens or H_2O_2 are often used to oxidise the metal centre, resulting in a labilisation of the metal-macrocycle bonds. However using this approach with phosphine containing macrocycles, oxidation of the phosphorus atoms has also been observed.[32] Secondly, the addition of strongly competing ligands to a solution of the complex can induce demetallation. The most common ligands used include CN^-, $EDTA^{4-}$, OH^- and S^{-2}. In phosphorus containing macrocycles, the agent most extensively used is KCN.[39]

1.8 Aims of This Research

Tri-donor small-ring macrocycles are an interesting class of compounds due to their potential in coordination chemistry. The increased stability gained through the macrocyclic coordination effect may give access to new or rare metal complexes, for example those of metals in low oxidation states, or those with unusual coordination numbers or geometries. Furthermore as six electron, neutral donors, these macrocycles may form robust metal-macrocycle fragments, whereby all other reactive sites are mutually *cis* and labilised by *trans* labilising donors. This may lead to interesting reactivity being exhibited by the ensuing complexes, which we are keen to explore.

Since no reported 9-membered triphosphorus macrocycle has been liberated from its metal template to date, there is a need to develop new synthetic approaches to access more reactive or labile macrocyclic complexes as precursors to the liberated, free macrocycle. In order to achieve this, a principle aim of this research is to explore the use of new or previously overlooked classes of phosphines as synthons for the assembly of such complexes.

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Chapter 2- Synthesis & coordination of Silylated & Secondary Phosphiranes

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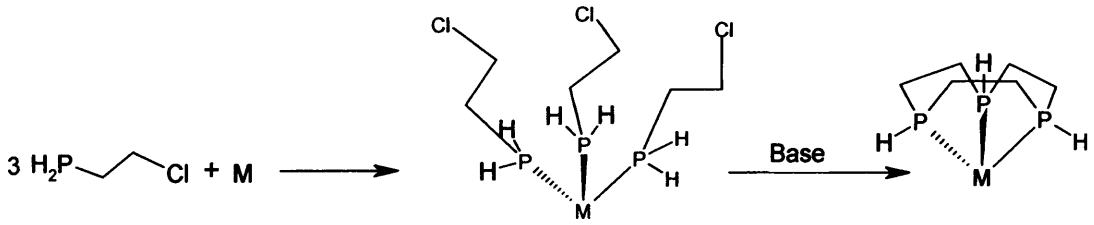
Cardiff University

2.1 Introduction

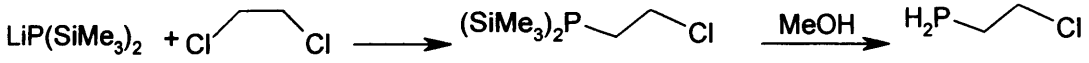
The use of simple, phosphorus containing haloalkyl moieties as synthons for P_3[9]ane macrocycles is of particular interest to our research group. The advantage of this approach is that the coordination of such ligands, and the subsequent cyclotrimerisation to form the desired macrocycle may proceed as a 'one pot' in a similar fashion to Norman's elegant use of allyl phosphine in the assembly of the parent [12]ane triphosphorus macrocycle.[1] Such precursors are frequently used in nitrogen, oxygen and sulfur [9]ane macrocyclic chemistry,[2] however no phosphorus analogues are reported in the literature. Our goal was to synthesise a halogenated-ethylphosphine, coordinate three units to a suitable metal centre, and induce cyclotrimerisation by addition of a base, as shown in scheme 2.1.



Scheme 2.1 (M = Cp^RFe^+, $Cr(CO)_3$)

There are few such phosphines reported in the literature. This is primarily due to their inherent instability as well as their tendency to react, often forming phosphirane species. For example, when sodium phosphide is added to dichloroethane, the three membered heterocycle, phosphirane is formed.[3] In order to overcome this issue our strategy involved the use of a bulkier, 'protected' phosphide. Our research has shown that tris(trimethylsilyl)phosphine may undergo lithiation selectively, forming $LiP(SiMe_3)_2$ in quantative yields.[4] Furthermore as P-Si bonds are prone to hydrolytic cleavage to form the parent P-H species, substituted trimethylsilyl phosphines are excellent candidates for sterically protected precursors to the parent primary phosphine.

The synthesis of chloroethyl phosphines is not trivial. Group 15 chloroethyl moieties are classed as mustard compounds and severe nerve poisons, and chloroethylphosphine is not reported in the literature. However, due to the potential of this compound as a precursor in phosphorus macrocyclic chemistry we developed the following synthetic route to synthesise chloroethylphosphine (scheme 2.2).



Scheme 2.2. The synthetic route to chloroethylbis(trimethylsilyl)phosphine, **2.1**, and chloroethylphosphine, **2.2.**

2.2 The Chemistry of Phosphiranes

The observation that the reaction of 1,2-dichloroethane with disodium phosphide yield phosphirane has also led us to consider phosphiranes, the smallest phosphorus heterocycle, as an attractive candidate as a precursor ligand in the assembly of [9]ane triphosphorus macrocycles. The development of more efficient routes to such macrocycles through template systems that allow access to the free ligands remains a major goal in the Edwards laboratories. Wild envisaged using phosphiranes as precursors for metal-directed cyclotrimerisation in 1996, and he prepared a number of facial *tris*-(1-phenylphosphirane) complexes for this purpose.[5] The intention was to promote cyclotrimersiation through a series of phosphirane ring-opening reactions achieved via the nucleophilic attack of coordinated phosphides at the carbon atoms of neighbouring phosphirane ligands. This, however, was not possible with the *fac*-$Mo(CO)_3(C_2H_4PPh)_3$ and $[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PPh)_3]^+$ complexes reported because the choice of 1-phenylphosphirane as the precursor precluded easy access to the phosphide. The generation of the necessary metal-bound $C_2H_4P^-$ anion

from coordinated C_2H_4PR requires R to be removable, preferably under relatively mild conditions.

The C_2H_4PH parent has been prepared by several methods, notably the reaction of disodium phosphide with 1,2-dihaloethane at low temperature.[3] These syntheses are, however, capricious with variable yields and the isolation of the compound can be frustrated by its thermal instability; phosphirane is reported to decompose during 24 hours at 25°C (when neat) to a mixture of ethyl phosphine, ethene and unidentified viscous products.[3] Stable phosphiranes are achieved when bulky alkyl or aryl substituents are introduced at the phosphorus. Thus 1-phenylphosphirane,[6] 1-mesitylphosphirane[7] and 1-*tert*-butylphosphirane[8] are distillable liquids and the coordination chemistry of these ligands has been explored by a number of groups including those of Kubiak,[16] Wild,[9] and Mathey.[10] In addition, Grützmacher has developed the chemistry of more complex phosphiranes that include a P-N function.[11]

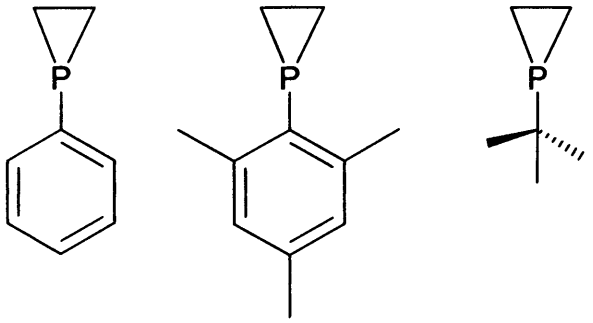


Figure 2.1. 1-phenylphosphirane,[12] 1-mesitylphosphirane[13] and 1-*tert*-butylphosphirane[14]

The succeptibility of P-Si bonds to hydrolytic cleavage in protic solvents make 1-trimethylsilylphosphirane an attractive candidate as a stable precursor to the thermally unstable parent phosphirane. Furthermore the parent phosphirane, C_2H_4PH, may give access

to coordinated phosphido complexes which may lead to the cyclotrimerisation reactions envisaged by Wild.[9]

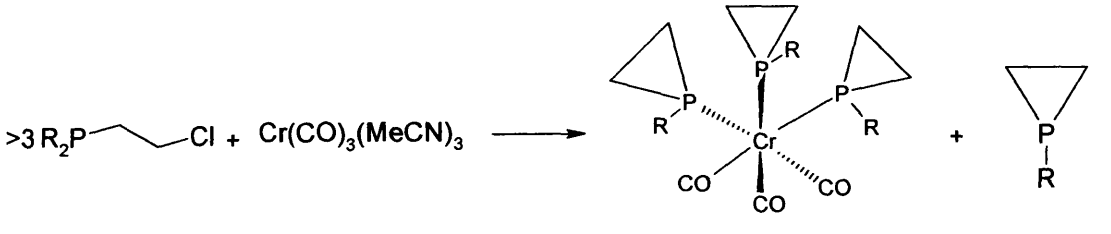
2.3 Results and Discussion

Synthesis of 2.1 and 2.2

The phosphine ligands **2.1** and **2.2** were prepared by slow addition of lithium bis(trimethylsilyl)phosphide to dichloroethane in an acetone / dry ice bath (scheme 2.2). The subsequent solutions were used 'in situ' and only characterised by ^{31}P NMR specroscopy, due to their likely instability upon isolation, as well as their toxicity. Compound **2.2** was obtained by addition of a small amount of methanol to **2.1**. The ^{31}P NMR spectra of both compounds show resonances in the expected regions; a singlet was observed at δ_P -176 ppm for **2.1** and a triplet at δ_P -126 ppm was observed in the spectrum of **2.2**, showing a one bond P-H coupling constant of 198 Hz, consistent with other primary phosphines.[15] The hydrolysis of **2.1** to **2.2** was followed by ^{31}P NMR spectroscopy, which showed the conversion to be facile. However, in both cases, the respective ^{31}P NMR spectra showed the presence of high-field signals (δ_P -319 ppm and -310 ppm for **2.1** and **2.2**, respectively). The position of these signals suggested the formation of a phosphirane species. Furthermore, in the case of **2.2**, the proton coupled spectrum was obtained and showed a doublet, again with a coupling constant in accordance with secondary phosphines.[16] The formation of unwanted phosphirane species was controlled by cooling the reaction mixtures in acetone and dry ice. However, despite these conditions, the formation of phosphirane (<10%) was always observed.

2.4 Coordination of 2.1 and 2.2 to Cr(0)

Upon coordination of **2.1** and **2.2** to $Cr(CO)_3(MeCN)_3$ both ligands were observed to intramolecularly cyclise. Thus, silylated and primary facial phosphirane complexes **2.7** and **2.8** were isolated from the reaction solutions (scheme 2.3). Furthermore ^{31}P NMR analysis of the reaction mixtures showed the complete conversion of residual free ligand to the respective phosphirane species. The facile ring closure of the coordinated phosphine may be rationalised by the increased lability of the P-R bond (where R = Si, **2.1** or H, **2.2**) as a result of coordination to the chromium centre. Due to back-bonding the phosphorus atom becomes more nucleophilic, and the chloroethyl pendant is attacked to form the three membered cycle. It is likely that the the cyclisation of the free phosphine is promoted by the basicity of the reaction mixture, or the gradual warming of the solution to room temperature.



Scheme 2.3 (R = $SiMe_3$ or H)

The ^{31}P $\{^1H\}$ NMR spectra of **2.7** and **2.8** show characteristically high-field resonances at δ_P -219.6 and -190.2 ppm, respectively. Although upfield from the free, linear phosphine ligands, **2.1** and **2.2**, these values are consistent with other coordinated phosphirane systems.[17] The ^{31}P NMR spectrum of **2.8** shows a one bond P-H coupling of 318 Hertz, and the signal is split into a doublet of poorly resolved multiplets, indicating the presence of only one bound proton. In the ^1H NMR spectrum of **2.7** the methyl protons are observed at δ_H 0.12 ppm, and the methylene protons in the C_2 backbone are observed at δ_H 0.75 ppm. However, in the secondary analogue, **2.8**, two sets of inequivalent protons are observed at δ_H

0.82 and 0.52 ppm. The P-H protons are observed at δ_H 1.09 ppm, and the $^1J_{H-P}$ coupling constant is in accordance with the ^{31}P NMR spectrum. In the ^{13}C $\{^1H\}$NMR spectra of **2.7** and **2.8** the carbonyl environments are observed at δ_C 230.1 and 226.5 ppm, respectively. Both signals appear as multiplets, and therefore no through metal C-P coupling constant could be deduced. The methylene signals also appear as multiplets; at δ_C 6.10 and, much further upfield, at δ_C 0.03 ppm. This difference reflects the steric presence of the trimethylsilyl group. The IR spectra of **2.7** and **2.8** (recorded as nujol mulls) show two carbonyl bands, consistent with facial, C_3 symmetric tricarbonyl complexes. In the IR spectrum of **2.7** these bands are observed at 1917 and 1815 cm^{-1}. These values of $\nu_{(CO)}$ are low compared to other analogous phosphine species, for example the values of the highest energy $\nu_{(CO)}$ stretch for *fac*-$Cr(CO)_3(P(OMe)_3)_3$[18] and *fac*-$Cr(CO)_3(PMe_3)_3$[19] are 1961 and 1923 cm^{-1}, respectively, suggesting that the $C_2H_4PSiMe_3$ ligand is a strong σ-donor and weak π-acceptor. Curiously, phosphiranes are generally regarded as poor sigma donors as a result of a contraction of the lone pair orbital, due to the acute C-P-C bond angle.[20] However, the presence of the inductively-donating $SiMe_3$ group at the phosphorus may enable greater sigma donation. The IR spectrum of **2.8** show the two carbonyl bands at 1959 and 1881 cm^{-1}, at considerably higher wavenumbers than those in **2.7**, suggesting lesser σ-donating properties of coordinated HPC_2H_4 over $Me_3SiPC_2H_4$.

The crystal structure of **2.7** was determined and is shown in figure 2.2. The complex has the expected pseudo-octahedral structure with C_3 symmetry in the solid state. All the interligand bond angles are close to the idealised 90° as anticipated. The average Cr-P bond distance of 2.377Å is somewhat longer than the average values of 2.348, 2.430 and 2.344Å observed for *fac*-$Cr(CO)_3(PH_3)_3$,[21] *fac*-$Cr(CO)_3(PEt_3)_3$,[22] and *fac*-$Cr(CO)_3(H_2PC(Me)CH_2)_3$.[23]

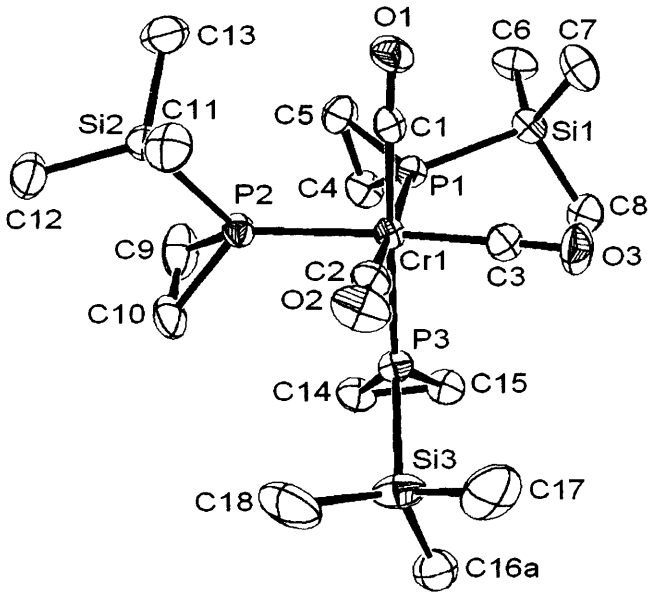


Figure 2.2 Ortep view of the complex $Cr(CO)_3(C_2H_4PSiMe_3)_3$, **2.7**. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): Cr1-P1, 2.3868(8); Cr1-P2, 2.3779(8); Cr1-P3, 2.3677(8); Cr1-C1, 1.844(2); Cr1-C2, 1.841(2); Cr1-C3, 1.837(2): C1-Cr1-C2, 89.56(10); C1-Cr1-C3, 89.54(10); C2-Cr1-C3, 87.30(10); P1-Cr1-P2, 92.73(3); P1-Cr1-P3, 91.83(3); P2-Cr1-P3, 90.70(3); P1-Cr1-C2, 176.29(8); P2-Cr1-C3, 174.55(8); P3-Cr1-C1, 177.26(7).

In order to study the reactivity of the coordinated P-$SiMe_3$ function, a toluene solution of **2.7** was treated with methanol. The desilylation process was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. As the intensity of the peak for **2.7** decreased, growth of a doublet at δ_P -220.0 (**1**, fig. 2.3), and triplet at -192.8 ppm (J_{P-P} = 41 Hz) (**3**, fig.2.2) attributable to an A_2B pattern assigned to the first intermediate $Cr(CO)_3(C_2H_4PSiMe_3)_2(C_2H_4PH)$ preceded the growth of a second A_2B pattern [δ_P -219.6 (t, J_{P-P} = 41 Hz), and -191.3 (d) ppm (**2** and **4** in fig. 2.3)] assigned to the second intermediate, $Cr(CO)_3(C_2H_4PSiMe_3)(C_2H_4PH)_2$ and finally a resonance due to the product **2.8** (δ_P –190.9) predominated (fig. 2.2). The desilylation is slow under ambient conditions, taking up to 5 days for completion. Conversely, the desilylation of

the free 1-trimethylsilylphosphirane, **2.3** to the parent phosphirane, **2.4**, is achieved within minutes under similar conditions.

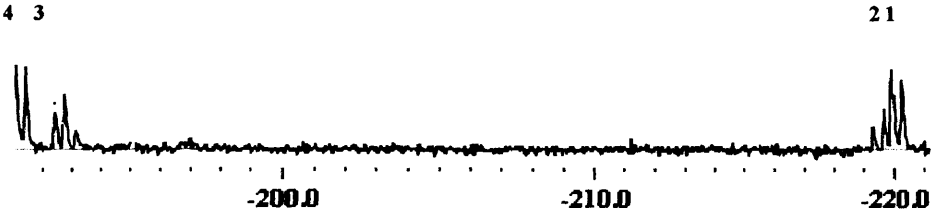


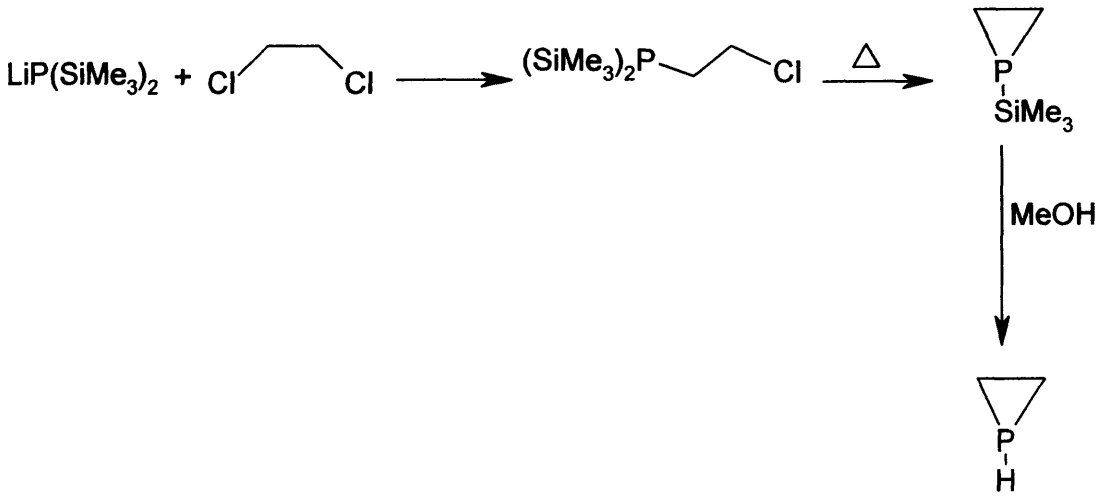
Figure 2.3. A ^{31}P {^{1}H} NMR spectrum showing the two intermediate species in the conversion of **2.7** to **2.8.**

2.5 Synthesis of phosphiranes 2.3-2.6 from linear precursors

Given that the linear phosphines **2.1** and **2.2** were observed to cyclise to their respective phosphirane in solution, we were interested in developing synthetic routes to access larger quantities of phosphiranes. Given the ease at which P-Si bonds are cleaved in the presence of protic solvents, 1-silylated phosphiranes are an attractive candidate as 'protected' sources of the parent, P-H function. Also, the steric bulk of the trimethylsilyl function may stabilise phosphiranes, and also give access to the thermally unstable parent phosphirane, through *in situ* protonolysis.

The ring-closure of **2.1** to give $C_2H_4PSiMe_3$ is effected upon heating **2.1** to 100 °C to expell Me_3SiCl. The resultant crude $C_2H_4PSiMe_3$ was distilled at 40 °C (10 mm Hg) to give the phosphirane, **2.3**, in 82% yield. It is noteworthy that no significant decomposition was observed when neat $C_2H_4PSiMe_3$ was heated at 150 °C for one hour. The ^{1}H NMR spectrum consists of a complex multiplet at δ_H 1.06 ppm for the four ring hydrogens and a doublet at δ_H 0.02 ppm ($^{3}J_{H\text{-}P}$ = 4.0 Hz) for the methyl hydrogens. The methyl carbons appear as a doublet ($^{2}J_{C\text{-}P}$ = 10.0 Hz) at δ_C 0.05 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum with the methylene carbons in the ring being observed as a doublet at δ_C 5.9

ppm with an absolute $^{1}J_{C\text{-}P}$ value of 41.6 Hz; all these observations accord with those for other phosphirane species.[24]

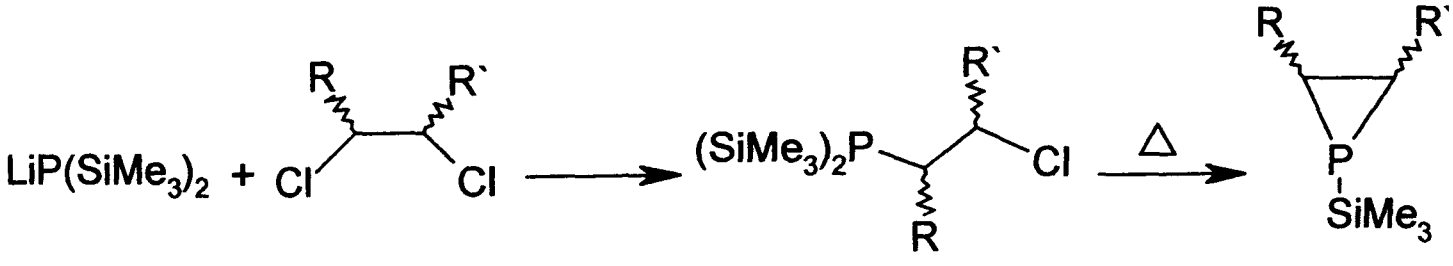


Scheme 2.4 The preparation of 1-trimethylsilylphosphirane and phosphirane.

Phosphirane, **2.4** was readily prepared as a solution in toluene or other unreactive organic solvent by treatment of 1-trimethylsilylphosphirane with an alcohol. Complete removal of the trimethylsilyl group from $C_2H_4PSiMe_3$ was achieved within minutes of adding MeOH to toluene solutions of $C_2H_4PSiMe_3$ (~1M in phosphirane) and the relatively dilute solutions of C_2H_4PH thus prepared were stable to decomposition at room temperature showing no noticeable deterioration (assessed by ^{31}P NMR spectroscopy) after several weeks at RT. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for a sample of C_2H_4PH prepared in C_6D_6 agree exactly with published data, however the $^{31}P\{^{1}H\}$ NMR chemical shift we observe for the phosphirane does not. The solutions of C_2H_4PH prepared from $C_2H_4PSiMe_3$ (either in deuterated or protic solvents) show a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum at δ_P = –309 ppm, some 32 ppm downfield of the reported chemical shift of δ_P = -341 ppm.[25] The chemical shifts of R_2PH species are usually downfield of the related R_2PSiMe_3 compounds and our phosphiranes follow this trend. The ^{31}P spectrum recorded at 121.7 MHz shows an apparent doublet of triplets with a $^{1}J_{P\text{-}H}$ of 160.0 Hz and a $^{2}J_{P\text{-}H}$ of 16.7 Hz. These patterns are largely in

The stability of phosphiranes has been studied extensively, most notably by Mathey. to the thermal instability of these systems, relatively few are known in comparison to th and O analogues, aziradines and oxiranes. Phosphiranes are destabilised by introdu bulky substituents at the ring carbons.[24] In 1969, Goldwhite *et al* reported the synthesis c methyl phosphirane in a 30% yield.[27] Goldwhite`s synthesis of this compound was trivial, requiring the use of a steel bomb charged with liquid ammonia, phosphine gas sodium metal. He also noted that the neat compound was extremely unstable, and there its coordination chemistry has not been explored.

However, the bulky $SiMe_3$ group in **2.3** has been shown to have a stabilising effect, s bulky substituents at the P atom increase stability. As a probe into the stabilising effect o $SiMe_3$ group, we prepared phosphiranes with substituents at the carbon atoms, using mod linear precursors (scheme 2.5).



Scheme 2.5. R = Me, R` = H (**2.5**), R = R` = Me (**2.6**).

To prepare the simplest C-substituted phosphirane, **2.5**, lithium bis(trimethylsilyl)phospl was added to a stirring solution of 1,2 dichloropropane. The reaction was followe $^{31}P\{^1H\}$ NMR spectroscopy, and a singlet in the spectrum of the reaction mixture at δ_P - ppm indicated the formation of the linear intermediate product, $(Me_3Si)_2PCH_2CH(CH_3)C$

was extremely malodourous and was found to be unstable when neat. In the ^{31}P

spectrum of **2.5**, there is evidence of decomposition of the product, however, all groups

protons associated with the proposed structure can be assigned. The C-H proton shift appe

at δ_H 1.47 ppm as a multiplet. The methylene protons are observed at δ_H 0.72ppm, and

methyl protons of the silyl group are observed atδ_H –0.01 ppm as a doublet (7 Hz).

methyl protons of the ring-substituent are observed as a doublet at δ_H –0.15 ppm, wit

coupling constant of 7 Hz. All four inequivalent carbon centres can be seen in the ^{13}C {

DEPT NMR spectrum of **2.5**. A doublet of 11 Hz at δ_C 21.17 ppm denotes the presence of

C-H carbon atoms, which couple to the phosphorus atom. The methylene carbon atom

observed as a doublet at δ_C 15.45 ppm, with a $^1J_{C-P}$ value of 26 Hz. The two respective

carbon environments are observed at δ_C 1.69 and –1.10 ppm as singlets. No fur

characterisation was carried out on this compound due to its inherent instability.

2.6, the dimethyl analogue was prepared using 2,3-dichlorobutane in the same procedur

for **2.5**. However we were unable to fully characterise this compound due to its inhe

instability. The compound was distilled and isolated pure. However, it was observe

decompose once neat. In the ^{13}C $\{^1H\}$ NMR spectrum of **2.6**, the methyl carbons

observed at δ_C 2.90 and 1.16 ppm, while the C-H carbons are observed at δ_C 24.98 ppm

the $^{31}P\{^1H\}$ NMR spectrum of **2.6** the phosphorus resonance is observed at δ -298 ppm, s

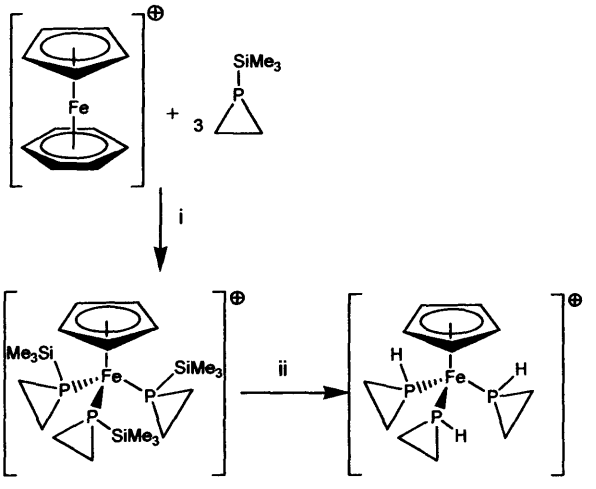
20 ppm downfield from the unsubstituted phosphirane, **2.3**. This compound was found t

extremely unstable and as a result its coordination chemistry was not examined.

quantitative yield (scheme 2.6). The complex shows a sharp singlet in the $^{31}P\{^1H\}$ NM spectrum at δ_p –205.6 ppm, corresponding to the coordinated 1-trimethylsilylphosphir in addition to the septet at δ_p –143.2 ppm due to the PF_6^- counterion ($^1J_{P\text{-}F}$ = 712 H Attempts to isolate and fully characterise this complex were frustrated by the rea desilylation of one or more of the $C_2H_4PSiMe_3$ ligands, even when every precaution l been taken to exclude water from the system. Evidence for the desilylation came fr $^{31}P\{^1H\}$ NMR analysis in solution where the presence of the intermediate species [($C_5H_5)Fe(C_2H_4PSiMe_3)_2(C_2H_4PH)]^+$ $(PF_6)^-$ was identified by a triplet at δ_p –164.2 ppm a doublet at δ_p –203.1 ppm during attempted work-up.

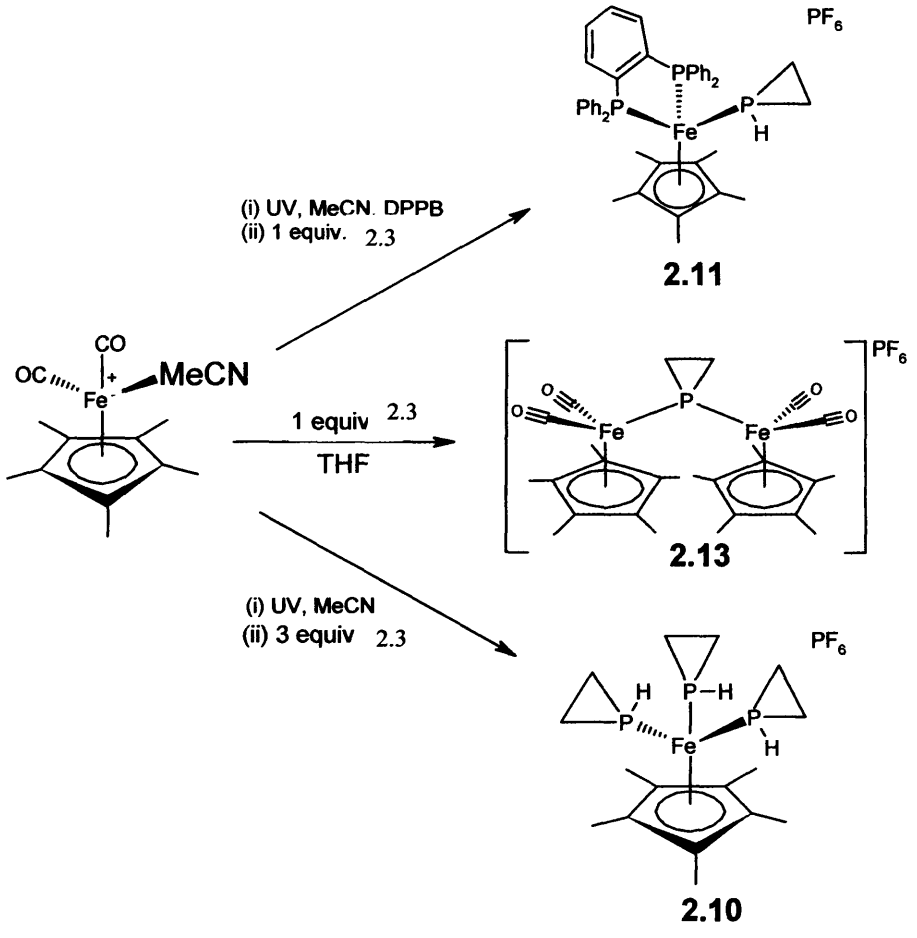
Protonolysis to **2.9** was achieved readily on addition of MeOH to a dichlorometh solution of the complex. Unlike the Cr and Mo species that took several days for t desilylation, complete loss of the trimethylsilyl groups occurred within minutes at RT **2.9**. The $[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PH)_3]PF_6$ complex, **2.9**, was readily recrystallised fi MeOH to afford brick-red crystals. The ^1H NMR spectrum of **2.9** recorded in CD_3N consists of two multiplets for the non-equivalent CH_2 ring protons at δ_H 0.88 ppm 1.39 ppm. A poorly resolved quartet is observed at δ_H 4.45 ppm due to cyclopentadienyl protons, as well as a doublet of multiplets at δ_H 1.08 ppm for the l protons of the secondary phosphines, with a one-bond coupling constant of 368 Hz. $^{13}C\{^1H\}$ NMR spectrum of **2.9** shows the ring carbons as an unresolved multiplet a 0.0 ppm. The carbons of the cyclopentadienyl ring appear as a singlet at δ_C 76.5 p The infrared spectrum of **2.9** recorded as a KBr disk shows two $\nu_{(P\text{-}H)}$ stretches at 2

cm^{-1}. Identification of **2.9** was unequivocally confirmed by it mass spectrum (TOF-MS, ES^+), which afforded the molecular ion at m/z = 301.03.



Scheme 2.6 The preparation of **2.9**. Conditions: i) DCM, sunlight, ii)) MeOH.

2.3 was found to readily coordinate to cationic Cp*Fe centres although P-Si bond activation was observed and subsequently three new complexes of the secondary phosphirane have been isolated. Our work has shown that the phosphirane may coordinate to the Cp^*Fe^+ precursor in a *tris* fashion, yielding the facial complex, **2.10**. However, by sequential coordination of a bidentate ligand, followed by addition of the phosphirane, we have been able to prepare the *mono*-phosphirane, bridged diphosphine complex, **2.11**. We have also observed the first example of a μ^2-bridging phosphirane complex, **2.13** upon coordination of **2.3** to $[Cp^*Fe(CO)_2]^+$.

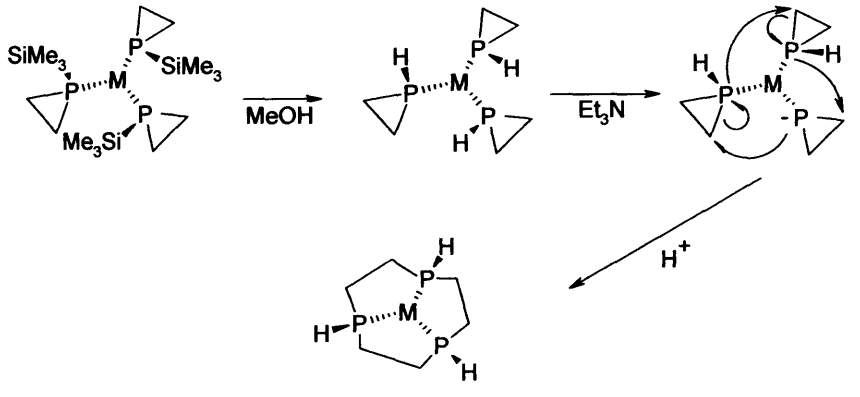


Scheme 2.7. The coordination chemistry of phosphirane to Cp^*Fe^+ centres.

2.10 was prepared by addition of three equivalents of **2.3** to an acetonitrile/ methanol solution of $[Cp^*Fe(MeCN)_3]PF_6$. After stirring overnight, the complexation was complete, as signified by a singlet at δ_P –166.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. This complex, once isolated was found to be very unstable when neat and stored in solution. In the ^1H NMR spectrum of **2.10**, the characteristic P-H shift appears at δ_H 3.25 ppm, with a one-bond P-H coupling constant of 400 Hz. The Cp*-methyl protons are seen as a singlet at δ_H 1.40 ppm, and the two sets of methylene protons are observed at δ_H 2.31 and 1.20 ppm, both as singlets. In the ^{13}C $\{^1H\}$ DEPT NMR spectrum of **2.10**, the Cp*-ring carbons are seen at δ_C 109.12 ppm as a singlet. A singlet at δ_C 8.84 ppm denotes the presence of the methylene carbon atoms, and the methyl carbons are seen as a singlet at δ_C 1.02 ppm. The

infrared spectrum of **2.10** shows a broad signal at 2363cm^{-1}, corresponding to a P-H stretch. Again, the mass spectrum of **2.10** shows the presence of the molecular ion at 371.09 amu, in 100% abundance.

The facial complex, **2.10** is an appealing candidate as a macrocyclic precursor complex. Pentamethyl Cp Iron(II) systems have been observed to induce more efficient formation of the macrocycle over the Cp analogue, due to the steric compression afforded by the methyl groups.[28] The availability of coordinated P-H functions in **2.10** allows access to the phosphido species upon addition of a base to a solution of the complex. It was hoped that the cyclotrimerisation would proceed in the manner shown in scheme 2.8.



Scheme 2.8 The proposed reaction scheme for the formation of a triphosphorus macrocycle from three coordinated phosphirane units.

Generation of the phosphido species was achieved by addition of 1.5 equivalents of triethylamine, and was accompanied by a darkening of the solution from orange to deep red. Upon stirring the solution for 4 hours, a ^{31}P NMR spectrum of the solution showed the presence of a broad resonance at δ_P -17 ppm, due to the phosphido species. The solution was warmed to reflux (THF) for 2 hours, and this action was accompanied by a darkening of the solution, and the precipitation of a small amount of insoluble, black material. The solution was allowed to cool to room temperature, and evaporated to dryness. Water was added in order to quench the mixture, and the ^{31}P NMR spectrum of the residual material showed that

the complex had decomposed, as no phosphorus resonances were observed. Similar results were observed using potassium tert-butoxide as a base.

2.11 was prepared by irradiating $[Cp^*Fe(CO)_2MeCN]PF_6$ in acetonitrile in the presence of bis(diphenylphosphino)benzene (DPPB), forming the intermediate species, $[Cp^*Fe(DPPB)MeCN]PF_6$, which gave a signal in the ^{31}P $\{^1H\}$NMR spectrum of δ_P 96 ppm. To this, was added one equivalent of **2.3**, followed by methanol, which yielded **2.11** after stirring for 12 hours at room temperature as red crystals. The ^{31}P $\{^1H\}$NMR spectrum of **2.11** shows a doublet corresponding to the coordinated DPPB at δ_P 91.8 ppm, with a $^2J_{P\text{-}P}$ value of 52 Hz. The coordinated phosphirane appears as a triplet at δ_P –140.5 ppm, with the same coupling constant. In the ^1H NMR spectrum of **2.11**, aryl resonances are observed at δ_H 7.63, 7.38 and 7.23 ppm. The P-H proton appears at δ_H 4.42 ppm, with a one-bond P-H coupling constant of 400 Hz. The Cp*-methyl protons are seen as a singlet at δ_H 1.40 ppm, and the methylene protons at δ_H 0.58 and 0.37 ppm as singlets. In the ^{13}C $\{^1H\}$ DEPT NMR spectrum of **2.11**, aryl resonances are observed at δ_C 133.38, 132.97, 131.26 and 128.83 ppm. The Cp*-ring carbons are seen at δ_C 90.04 ppm as a singlet. A singlet at δ_C 10.07 ppm denotes the presence of the five equivalent Cp*-methyl carbon atoms, while the methylene carbon atoms appear at δ_C 1.01 ppm. The infrared spectrum of **2.11**, recorded as a KBr disk shows the P-H stretching frequency at 2336 cm^{-1}. A mass spectrum of **2.11** afforded the molecular ion at 697.20 amu in 100% abundance, and the micro analysis of **2.11** was found to be within reasonable limits.

A single crystal of **2.11** was analysed by X ray diffraction, and is shown below (figure 2.4).

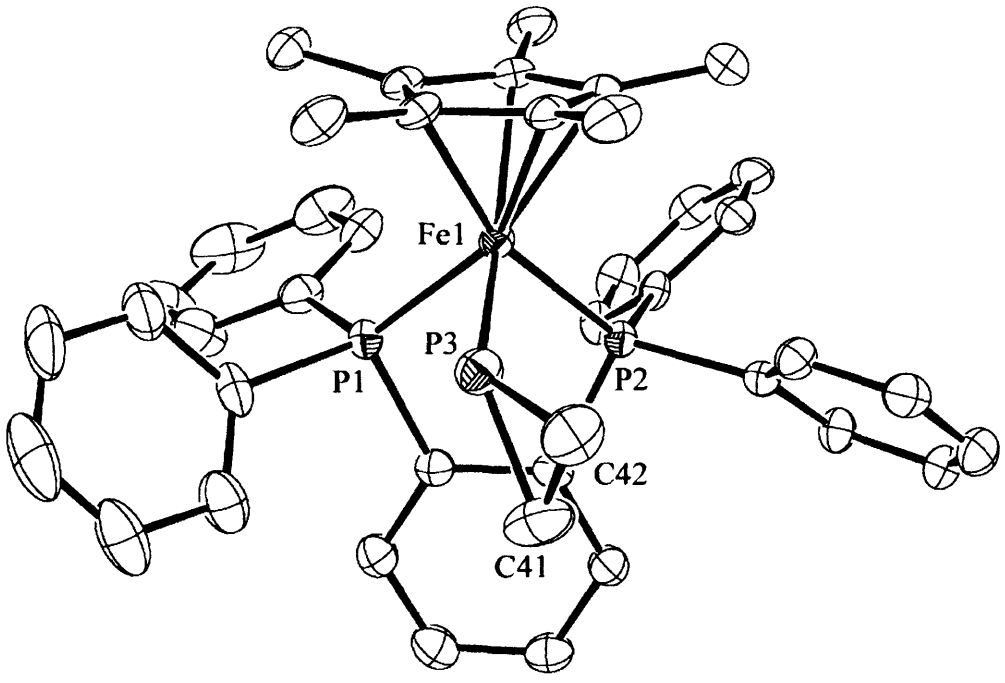


Figure 2.4. The structure of *Fac*-[(η^5-Cp*)(DPPB)Fe(HPC_2H_4)]PF_6, **2.11**. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): P(1)-Fe(1) = 2.2147(9); P(2)-Fe(1) = 2.2051(9); P(3)-Fe(1) = 2.2003(10); P(3)-C(42) = 1.828(4); P(3)-C(41) = 1.815(4); C(41)-C(42) = 1.499(6); P(3)-H = 1.000; P(1)-Fe(1)-P(2) = 85.18(3); P(1)-Fe(1)-P(3) = 86.62(4); P(2)-Fe(1)-P(3) = 94.96(4).

The solid state structure of **2.11** shows considerable deviation from the idealised octahedral configuration, with P-Fe-P bond angles of 86.62 (4), 85.18 (3) and 94.96 (4)° as a result of the distortions imposed by the chelating DPPB and Cp* ligands. The Fe-P bond lengths (2.2147 (9), 2.051 (9) & 2.2003(10) Å) are in line with those reported for the tris(phenylphosphirane) iron(II) complex reported by Wild (2.197 (3), 2.193 (4) and 2.186 (4) Å).[21] However, the interligand P-Fe-P bond angles were much closer to the ideal 90 degrees in Wilds complex, as there were no distortions imposed by the coordination of chelating ligands. In a phosphetane iron (II) complex structurally characterised by Wild (shown

below), the interligand bond angles are much closer to those obtained for **2.11**, at 85.8 (2) and 98.1 (2)°, due to the constraints of the 1,2-phenylenebis-(methylphenyl)phosphine ligand.[29] In this complex, the (phosphetane) P-Fe bond distance is comparable to that of **2.11**, and that in the tris(phenylphosphirane) complex, at 2.193 (7) Å. These observations suggest that the weaker σ-donating abilities of phosphiranes over their phosphetane analogues is a small factor in these specific systems.

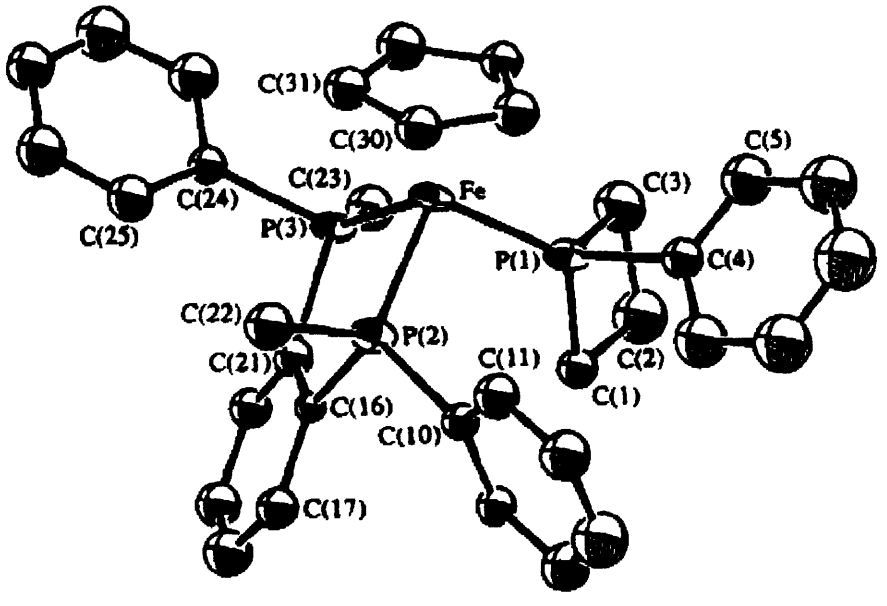


Figure 2.5. The solid state structure of Wilds phenylphosphetane Iron(II) complex.[27]

In attempting to prepare $[Cp^*Fe(CO)_2(HPC_2H_4)]PF_6$, the dicarbonyl derivative of **2.11**, the phosphirane unit was found to bridge two iron centres via deprotonation to the coordinated phosphide species. The dimerisation appears to be facile, given that no intermediate η^1-phosphirane or phosphido species can be observed in the ^{31}P NMR spectrum of the reaction mixture. Subsequent attempts to prepare $[Cp^*Fe(CO)_2(HPC_2H_4)]PF_6$ using more controlled reaction conditions (dropwise addition of metal to ligand) failed, resulting only in the formation of **2.13**. Given that phosphirane may coordinate to $[Cp^*FeL_2]^+$ centres in a η^1-fashion, such as in **2.11**, this anomaly is interesting. It is likely that the carbonyl groups,

through their pi-acidity, have an activating effect on the P-H function of the phosphirane, by increasing the electrophilicity of the metal centre. This inductive effect weakens the P-H bond due to the movement of bonding electrons from the P-H bond. This reactivity is an extension of previous observations made by us; in reactions with iron (II) complexes and 1-trimethylsilylphosphirane, the P-Si bond is labilised to such an extent that desilylation is facile, and subsequently no iron (II) complexes of the silylated phosphirane, **2.3** have not been isolated.

2.13 was prepared by addition of **2.3** to a DCM solution of $[Cp^*Fe(CO)_2MeCN]PF_6$. The ^{31}P NMR spectrum of the dark red solid, **2.13** shows the coordinated phosphine at δ_P –150.6 ppm as a singlet. Evidence of the proposed dimeric structure is seen in the ^1H NMR spectrum of **2.13**. A singlet is observed at δ_H 1.78 ppm corresponding to the methyl protons of the Cp*, and two further singlets are observed at δ_H 1.91 and 1.31ppm, which intergrate to 30:2:2, corresponding to the methyl protons and two sets of methylene protons respectively. In the ^{13}C $\{^1H\}$ DEPT NMR spectrum of **2.13**, the carbonyl groups appear as a doublet at δ_C 212.94 ppm, with a $^2J_{C\text{-}P}$ value of 26 Hz. The methylene carbon atoms are seen as a doublet at δ_C 11.66 ppm ($^1J_{C\text{-}P}$ = 23 Hz). At δ_C 8.85 ppm the methyl carbons are seen as a singlet. The Infrared spectrum of **2.13** was recorded, and the carbonyl stretches are at 2015, 1961 and 1949 cm^{-1}. No P-H stretches are seen in the expected area, which is in agreement with the proposed structure. The mass spectrum of **2.13** afforded the molecular ion in 100% abundance, at 553.21 amu.

2.7 Coordination of Phosphirane to other d^6 Metal Centres

The d^6 metal centres Mn(I), Fe(II) and Co(III) show increasing electrophilicity along the series, due to the increased cationic charge. In complex **2.13**, the formation of the bridging

phosphido donor is attributed to the electrophilicity of the Fe(II) centre, which inductively weakens the P-H bond. This electrophilicity is undoubtedly amplified by the presence of the strongly π-acidic carbonyl groups, since in complexes where there are no carbonyl groups on the Fe(II) centre, such as **2.10** and **2.11,** the formation of phosphido species is not observed

Mono-phosphirane complexes of manganese (I) and cobalt (III) were prepared in order to investigate the formation of phosphido bridged dimers in a series of increasingly harder metal centres.

The manganese complex, **2.12**, was prepared by the addition of one equivalent of **2.4** to manganese pentacarbonyl bromide in the presence of silver triflate. Although we were unable to fully characterise this complex, we have been able to ascertain the bonding mode of the phosphirane. Firstly, the IR spectrum of **2.12** shows two P-H bands in the expected region (a second band due to impurity which could not be removed), at 2342 and 2308 cm^{-1}. A ^{31}P NMR spectrum of **2.12** shows a doublet, with a one bond P-H coupling constant of 320 Hz, indicating that the P-H bond remains intact. The mass spectrum of **2.12** also shows the presence of the proposed monomeric cation in 100% abundance, confirming the structure as shown in figure 2.6

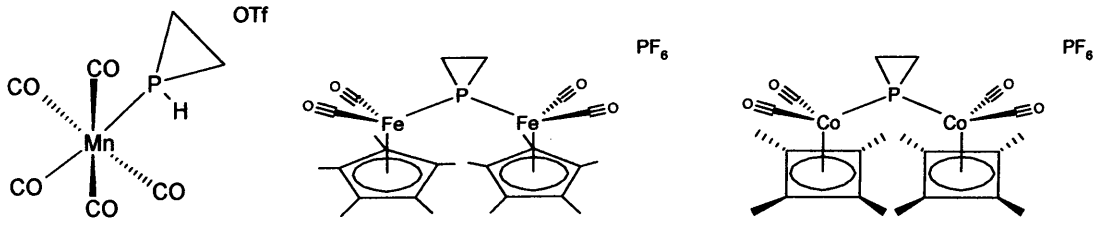


Figure 2.6. The structures of **2.12** , **2.13** and **2.14,** respectively.

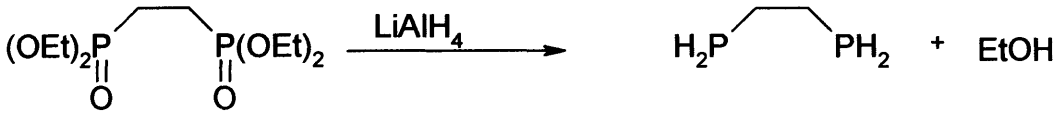
The cobalt complex, **2.14**, was prepared by the addition of **2.4** to a DCM solution of $Cb^*Co(CO)_2I$ in the presence of silver hexafluorophosphate. The addition of the ligand

affected an immediate colour change from purple to brown, and the ^{31}P NMR spectrum of **2.14** showed a singlet at δ_P -198 ppm, indicating a loss of hydrogen. The infrared spectrum of **2.14** also shows three carbonyl bands at 2119, 2072 and 2027 cm^{-1}, and there is an absence of any P-H stretch. Again, analysis of this complex by mass spectrometry gave the molecular ion of the dimeric species in 100% abundance.

It is noteworthy to mention that, upon leaving **2.14** in solution for a period of weeks, ^{31}P NMR spectra of this solution taken at regular intervals showed the gradual growth of a further peak, at δ_P 166 ppm accompanied by a decrease in intensity of the peak associated with **2.14**. Due to the insolubility of this unknown compound we were unable to gather any further spectroscopic evidence to confirm the proposed trend in dimer formation along the series.

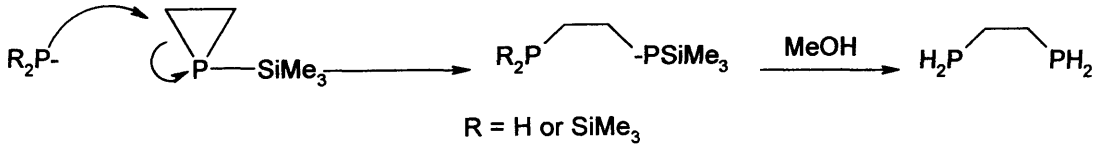
2.8 Reactivity of free phosphiranes 2.3 and 2.4

Work published by the Wild group has shown that phosphiranes may undergo ring opening upon reactions with nucleophiles.[27,30] In particular, Wild was able to demonstrate that 1-phenylphosphirane could be converted to 1,2-diphosphino ethane moieties using phosphido nucleophiles. However, he was only able to access the di(tertiary)phosphinoethane as a result. Currently, the synthesis of the diprimary parent, 1,2-bisphosphinoethane, is prepared by reduction of the bis(diethyl)phosphonate (scheme 2.9).[31]



Scheme 2.9

The problem with this route is that a by-product of the reduction, ethanol, is not easily separated from the phosphine during work up. Therefore, it is very difficult to obtain 1,2-diphosphinoethane in a pure state. We conducted small scale reactions in order to determine whether 1,2-bisphosphinoethane could be prepared upon reaction of **2.3** with the phosphorus containing nucleophiles, $NaPH_2$ and $LiP(SiMe_3)_2$ (scheme 2.10)



Scheme 2.10

Sodium phosphide, $NaPH_2$, has been prepared by the Edwards group by addition of two equivalents of ammonium chloride to trisodium phosphide in liquid ammonia.[32] Following

this protocol, a small amount of the nucleophile was prepared, and **2.3** was added. The solution was allowed to warm gradually with stirring. After 12 hours, the reaction was quenched with methanol and filtered. Analysis of the filtrate by $^{31}P\{^{1}H\}$ NMR showed the presence of numerous phosphorus environments, assigned to, **2.4** (δ_P = -309 ppm), PH_3 (δ_P = -236 ppm) and 1,2-bisphosphinoethane (δ_P = -126 ppm), as shown in figure 2.7.

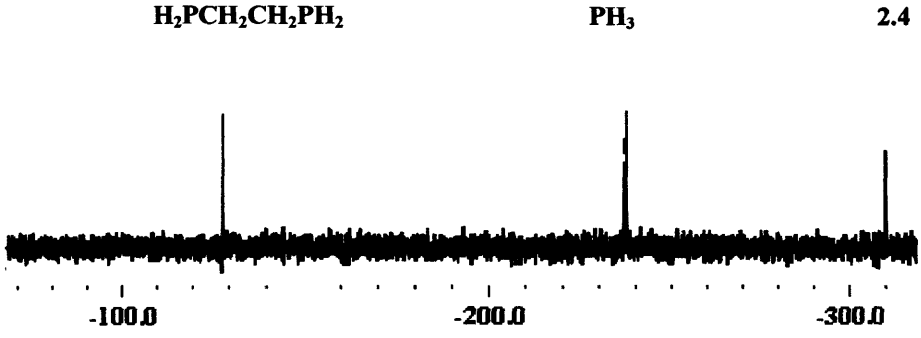


Figure 2.7. A representative $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture of **2.4** with a phosphide.

A proton-coupled spectrum was measured, and the three resonances were split into a quartet at δ_P = -236 ppm ($^{1}J_{P\text{-}H}$ = 198 Hz), a doublet at δ_P = -309 ppm (195 Hz) and a triplet at δ_P = -126 ppm (201 Hz).

2.3 was also added to a solution of lithium bis(trimethylsilyl)phosphide in 40/60 petroleum ether. Again, upon stirring for 12 hours, the solution was quenched with methanol and filtered. The ^{31}P NMR spectrum of this reaction mixture showed the presence of the three phosphines **2.4**, PH_3 and 1,2-bisphosphinoethane.

Both reactions demonstrated that 1,2-bisphosphinoethane is formed upon reaction of a phosphide species with **2.3**. However, in both cases, the reactions were not quantitative. Subsequently, we were unable to isolate 1,2-bisphosphinoethane from the reaction mixture. The reaction of sodium phosphide with **2.3** appeared to be the more efficient of the two. This is attributed to the steric difference between the nucleophiles; the large $SiMe_3$ groups in $LiP(SiMe_3)_2$ somewhat hinder the attack of the phosphide at the ring carbon.

2.9 Conclusion

We have developed an efficient route to 1-trimethylsilylphosphiranes, which can be converted to the parent phosphirane species by methanolysis. The steric bulk of the $SiMe_3$ substituent at the phosphorus has a stabilising effect, whereas the introduction of methyl substituents at the ring carbons was observed to destabilise the ensuing phosphiranes.

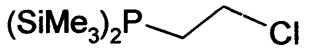
1-trimethysilylphosphirane readily coordinates to a range of metal centres, and IR studies have shown 1-trimethylsilylposphirane to be a relatively strong net donor, although the P-Si bond is labilised upon coordination. This is more prevalent in harder, more electrophilic metal centres such as Fe(II), where desilylation is facile. Phosphirane has been shown to coordinate to the 'harder' metal centres Co(III) and Fe(II) in a bridging fashion as the P-H bond is inductively weakened upon coordination, thus forming the required phosphido species.

Attempts to instigate cyclotrimerisation of facial tris phosphirane complexes to the desired [9]ane triphosphorus macrocycle using base were unsuccessful, due to the instability of the ensuing phosphido complexes.

Using two sources of P^-, $NaPH_2$ and $LiP(SiMe_3)_2$, we have shown that phosphirane species are susceptible to ring opening, leading to the formation of bisphosphinoethane. Due to the difficulty in accessing pure bisphosphinoethane using existing methods, it may be envisaged this route may be used as a more convenient route to the ligand. Furthermore, using phosphiranes with substituents at the carbon atoms, the ring opening reaction of phosphirane may yield more exotic, chiral bisphosphines. Our preliminary results in this field indicate that there is merit to this strategy, once refined.

2.10 Addendum

Below are the structures of the compounds referred to throughout this chapter.



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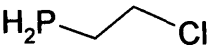

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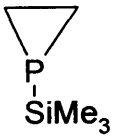

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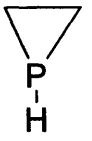

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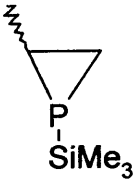

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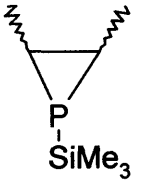

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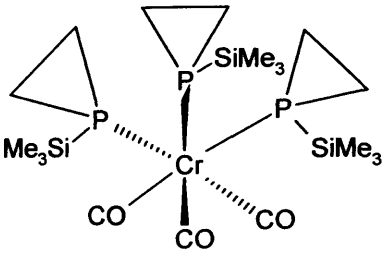

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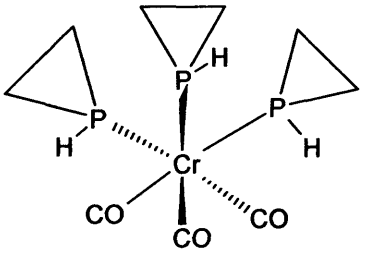

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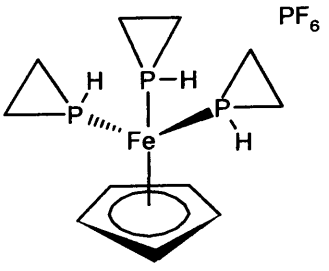

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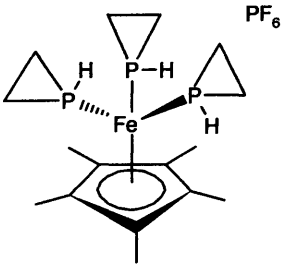

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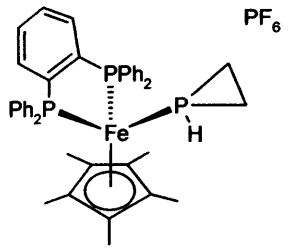

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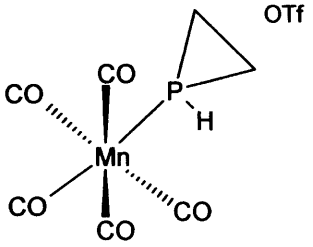

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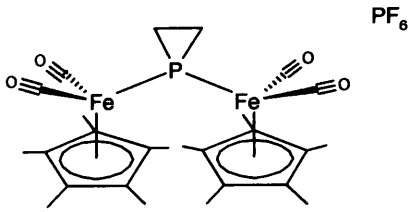

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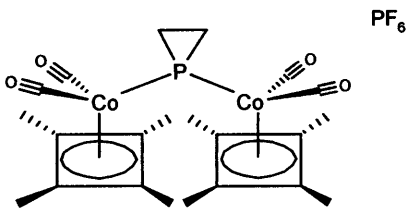

2.14

2.11 Experimental

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk and glovebox techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. The metal precursor complexes *fac*-$Cr(CO)_3(MeCN)_3$,[33] $[Cp^*Fe(CO)_2(MeCN)]PF_6$,[34] $[Cb^*CoI(CO)_2]PF_6$[35] and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)](PF_6)$[36] were prepared by literature methods. All deuterated solvents were dried (3Å molecular sieves) and degassed by freeze-thaw methods prior to use. $LiP(SiMe_3)_2$ was prepared by the addition of one equivalent of MeLi to a THF solution of $P(SiMe_3)_3$. The solution was stirred overnight, pumped to dryness and the grey residue was redissolved in petrol and used without further purification or characterisation. All other chemicals were obtained commercially, and used as received. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane ($\delta = 0$ ppm). Unless stated otherwise, infrared spectra were recorded as KBr disks on a Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd, UK.[37]

Chloroethylsbis(trimethylsilyl)phosphine (**2.1**)

$LiP(SiMe_3)_2$ (2.30 g, 12.5 mmol, prepared from $P(SiMe_3)_3$) in 40/60 petroleum ether (30 mL) was added dropwise to a stirred solution of 1,2-dichloroethane (1.2 mL, 15 mmol) in 40/60 petroleum ether (50 mL) in a well maintained acetone / dry ice bath. Once the addition was

complete, the cloudy mixture was filtered (cold) and used *in situ* for coordination in **2.7**. $^{31}P\{^{1}H\}$ NMR (121.7 MHz) δ -176.0 ppm.

Chloroethylphosphine (**2.2**)

A solution of chloroethylbis(trimethylsilyl)phosphine (approximately 6 mmol in 30 mL 40/60 petroleum ether) was cooled to -78 °C, and MeOH (5 mL) was added. Due to the tendency of this compound to cyclise to form phosphirane, this compound was not worked up, and was used *in situ* for coordination in **2.8**. $^{31}P\{^{1}H\}$ NMR (121.7 MHz) δ -126.4 (s), ^{31}P NMR (121.7 MHz) δ -126.2 (t, $^{1}J_{P\text{-}H}$ = 198 Hz) ppm.

1-trimethylsilylphosphirane (**2.3**)

A solution of $LiP(SiMe_3)_2$ (4.65 g, 25.2 mmol, prepared from $P(SiMe_3)_3$) in 40/60 petroleum ether (50 ml) was added dropwise to a stirred solution of 1,2-dichloroethane (2.38 ml, 30.2 mmol) in 40/60 petroleum ether (50 ml) in a manner similar to that previously described.[38] After stirring for 12 hrs, the mixture was filtered and the volatile materials were removed from the filtrate under reduced pressure. The crude $(MeSi)_2PCH_2CH_2Cl$, **2.1**, was transferred to a distillation apparatus and heated slowly to 100 °C to expel Me_3SiCl. After the removal of the trimethylchlorosilane was complete, the resultant oily residue was distilled at 40 °C (10 mm Hg) to give 1-trimethylsilylphosphirane as a clear, very slightly yellow liquid. Yield = 2.6 g (77%). ^{1}H NMR (C_6D_6, 500 MHz) δ 1.06 (m, 4H), 0.02 (d, J= 4.0 Hz, 9H) ppm. $^{13}C\{^{1}H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 5.95 (d, J =41.5 Hz, CH_2), 0.04 (d, J =10.0 Hz, CH_3) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 121.7 MHz) δ -318.3 ppm.

Phosphirane (**2.4**)

To a stirred solution of $C_2H_4PSiMe_3$ in toluene (10 ml of a 10% w/v solution) was added MeOH (0.5 ml) at room temperature. $^{31}P\{^1H\}$ NMR analysis of the solution showed complete conversion of **2.3** to C_2H_4PH within minutes, as indicated by the presence of a single peak at –309 ppm that appeared as a doublet of multiplets in the ^{31}P NMR spectrum. ^1H and ^{13}C NMR spectra obtained following addition of MeOD to a C_6D_6 solution of **2.3** on an NMR scale confirmed the formation of C_2H_4PH (as the sole phosphorus containing product) and Me_3SiOMe; the spectra were in full agreement with those published previously.[39]

1-trimethylsilyl, 2-methylphosphirane (**2.5**)

$LiP(SiMe_3)_2$ (7 mmol, in 50 mL 40/60 petroleum ether) was added dropwise to a stirred solution of 1,2-dichloropropane (0.8 g, 7 mmol in 10 mL 40/60 petroleum ether) at –78 °C. The solution was stirred overnight, the mixture was filtered and the volatile materials were removed from the filtrate by distillation. The crude $(MeSi)_2PCH_2CH(CH_3)Cl$ (δ_p -178 ppm) was transferred to a distillation apparatus and heated slowly to 100 °C. After the removal of trimethylchlorosilane, the resultant oily residue was distilled at 55 °C (10 mm Hg) to give 1-trimethylsilyl,2-methylphosphirane as a dark yellow liquid. Yield = 0.58 g (56%). ^1H NMR (C_6D_6, 500 MHz) δ 1.47 (m, CH, 1H), 0.72 (m, CH_2, 2H), -0.01 (d, J = 6 Hz, Si-CH_3, 9H), -0.15 (d, J= 7 Hz, CH_3, 3H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 21.17 (d, J= 11 Hz, *C*H), 15.45 (d, J = 26 Hz, *C*H_2), 1.69 (s, CH_3), -1.10 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ -290.1 ppm.

1-trimethylsilyl, 2,3-dimethylphosphirane (**2.6**)

$LiP(SiMe_3)_2$ (7 mmol, in 50 mL 40/60 petroleum ether) was added dropwise to a stirred solution of 2,3-dichlorobutane (0.89 g, 7 mmol in 10 mL 40/60 petroleum ether) at –78 °C. The solution was stirred overnight, the mixture was filtered and the volatile materials were removed from the filtrate by distillation. The crude $(MeSi)_2PCH(CH_3)CH(CH_3)Cl$ was transferred to a distillation apparatus and heated slowly to 100 °C. After the removal of trimethylchlorosilane, the resultant oily residue was distilled at 58 °C (10 mm Hg) to give 1-trimethylsilyl,2,3-dimethylphosphirane as a dark yellow liquid. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 24.98 (m, *C*H), 2.90 (s, CH_3), 1.16 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ -298.2 ppm.

Fac-$Cr(CO)_3(C_2H_4PSiMe_3)_3$ (**2.7**)

To a stirring suspension of *fac*-$Cr(CO)_3(MeCN)_3$ in toluene (200 mg, 7.71×10^{-4} mol in 20 mL) was added a large excess of **2.1** (from the crude reaction mixture). The complex went into solution immediately upon addition of the phosphine. After stirring at room temperature for ca. 12 hours, the solution was filtered, and all volatiles were removed *in vacuo*. The remaining solid was crystallised from 40/60 petroleum ether at -35 °C, yielding bright yellow crystals. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ -219.6 (s) ppm. ^1H NMR (C_6D_6, 500 MHz) δ 0.75 (m, 12H), 0.12 (s, 27H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 230.10 (m, *C*O), 6.10 (m, CH_2), 0.01 (m, CH_3) ppm. IR (nujol): 1917vs, 1815vs cm^{-1} (ν_{CO}). ES-MS: *m/e* 533 amu ($[M]^{\cdot+}$).

Fac-$Cr(CO)_3(C_2H_4PH)_3$ (**2.8**)

To a stirring suspension of *fac*-$Cr(CO)_3(MeCN)_3$ in toluene (200 mg, 7.71 x 10^{-4} mol in 20 mL) was added a large excess of the crude phosphine, **2.2**. The reaction mixture was left to stir overnight, and the solution was filtered to remove insoluble materials. All volatile solvents (and excess phosphine) were removed under reduced pressure (into a pre-trap), and **2.8** was crystallised from 40/60 petroleum ether at -35 °C. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ -190.2 (s) ppm. ^1H NMR (C_6D_6, 500 MHz) δ 1.09 (dm, $^1J_{H-P}$ 315 Hz, 3H, 0.82 (m, 6H), 0.52 (m, 6H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 226.51 (m, *C*O), 0.03 (m, *C*H_2) ppm. IR (nujol): 2319w (ν_{PH}), 1959vs, 1881vs cm^{-1} (ν_{CO}).

Fac-$[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PH)_3](PF_6)$ (**2.9**)

To a dark yellow solution of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)](PF_6)$ (100 mg, 2.91 x 10^{-4} mol) in dichloromethane (20 mL), was added a solution of 1-trimethylsilylphosphirane (3.5 equivalents, 1 mmol, 132 mg), and the mixture stirred in sunlight (12h.) after which time the colour had decome dark red. Methanol (1 mL) was added, and the solution was allowed to stir for a further 4 h. The product was isolated by removal of the volatile solvents under reduced pressure, and recrystallised readily from MeOH at -35°C. Yield = 97mg (75%). ^1H NMR (CD_3NO_2 500 MHz) δ 4.45 (q, Cp 5H) 1.08 (d m, $^1J_{P-H}$ = 368 Hz, P-H, 3H), 0.80, 1.39, 0.88 (m, CH_2, 12H) ppm. $^{13}C\{^1H\}$ DEPT NMR (CD_3NO_2, 125.8 MHz) δ 76.5 (s, Cp), 0.01 (m, CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121.7 MHz) δ -170.0 (s) δ -143.2 (h, $^1J_{P-F}$ = 708 Hz) ppm. IR (KBr): 2963 w, 2344, 2340 w (ν_{PH}), 1451 w, 1421 w, 1027 s, 997 s, 841 vs,

cm^{-1}. *Anal,:* calc for $[(\eta^5\text{-}C_5H_5)Fe(HPC_2H_4)_3](PF_6)$: C, 29.62; H, 4.52. Found: C, 29.16; H, 4.00. ES-MS: *m/e* 301.03 amu ($[M]\cdot^+$).

Fac-$[(\eta^5\text{-}C_{10}H_{15})Fe(C_2H_4PH)_3]PF_6$ (**2.10**).

$[Cp^*Fe(CO)_2(MeCN)]PF_6$ (200 mg, 4.6 x 10^{-4} mol) was irradiated with ultraviolet radiation in acetonitrile (170 mL) for 24 hours. The pale yellow solution darkened to a deep red colour overnight, due to the stoichiometric formation of the intermediate $[Cp^*Fe(MeCN)_3]PF_6$ species. At this stage, the solution was concentrated to ca. 50 mL. To this solution was added 3.5 equivalents of 1-trimethylsilylphosphirane (215 mg) and the reaction mixture was stirred for 24 h, after which time methanol (1 mL) was added. Following stirring for a further 1 h, the solution was pumped to dryness *in vacuo*, and the resultant residue was washed with petrol. Yield = 165 mg (70%). ^1H NMR ($CDCl_3$ 500 MHz): δ 3.25 (d, P-H, $^1J_{P\text{-}H}$ = 370 Hz, 3 H), 2.31 (s, CH_2, 6 H), 1.44 (s, CH_3, 15 H) 1.20 (s, CH_2, 6 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 109.12 (s, Cp*), 8.84 (s, CH_2), 1.02 (s, CH_3) ppm. $^{31}P\ \{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ -144.5 (h, $^1J_{P\text{-}F}$ = 711 Hz). -166.6 (br, s) ppm. IR : 2363 br, (ν_{PH}), 1958 s, 1654 s, 1457 s, 1028 m, 843 s, cm^{-1} M.S: ES-MS: *m/e* 371.09 amu ($[M]\cdot^+$, 100%).

Fac-$[(\eta^5\text{-}Cp^*)(DPPB)Fe(HPC_2H_4)]PF_6$ (**2.11**)

$[Cp^*Fe(CO)_2(MeCN)]PF_6$ (200 mg, 4.6 x 10^{-4} mol) was irradiated with ultraviolet radiation in acetonitrile (170 mL) in the presence of 1,2-bis(diphenylphosphino)benzene *(DPPB)* (210 mg, 5 x 10^{-4} mol) for 24 hours. The resultant red solution of the intermediate $[Cp^*Fe(DPPB)(MeCN)]PF_6$ species was concentrated to ca. 50 mL. To this solution was added one equivalent of 1-trimethylsilylphosphirane (61 mg) and the reaction mixture was

stirred for 24 h, after which time methanol (1 mL) was added. After stirring for a further 1 h, the solution was pumped to dryness *in vacuo*, and the resultant red solid was washed with petrol (10 mL). Red crystals of $[Cp^*(DPPB)Fe(HPC_2H_4)]PF_6$ were obtained by diffusion of ether into a concentrated methanol solution of the complex at -35°C. Yield = 220 mg (57 %). ^1H NMR ($CDCl_3$ 500 MHz): δ 7.63 (s, *Ar*-H, 12H), 7.38 (m, *Ar*-H, 6 H), 7.23 (m, *Ar*-H, 6 H), 4.42 (d, P-H, $^1J_{P-H}$ = 400 Hz, 1 H), 1.40 (br s, CH_3, 15 H), 0.58 (s, CH_2, 2 H) 0.37 (s, CH_2, 2 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 133.38 (s, *Ar*-C), 132.97 (s, *Ar*-C), 131.26 (d, *J* =55 Hz, Ar-C), 128.83 (d, *J*= 44 Hz, Ar-C), 90.04 (s, Cp*), 10.07 (s, CH_3), 1.01 (s, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 91.8 (d, *J* =52 Hz) δ -140.5 (t, *J*= 52 Hz), δ -144.5 (h, $^1J_{P-F}$ = 712 Hz) ppm. IR : 3056 m, 2961 m, 2911 m, 2336 s, (ν_{PH}), 1482 s, 1435 s, 838 vs. cm^{-1}M.S: ES-MS: *m/e* 697.20 amu ($[M]^{\cdot+}$, 100%) *Anal.* Calc. For $C_{42}H_{44}P_4F_6Fe$: C, 59.87; H, 5.26. Found: C, 59.61; H, 5.06%.

$[Mn(CO)_5(C_2H_4PH)]CF_3SO_3$ (**2.12**)

To a stirring solution of manganese pentacarbonyl bromide (200 mg, 7.28 x 10^{-4} mol in 10 mL DCM + 0.5 mL MeOH) was added **2.3** (1.5 equiv., 1.44 g) in the presence of silver triflate (1.1 equiv, 206 mg). The solution was stirred in the absence of bright or direct sunlight for ca 12 h. The resultant mixture was then filtered to remove silver containing solids, and pumped to dryness. The solid was washed sequentially with petrol (2 x 20 mL), followed by cold diethyl ether (2 x 10 mL). The yellow powder was then thoroughly dried *in vacuo*. ^1H NMR (CD_3NO, 500 MHz): δ -0.90 (s, CH_2, 4 H), - 0.40 (d, $^1J_{H-P}$ = 320 Hz, P-H, 1 H) ppm. ^{31}P NMR (CD_3NO, 121.7 MHz): δ -200.0 (d, *J* = 320 Hz) ppm. IR : 2342, 2308 cm^{-1} s, (ν_{PH}), 2012, 1980 br (υ_{CO}) M.S: ES-MS: *m/e* 254.9 amu ($[M]^{\cdot+}$, 100%)

$[Cp^*Fe(CO)_2]_2(\mu^2\text{-}PC_2H_4)PF_6$ (**2.13**)

To a solution of $[Cp^*Fe(CO)_2(MeCN)]PF_6$ (200 mg, 4.6 x 10^{-4} mol) in THF (50 mL) was added one equivalent of trimethylsilylphosphirane (61 mg) and methanol (1 mL). The pale yellow solution was stirred overnight, after which time the solution turned dark-red. The solvent and excess ligand was removed under reduced pressure, and the complex was washed in petrol (50 ml), followed by diethyl ether (25 ml). The crude solid was re dissolved in THF and crystallised by slow diffusion of petrol into the solution. Yield = 121 mg (75 %). ^1H NMR ($CDCl_3$ 500 MHz): δ 1.78 (s, CH_3, 30 H), 1.91 (s, CH_2, 2 H) 1.31 (s, CH_2, 2 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 212.94 (d, CO, $^2J_{C\text{-}P}$ = 26 Hz), 97.88 (s, Cp*), 11.66 (d, CH_2, $^1J_{C\text{-}P}$ = 23 Hz), 8.85 (s, CH_3) ppm. ^{31}P NMR ($CDCl_3$, 121.7 MHz): δ -150.6 (s), -144.5 (h, $^1J_{P\text{-}F}$ = 710 Hz) ppm. IR : 2015, 1961, 1949 s (ν_{CO}), 1489 s, 1386 s, 1077 m, 1026 m, 839 s cm^{-1} M.S: ES-MS: *m/e* 553.21 amu ($[M]^{\cdot+}$, 100%).

$[Cb^*Co(CO)_2]_2(\mu^2\text{-}PC_2H_4)PF_6$ (**2.14**)

$Cb^*Co(CO)_2I$ (100 mg, 2.86 x 10^{-4} mol) was dissolved in DCM and methanol (10 mL and 0.5 mL, respectively) in the presence of $AgPF_6$ (137 mg), and the solution was kept away from direct sunlight light. To this was added **2.3**, and the solution was left to stir overnight. After this time, the colour of the solution was observed to have changed colour from purple to brown. The solution was filtered, pumped to dryness and washed with petrol (2 x 20 mL), and diethyl ether (2 x 20 mL). ^1P NMR ($CDCl_3$, 121.7 MHz): δ -198.0 (s), -144.5 (h, $^1J_{P\text{-}F}$ = 710 Hz) ppm. IR : 2119, 2072, 2027 cm^{-1} s (ν_{CO}). M.S: ES-MS: *m/e* 505.04 amu ($[M]^{\cdot+}$, 100%).

Reaction of **2.3** with $LiP(SiMe_3)_2$

1.65×10^{-4} mol of $LiP(SiMe_3)_2$ was prepared and added dropwise (in 50 mL of 40/60 petroleum ether) to a stirring solution of **2.3** (in 20 mL 40/60 petroleum ether). The mixture was refluxed for 3 days and allowed to cool. The volume of the solution was reduced to ca. 15 mL under reduced pressure and methanol was added (5 mL). ^{31}P NMR showed the presence of **2.4**, PH_3, and 1,2-bisphosphinoethane.

Reaction of **2.3** with $NaPH_2$

0.5 g of Na_3P (5×10^{-3} mol) was suspended in liquid ammonia and two equivalents of ammonium chloride (0.53 g) was added grain-wise. The solution was stirred for ca 2 h and the temperature was maintained using a dry ice / acetone bath. After this time, a solution of **2.3** was added (0.3 g, 1.27×10^{-3} mol in 40 mL of 40/60 petroleum ether). The solution was stirred under an atmosphere of nitrogen overnight. After this point, the solution was concentrated to ca. 15 mL and MeOH (15 mL) was added.

2.12 References

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Chapter 3-Preparation & Reactivity of Manganese(I) PN_2 mixed-donor Macrocyclic Complexes

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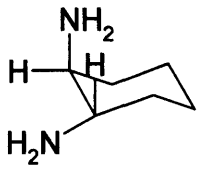
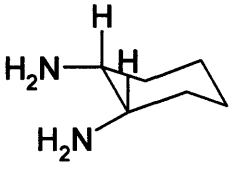
3.1 Introduction

The Edwards group is interested in mixed donor macrocycles with group 15 donor atoms, as a combination of donors may impart differing characteristics on *trans* bound ligands, which may lead to interesting reactivity. Previous attempts to introduce N and As donors into the [9]ane macrocycle using our P_3 approaches have largely remained fruitless, although a series of iron complexes of P_2As have been reported.[1] Although there are no reported examples of N_2P macrocycles in the literature, there are some examples of larger macrocycles of this type. In 1980, the Kyba group published a series of 11-membered tridonor macrocycles including N_2P and P_2N-[11]ane macrocycles by high dilution methods.[2] Larger macrocycles of this type have also been reported, such as the [18]ane P_4N_2 macrocycle published by Ciampolini (shown in figure 1.10 in chapter 1).[3] However, all of these routes involved the use of high dilution techniques. Our synthetic route is based around the coordination of *cis* and *trans* 1,2-diaminocyclohexane (fig. 3.1) to manganese(I), and subsequent intramolecular coupling of a coordinated phosphine to the diamine.



(i)

1R, 2R-diaminocyclohexane (trans)



(ii)

1R, 2S-diaminocyclohexane (cis)

Figure 3.1.

It is conceivable that PN_2 macrocycles may be liberated from their templates under milder conditions than the P_3 analogue. This may avoid the unwanted oxidation of the phosphine during liberation. Another benefit of P,N-mixed ligands is that quaternization of the nitrogen donor may give enhanced solubility in polar solvents, over the triphosphine analogue. 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 addition, both forms of diaminocyclohexane adopt different conformations around the metal centre in a chelate. This may lead to interesting shape distortions around the metal coordination sphere and therefore the steric considerations of the conformation of the cyclohexyl ring may have an effect on the reactivity of the ensuing complexes.

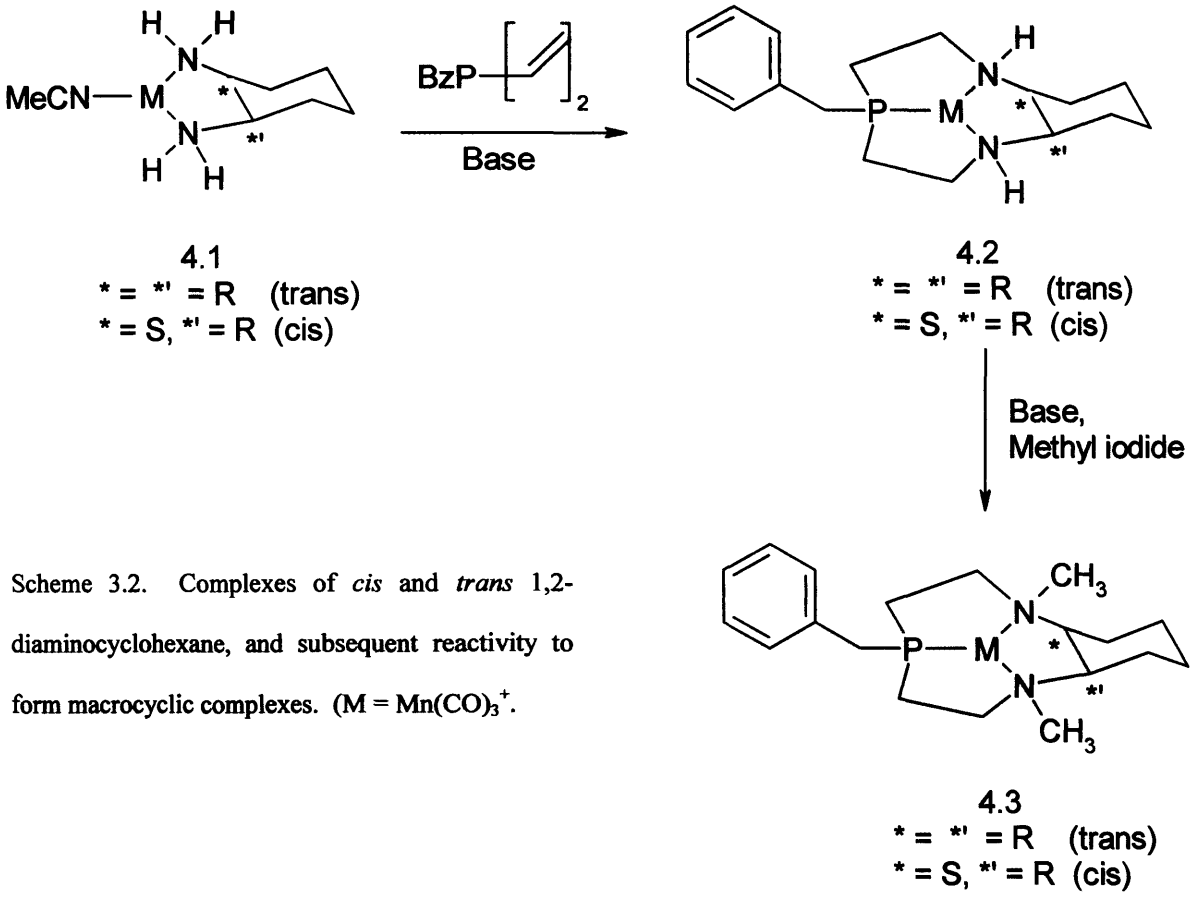
3.2 Results & Discussion

Chelating complexes of *cis* and *trans* diaminocyclohexane were prepared by addition of a stoichiometric amount of diamine to DCM solutions of $[(Mn(CO)_3(MeCN)_3]PF_6$. The reactions were followed by solution infrared spectroscopy, which showed the gradual disappearance of carbonyl bands associated with the starting complex, and the emergence of those of the products, **3.1(*trans*)** and **3.1(*cis*)**. The IR spectra of **3.1(*trans*)** and **3.1(*cis*)** are similar, and provide evidence for the proposed structures. The carbonyl stretch patterns are consistent with low symmetry *fac*-$Mn(CO)_3$ complexes, showing three bands for each; 2045, 1932 and 1818 cm^{-1} for **3.1(*trans*)**, and 2033, 1922 and 1883 cm^{-1} for **3.1(*cis*)**. Two bands are observed for the symmetric and asymmetric N-H stretches at 3347 and 3298 cm^{-1} in **3.1(*trans*)** and at 3344 and 3288 cm^{-1} in **3.1(*cis*)**. Acetonitrile stretches at 2359 and 2333 cm^{-1} are observed for **3.1(*trans*)** and **3.1(*cis*)**, respectively.

The ^1H NMR spectra of **3.1(*trans*)** and **3.1(*cis*)** show four distinct N-H environments, at δ_H 5.18, 4.94, 4.15 and 4.00 ppm, and δ_H 4.45, 4.18, 3.93 and 3.80 ppm, respectively. These resonances are characteristically broad, indicative of the ^{14}N quadrupole. The methyl resonance of the acetonitrile donor appears at δ_H 2.50 in **3.1(*trans*)** and δ_H 1.95 in **3.1(*cis*)**, compared to δ_H 2.10 ppm for free acetonitrile. The two inequivalent C-H environments appear at δ_H 2.38 and 2.34 ppm in the *trans* isomer, **3.1(*trans*)**, while in the *cis* analogue, **3.1(*cis*)**, they appear somewhat downfield at δ_H 3.17 and 3.09 ppm. The difference in chemical shift between the two isomers may be attributed to the different steric properties of the coordinated *cis* and *trans* forms of 1,2-diaminocyclohexane (figure 3.3).

Complexes **3.1(*trans*)** and **3.1(*cis*)** were also characterised by high resolution mass spectrometry and their spectra showed the presence of the molecular ion within agreeable

limits. Surprisingly, **3.1(*trans*)** and **3.1(*cis*)** were observed to decompose readily in a range of solvents over a relatively short timeframe. Therefore, the diamine, mono(acetonitrile) manganese complexes of **(*trans*)** and **(*cis*)** were used *in situ* for the preparation of **3.2(*trans*)** and **3.2(*cis*)** (scheme 3.2).



4.1
* = *' = R (trans)
* = S, *' = R (cis)

4.2
* = *' = R (trans)
* = S, *' = R (cis)

4.3
* = *' = R (trans)
* = S, *' = R (cis)

Scheme 3.2. Complexes of *cis* and *trans* 1,2-diaminocyclohexane, and subsequent reactivity to form macrocyclic complexes. (M = $Mn(CO)_3^+$.

The subsequent substitution of acetonitrile by benzyldivinylphosphine in **3.2(*trans*)** and **3.2(*cis*)** was achieved by the addition of the phosphine in DCM. The reactions were followed by ^{31}P NMR spectroscopy, which showed the formation of numerous irresolute signals downfield from that of the free ligand in both instances. It was clear from this information that the coordinated vinyl functions were coupling to the amines by intramolecular hydroamination, since downfield signals of this nature are often observed in the triphosphorus analogue.[11] In order to promote further reaction towards the macrocycle, the

DCM was removed *in vacuo,* the residues dissolved in THF, and potassium-*tert*-butoxide added thereto. Macrocyclic complexes **3.2(*trans*)** and **3.2(*cis*)** were isolated after an aqueous quench of the mixtures and their respective ^{31}P NMR shifts are characteristically downfield (δ_P 104 and 103 ppm, respectively). The IR spectra of **3.2(*trans*)** and **3.2(*cis*)** show the absence of MeCN stretches, as well as a reduction in the number of N-H bands, from two to one (3291 and 3500 cm^{-1}, respectively), consistent with the formation of the macrocycle. The carbonyl stretching frequencies are observed at 2016, 1918 and 1845 cm^{-1} for **3.2(*trans*)** and 2019, 1910 and 1830 cm^{-1} for **3.2(*cis*)**, to a lower frequency from **3.1(*trans*)** and **3.1(*cis*)**. This is due to increased electron density at the metal, as a result of substitution of acetonitrile (π-acceptor) by the phosphine, which may be regarded as a greater net donor. Additionally, a consequence of macrocycle formation is the contraction of metal-macrocycle donor bond length which amplifies this effect.

Table 3.1 shows the change in CO stretching frequencies in the series of complexes of **(*trans*)**. Again, a shift to a lower frequency is observed upon methylation of **3.2(*trans*)** to form the dimethyl analogue, **3.3(*trans*)**. This is consistent with the greater electron donating properties of the methyl substituted amines over their secondary analogues in **3.2(*trans*)**.

Complex	No.	ν_{CO} /cm^{-1}		
$[Mn(CO)_3(1R,2R\text{-}CHXN)(MeCN)]PF_6$	**3.1(*trans*)**	**2045**	**1932**	**1818**
$[Mn(CO)_3([9]ane_{trans}N_2P)]PF_6$	**3.2(*trans*)**	**2016**	**1918**	**1845**
$[Mn(CO)_3([9]ane_{trans}N_2(Me)_2P)]PF_6$	**3.3(*trans*)**	**2004**	**1907**	**1838**

Table 3.1. Infrared stretches of carbonyl groups in complexes of *(trans)*1R, 2R- diaminocyclohexane, **(*trans*)**.

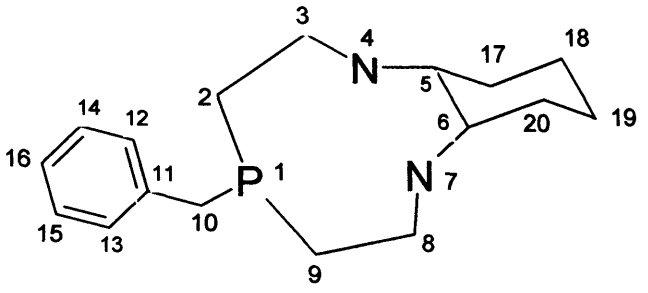


Figure 3.2. Numbering scheme for NMR assignments of complexes. $Mn(CO)_3^+$ omitted and stereochemistry not specified for clarity.

The ^{13}C $\{^1H\}$NMR spectrum of **3.2(*trans*)** shows that the CH_2 environments directly adjacent to the P atom (2,9 & 10) give $^1J_{C\text{-}P}$ values in the region of 20 Hz, and their resonances appear as doublets at δ_C 29.75, 21.92, and 31.76 ppm, respectively. The carbon environments of 3 and 8 are also coupled to the phosphorus atom, appearing as doublets (8 Hz) at δ_C 51.09 and 43.03 ppm. Two singlets account for the CH groups (5 & 6) at δ_C 68.86 and 58.93ppm. In the aromatic region, the quaternary carbon environment, 11, is observed as a doublet at δ_C 133.69 ppm, with a coupling constant of 8 Hertz.

In the ^1H NMR spectrum of **3.2(*trans*)**, the N-H resonances are characteristically broad, appearing as singlets at δ_H 5.43 and 5.14 ppm. A series of multiplets at δ_H 7.50-7.70 ppm denote the presence of 5 aromatic protons, however these are poorly resolved. The benzyl CH_2 protons resonate at δ_H 3.62 ppm as a doublet, with a two bond H-P coupling constant of 11 Hz. The CH_2 environments at 2 and 9 are observed as a doublet and a multiplet at δ_H 2.51 and 2.27ppm, with the doublet showing a $^2J_{H\text{-}P}$ value of 10 Hz. Two quartets at δ_H 2.73 and 2.70 (7 Hz) are due to the CH_2 protons of 3 and 8. Microanalysis and accurate mass spectrometry was in line with the formulation of **3.2(*trans*)**.

Interestingly, the formation of **3.2(*cis*)** appears to be far less efficient than for the trans analogue, **3.2(*trans*)**. This may be rationalised by examining the configuration of the

cyclohexyl rings in relation to the metal centres in the *cis* and *trans* isomers. The absolute configurations of both isomers in relation to manganese are fixed, as shown in figure 3.3. In the *trans* isomer the cyclohexyl ring is in the λ form and by constructing a model, the cyclohexyl ring is orientated in the square plane of the metal centre.[4] This configuration is sterically the most unobtrusive, and the incumbent bulky phosphine is able to occupy the remaining coordination site with little steric hindrance. In the *cis* analogue, the cyclohexyl ring adopts a δ configuration with respect to the metal centre. In this configuration, the ring lies almost parallel to the z-axis and may act as a steric obstacle for the approaching phosphine.

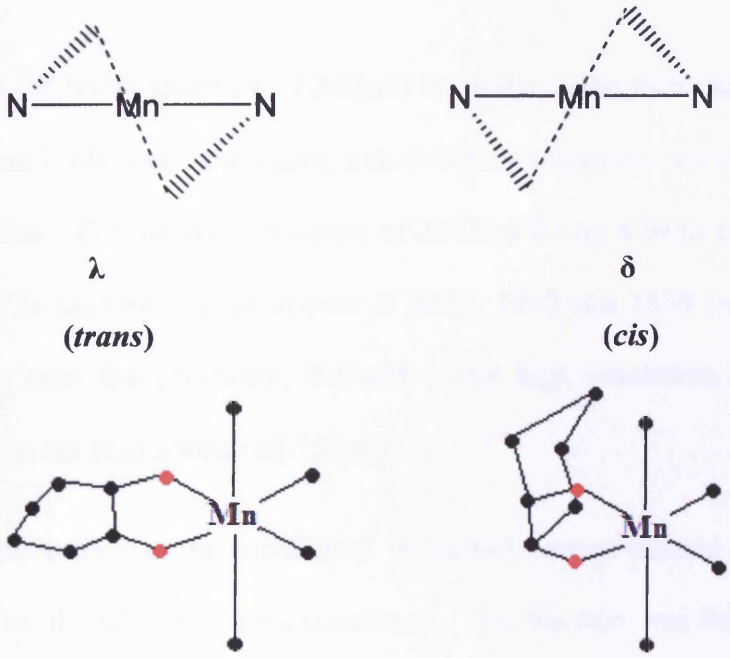


Figure 3.3. The absolute configurations of both isomers of 1,2-diaminocyclohexane with respect to the manganese centre.

This steric difficulty appears to be reflected in the yield of **3.2(*cis*)**, which is substantially lower than that of the *trans* analogue. The complex **3.2(*cis*)** was characterised by accurate mass spectrometry, IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and microanalysis.

In the ^{1}H NMR spectrum of **3.2(*cis*)**, three separate aromatic resonances are observed in the expected region, integrating to 5 protons. Two broad singlets at δ_H 4.69 and 2.38 show the presence of two inequivalent amine protons, while the characteristic benzyl methylene proton resonance is observed at δ_H 3.65 ppm as a doublet with a $^{2}J_{H\text{-}P}$ value of 14 Hertz. All other resonances appear in the aliphatic region of the spectrum, and their integrals accord with the formula of **3.2(*cis*)**. In the ^{13}C NMR spectrum of **3.2(*cis*)**, all aromatic resonances are observed. However, no carbonyl peaks were observed despite increasing both the number of acquisition scans and the pulse delay of the NMR experiment. The benzyl methylene carbon exhibits a one bond phosphorus coupling, and is observed as a doublet at δ_C 31.97 ppm with a coupling constant of 25 Hertz

Unsurprisingly, the ^{31}P NMR spectrum of **3.2(*cis*)** is similar to the *trans* analogue, **3.2(*trans*)**. A peak at δ_P 103 ppm is observed and again, a shift of this magnitude is a classic indication of macrocycle formation. The infrared spectrum of **3.2(*cis*)** shows a band at 3500 cm^{-1} due to the N-H stretch. The carbonyl bands appear at 2019, 1910 and 1830 cm^{-1}, which are at a lower wavenumber than the precursor, **3.1(*cis*)**. The high resolution mass spectrum of **3.2(*cis*)** also confirms the formulation of **3.2(*cis*)**.

Methylation of **3.2(*trans*)** was accomplished by initial base-promoted generation of the diamide, followed by the addition of iodomethane. The reaction was followed by solution IR, and the progress of the reaction was characterised by the disappearance of the N-H bands associated with **3.2(*trans*)**. The three carbonyl bands for **3.3(*trans*)** are listed in table 3.1. The ^{1}H NMR spectrum of **3.3(*trans*)** gives evidence for methylation, with the CH_3 protons appearing at δ_H 1.18 ppm as well as the absence of N-H resonances. Again, the aromatic protons are poorly resolved at δ_H 7.27 ppm. All other resonances appear in the expected region. In the $^{13}C\ \{^{1}H\}$ DEPT NMR spectrum **3.3(*trans*)** the carbon environments in close

proximity to the N atoms are shifted significantly downfield from the disecondary analogue, **3.2(*trans*)**. The resonances of the C-H carbons (5 & 6) are observed at δ_C 73.49 and 65.63 ppm, some 4.6 and 6.7 ppm downfield, respectively. The carbon atoms at positions 3 and 8 are also downfield, appearing at δ_C 69.90 and 55.85 ppm, compared to shifts of δ_C 51.09 and 43.03 ppm for **3.2(*trans*)**. The methyl resonance can also be observed for **3.3(*trans*)**, at δ_C 15.07 ppm. The high resolution mass spectrum and microanalysis of **3.3(*trans*)** also confirmed its formulation.

Similarly, the IR spectrum of **3.3(*cis*)** show the absence of characteristic N-H bands, and the carbonyl bands have shifted to 2104, 1908 and 1835 cm^{-1}. A singlet in the ^1H NMR spectrum at δ_H 2.05 ppm is seen for the 6 methyl protons, and a C-H correlation spectrum confirms the resonance at δ_C 28.79 ppm in the ^{13}C NMR spectrum for the CH_3 groups. The ^{31}P NMR spectrum of **3.3(*cis*)** shows no significant shift upon methylation, which is expected as the phosphorus environment is not in close proximity to the methylated amines. The molecular ion of **3.3(*cis*)** is observed at 457.1430 ***m/e*** amu in the high resolution mass spectrum, and the microanalysis of **3.3(*cis*)** was found to be within reasonable limits.

3.3 Attempts to prepare 11- membered PN_2 macrocycles from 3.1(*trans*) and 3.1(*cis*).

The ability of coordinated allyl functions to undergo free radical initiated intramolecular hydrophosphination has been utilised to synthesise a range of macrocyclic compounds, and those of Norman[5] are of particular interest (shown in scheme 1.5 in chapter 1). Larger macrocycles have also been assembled using this methodology. In 2000 Gladysz published the 45-membered triphosphorus macrocyclic complex shown below.[6]

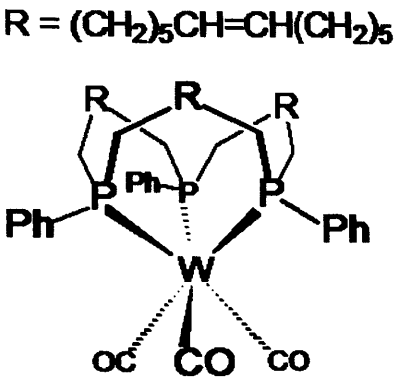
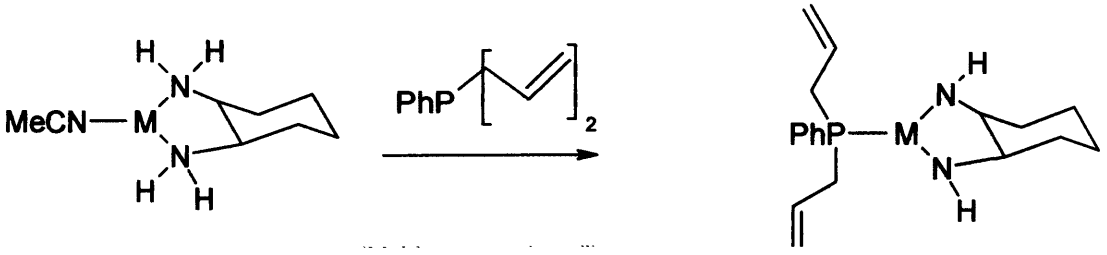


Figure 3.4. The 45-membered triphosphorus macrocycle prepared by Gladysz.[6]

We were interested to determine whether larger 11-membered macrocycles could be prepared using this approach, and therefore compounds **3.4(*trans*)** and **3.4(*cis*)** were prepared (scheme 3.3).



Scheme 3.3. The preparation of bis(allyl)phenylphosphine complexes **3.4(*trans*)** and **(*cis*)** as macrocyclic synthons. (M= $Mn(CO)_3^+$).

The addition of bis(allyl)phenylphosphine to complex **3.1(*trans*)** was followed by ^{31}P NMR spectroscopy, which showed the gradual disappearance of signal associated with the free ligand, and the emergence of a broad signal at δ_P 37 ppm. The infrared spectrum of **3.4(*trans*)** shows the N-H bands at 3352 and 3258 cm^{-1}, while the carbonyl bands are observed at 2004, 1907 and 1838 cm^{-1}. Again, substitution of the acetonitrile ligand by the phosphine in **3.1(*trans*)** results in a reduction in the carbonyl stretching frequency, consistent with the greater sigma donating ability of the phosphine over the acetonitrile donor. The allyl

protons are visible in the ^{1}H NMR spectrum at δ_H 5.89, 5.77 (both C-H), while the two sets of inequivalent methylene protons appear as doublets of doublets at δ_H 5.32 and 5.20 ppm for the germinal CH_2 groups. This is due to the two bond coupling to the phosphorus atom (32 and 28 Hertz, respectively), and the two bond coupling to the inequivalent protons (16, 12 Hertz). The allyl methylene carbon atoms appear significantly downfield in the ^{13}C $\{^{1}H\}$ NMR spectrum of **3.4(*trans*)** at δ_C 122.00 and 121.92. Both signals give rise to one bond C-P coupling constants of 25 Hertz, which is consistent with the macrocyclic complex **3.3(*trans*)**. All other resonances agree with the formulation of **3.4(*trans*)**.

In the cis analogue, **3.4(*cis*)**, the IR spectrum shows two N-H bands at 3337 and 3297 cm^{-1}. The carbonyl bands appear at 2029, 1917 an 1853 cm^{-1}, again, at lower wavenumbers than the acetonitrile precursor. The ^{31}P NMR spectrum of **3.4(*cis*)** shows a singlet at δ_P 48 ppm, associated with the coordinated phosphine. A single crystal of **3.4(*cis*)** was obtained for x-ray analysis by diffusion of petrol into a saturated solution of **3.4(*cis*)** in DCM. The structure is shown overleaf (figure 3.5).

The structure of **3.4(*cis*)** shows that the chelating diamine adopts a δ conformation around the metal centre, as shown in figure 3.3. As a result, the cyclohexyl backbone is shown to fold back somewhat. The carbonyl group which is cis to the diamine (C9) is therefore folded away from the steric bulk of the cyclohexyl backbone, and the Mn-C-O bond angle is 171.3(4)°, significantly distorted from the idealised 180°. The other two Mn-carbonyl bond angles are more linear, with Mn-C-O angles in the region of 177°. Other L-Mn-L bond angles suggest a *pseudo*-octahedral structure, with the angles in the region of 90°. The N-Mn-N bond angle is shown to be 79.7(12)°, due to the influence of the 5-membered chelate. In the carbonyl group trans to the phosphine (C9), the metal-carbon bond is lengthened (1.841(5)Å) in comparison to the other two (1.800(5) & 1.799(4)Å). This observation

concurs with the greater π-acidity of the phosphine over the diaminocyclohexane ligand. However, all three metal-carbon bonds are shown to be in line with those of facial tricarbonyl complexes of group 15 donors published by Reid, which show them to be around 1.80Å.[7]

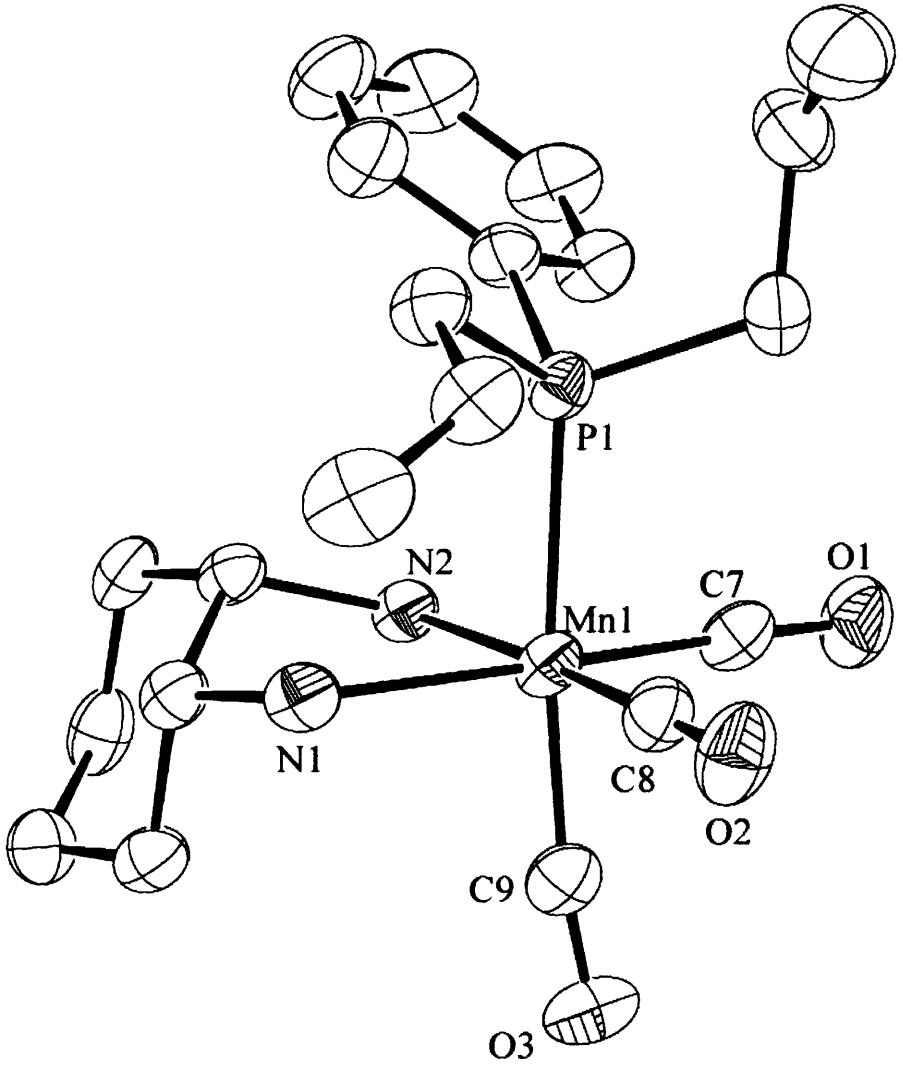


Figure 3.5 ORTEP view of the solid state structure of **3.4(*cis*)**. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): N(1)-Mn(1) = 2.099(3); N(2)-Mn(1) = 2.101(3); P(1)-Mn(1) = 2.354(13); Mn(1)-C(7) = 1.800(4); Mn(1)-C(8) = 1.799(4); Mn(1)-C(9) = 1.841(5); C(7)-O(1) = 1.149(5); C(8)-O(2) =

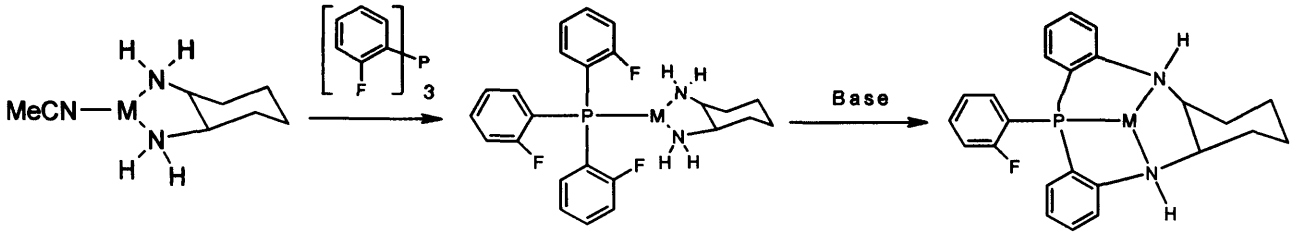
1.150(5); C(9)-O(3) = 1.139(5). Mn(1)-C(7)-O(1) = 177.3(4); Mn(1)-C(8)-O(2) = 177.5(4); Mn(1)-C(9)-O(3) = 171.3(4); C(8)-Mn(1)-C(7) = 91.31(19); C(8)-Mn(1)-C(9) = 86.44(19); C(7)-Mn(1)-C(9) = 88.29(19); C(8)-Mn(1)-N(1) = 93.41(16); C(9)-Mn(1)-N(1) = 91.61(17); C(7)-Mn(1)-N(2) = 95.60(16); C(9)-Mn(1)-N(2) = 94.98(16); N(1)-Mn(1)-N(2) = 79.70(12); C(8)-Mn(1)-P(1) = 88.10(14); C(7)-Mn(1)-P(1) = 87.90(14); N(1)-Mn(1)-P(1) = 92.65(10); N(2)-Mn(1)-P(1) = 90.92(10).

Attempts to ring close complex **3.4(*trans*)** to the macrocycle using the free radical initiator, 1,1'-azobis(cyclohexanecarbonitrile) in toluene (80 °C, 12 h) have proved unsuccessful. The only identifiable phosphorus containing compound from the subsequent reaction mixture was found to be that of the starting complex, **3.4(*trans*)**. However the lack of reactivity is not entirely suprising given that the radical initiation of this reaction depends largely on the homolytic cleavage of the N-H bond. In phosphine analogues, the P-H bond is far more susceptible to homolytic cleavage, as the electronegativity of phosphorus is relatively close to that of hydrogen (2.19 and 2.20 on the Pauling scale, respectively). However, the increased electronegativity of the nitrogen atom (3.04 on the Pauling scale) may hinder the formation of the required N radicals.

3.4 Attempts to prepare benzannulated PN_2 macrocycles from 3.1(*trans*)

Previously, benzannulated triphosphorus macrocycles have been assembled on manganese centres using tris(orthofluorophenyl)phosphine (analogous to that shown on Cp^RFe^+ centres in scheme 3.1).[18] We were keen to expand the number of PN_2 macrocycles using this approach (scheme 3.4). Therefore, **3.1(*trans*)** was stirred in the presence of tris(orthofluorophenyl) phosphine in a number of solvents at room temperature. However,

the phosphine did not coordinate to the manganese centre under these conditions. Attempts to coordinate the phosphine to the manganese centre by refluxing in chlorobenzene (131 °C) and nitromethane (100-103 °C) over various periods of time were more successful, with downfield shifts being observed in the ^{31}P NMR spectra of the reaction mixtures, showing traces of phosphine containing complexes in the expected region (δ_P 50 – 65 ppm).[17] However the thermal instability of the ensuing complexes resulted in decomposition upon further heating. Consequently, we were unable to isolate or identify any phosphorus containing manganese complexes.

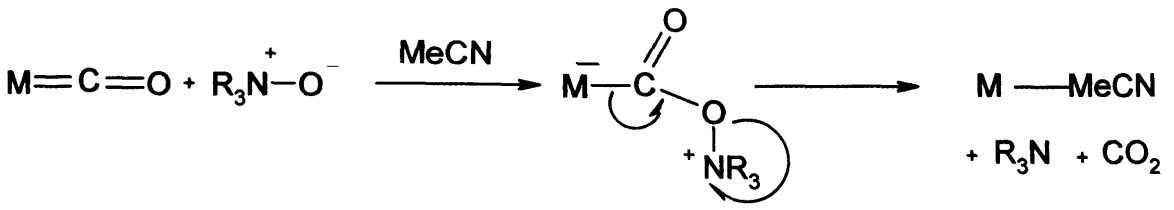


Scheme 3.4. The proposed reaction scheme for the preparation of di-benzannulated macrocycles. (M= $Mn(CO)_3^+$).

3.5 Towards Macrocycle Liberation

Reactions with 4-methylmorpholine-N-oxide

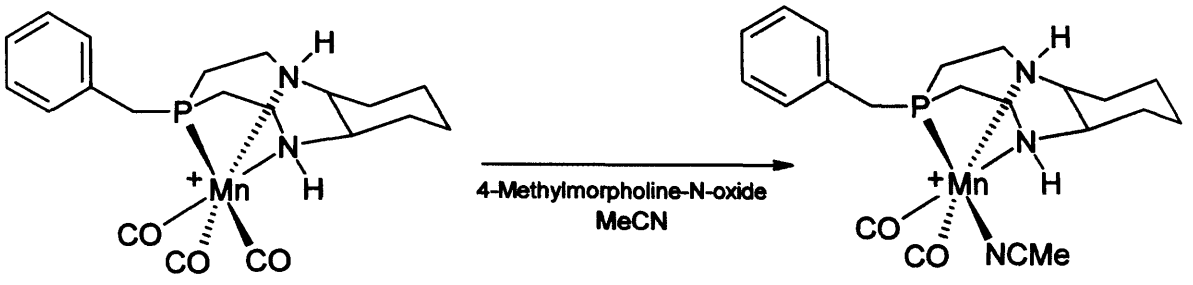
The reactions of metal complexes with trialkyl-N-oxides have been extensively studied.[8] Of particular interest, is the ability of these moieties to remove carbonyl ligands from the metal centre, according to the mechanism shown in scheme 3.5, below. Replacement of a carbonyl ligand with more labile donors enables the introduction of strongly oxidising ligands, such as halides, to the coordination sphere of the metal. By oxidising the metal centre, it may be envisaged that the metal-macrocycle bonding is labilised.



Scheme 3.5. The mechanism of decarbonylation using trialkyl-N-oxides in the presence of acetonitrile.

Work conducted by Koelle[9] and Brown[10] has shown that for this process to occur, the υ(CO) value of the target carbonyl must be more than 2000 wavenumbers. However, recent research conducted within our group has shown that the decarbonylation of $(L)M(CO)_3^+$ species (where M= Re, Mn and L = P_3 or P_2NHC macrocycle) by this method is non selective as mixtures of all possible products are observed from these reactions.[11,12]

In the case of N_2P systems it may be envisaged that decarbonylation proceeds selectively, given the greater difference in the *trans* effect between the two sets of donors, P and N. We have conducted decarbonylation reactions using the decarbonylation reagent 4-methylmorpholine-N-oxide. When a 1:1 stoichiometric ratio of N-oxide to **3.3(*trans*)** in MeCN was employed, the ^{31}P NMR spectrum of the reaction mixture showed a downfield shifted resonance at δ_P 112 ppm, some 9 ppm downfield from the starting complex. From this information, it is evident that the metal-macrocycle unit has remained intact, as the magnitude of the shift is relatively small and the chemical shift is characteristic of a 9-membered phosphorus macrocycle. Also, the fact that only one resonance is observed in the reaction mixture after 24 h indicates that decarbonylation of **3.3(*trans*)** to $[(N_2P)Mn(CO)_2(MeCN)]PF_6$ is selective. Thus compound **3.5(*trans*)** was isolated.



Scheme 3.6. The selective decarbonylation of **3.5(*trans*)**.

The infrared spectrum of **3.5(*trans*)** is consistent with the proposed structure. The carbonyl bands are observed at 1930 and 1847 cm^{-1}. Furthermore, the presence of a coordinated acetonitrile ligand is shown by a stretch at 2345 cm^{-1}. This stretch is at a higher wavenumber than those observed in the precursor, $[Mn(CO)_3(MeCN)_3]PF_6$, which show two bands at 2327 and 2301 cm^{-1}. The mass spectrum of **3.5(*trans*)** also shows the presence of the molecular cation at 442.15 amu. The ^1H NMR spectrum of **3.5(*trans*)** is characteristically broad, consistent with a lowering of local symmetry around the metal centre, as well as the quadrupolar nature of the manganese atom. However, the aromatic resonance (a broad singlet at δ_H 7.64 ppm) integrates to 5 protons, while the unresolved, upfield resonances integrate to 25. Therefore, although being uninformative and broad, the ^1H NMR spectrum of **3.5(*trans*)** supports the formulation. In the ^{13}C $\{^1H\}$NMR spectrum of this compound, the methyl carbon of the coordinated acetonitrile group is clearly visible, at δ_C 4.68 ppm.

Upon reaction of **3.3(*trans*)** with a large excess of N-oxide, the ^{31}P NMR spectrum of the reaction mixture showed the gradual emergence of a signal at δ_P 36 ppm over the course of 3 weeks. This was also accompanied by a gradual change in solution colour from yellow to colourless. However, we were unable to gain any further insight into the product of this reaction as the amount of material recovered was insufficient for full analysis.

Reactions with H_2O_2 and Br_2

The use of strong oxidising conditions to demetallate macrocyclic complexes has been well documented.[1,13] Macrocycles have been liberated from their metal templates, using potassium cyanide.[14] However, due to the stability of the smaller chelate macrocyclic complexes, more exhaustive measures are required to demetallate the 9-membered triphosphine and 14-membered tetraphosphine of Edwards and Stelzer, respectively.[1,13] Both dibromine and hydrogen peroxide are strong candidates for these reactions as they oxidise the metal centre, thus labilising the metal-macrocycle bonds. In the case of dibromine, the liberated phosphine is then oxidised to a pentavalent phosphorus species, which is then attacked by water to form the phosphine oxide. These reactions are carried out in aqueous solution and the resultant phosphine oxide is isolated from the aqueous phase.

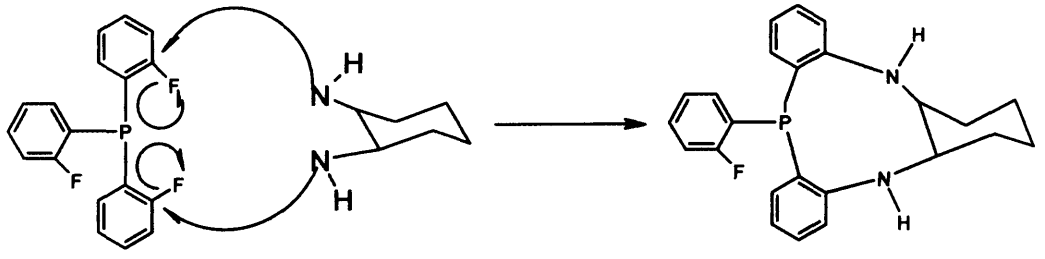
The reaction between **3.3(*trans*)** and bromine was carried out in a mixture of DCM and water. Addition of an excess of bromine caused an instant exothermic reaction, which made the solution warm. The solution was stirred vigorously in air until most of the bromine had evaporated, and the aqueous layer was isolated. Two singlets at δ_P 47 and 49 ppm in the ^{31}P NMR of the aqueous phase showed the presence of two new phosphorus containing environments. Shifts in this region have been observed in similar P_3 systems upon reaction with bromine (δ_P 38.91 and 32.91[2]), indicating the formation of phosphine oxide. In the IR spectrum of the isolated solid, the P=O band is clearly observed at 1071 cm^{-1}, and the high resolution mass spectrum confirmed the presence of the free macrocycle oxide. We were unable to obtain any other spectroscopic data due to the insolubility of the oxide in suitable solvents.

Reaction of **3.3(*trans*)** with an acidified aqueous hydrogen peroxide solution also led to the formation of the phosphine oxide, as confirmed by mass spectrometry. However, the yields were considerably lower than the corresponding reaction with bromine, and no further data was obtainable from the solid recovered from this reaction.

Attempts to reduce the P=O bond using $LiAlH_4$ in THF were unsuccessful, again, due to the insolubility of the proposed phosphine oxide.

3.6 Non-Templated Reactions

Given that the inversion barrier of amines is considerably smaller than that for analogous phosphines (24.2 kJ/mol for NH_3 compared to 132 KJ/mol for PH_3), we were keen to explore whether the free 9-membered macrocycle could be assembled in the absence of a metal template. One of the main functions of the metal template in the assembly of triphosphorus macrocycles is to ensure stereochemical control over the conformation of the phosphorus atoms, as these are fixed in the free phosphine at ambient temperature due to the high inversion energy. However due to the lower inversion barriers of amines, the comformation of the P atom is irrelevant (scheme 3.6), as the interconversion of the various *anti* forms to the desired *syn* is facile.



Scheme 3.6. The proposed scheme for the non-template assisted assembly of the 9-membered PN_2 macrocyclic compound.

Firstly, the diamine was dissolved in THF and two equivalents of base were added. To the subsequent diamide, 1 equivalent of tris(orthofluorophenyl) phosphine was added and the reaction stirred for one week. The ^{31}P NMR of the reaction mixture showed only the presence of the starting phosphine, indicating that no reaction had taken place. The reaction mixture was heated to reflux for a further week, however the ^{31}P NMR spectra showed no reaction.

One possible explanation for the lack of reactivity of the phosphine may be due to the fact that the Ar-F bond is not reactive enough when not coordinated. It was therefore decided to 'activate' the Ar-F bond by oxidising the phosphine, which should inductively weaken the aryl fluoride bond. It was hoped that this may lead to the benzannulated bridged macrocycle oxide. Although our priority is to obtain the free (unoxidised) macrocycle, we hoped that we could obtain enough of the oxidised macrocycle to attempt reduction reactions on a workable scale.

The oxidisation of tris(orthofluoro)phosphine was achieved by treatment of the phosphine with hydrogen peroxide. The ^{31}P NMR spectrum of the oxide shows a singlet at δ_P 15.4 ppm, and the infrared spectrum shows the P=O band at 1136 cm^{-1}. Four aromatic environments are observed in the ^{1}H NMR spectrum, with resonances at δ_H 7.64, 7.52, 7.25 and 7.05 ppm, with equal integrations. The ^{13}C $\{^{1}H\}$NMR spectrum of the phosphine oxide shows six aromatic resonances in the expected region, and all other data corresponds to the formulation of tris(orthofluorophenyl) phosphine oxide.

The reaction of the phosphine oxide and the diamine was carried out under identical conditions to that of the phosphine and diamine (scheme 3.6). The THF mixture was stirred for 1 day at room temperature. At this point, analysis of the mixture by ^{31}P NMR spectroscopy showed no reaction. The mixture was then heated at reflux, at which point it became cloudy and a precipitate formed. After 1 week of refluxing in THF, the solution was filtered and pumped to dryness. The yellow oily residue was shown to contain a mixture of the diamine and phosphine oxide (by NMR spectroscopy), confirming that no reaction had taken place.

3.7 Conclusions

In conclusion, the two isomeric forms of 1,2-diaminocyclohexane have been used as synthons in the assembly of 9-membered PN_2 macrocycles on a cationic manganese centre via intramolecular hydroamination of coordinated vinyl functions. As both the *cis* and *trans* forms of the diamine adopt different chelate conformations around the metal centre in a chelate, the different spatial arrangements in the two coordinated forms greatly affect the efficiency and yield of macrocycle formation. Subsequently, the formation of macrocycles containing the *trans*-cyclohexane backbone are formed more efficiently than those of the *cis* analogue.

Attempts to prepare the benzannulated analogues using tris(orthofluorophenyl)phosphine were unsuccessful, due to the failure of the phosphine to coordinate to the manganese centre. Attempts to prepare this macrocycle using high-dilution techniques with the phosphine and the 'activated' phosphine oxide were also unsuccessful.

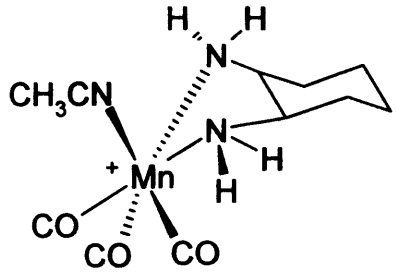
Using complexes **3.1(*trans*)** and **3.1(*cis*)**, we were able to coordinate bis(allyl)phenyl phosphine, yielding the novel complexes **3.4(*trans*)** and **3.4(*cis*)**. However, attempts to ring close the complex to the [11]ane PN_2 macrocycle using a free radical initiator failed.

The parent [9]aneP(benzyl)$N_2(H)_2$ macrocyclic complexes undergo methylation of the N-H bonds to yield the air stable [9]aneP(benzyl)$N_2(Me)_2$ analogue. Reactivity studies have shown that the macrocycle may be liberated from the metal centre using the strong oxidising agents dibromine and acidified hydrogen peroxide. However in both instances the phosphine donor is irreversibly oxidised and the oxide is too insoluble to reduce easily. Attempts to substitute solublising functions at the nitrogen donors were unsuccessful.

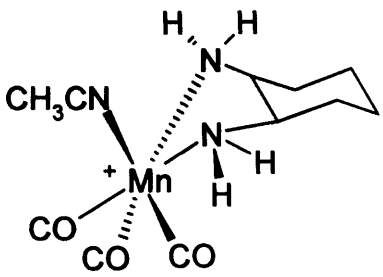
We have demonstrated that, using 4-methylmorpholine-N-oxide, it is possible to remove one carbonyl group from the metal centre. Furthermore due to the relative *trans* effect of the macrocycle donors the decarbonylation is selective, and only the carbonyl *trans* to the phosphine is removed.

3.8 Addendum

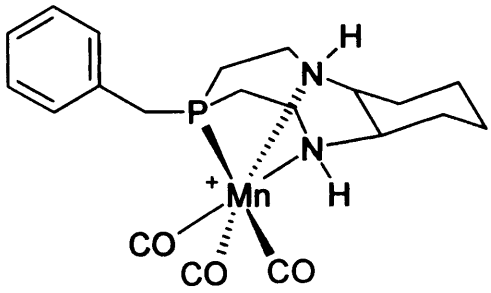
Below are the structures of the compounds referred to throughout this chapter.



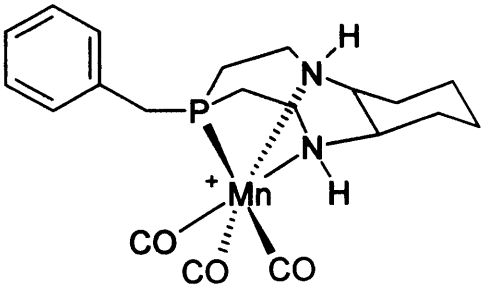
3.1(*trans*) *(CHX = trans)*



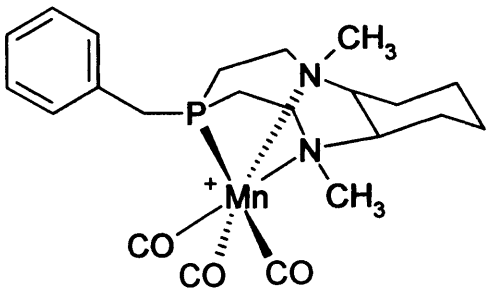
3.1(*cis*) *(CHX = cis)*



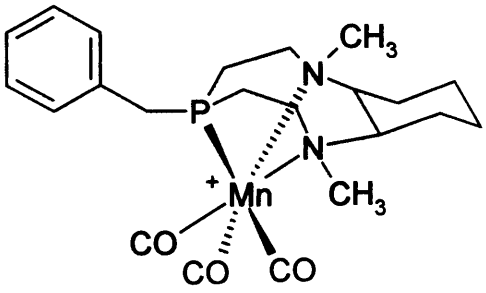
3.2(*trans*) *(CHX = trans)*



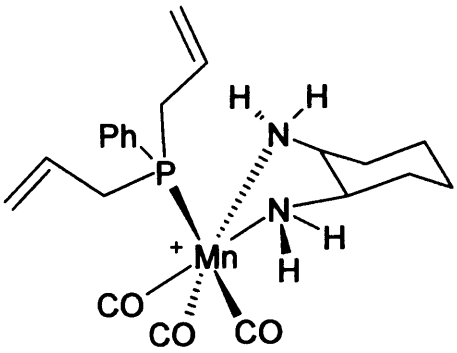
3.2(*cis*) *(CHX = cis)*



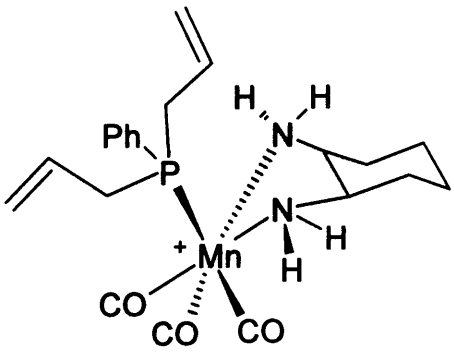
3.3(*trans*) *(CHX = trans)*



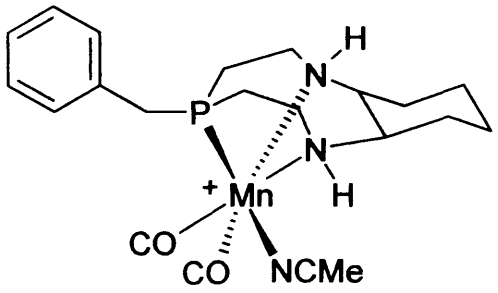
3.3(*cis*) *(CHX = cis)*



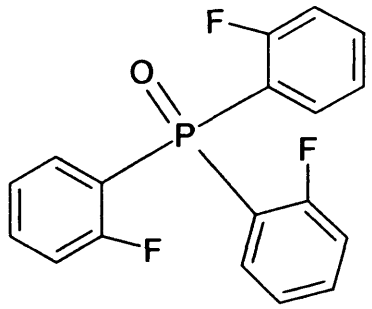
3.4(*trans*) *(CHX = trans)*



3.4(*cis*) *(CHX = cis)*



3.5(*trans*) *(CHX = trans)*



Tris(orthofluorophenyl)phosphine oxide

3.9 Experimental

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line techniques, unless otherwise stated. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. Metal precursor complex $[Mn(CO)_3(MeCN)_3]PF_6$,[15] 1R,2R-diaminocyclohexane (i)[16], benzyldivinylphosphine[17] and tris(orthofluorophenyl) phosphine[18] were prepared according to previously reported methods. All other chemicals were obtained commercially, and used as received. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 (δ = 0 ppm). ^{1}H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane (δ = 0 ppm). Unless stated otherwise, infrared spectra were recorded as nujol mulls on a Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd, UK.
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Complexes of *(trans)*1R, 2R- diaminocyclohexane

Synthesis of $[Mn(CO)_3$(1R,2R-diaminocyclohexane)$(MeCN)]PF_6$ (**3.1(*trans*)**)

To a stirring solution of $[Mn(CO)_3(MeCN)_3]PF_6$ (150 mg, 3.68×10^{-4} mol in 15 mL MeCN), was added one equivalent of diamine (***trans***) (0.04 g). The solution was stirred overnight under an atmosphere of dinitrogen, afterwhich time a pale yellow precipitate had formed. The solution was pumped to dryness and washed sequentially with petrol (10 mL) and diethyl

ether (10 mL). The resultant yellow powder was dried *in vacuo* to yield **3.1(*trans*)** (125 mg, 76 %). ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ 5.18 (br s, N-H, 1H), 4.94 (br s, N-H, 1H), 4.15 (br s, N-H, 1H), 4.00 (br s, N-H, 1H), 2.80 (m, 2H), 2.50 (s, CH_3, 3H), 2.38 (s, C-H, 1H), 2.34 (s, C-H, 1H), 1.00-1.80 (m, 6H) ppm. HR.M.S: ES-MS: *m/e* 294.0653 amu (100%) ($[M]^{\cdot+}$). IR : 3347, 3298 s (ν_{NH}), 2944, 2867 s (ν_{CH}), 2359 w (MeCN), 2045, 1932, 1818 vs (ν_{CO}), 1601 s, 1451 w, 1139 s 838 (PF_6) cm^{-1} .

Synthesis of $[Mn(CO)_3([9]ane_{trans}N_2P)]PF_6$ **(3.2(*trans*))**

Manganese tricarbonyl (1R, 2R-diaminocyclohehane) acetonitrile hexafluorophosphate **(3.1(*trans*))** was dissolved in DCM (150 mg, 3.42 x 10^{-4}mol in 10 mL) and a solution of benzyldivinylphosphine was added (0.05 g from a standard solution in toluene). The solution was stirred for ca. 4 h, and the ^{31}P NMR spectrum of the crude reaction mixture showed the presence of free ligand (δ_P -18 ppm), as well as two further, broadenned peaks at δ_P 36 and δ_P 64 ppm, indicating the presence of two coordinated phosphine environments. The reaction mixture was pumped to dryness, redissolved in THF and an excess of potassium-*tert*-butoxide (0.1 g) was added. The colour of the solution turned from pale yellow to dark red instantly upon the addition of base. The reaction was stirred under dinitrogen for 2 days and all solvent was removed under reduced pressure. The red solid was quenched upon the addition of degassed water (5 mL), which was subsequently filtered off, yielding a yellow powder. The solid was sequentially washed with petrol (10 mL) and diethyl ether (10 mL), affording **3.2(*trans*)**. Yield 160 mg (82%). ^{1}H NMR (CD_3CN, 500 MHz): δ 7.50-7.70 (m, Ar-H, 5H), 5.43 (s, N-H, 1H), 5.14 (s, N-H, 1H), 3.62 (d, $^2J_{H\text{-}P}$ = 11 Hz, CH_2Ph, 2H), 2.73 (q, $^3J_{H\text{-}P}$ = 7 Hz CH_2N, 1H), 2.70 (q, $^3J_{H\text{-}P}$ = 7 Hz CH_2N, 1H), 2.51 (d, $^2J_{H\text{-}P}$ = 10Hz, CH_2P, 1H), 2.46 (t, J =11 Hz, CH, 1H), 2.27 (m, CH_2P, 1H), 2.19 (m, CH_2, 2H), 2.06 (m, CH_2, 2H), 1.72 (m,

CH_2, 2H), 1.64 (m, CH_2, 2H), 1.24 (m, CH_2, 2H), 1.06 (m, CH_2, 2H), 0.81 (m, CH_2, 2H) ppm. $^{13}C\{^1H\}$ DEPT NMR (CD_3CN, 125.8 MHz): δ 133.69 (d, $^2J_{C\text{-}P}$ = 8 Hz, Ar-C), 131.28 (s, Ar-C), 129.71 (d, J = 4 Hz, Ar-C), 129.08 (d, J = 3 Hz, Ar-C), 128.73 (s, Ar-C), 127.40 (d, J = 4Hz, Ar-C), 68.86 (s, C-H), 58.93 (s, C-H), 51.09 (d, $^2J_{C\text{-}P}$ = 8 Hz, CH_2N), 43.03 (d, $^2J_{C\text{-}P}$ = 8 Hz, CH_2N), 31.76 (d, $^1J_{C\text{-}P}$ = 24 Hz, CH_2Ph), 30.63 (s, CH_2), 30.19 (s, CH_2), 29.76 (s, CH_2), 29.75 (d, $^1J_{C\text{-}P}$ = 21 Hz, CH_2P), 23.88 (s, CH_2), 21.92 (d, $^1J_{C\text{-}P}$ = 19 Hz, CH_2P) ppm. $^{31}P\ \{^1H\}$ NMR (CD_3CN, 121.7 MHz): δ 104 (s), −143 (h, $J_{P\text{-}F}$ = 712 Hz, PF_6) ppm. HR.M.S: ES-MS: *m/e* 421.1130 amu (100%) ($[M]^{\cdot+}$). IR : (KBr) 3291 (ν_{NH}), 2930, 2862 (ν_{CH}), 2016, 1918, 1845, 1721 (ν_{CO}),1495 w, 1450 s, 1405 w, 1286 s, 1117, 1066 w, 840 (PF_6) cm^{-1}. (CH_2Cl_2) 2020, 1941, 1919 (ν_{CO}) cm^{-1}. *Anal.* Calc. For $MnC_{20}H_{27}P_2N_2O_3F_6$: C, 41.83; H, 4.74; N, 4.80. Found: C, 41.79; H, 4.72; N, 4.78.

Synthesis of $[Mn(CO)_3([9]ane_{trans}N_2(Me)_2P)]PF_6$ **(3.3(*trans*))**

225 mg (3.92 x 10^{-4} mol) of **3.2(*trans*)** was dissolved in THF (10 mL) and stirred under dinitrogen. A solution of potassium-*tert*-butoxide (0.1 g in 5 mL THF) was added dropwise at -78 C, and the mixture was allowed to warm to room temperature. An excess of iodomethane (0.5 g) was added to the red solution and stirred overnight. After this time, a pale yellow precipitate had formed and the solvent was removed under reduced pressure. The pale yellow solid was washed sequentially with petrol (10 mL) and ether (10 mL), before drying in air, yielding **3.3(*trans*)**. 150 mg (64%). ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.27 (br s, Ar-H, 5H), 3.71 (br s, CH_2, 2H), 3.33 (m, CH_2, 2H), 3.23 (s, CH_2, 2H), 2.92 (s, CH_2, 2H), 2.80 (s, CH_2, 2H), 2.50-1.47 (m, CH_2, 8H), 1.18 (s, CH_3, 6H) ppm. $^{13}C\{^1H\}$ DEPT NMR (CD_2Cl_2, 125.8 MHz): δ 221.59 (br s, eq CO), 215.38 (br s, ax CO), 132.32 (m, Ar-C), 129.91 (m, Ar-C), 129.76 (m, Ar-C), 129.37 (m, Ar-C), 129.06 (s, Ar-C), 127.86 (s, Ar-C),

73.49 (s, CH), 65.63 (s, CH), 61.90 (s, CH_2N), 55.85 (s, CH_2N), 33.16 (d, J = 25 Hz, CH_2), 29.82 (d, J = 19 Hz, CH_2), 26.02 (s, CH_2), 24.65 (d, J = 16 Hz, CH_2), 24.31 (s, CH_2), 23.84 (d, J = 16 Hz, CH_2), 15.07 (s, CH_3) ppm. ^{31}P $\{^1H\}$ NMR (CD_2Cl_2, 121.7 MHz): δ 103.0 (s), –143.8 (h, J_{P-F} = 714 Hz, PF_6) ppm. M.S: ES-MS: *m/e* 457.1435 amu (100%) ($[M]^{\cdot+}$). IR : 2922, 2859 (ν_{CH}), 2004, 1907, 1838 (ν_{CO}), 1448 s, 836 (PF_6) cm^{-1}. *Anal.* Calc. For $C_{22}H_{31}P_2N_2F_6O_3Mn$: C, 43.87; H, 5.19; N, 4.65. Found: C, 44.03; H, 5.24; N, 4.81.

Synthesis of $[Mn(CO)_3$(1R,2R-diaminocyclohexane)$PhP(allyl)_2]PF_6$ **(3.4(*trans*))**

To a solution of **3.1(*trans*)** (150 mg, 3.4 x 10^{-4} mol in 20 mL DCM) was added 1.1 equivalents of diallylphenyl phosphine. The solution was stirred for ca. 2 days, and pumped to dryness. The residue was then washed with diethyl ether, followed by petrol (10 mL) Yield 150 mg (66%). ^1H NMR ($(CD_3)_2CO$, 500 MHz): δ 7.66 (t, J = 8 Hz, Ar-H, 2H), 7.56 (m, Ar-H, 2H), 7.23 (m, Ar-H, 1H), 5.89 (br s, allyl C-H, 1H), 5.77 (br s, allyl C-H, 1H), 5.32 (dd, $^2J_{H-P}$ = 32 Hz, $^2J_{H-H}$ = 16 Hz, allyl CH_2, 2H), 5.20 (dd, $^2J_{H-P}$ = 28 Hz, $^2J_{H-H}$ = 12 Hz, allyl CH_2, 2H), 4.83 (m, CH_2, 2H), 4.25 (br s, N-H, 1H), 3.33 (m, CH_2, 2H), 3.27 (m, CH_2, 2H), 3.00 (br s, N-H, 1H), 2.44 (m, CH_2, 1H), 2.18 (m, C-H, 1H), 1.80 (m, C-H, 1H), 1.46 (m, 3H), 0.94 (m, 2H), o.57 (m, 2H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($(CD_3)_2CO$, 125.8 MHz): δ 131.87 (m, Ar-C), 131.08 (d, J = 7 Hz, Ar-C), 130.11 (d, J = 6 Hz, Ar-C), 122.00 (d, $^1J_{C-P}$ = 25 Hz, allyl CH_2), 121.92 (d, $^1J_{C-P}$ = 25 Hz, allyl CH_2), 60.76 (s, C-H), 59.39 (s, C-H), 35.55 (s, CH_2), 34.52 (s, CH_2), 30.45 (m, CH_2), 30.24 (s, CH_2), 28.94 (s, CH_2), 24.84 (d, J = 8 Hz, CH_2) ppm. ^{31}P $\{^1H\}$ NMR ($(CD_3)_2CO$, 121.7 MHz): δ 37.1 (s), –143.7 (h, J_{P-F} = 708 Hz, PF_6) ppm. IR : 3352, 3258 (ν_{NH}), 2922, 2859 (ν_{CH}), 2004, 1907, 1838 (ν_{CO}), 836 (PF_6) cm^{-1}. *Anal.* Calc. For $C_{21}H_{29}P_2N_2F_6O_3Mn$: C, 42.87; H, 4.97; N, 4.76. Found: C, 42.99; H, 4.82; N, 4.81.

Complexes of *(cis)*1R, 2S- diaminocyclohexane

Synthesis of $[Mn(CO)_3(1R,2S\text{-diaminocyclohexane})(MeCN)]PF_6$ **(3.1(*cis*))**

To a stirring solution of $[Mn(CO)_3(MeCN)_3]PF_6$ (150 mg, 3.68×10^{-4} mol in 15 mL MeCN), was added 1R,2S-diaminocyclohexane (***cis***) (0.04 g). The solution was stirred overnight under nitrogen. The solution was pumped to dryness and washed sequentially with petrol (10 mL) and diethyl ether (10 mL). The resultant yellow powder was dried under reduced pressure. yield 110 mg (69%). ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ 4.45 (br s, N-H, 1H), 4.18 (br s, N-H, 1H), 3.93 (br s, N-H, 1H), 3.80 (br s, N-H, 1H), 3.17 (s, C-H, 1H), 3.09 (s, C-H, 1H), 2.39 (s, CH_2, 1H), 1.93 (s, MeCN, 3H), 1.54 (br m, 6H, 1.32 (br s, 2H) ppm. HR.M.S: ES-MS: *m/e* 294.0658 amu (100%) ($[M]^{\cdot+}$). IR : 3344, 3288 s (ν_{NH}), 2944, 2855 s (ν_{CH}), 2333 w (MeCN), 2033, 1922, 1883 s (ν_{CO}), 1594 s, 1488 w, 1444 w, 1394 w, 1083 w, 838 vs (PF_6) cm^{-1} .

Synthesis of $[Mn(CO)_3([9]ane_{cis}N_2P)]PF_6$ **(3.2(*cis*))**

Compound **3.1(*cis*)** (150 mg, 3.42×10^{-4} mol) was dissolved in DCM (10 mL) and a solution of benzyldivinylphosphine was added (0.05 g, mol in from a standard solution in toluene). The solution was stirred for ca. 4 h. The reaction mixture was pumped to dryness, redissolved in THF and an excess of potassium-*tert*-butoxide (0.1 g) was added. The red solution was stirred under dinitrogen for 2 days and all solvent was removed under reduced pressure. The mixture was quenched upon the addition of degassed water (5 mL) and filtered off, yielding a yellow powder. The solid was sequentially washed with petrol (10 mL) and diethyl ether (10 mL), affording **3.2(*cis*).** Yield 75 mg (40 %). ^{1}H NMR (CD_3CN, 500 MHz): δ 7.34 (m, Ar-H, 1H), 7.30 (s, Ar-H, 2H), 7.29 (m, Ar-H, 2H), 4.69 (br s, N-H, 1H), 3.65 (d,

$^{2}J_{H\text{-}P}$ = 14 Hz, benzyl CH_2, 2H), 3.24 (m, 2H), 3.18 (m, 2H), 2.65 (m, 2H), 2.50 (s, C-H, 2H), 2.38 (br s, N-H, 1H), 1.99 (s, 2H), 1.00-1.90 (m, 8H) ppm. $^{13}C\{^{1}H\}$ DEPT NMR (CD_3CN 125.8 MHz): δ 129.47 (d, J = 4 Hz, Ar-C), 128.82 (d, J = 4 Hz, Ar-C), 128.55 (m, Ar-C), 127.88 (m, Ar-C), 127.15 (d, J = 3 Hz, Ar-C), 126.67 (m, Ar-C), 66.01 (s, C-H), 61.70 (s, C-H), 53.41 (m, CH_2), 31.97 (d, $^{1}J_{C\text{-}P}$ = 25 Hz, benzyl CH_2), 29.59 (s, CH_2), 25.67 (m, CH_2), 25.43 (m, CH_2), 21.07 (m, CH_2), 20.84 (m, CH_2), 19.38 (s, CH_2) ppm. $^{31}P\ \{^{1}H\}$ NMR (CD_3CN, 121.7 MHz): δ 103.0 (s), −143.9 (h, $J_{P\text{-}F}$ = 712 Hz, PF_6) ppm. HR.M.S: ES-MS: 338.15 *m/e* amu ($[M - Bz]^{\cdot +}$). IR : 3500 s (ν_{NH}), 2927 s (ν_{CH}), 2019, 1910, 1830 vs (ν_{CO}), 840 vs (PF_6) cm^{-1}. *Anal.* Calc. For $MnC_{20}H_{27}P_2N_2O_3F_6$: C, 41.83; H, 4.74; N, 4.80. Found: C, 41.90; H, 4.86; N, 4.74.

Synthesis of $[Mn(CO)_3([9]ane_{cis}N_2(Me)_2P)]PF_6$ **(3.3(*cis*))**

225 mg (3.92 x 10^{-4} mol) of **3.2(*cis*)** in THF (10 mL) was stirred under dinitrogen. A solution of potassium-*tert*-butoxide (0.1 g in 5 mL THF) was added slowly in an acetone/dry ice bath, and the mixture was allowed to warm to room temperature. An excess of iodomethane (0.5 g) was added to the red solution and stirred overnight. The resultant yellow solution was pumped to dryness, and the pale yellow solid was washed sequentially with petrol (10 mL) and ether (10 mL), before drying in air, yielding **3.3(*cis*)**. Yield 100 mg (43%). ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ 7.24 (d, J = 14 Hz, Ar-H, 1H), 7.21 (t, J = 5 Hz, 2H), 7.13 (m, Ar-H, 2H), 3.90 (d, $^{2}J_{H\text{-}P}$ = 14 Hz, CH_2P, 2H), 3.55 (m, CH_2, 1H), 3.44 (m, CH_2, 1H), 3.24 (m, CH_2, 2H), 2.93 (s, CH, 1H), 2.10-2.90 (m, 8H), 2.05 (s, CH_3, 6H), 1.75 (m, CH_2, 2H), 1.71 (m, CH_2, 2H), 1.32 (m, CH_2, 1H) ppm. $^{13}C\{^{1}H\}$ DEPT NMR ($(CD_3)_2CO$ 125.8 MHz): δ 129.81 (d, J = 5 Hz, Ar-C), 129.13 (d, J = 3 Hz, Ar-C), 129.08 (m, Ar-C), 127.56 (d, J = 4 Hz, Ar-C), 65.11 (m, CH_2), 65.00 (m, CH_2), 64.25 (d, J = 10 Hz, CH_2), 55.23 (s, CH_2), 53.66

(s, CH), 31.89 (d, J = 26 Hz, CH_2P), 29.14 (d, J = 5 Hz, CH_2), 28.95 (s, CH_3), 28.82 (m, CH_2), 28.79 (s, CH_3), 28.67 (m, CH_2), 28.66 (m, CH_2) ppm. ^{31}P $\{^1H\}$ NMR ($(CD_3)_2CO$, 121.7 MHz): δ 105.3 (s), –144.5 (h, J_{P-F} = 710 Hz, PF_6) ppm. HR.M.S: ES-MS: 457.1430 *m/e* amu ($[M]^{\cdot+}$). IR : 2932, 2828 (ν_{CH}), 2104, 1908, 1835 (ν_{CO}), 840 (PF_6) cm^{-1}. *Anal.* Calc. For $MnC_{22}H_{31}P_2N_2O_3F_6$: C, 43.87; H, 5.19; N, 4.65. Found: C, 43.21; H, 5.87; N, 4.90.

Synthesis of $[Mn(CO)_3$(1R,2S-diaminocyclohexane)$PhP(allyl)_2]PF_6$ **(3.4(*cis*))**

To a solution of **3.1(*cis*)** (150 mg, 3.4 x 10^{-4} mol in 20 mL DCM) was added 1.1 equivalents of diallylphenyl phosphine. The solution was stirred for ca. 2 days, and pumped to dryness. The residue was then washed with diethyl ether, followed by petrol (10 mL) Yield 75 mg (38%). $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$ 125.8 MHz): δ 129.53 (m, Ar-C), 127.71 (m, Ar-C), 121.16 (m, Ar-C), 117.05 (br s, Allyl CH_2), 78.15 (s, C-H), 53.50 (s, C-H), 30.97 (m, CH_2), 29.80 (m, CH_2), 27.70 (br m, CH_2), 25.00 (m, CH_2), 20.00 (m, CH_2) ppm. ^{31}P $\{^1H\}$ NMR ($(CD_3)_2CO$, 121.7 MHz): δ 48.2 (s), –144.8 (h, J_{P-F} = 710 Hz, PF_6) ppm. HR.M.S: ES-MS: 441.12 *m/e* amu ($[M]^{\cdot+}$). IR : 3337, 3297 s (ν_{NH}), 2937, 2863 s (ν_{CH}), 2029, 1917, 1853 vs (ν_{CO}), 1634 s, 1579 m, 1435 w, 840 vs (PF_6) cm^{-1}. *Anal.* Calc. For $C_{21}H_{29}P_2N_2F_6O_3Mn$: C, 42.87; H, 4.97; N, 4.76. Found: C, 42.69; H, 5.11; N, 4.69.

Towards Macrocycle Liberation

Reaction of $[Mn(CO)_3([9]ane_{trans}N_2(Me)_2P)]PF_6$ (**3.3(*trans*)**) with Br_2.

90 mg (1.5×10^{-4} mol) of **3.3(*trans*)** was dissolved in DCM (10 mL) and an excess of bromine (0.5 mL) was added to the solution with vigorous stirring. The solution became warm upon the addition of the bromine, and a colour change from pale yellow to red-brown was observed. The solution was allowed to cool to room temperature, and water was added (20 mL). The mixture was stirred for ca. 2 days and the aqueous phase was isolated and pumped to dryness, yielding an insoluble white solid. Yield 30 mg. ^{31}P $\{^1H\}$ NMR ($(CD_3)_2SO$, 121.7 MHz): δ 49 (s), 47 (s) ppm. HR.M.S: ES-MS: 335.2237 *m/e* amu ($[M]^{\cdot+}$). IR : 1071 ($\nu_{P=O}$) cm^{-1}

Reaction of $[Mn(CO)_3([9]ane_{trans}N_2(Me)_2P)]PF_6$ (**3.3(*trans*)**) with H_2O_2.

An aqueous suspension of **3.3(*trans*)** (30 mg, 5×10^{-5} mol in 2 mL water) was acidified with concentrated HCl (8 drops) and H_2O_2 (30% aqueous solution, 1 mL) was added to the resultant solution. A colour change was observed instantly after the addition of the peroxide from yellow to red. As the reaction proceeded, the colour of the solution slowly lightened and a precipitate formed over the course of 24 h. The precipitate was filtered and washed with water (5 mL) to give a white powder. Yield 15 mg. MS:ES-MS: 335 amu (100%) ($[M]^{\cdot+}$).

Reaction of $[Mn(CO)_3([9]ane_{trans}N_2P)]PF_6$ (**3.2(*trans*)**) with 4-methylmorpholine-N-oxide

To a cold solution of **3.2(*trans*)** in acetonitrile (73 mg, 1.2 x 10^{-4} mol in 5 mL, -20 °C) was added dropwise a solution of 4-methylmorpholine-N-oxide (0.016 g, 1 equiv., in 5 mL MeCN). The solution was allowed to gradually warm to rtp, with stirring. After stirring for ca. 24 h the mixture was pumped to dryness and washed with petrol (10 mL), Yielding the de-carbonylated complex, **3.5(*trans*)**. ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.64 (br s, Ar-H, 5H), 1.00-3.90 (br m, 25H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$ 125.8 MHz): δ 131.89 (br s, Ar-C), 130.8 (m, Ar-C), 68.60 (s, C-H), 64.30 (s, CH_2), 63.80 (s, CH_2),57.40 (s, C-H), 55.26 (s, CH_2), 33.95 (s, CH_2), 31.36 (s, CH_2), 29.30 (d, $^2J_{C\text{-}P}$ = 23 Hz, benzyl CH_2), 26.75 (m, CH_2), 26.40 (m, CH_2), 4.68 (s, CH_3), ppm. $^{31}P\ \{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 112 (s), –144 (h, $J_{P\text{-}F}$ = 710 Hz, PF_6) ppm. M.S: ES-MS: 442.15 *m/e* amu ($[M]\cdot^+$). IR : 2936, 2861 s (ν_{CH}), 2345 w (ν_{MeCN}), 1930, 1847 vs (ν_{CO}), 1496 s, 1454 s, 1412 w, 840 s (PF_6) cm^{-1}

Non-Template Reactions

Preparation of tris(orthofluorophenyl)phosphine oxide.

Tris(orthofluorophenyl)phosphine (250 mg, 7.9 x 10^{-4} mol) was dissolved in DCM (10 mL) and water (10 mL) was added. The two phases were stirred vigorously in air as hydrogen peroxide (1 mL of 30% solution) was added. The mixture was stirred overnight and the DCM layer was isolated, dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure to yield an off white solid. Yield 245 mg (94%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (t, J = 8 Hz, Ar-H, 1H), 7.52 (s, Ar-H, 1H), 7.25 (m, Ar-H, 1H), 7.05 (d, J = 5 Hz, Ar-H, 1H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 165.50 (s, Ar-C), 161.48 (s, Ar-C), 135.02 (s, Ar-C), 133.80 (m, Ar-C), 125.65 (d, J = 12 Hz, Ar-C), 116.38 (m, Ar-C) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 15 (s) ppm. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 283 MHz): δ -101.7 (s) ppm. M.S: ES-MS: *m/e* 333.0658 amu (100%) ($[M]^{\cdot+}$). IR : 1601, 1572, 1475, 1442, 1267, 1219, 1188, 1136 ($\nu_{P=O}$) cm^{-1}. *Anal.* Calc. For $C_{18}H_{12}POF_3$: C, 43.87; H, 5.19; N, 4.65. Found: C, 43.93; H, 5.14; N, 4.61.

Reaction of tris(orthofluorophenyl)phosphine oxide with 1R, 2R-diaminocyclohexane.

A mixture of diamine (120 mg, 1x10^{-3}.mol), phosphine oxide (1 equivalent, 350 mg) and potassium-*tert*-butoxide (236 mg) was dissolved in THF and stirred under nitrogen. The colour of the solution became gradually pale yellow and the mixture was allowed to stir overnight. A ^{31}P NMR spectrum of the crude reaction mixture showed the presence of the phosphine oxide starting material as the only phosphorus environment present. The mixture was heated to reflux for 1 week, and regular analysis of the mixture by ^{31}P NMR showed no reaction.

3.10 References

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Chapter 4- Synthesis & Coordination of Linear triphosphines

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4.1 Introduction

Although there are a number of synthetic routes to triphosphorus macrocycles involving mono- and / or bidentate precursors, or a combination of the two, the synthesis of a linear macrocycle precursor ligand with all three phosphorus donors in the chain is of particular interest. By performing various disconnections on the parent [9]ane P_3 macrocycle, it is clear that there are a number of approaches to assemble the desired macrocycle; 1+1+1, 2+1, and finally, '3+0' (where the number signifies the number of donor atoms in the coordinated ligands, figure 4.1). Whilst the first two approaches are widely used, the '3+0' approach has been overlooked.

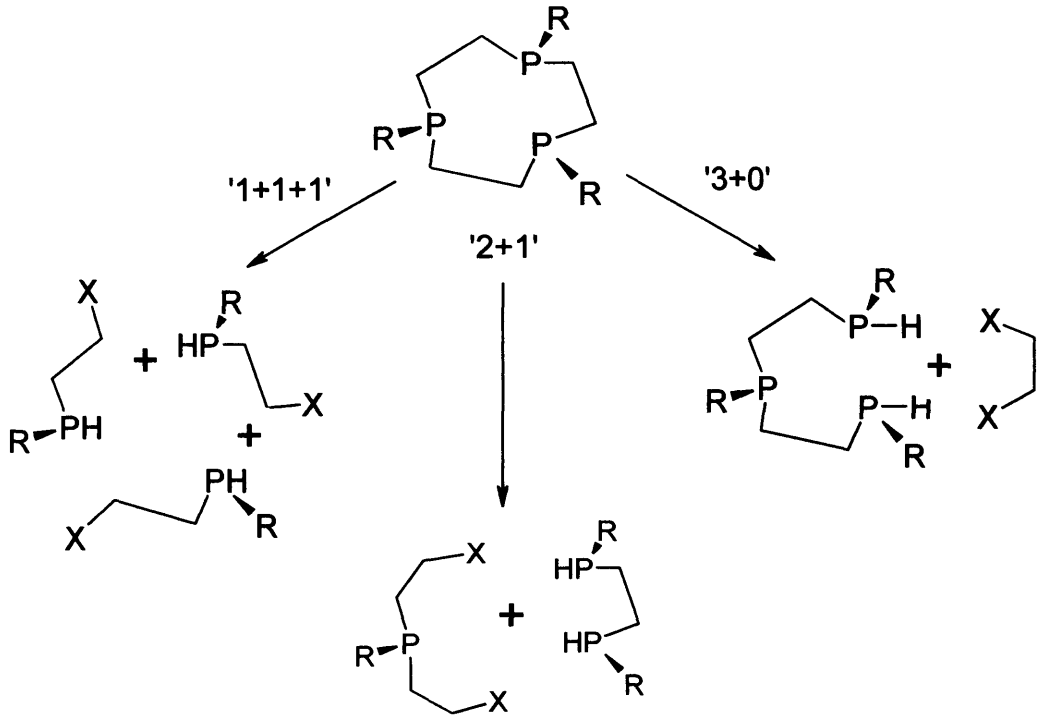
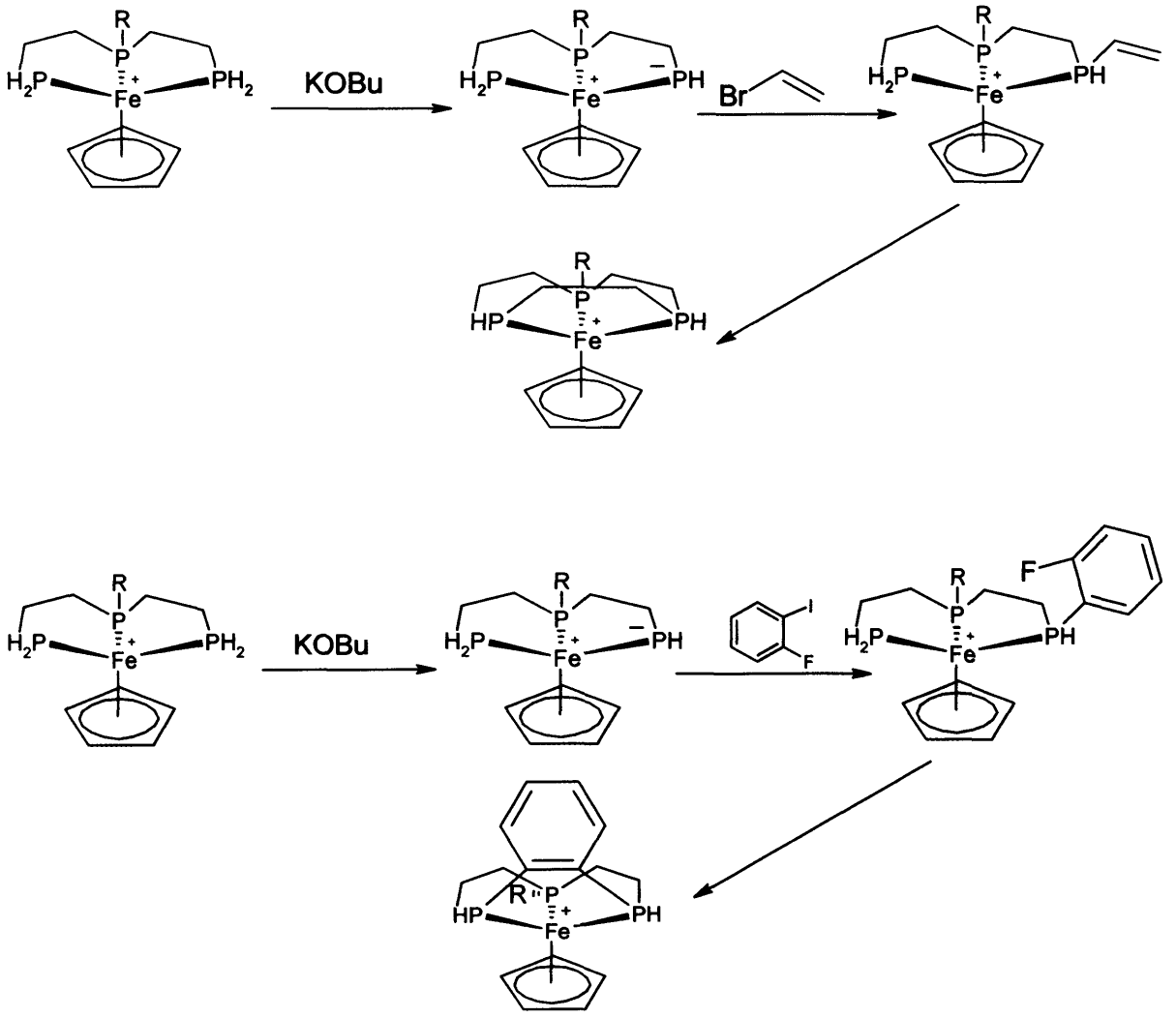


Figure 4.1. The possible disconnections of a [9]ane P_3 macrocycle.

In order for this approach to yield the desired macrocycle, the triphosphine starting ligand must have appropriately reactive functions at each terminus. The subsequent complex may then undergo substitution at either terminus, thus 'tethering' together

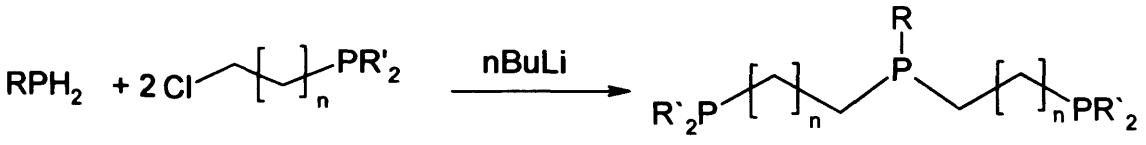
the two outermost phosphine donors (scheme 4.1). Our synthetic strategy involves the preparation of a linear P_3 ligand with two primary phosphines at each terminus. Once coordinated, this will allow access to the reactive phosphide functions which may then be substituted with appropriate bridging functions.



Scheme 4.1. The proposed route to triphosphorus macrocycles with benzannulated and aliphatic backbones from a linear P_3 unit.

4.2 Examples of Linear Triphosphines

The chemistry of linear triphosphorus species with hydrocarbon bridges has been thoroughly explored. In particular, a series of tri-tertiary phosphines of this nature have been prepared by Meek using $RPLi_2$ / $Cl(CH_2)_nPR_2$ coupling reactions.[1] More recently, Peters has demonstrated the versatility of Meek`s approach by incorporating aromatic bridging functions into the backbone.[2] The most common route is a *two-fold* electrophilic substitution at an alkyl phosphide, by two equivalents of a halo-alkyl or aryl phosphine (scheme 4.2).



Scheme 4.2. The general preparatory method for a variety of tritertiary linear phosphines.

Indeed, a large number of tritertiary linear triphosphines have been prepared and subsequently utilised in various catalytic systems using this approach, notably so in the protonolysis of cationic Pt-CH_3 bonds.[3] Although these preparations are synthetically reliable and generally high yielding, our requirement for P-H functions at both termini precludes the use of (haloalkyl) primary phosphines, or strongly basic reagents (ie. nBuLi) to form the required alkyl phosphide.

Tertiary-disecondary, and tertiary-diprimary phosphines have been reported using other well-known organophosphorus routes, although their coordination chemistry has not been as thoroughly investigated. The first such example of a tertiary-diprimary phosphine, 4-phenyl-1,4,7-triphosphaheptane was reported in 1973 by King (fig. 4.2).[4] This was achieved by a base catalysed coupling of phenylphosphine with vinyl diethyl phosphonate, followed by lithium aluminium hydride reduction.

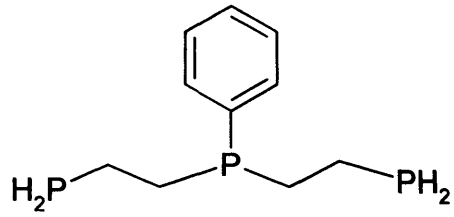


Figure 4.2. 4-phenyl-1,4,7-triphosphaheptane.

Surprisingly, no complexes of this ligand are reported in the literature. However Katti *et al* have shown that this ligand readily undergoes formylation of the P-H bonds in the presence of formaldehyde in ether to form the water soluble tripod, $PhP(CH_2CH_2P(CH_2OH)_2)_2$.[5]

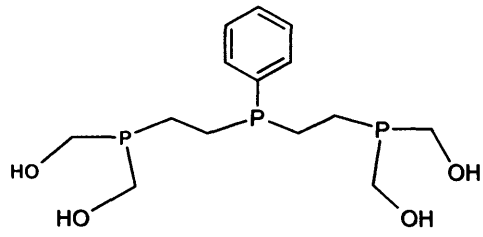
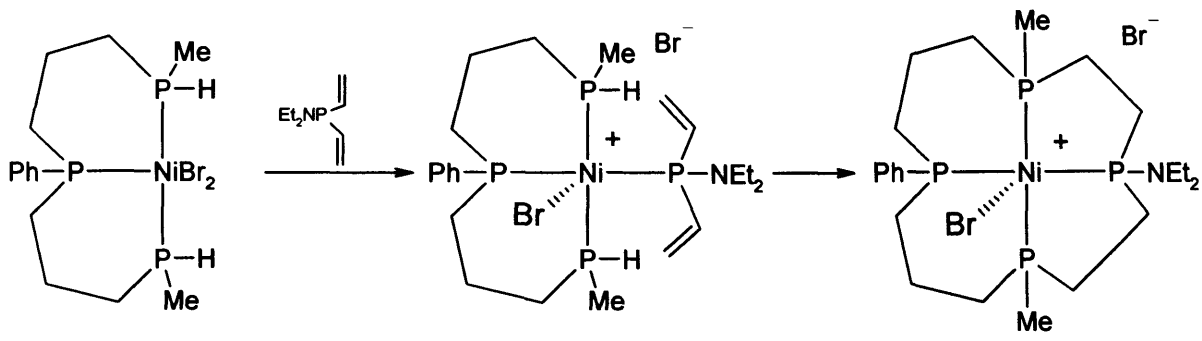


Figure 4.3. The water soluble triphosphine, $PhP(CH_2CH_2P(CH_2OH)_2)_2$.

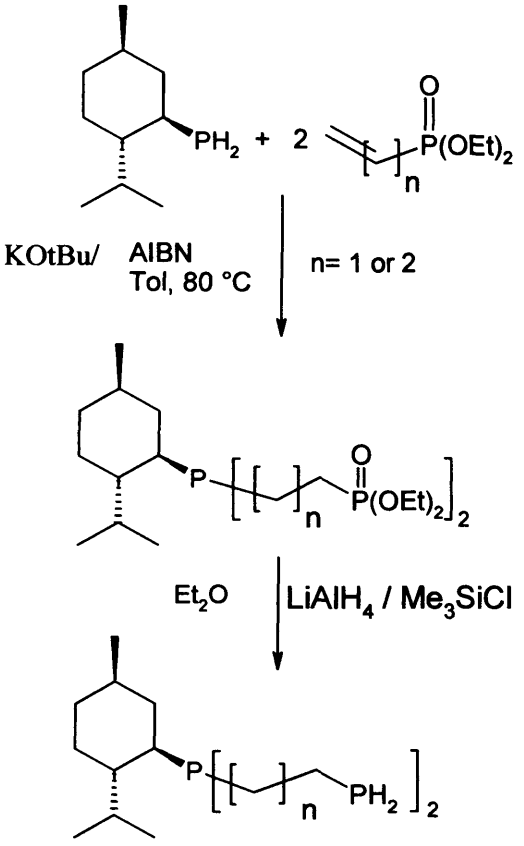
Using King's methodology, Steltzer has prepared the tertiary-disecondary phosphine, $PhP((CH_2)_3P(H)Me)_2$ using a modified starting phosphine, allylmethyl-ethylphosphinite.[6] Steltzer has shown that coordinated P_3 systems such as these can exhibit interesting reactivity, as the P-H function is easily substituted *via* the phosphide intermediate. Stelzer's work is significant, as this approach led to the preparation of the first reported tetraphosphamacrocycle on a Ni(II) template, achieved by intramolecular hydrophosphination of the coordinated triphosphine with a divinyl phosphine species (scheme 4.3).[7]



Scheme 4.3. The preparation of P_4 macrocycles from intramolecular hydrophosphination of a coordinated linear P_3 unit with a divinyl phosphine on a nickel(II) template.

Given the susceptibility of coordinated primary or secondary phosphine functions to undergo substitution, we believe that triphosphorus systems such as those reported by Stelzer[6] and King[4] may be useful candidates for novel routes towards small chelate triphosphorus macrocycles. We therefore report the preparation of two novel triphosphine ligands, 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane (**4.1**), and 4-(1R,2S,5R-menthyl)-1,5,9-triphosphanonane (**4.2**).

4.3 Results and Discussion- Ligand Synthesis



Scheme 4.4. Synthesis of ligands **4.1** and **4.2** (n = 1 or 2, respectively).

The synthesis of the seven and nine membered triphosphines, **4.1** and **4.2** are outlined in Scheme 4.4. The mixtures of menthylphosphine, AIBN and the appropriate phosphonate were heated in toluene for ca. 80 h. This yielded the appropriate tertiary-phosphine bisphosphonate in quantative yield, as very viscous oils in both cases. The $^{31}P\{^{1}H\}$ NMR resonances for the phosphonate intermediates were observed at δ_P -20.1 (t, 29 Hz) and -30.0 (d, 29 Hz) ppm for **4.1**, and δ_P –34.8 (s) and -30.0 (s) ppm for **4.2**. No further characterisation was made at this stage of the preparation. Reduction of the two $P(O)(OEt)_2$ groups was carried out using lithium aluminium hydride. Although some product was lost at this stage of the preparation -as is common with $LiAlH_4$ reductions- yields of 53 % and 41 % were obtained for the syntheses **4.1** and

4.2, respectively. Both ligands were found to be stable indefinitely in toluene in the absence of oxygen.[8]

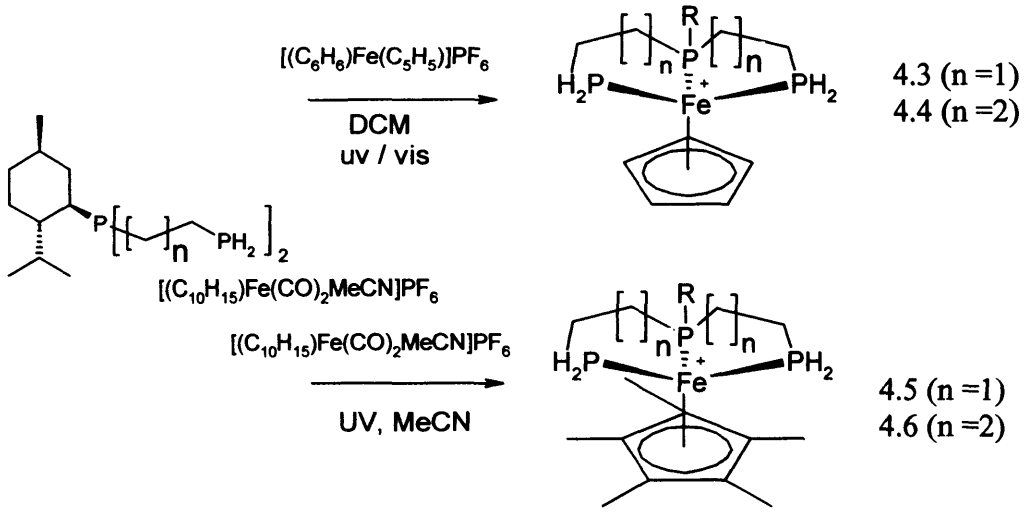
Both ligands exhibited similar patterns in their respective $^{31}P\{^{1}H\}$ NMR spectra. The $^{31}P\{^{1}H\}$ NMR spectrum of **4.1** shows an apparent doublet at δ_P - 128.3 ppm due to the two primary phosphine groups, with a three bond coupling constant of $^{3}J_{P\text{-}P}$ = 14.8 Hz. The tertiary phosphorus atom appears as a triplet in the expected region, at δ_P – 24.7 ppm. The ^{1}H NMR spectrum for **4.1** consists of a doublet of multiplets at δ_H 2.75 ppm ($^{1}J_{P\text{-}H}$ = 175 Hz) for the P-H protons, with the coupling constant in accordance with other primary, non-coordinated phosphines.[9] The methyl protons appear as three doublets at δ_H 0.70, 0.80 and 0.83 ppm ($^{3}J_{H\text{-}H}$ = 7, 9, 6 Hz, respectively). All other resonances appear in the δ_H 0.90 – 1.72 ppm region as a number of unresolved multiplets, although their relative intensities are in agreement with the empirical formula of the ligand. In the $^{13}C\{^{1}H\}$ DEPT spectrum of **4.1** the methyl carbons appear as three singlets at δ_C 15.12, 21.65 and 22.70 ppm. Two doublets are observed for two of the C-H groups ($J_{C\text{-}P}$ = 12 Hz), while two singlets at δ_C 33.70 and 44.90 ppm are assigned to the two remaining C-H carbons. Five multiplets appear as a result of the methylene carbon atoms, at δ_C 11.10, 27.58, 28.17, 29.79 and 30.28 ppm. A doublet is observed for one of the methylene groups at δ_C 36.25 ppm ($J_{C\text{-}P}$ = 18 Hz), while a singlet at δ_C 35.00 ppm is seen for a further methylene resonance.

The $^{31}P\{^{1}H\}$ NMR spectrum of **4.2** does not exhibit any phosphorus coupling, presumably due to the additional chain length separating the phosphorus atoms. The primary phosphines therefore appear as a singlet at δ_P –138.9 ppm, almost 10 ppm upfield from the seven membered analogue, **4.1**. The tertiary phosphine appears at δ_P –32.3 ppm, again, upfield from the seven membered analogue. The ^{1}H NMR

1.80ppm region. In the $^{13}C\{^1H\}$ DEPT spectrum of **4.2**, the methyl carbons are coupled to the phosphorus atoms and are therefore observed as three singlets at 15.54, 21.51 and 22.05 ppm. Two doublets at δ_C 27.60 and 36.13 ppm are assigned C-H carbons, with both showing $J_{C\text{-}P}$ values of 21 Hz. The two other C-H resonan occur as singlets at δ_C 33.72 and 44.95 ppm. Multiplets for the methylene car atoms are observed at δ_C 16.47, 23.10, 25.76, 30.07 and 30.73 ppm, while two sing at δ_C 34.65 and 35.19 ppm account for the remaining CH_2 groups.

4.4 Coordination of 4.1 and 4.2 to $CpFe^+$ Templates

$CpFe^+$complexes of **4.1** and **4.2** were readily precipitated from concentrated methanol solutions at low temperature, yielding tan solids in both instances. The complexes themselves were prepared by the addition of one equivalent of **4.1** or **4.2** to dichloromethane solutions of $[(\eta^5\text{-}C_5H_5)Fe\ (\eta^6\text{-}C_6H_6)]PF_6$. The aryl functions were displaced by the triphosphine upon exposure to sunlight with stirring for ca. 24 h (Scheme 4.5, complexes **4.3** and **4.4**).



Scheme 4.5. The coordination of ligands **4.1** and **4.2** to Fe $_{(II)}$ centres (R = (1R,2S,5R-menthyl)).

Complex **4.3** shows the characteristic downfield shift in its $^{31}P\ \{^1H\}$ NMR spectrum. Upon coordination, all three phosphorus environments become chemically inequivalent. Therefore all three phosphorus resonances are split into doublets of doublets in the $^{31}P\ \{^1H\}$ NMR spectrum, according to the 2nI + 1 rule.[10] However, the doublet of doublets concurrent with the tertiary phosphine overlap, and therefore the tertiary phosphine appears as a virtual triplet at δ_P 132.9 ppm ($^2J_{P\text{-}P'}$ = 27 Hz). The two primary coordinated phosphines appear as doublets of doublets at δ_P 11.5 and 10.1 ppm, with two bond phosphorus coupling constants in the region of 25-30 Hz. In

addition, a septet at δ_p –143.2 ppm is observed due to the PF_6^- counterion ($^1J_{P\text{-}F}$ = 712 Hz). This pattern is seen in all iron complexes of **4.1** and **4.2**, and is illustrated in figure 4.4, below.

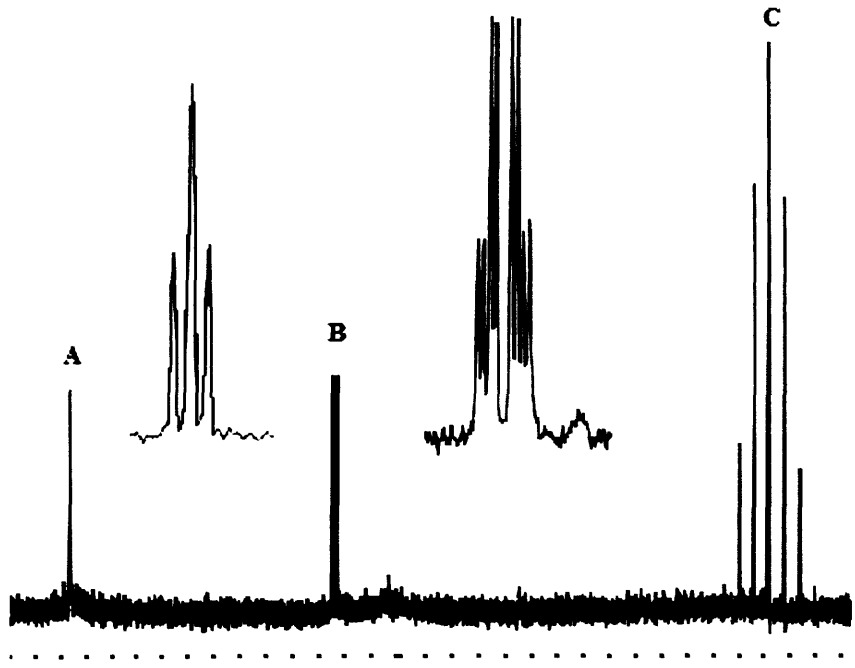


Figure 4.4. A representative $^{31}P\{^1H\}$ NMR spectrum showing the coupling patterns in Cp^RFe^+ complexes of **4.1** and **4.2**.

Signal **A** is due to the coordinated tertiary phosphine, and the expansion shows the overlapping of the doublet of doublets, yielding a virtual triplet with an integration approximating to 1:2:1. The two primary phosphine donor signals are observed as two independent doublets of doublets (**B**), with an obvious roofing effect as the signals are within close proximity to each other, consistent with an ABX spectrum. The heptet (**C**) is consequent to the hexafluorophosphate anion.

The ^1H NMR spectrum of **4.3** consists of a singlet at δ_H 4.50 ppm due to the resonance of the cyclopentadienyl protons. The four non-equivalent P-H protons appear as doublets of doublets at δ_H 5.41, 4.85, 4.55 and 3.75 ppm giving the characteristic $^1J_{H\text{-}P}$ value of 340 Hz. The methyl protons appear as distinct doublets at δ_H 0.80 ($^2J_{H\text{-}H'}$ = 9

Hz), 0.90 ($^2J_{H\text{-}H'}$ = 8 Hz), 0.93 ppm ($^2J_{H\text{-}H'}$ = 7 Hz). All other resonances appear within the expected region (δ_H 1.00 – 2.40 ppm) as a series of multiplets. The $^{13}C\{^1H\}$ DEPT spectrum of **4.3** consists of a quartet at δ_c 76.59 ppm due to the cyclopentadienyl resonances, which couple to the coordinated P atoms ($^2J_{C\text{-}P}$ = 41 Hz). The methyl carbons appear as singlets at δ_c 16.30, 22.01, and 22.54 ppm. The two inequivalent methylene carbon atoms in the P-P bridging chains of **4.3** are observed as two doublets at δ_c 15.00 and δ_c 30.00 ppm. A doublet is observed at δ_c 25.42 ppm ($^2J_{C\text{-}P}$ = 10 Hz) due to the methylene carbon at the menthyl group. Two singlets at δ_c 34.00 and 37.00 ppm account for the other methylene carbons present. The IR spectrum of **4.3** shows the characteristic $\nu_{(PH)}$ stretch at 2323 cm^{-1}. This value is in line with other iron (II) complexes of chelating primary phosphines, which we have recently published.[11] The molecular ion (M^+ = 413.10 amu) is apparent in the mass spectrum of **4.3**, and the elemental composition data is in accordance with its empirical formula.

The $^{31}P\ \{^1H\}$ NMR spectrum of complex **4.4** shows a downfield shift from the starting ligand, **4.2**, with the tertiary phosphine resonance appearing as a virtual triplet at δ_P 41.7 ppm. This is again due to the overlap of the doublet of doublets consistent with a coordinated phosphine coupling to two other non-equivalent environments. The two primary phosphine terminals give rise to two doublets of doublets at δ_P –27.8 and -31.0ppm. Both signals give rise to a coupling constant of in the region of 60 Hz. Again, the PF_6^- counterion gives rise to a septet at δ_p –143 ppm ($^1J_{P\text{-}F}$ = 710 Hz). Due to the increased fluxionality of the six membered chelate over its five membered analogue, **4.3**, the identification of **4.4** by its ^1H NMR spectrum was frustrated by peak broadening. However by measuring the spectrum at high temperature (393 K) in d-DMSO, all peaks were satisfactorily resolved. A sharp singlet at δ_H 4.61 ppm is

assigned to the cyclopentadienyl protons. Four doublets of doublets at δ_H 6.08, 5.35, 4.59 and 3.70 ppm show the presence of four in-equivalent P-H environments, with respective $^1J_{H\text{-}P}$ values of 355, 352, 348 and 352 Hz. Once again, the methyl protons appear as distinct doublets at δ_H 0.89 ($^2J_{H\text{-}H'}$ = 8 Hz), 0.90 ($^2J_{H\text{-}H'}$ = 7 Hz), 0.92 ppm ($^2J_{H\text{-}H'}$ = 8 Hz), with the remaining protons giving rise to a series of multiplets within the δ_H 1.10 – 2.30 ppm region. In the $^{13}C\{^1H\}$ DEPT spectrum of **4.4**, the methyl carbons are observed as three singlets at δ_C 15.85, 20.82 and 21.89 ppm. The Cp carbon atoms appear as a singlet, characteristically downfield, at δ_C 79.31 ppm, with no phosphorus splitting. All four C-H peaks are observed as three multiplets at δ_C 32.96, 44.69 and 52.97 ppm, and a singlet at δ_C 28.44 ppm. The methylene carbons appear as four singlets at δ_C 12.57, 21.98, 22.24, and 39.59 ppm, as a doublet at δ_C 24.77 ppm ($J_{C\text{-}P}$ = 5 Hz), and a doublet at δ_C 28.50ppm ($J_{C\text{-}P}$ = 7 Hz). The infrared spectrum of **4.4** shows the $\nu_{(PH)}$ stretch at 2311 cm^{-1}. The mass spectrum of **4.4** afforded the molecular ion at 441.17 amu, showing the presence of the expected mono-cationic species $[CpFeP_3]^+$. The elemental analysis of **4.4** is also consistent with its formula.

4.5 Coordination of 4.1 and 4.2 to Cp*Fe$^+$ Templates

Pentamethyl-Cp derivatives of **4.3** and **4.4** were prepared by addition of **4.1** or **4.2** to acetonitrile solutions of $[Cp^*Fe(MeCN)_3]PF_6$, prepared *in situ* by uv photolysis of $[Cp^*Fe(CO)_2MeCN]PF_6$ in acetonitrile. The ligands themselves were not included in the photolysing mixture, due to the potential for P-C bond cleavage under such conditions. However, addition of one equivalent of ligand to the tris-acetonitrile

intermediate, followed by stirring overnight, yielded the desired complexes **4.5** and **4.6.**

Complex **4.5** was isolated in a 62% yield as tan crystals, and exhibited the expected pattern in the $^{31}P\{^{1}H\}$ NMR spectrum with the coordinated tertiary phosphine being observed as a virtual triplet at δ_P 123.3 ppm, with a two bond coupling constant of 15 Hz. Two doublets of doublets are observed at δ_P 21.9 and 20.3 ppm for the two primary phosphine groups, and the coupling constants are of the same magnitude as that of the tertiary phosphine, somewhat lower than the Cp analogue, complex **4.3.** Three doublets are observed in the ^{1}H NMR spectrum, corresponding to three of the four inequivalent P-H environments at δ_H 4.83, 4.59 and 4.47 ppm, with respective $^{1}J_{H\text{-}P}$ couplings of 332, 330 and 328 Hz. Again, a complex series of poorly resolved multiplets is seen in the δ_H 1.70 – 2.30 ppm region, corresponding to the methylene and CH groups of the ligand. The methyl protons of the Cp* are seen as a singlet at δ_H 1.65 ppm, while two multiplets are visible for two methyl groups at δ_H 0.95 and 0.89 ppm. The remaining methyl protons are seen as a doublet ($^{3}J_{H\text{-}H}$ = 12 Hz) at δ_H 0.76 ppm. In the $^{13}C\{^{1}H\}$ DEPT spectrum of **4.5**, the methyl carbons are observed as three singlets at δ_C 15.09, 14.26 and 8.95 ppm. The Cp* carbon atoms appear as a singlet, characteristically downfield, at δ_C 86.78 ppm. The infrared spectrum of **4.5** shows the characteristic P-H stretch as a broad singlet at 2341 cm^{-1}, and the high-resolution mass spectrum of **4.5** shows the presence of the molecular ion at 483.2161 amu, in 100% abundance.

4.6 was isolated by vapour diffusion of petrol into a concentrated methanol solution of **4.6**. A virtual triplet in the $^{31}P\{^{1}H\}$ NMR spectrum of **4.6** at δ_P 42.5 ppm ($^{2}J_{P\text{-}P}$ = 50 Hz) comfirms the coordination of the tertiary phosphorus atom. Two doublets of doublets are observed for the terminal phosphines, one at δ_P –11.1 ppm, and the

second at δ_P –15.4 ppm. All show two bond P-P coupling constants in the region of 45 Hz, showing the inequivalence of all three phosphorus environments. The $^{31}P\{^1H\}$ NMR data for complexes **4.3-4.6** are outlined in table 4.1.

Complex	$\delta_{p\ tert.}$	$^2J_{P\text{-}P}$	$\delta_{p\ Prim.}$	$^2J_{P\text{-}P\ (mean)}$
4.3	132.9	27	11.5, 10.1	27
4.4	41.7	65	-27.8, -31.0	59
4.5	123.3	15	21.9, 20.3	15
4.6	42.5	46	-11.1, -15.4	46

Table 4.1. The $^{31}P\ \{^1H\}$ NMR data for complexes **4.3-4.6**. δ_p values are quoted in ppm and coupling constants are given in hertz. The coupling constants for the primary phosphine signals are given as the mean value of the four.

The data in table 4.1 shows that the through-metal P-P coupling constants in the smaller chelate complexes (ie. Complexes of **4.1**, shown in the shaded rows) are smaller than those of their larger chelate analogues (complexes of **4.2**, in the white rows). Increasing the size of the chelate from five members to six, and therefore the P-M-P angle, leads to an approximately two-fold increase in the magnitude of the coupling constants (**4.3→4.4**). In the case of the Cp* complexes, this effect is even more pronounced, with a three-fold increase in $^2J_{P\text{-}P}$ values from **4.5→4.6**. This observation has been made in P_3 macrocyclic systems, such as those reported by Edwards *et.al* in 2006.[15] Furthermore, the absolute difference in chemical shift between the tertiary coordinated phosphine and the two primary phosphine shifts ($\delta_{p\ tert.} - \delta_{p\ Prim.}$) decreases from the Cp complexes to the Cp* analogues. Again, this pattern has been observed previously in P_3 macrocyclic systems, and may be rationalised by the increased steric compression of the Cp* system causing a

electron density at the metal centre. This effect may be a cause of the g coordination shift of the primary phosphines in complexes **4.5** and **4.6** over th **4.3** and **4.4**.

In the ^{1}H NMR spectrum of **4.6,** three of the four inequivalent P-H environmen be assigned, at δ_H 5.10, 4.96 and 4.86 ppm, which all exhibit P-H coupling con in line with those of coordinated primary phosphines. Again, the region betwe 1.30 – 2.00 ppm has a large number of irresolute multiplets, correspondi numerous, coincidental proton environments. Three doublets are seen for the respective groups of methyl protons, at δ_H 1.01, 0.99 and 0.80 ppm, with $^{3}J_{H\text{-}H}$ v of 6,7, and 7 Hz, respectively. Again, the Cp*-methyl protons are not coupled are observed as a singlet at δ_H 1.49 ppm. In the $^{13}C\{^{1}H\}$ DEPT spectrum of **4.** Cp* carbon atoms appear as a singlet at δ_C 91.84 ppm, while all other resonance in the expected regions. The infrared spectrum of **4.6** shows a broad signal at cm^{-1}, which is assigned to the P-H stretch. The high-resolution mass spectrum c shows the presence of the molecular ion at 511.2461 amu.

4.7 (n =1)
4.8 (n =2)

Scheme 4.6. The coordination of **4.1** and **4.2** to $Mo(CO)_3$. (R = (1R,2S,5R-menthyl)).

4.1 was found to readily coordinate to molybdenum tricarbonyl upon stirring a tolu solution of mesitylene molybdenum tricarbonyl in the presence of **4.1** overni forming the desired fac-$(P_3)Mo(CO)_3$ adduct. Thus, complex **4.7** may be isol from concentrated petrol solutions as straw-coloured crystals. Interestingly tertiary coordinated phosphine does not directly couple through the Mo centre the other P atoms. This observation was also made by Norman on [12]ane$P_3Mo(CO)_3$ species.[12] The ^{31}P $\{^1H\}$ NMR spectrum of **4.7** therefore sho singlet at δ_P 96.2 ppm, corresponding to the coordinated tertiary phosphine and doublets are observed at δ_P –50.1 ppm and -51.6 ppm ($^2J_{P\text{-}P}$ = 20, 23 Hz, respectiv corresponding to the two inequivalent primary coordinated phosphines. The four functions are clearly visible in the ^1H NMR spectrum of **4.7,** with doublets at δ_H ($^1J_{H\text{-}P}$ = 380 Hz) 3.90 ($^1J_{H\text{-}P}$ = 381 Hz), 4.35 ($^1J_{H\text{-}P}$ = 377 Hz) and 4.71 ppm ($^1J_{H\text{-}P}$ = Hz). Again, the $^1J_{H\text{-}P}$ values are typical of coordinated primary phosphines. T doublets at δ_H 0.71 ($^2J_{H\text{-}H'}$ = 8 Hz), 0.79 ($^2J_{H\text{-}H'}$ = 8 Hz), and 0.88 ($^2J_{H\text{-}H'}$ = 7 represent the methyl protons and all other resonances lie in between δ_H 1.00 – ppm as indiscreet multiplets, although the integrals do accord exactly with the forı of the complex. In the $^{13}C\{^1H\}$ DEPT spectrum of **4.7**, the carbonyl carbons observed as a singlet at δ_C 222.81 ppm. This is surprising, given that in **4.**

carbonyl groups are chemically inequivalent, and therefore should exhibit three separate carbonyl resonances. Again, the CH_3 environments of the menthyl group are not coupled, and therefore appear as singlets at δ_C 15.64, 20.95, 21.23 ppm, although they are slightly broadened. Two singlets at δ_C 27.06 and 46.14 ppm denote the presence of two CH groups, while the remaining two appear as doublets at δ_C 33.55 and 40.86ppm with $^2J_{C\text{-}P}$ values of 13 Hz, in both cases. A singlet consequent to a CH_2 group is seen at δ_C 37.71 ppm, while the other methylene carbons are observed as multiplets (δ_C 13.56, 18.00, 26.11 and 34.29 ppm), and two doublets (δ_C 24.75 ppm, $J_{C\text{-}P}$ = 10 Hz and δ_C 28.70 ppm, $J_{C\text{-}P}$ = 5 Hz). The infrared spectrum of **4.7** show the two $\nu_{(PH)}$ stretches at 2336 and 2359 cm^{-1}, while the $\nu_{(CO)}$ stretches appear as two bands at 1862 and 1949 cm^{-1}. Since diprimary-chelating triphosphine complexes of Mo are not reported, it is impossible to directly compare the carbonyl stretching frequencies of **4.7** with those of analogous Mo systems. However, in work published by Norman (figure 4.5) in 1982, the carbonyl IR stretches of complexes (**i**) and (**ii**) were observed at $\nu_{(CO)}$ 1954, 1864 cm^{-1}(**i**), and $\nu_{(CO)}$ 1918, 1815 cm^{-1}(**ii**).[12]

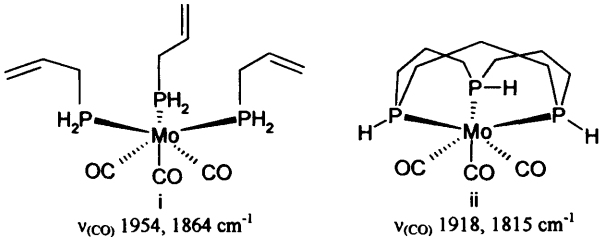


Figure 4.5. The $\nu_{(CO)}$ stretching frequencies of *fac*-$P_3Mo(CO)_3$ complexes (**i**) and (**ii**).

The higher $\nu_{(CO)}$ stretching frequencies in **4.7** suggest a relatively poor σ-donation capability in comparison to (**ii**). Indeed this is to be expected; given that in (**ii**) there are two electron-donating alkyl functions at each coordinated phosphine. Consequently, the IR spectrum of **4.7** shows the $\nu_{(CO)}$ stretches to be in the same

proximity to those in the tri-primary complex, (i). Identification of **4.7** was unequivocally confirmed by it mass spectrum (TOF-MS, ES^+), which afforded the molecular ion at m/z = 472.29 amu.

Yellow crystals of **4.8** were isolated in a 64 % yield from a concentrated toluene solution. The $^{31}P\{^1H\}$ NMR spectrum of **4.8** exhibits a virtual triplet at δ_P 9.27 ($^2J_{P\text{-}P}$ = 30 Hz), and two doublets of doublets at -73.8 and -75.4 ppm, with coupling constants in the region of 25-26 Hz. In the ^1H NMR spectrum of **4.8,** doublets at δ_H 0.86, 0.71 and 0.15 ppm are observed for the methyl protons, with $^2J_{H\text{-}H'}$ coupling constants of 10, 12 and 11 Hz. The four P-H resonances are observed at δ_H 4.25, 4.01, 3.60 and 3.42 ppm. Again, the magnitude of the $^1J_{H\text{-}P}$ values are typical of that coordinated primary phosphines. In the $^{13}C\{^1H\}$ DEPT spectrum of **4.8**, the carbonyl groups appear as a broad signal at δ_C 221.60 ppm, while the infrared spectrum of **4.8** shows the carbonyl stretching frequency at 1949 cm^{-1}. A broad signal at 2359 cm^{-1}, assigned to the P-H stretch is also present. The high-resolution mass spectrum of **4.8** shows the presence of the molecular ion at 497.0945 amu.

4.7 Reactivity Studies

Following on from work conducted by the Stelzer group on tetradentate analogues, we were keen to explore the possibility of ring closure reactions on complexes **4.3-4.6**, using various ring closure reagents.[7] Complexes of iron(II) were selected, over the molybdenum analogues, as the cationic charge of the metal centre was anticipated to give more stable phosphido complexes upon deprotonation of the coordinated phosphine. The strategy involved the formation of a neutral, mono-deprotonated phosphido complex, followed by the electrophilic substitution of the bridging function at one of the terminal phosphines. The subsequent primary, tertiary, secondary triphosphine complex may then undergo further reaction to tether the macrocycle together. Our strategy is outlined in scheme 4.1.

Work carried out by Whatton and Edwards has shown that electrophilic substitutions on similar systems are capricious.[13] Using dihalo alkanes such as dichloroethane, they were unable to access the desired macrocycle. One observation was that, while the neutral phosphido complex was easily obtained, the substitution was capricious and low yielding. Furthermore, the subsequent chloroethyl pendant arm was too fluxional to couple to the primary phosphine terminus. Additionally, Whatton was not able to isolate any product from these substitution reactions. Taking this into account, our synthetic strategy involved the use of the more rigid bridging functions, iodofluorobenzene and vinyl bromide.

Iron complexes of **4.1** and **4.2** were treated with one equivalent of KO^{t}Bu in THF, and in each instance a colour change was observed immediately, from orange to dark red. The ^{31}P NMR spectrum of the phosphido complex showed the presence of an additional peak, denoting the presence of a phosphide species. These additional peaks

obtained. Again, a darkening of the reaction mixture was observed and the genera

of phosphide species was confirmed by ^{31}P NMR spectroscopy. The Vinylbro

was bubbled through a cooled solution of the complex, and stirred continuousl

ca. 48 hours, with the temperature maintained at -40 °C. Upon spectrosc

examination of the reaction mixture, no reaction had taken place.

For reactions using 1-fluoro,2-iodobenzene as a ring closing agent, the generatio

the phosphide complex was carried out under the same conditions. A solution

fluoro,2-iodobenzene was added dropwise at -78 °C, and the mixture was allow

warm slowly to ambient temperature. ^{31}P NMR spectroscopy showed that no rea

had taken place after 24 hours. The solution was warmed to reflux, and re

analysis of the reaction mixture showed no evidence of the desired product.

solution was pumped to dryness after a week of refluxing, and redissolve

chlorobenzene. However, despite refluxing the reaction mixture for a further we

the higher temperature, no reaction had taken place.

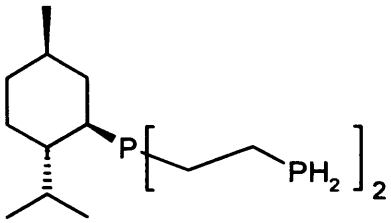
4.8 Conclusion

In conclusion, two novel triphosphine ligands, 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane (**4.1**), and 4-(1R,2S,5R-menthyl)-1,4,7-triphosphanonane (**4.2**) have been shown to coordinate to d^6 metal centres readily, forming bis-chelate complexes which are intrinsically stable. There was no evidence of bridging phosphine complexation in the reaction mixture, therefore the formation of the desired facial bi-chelate complex is selective over the formation of bridged polymetallic species.

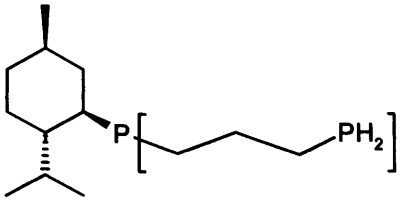
The subsequent complexes are prone to deprotonation of the terminal phosphine to give access to the phosphido complex. However due to the lack of stereochemical control over the substitution, and the lack of reactivity of the P^- terminus towards bridging electrophiles, we were unable to isolate any macrocycle or substituted phosphido complexes. It is therefore concluded that the 3+0 route to small ring chelate triphosphorus macrocycles is not as efficient as the other, better known routes

4.9 Addendum

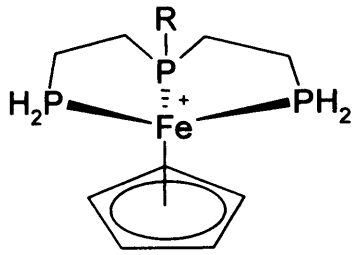
Below are the structures of the compounds referred to throughout this chapter.



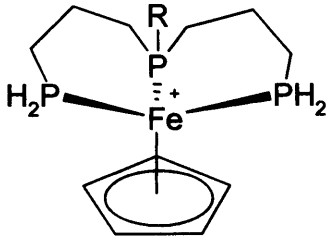
4.1



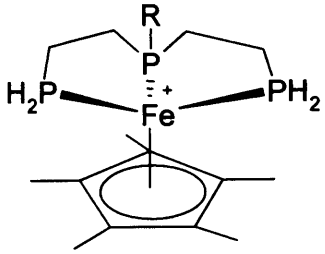
4.2



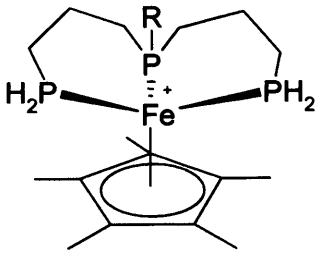
4.3 (R = (*1R,2S,5R-menthyl*))



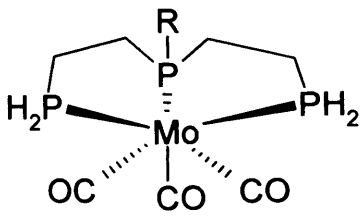
4.4 (R = (*1R,2S,5R-menthyl*))



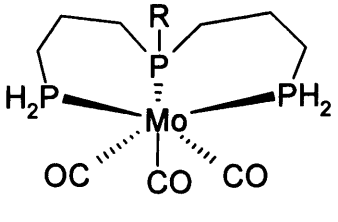
4.5 (R = (*1R,2S,5R-menthyl*))



4.6 (R = (*1R,2S,5R-menthyl*))



4.7 (R = (*1R,2S,5R-menthyl*))



4.8 (R = (*1R,2S,5R-menthyl*))

4.8 Experimental

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk and glovebox techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. The metal precursor complexes (η^6-1,3,5-trimethylbenzene)$Mo(CO)_3$,[14] *fac*-$Cr(CO)_3(MeCN)_3$,[15] and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)](PF_6)$[16] were prepared by literature methods. All deuterated solvents were dried (3Å molecular sieves) and degassed by freeze-thaw methods prior to use. All other chemicals were obtained commercially, and used as received. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 (δ = 0 ppm). ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane (δ = 0 ppm). Unless stated otherwise, infrared spectra were recorded as KBr disks on a Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd, UK.[17]

4-(1R, 2S, 5R-menthyl)-1,4,7-triphosphaheptane **(4.1)**

(1R, 2S, 5R)-menthyl phosphine (0.04 mol, 6.93 g), vinyl diethyl phosphonate (0.08 mol, 13.13 g) and two equivalents of KOtBu were dissolved in toluene (50 mL) and heated to 80 °C for 84 hours. After this stage, all volatile materials were removed under reduced pressure, with heating up to 100 °C. The two subsequent phosphonate terminal groups were reduced by the dropwise addition at 0 °C, of equimolar quantities of $LiAlH_4$ and trimethylsilylchloride (0.0625 mol). The mixture was

allowed to warm to room temperature and stirred for a further 2 h. The mixture was then re-cooled in an ice bath, and hydrolysed by the dropwise addition of water (2.35 mL), 15% aqueous NaOH (2.35 mL), and a further aliquot of water (7 mL). The organic layer was isolated, dried over $MgSO_4$, and all volatiles removed *in vacuo* to yield a clear, viscous oil. Yield = 6.3 g (53%).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 2.75 (dm, $^1J_{P\text{-}H}$ = 175 Hz, P-H, 4 H), 0.90-1.72 (m, 18 H), 0.83 (d, $^3J_{H\text{-}H}$ = 6 Hz, CH_3, 3 H), 0.80 (d, $^3J_{H\text{-}H}$ = 9 Hz, CH_3, 3 H), 0.70 (d, $^3J_{H\text{-}H}$ = 6 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 44.90 (s, CH), 36.25 (d, $J_{C\text{-}P}$ = 18 Hz, CH_2), 36.21 (d, J = 12 Hz, CH), 35.00 (s, CH_2), 33.70 (s, CH), 30.28, 29.79, 28.17, 28.09, 27.58 (m, CH_2), 22.70, 21.65, 15.12 (s, CH_3), δ 11.10 (m, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ -24.7 (t, $^3J_{P\text{-}P}$ = 15 Hz), -128.3 (d, $^3J_{P\text{-}P}$ = 15 Hz) ppm.

5-(1R,2S,5R-menthyl)-1,5,9-triphosphanonane **(4.2)**

1R,2S,5R-menthyl phosphine (0.04 mol, 6.93 g), allyl diethyl phosphonate (0.08 mol, 14.25 g) and 0.5 g of AIBN were combined in a toluene solution (50 mL) and heated to 80 °C for 84 hours. After cooling to rtp. all solvents were removed *in vacuo*, with heating up to 100 °C. Reduction by dropwise addition at 0 °C, of equimolar quantities of $LiAlH_4$ and trimethylsilylchloride (0.0625 mol) yielded the desired primary terminal groups. The mixture was allowed to warm to room temperature with stirring for ca. 2 h. Once cooled in an ice bath, the slurry was hydrolysed by the dropwise addition of water (2.35 mL), 15% aqueous NaOH (2.35 mL), followed by another portion of water (7 mL). The organic layer was dried over $MgSO_4$, and all volatiles removed *in vacuo* to yield a clear, viscous oil. Yield = 5.3 g (41%).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 2.65 (dm, $^1J_{P-H}$ = 173 Hz, P-H, 4 H), δ 1.00-1.80 (m, 20 H), δ 0.88 (d, $^3J_{H-H}$ = 7 Hz, CH_3, 3 H), δ 0.81 (d, $^3J_{H-H}$ = 9 Hz, CH_3, 3 H), δ 0.68 (d, $^3J_{H-H}$ = 7 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 44.95 (s, CH), δ 36.13 (d, 21 Hz, CH), δ 35.19, δ 34.65 (s, CH_2), δ 33.72 (s, CH), δ 30.73, δ 30.07 (m, CH_2), δ 27.60 (d, J = 21 Hz, CH), δ 25.76, δ 23.10 (m, CH_2), δ 22.05, δ 21.51 (s, CH_3), δ 16.47 (m, CH_2), δ 15.54 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ -32.3 (s), δ -138.9 (s) ppm.

Fac-(η^5-Cyclopentadiene)4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane Iron (II) hexafluorophosphate **(4.3)**

One molar equivalent of 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane (85 mg from a toluene solution) was added to cyclopentadienyl iron (II) benzene (100 mg, 2.9 x 10^{-4} mol) in CH_2Cl_2 (20 mL). The yellow solution was stirred in direct sunlight for ca. 12 h at room temperature to yield an orange solution. The solution was filtered and the solvent removed under reduced pressure. Orange crystals of fac-(η^5-Cyclopentadiene) 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane Iron (II) hexafluorophosphate were obtained from MeOH at -35°C. Yield = 125 mg (77 %).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 5.41, δ 4.85, δ 4.55 (dd, $^1J_{P-H}$ = 340 Hz, P-H, 3 H), δ 4.50 (s, Cp, 5 H) δ 3.75 (dd, $^1J_{P-H}$ = 340 Hz, P-H,1H), δ 1.00-2.40 (m, 18 H), δ 0.93 (d, $^3J_{H-H}$ = 7 Hz, CH_3, 3 H), δ 0.90 (d, $^3J_{H-H}$ = 8 Hz, CH_3, 3 H), δ 0.80 (d, J = 9 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 76.59 (t, J = 41 Hz, Cp), δ 46.76 (s, CH), δ 42.73 (d, $^1J_{P-C}$ = 19 Hz, CH), δ 37.00, δ 34.00 (s, CH_2), δ 33.60 (d, $^2J_{P-C}$ = 14 Hz, CH), δ 30.00 (d, J = 137 Hz, CH_2), δ 29.40 (d, J = 5 Hz, CH),

δ 25.42 (d, J = 10 Hz, CH_2) δ 22.54 (s, CH_3), δ 22.01 (s, CH_3), δ16.30 (s, CH_3), δ 15.00 (d, J = 244 Hz, CH_2) ppm. ^{31}P {^1H} NMR ($CDCl_3$, 121.7 MHz): δ 132.9 (virt. t, $^2J_{P\text{-}P}$ = 27 Hz) δ 11.5 (dd, $^2J_{P\text{-}P}$ = 26 Hz, $^2J_{P\text{-}P}$ = 24 Hz), δ 10.1 (dd, $^2J_{P\text{-}P}$ = 27 Hz, $^2J_{P\text{-}P}$ = 29 Hz), δ –143.2 (h, $J_{P\text{-}F}$ = 708 Hz, PF_6) ppm. IR : 3395 br, 3233, 3180 ($\upsilon_{C\text{-}H}$), 2323 s, (ν_{PH}), 1634 s, 1420 s, 1295 vs, 824 cm^{-1}. M.S: ES-MS: ***m/e*** 413.1 amu ($[M]^{\cdot+}$) *Anal.* Calc. For $C_{19}H_{36}P_4F_6Fe$: C, 40.88; H, 6.50. Found: C, 40.11; H, 6.42.

Fac-(η^5-Cyclopentadiene) 4-(1R,2S,5R-menthyl)-1,4,7 triphosphanonane Iron (II) hexafluorophosphate **(4.4)**

One molar equivalent of 4-(1R,2S,5R-menthyl)-1,4,7-triphosphanonane (90 mg from a toluene solution) was added to cyclopentadienyl iron (II) benzene (100 mg, 2.9 x 10^{-4} mol) in CH_2Cl_2 (20 mL). The solution was stirred in direct sunlight for ca. 12 h at room temperature to yield an orange solution. The solution was filtered and the solvent removed *in vacuo*. Orange crystals of fac-(η^5-Cyclopentadiene) 4-(1R,2S,5R-menthyl)-1,4,7-triphosphanonane Iron (II) hexafluorophosphate were precipitated from MeOH at -35°C. Yield = 110 mg (65 %).

^1H NMR (d-DMSO, 393 K, 500 MHz): δ 6.08 (dd, $^1J_{P\text{-}H}$ = 355 Hz, P-H, 1 H), δ 5.35 (dd, $^1J_{P\text{-}H}$ = 352 Hz, P-H, 1H), δ 4.61 (s, Cp, 5 H), δ 4.59 (dd, $^1J_{P\text{-}H}$ = 348 Hz, P-H, 1 H), δ 3.70 (dd, $^1J_{P\text{-}H}$ = 352 Hz, P-H,1H), δ 1.10-2.30 (m, 22 H), δ 0.92 (d, $^3J_{H\text{-}H}$ = 8 Hz, CH_3, 3 H), δ 0.90 (d, $^3J_{H\text{-}H}$ = 7 Hz, CH_3, 3 H), δ 0.89 (d, $^3J_{H\text{-}H}$ = 8 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 79.31 (s, Cp), δ 52.97, δ 44.69 (m, CH), δ 39.59 (s, CH_2), δ 32.96 (m, CH), δ 32.02 (m, CH_2), δ 28.50 (d, J = 10 Hz, CH_2), δ 28.44 (s, CH), δ 24.77 (d, J = 5 Hz, CH_2), δ 22.24, δ 21.98 (s, CH_2), δ 21.89, δ 20.82, δ 15.85 (s, CH_3), δ 12.57 (s, CH_2) ppm. ^{31}P {^1H} NMR ($CDCl_3$, 121.7 MHz):

δ 41.7 (virt. t, $^2J_{P\text{-}P}$ = 65 Hz), δ -27.8 (dd, $^2J_{P\text{-}P}$ = 60 Hz, $^2J_{P\text{-}P}$ = 59 Hz), δ -31.0 (dd, $^2J_{P\text{-}P}$ = 58 Hz, $^2J_{P\text{-}P}$ = 60 Hz) δ –143 (h, $J_{P\text{-}F}$ = 712 Hz, PF_6) ppm. M.S: ES-MS: *m/e* 441.17 amu ($[M]^{\cdot+}$). IR : 3430 br, 2928, 2869 vs (υ_{CH}), 2311 s, (ν_{PH}), 1696 w, 1654 w, 850 cm^{-1}. *Anal.* Calc. For $C_{21}H_{40}P_4F_6Fe$: C, 43.02; H, 6.88. Found: C, 42.86; H, 6.73.

Fac- (η^5-Pentamethylcyclopentadiene)4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane Iron (II) hexafluorophosphate **(4.5)**

$[Cp^*Fe(CO)_2MeCN]PF_6$ (200 mg, 4.6 x 10^{-4} mol) was dissolved in acetonitrile and irradiated with ultraviolet radiation for 12 h, after which time the yellow solution had turned to deep-red, due to the intermediate species, $[Cp^*Fe(MeCN)_3]PF_6$. The solution was concentrated to a volume of ca. 50 mL, by removal of excess acetonitrile *in vacuo*. To this solution, one equivalent of **4.1** (130 mg) was added, and the mixture was stirred overnight. The subsequent red-brown solution was filtered, and the solvent removed under reduced pressure. The residue was washed with petrol (50 mL), followed by ether (20 mL). Tan crystals of **4.5** were grown from a concentrated methanol solution at -35°C. Yield = 180 mg (62 %).

^1H NMR ($CDCl_3$, 500 MHz): δ 4.83 (d, $^1J_{H\text{-}P}$ = 332 Hz, P-H, 1H), 4.59 (d, $^1J_{H\text{-}P}$ = 330 Hz, P-H, 1H), 4.47 (d, $^1J_{H\text{-}P}$ = 328 Hz, P-H, 1H), 2.30-1.70 (m, 18 H), 1.65 (s, Cp^*-CH_3, 15H), 0.95, 0.89 (m, CH_3, 6 H), 0.76 (d, $^3J_{H\text{-}H}$ = 12 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 86.78 (s, Cp^*), 44.60 (s, CH), 33.15 (m, CH), 32.00 (s, CH_2), 28.16 (s, CH_2), 24.00 (s, CH_2), 15.09 (s, CH_3), 14.26 (s, CH_3), 8.95 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 123.3 (virt. t, $^2J_{P\text{-}P}$ = 15 Hz), 21.9 (dd, $^2J_{P\text{-}P}$ = 14 Hz, $^2J_{P\text{-}P}$ = 15 Hz), 20.3 (dd, $^2J_{P\text{-}P}$ = 15 Hz, $^2J_{P\text{-}P}$ = 16 Hz), -143.8 (h, $J_{P\text{-}$

$_F$ = 708 Hz, PF_6) ppm. M.S: ES-MS: *m/e* 483.2161 amu (100% $[M]^{\cdot+}$). IR : 2958 w, 2871 s, 2360, 2341 s (ν_{PH}) 1950 br, 1559 w, 1456 s, 1386 s, 1026 br, 841 vs cm^{-1}.

Fac- (η^5-Pentamethylcyclopentadiene) 4-(1R,2S,5R-menthyl)-1,4,7-triphosphanonane Iron (II) hexafluorophosphate **(4.6)**

To a stirring solution of $[Cp^*Fe(MeCN)_3]PF_6$ (4.6×10^{-4} mol in 50 mL acetonitrile, prepared in a similar manner as described in **4.5**) was added a stoichiometric amount of **4.2** (135 mg). The solution was allowed to stir overnight, and the solvent was removed under reduced pressure. The residue was washed with petrol (50 mL), followed by ether (20 mL). Crystals of **4.6** were grown by diffusion of petrol into a concentrated methanol solution of **4.6**. Yield = 180 mg (60%).

^1H NMR ($CDCl_3$, 500 MHz): δ 5.10 (d, $^1J_{H-P}$ = 301 Hz, P-H 1H), 4.96 (d, $^1J_{H-P}$ = 309 Hz, P-H, 1H), 4.86 (d, $^1J_{H-P}$ = 282 Hz, P-H, 1H), 2.00-1.30 (m, 22 H), 1.49 (s, Cp^*-CH_3, 15H), 1.01 (d, $^3J_{H-H}$ = 6 Hz, CH_3, 3 H), 0.99 (d, $^3J_{H-H}$ = 7 Hz, CH_3, 3 H), 0.80 (d, $^3J_{H-H}$ = 7 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 91.84 (s, Cp^*), 54.00 (s, CH), 53.24 (m, CH), 33.00 (m, CH_2), 32.32 (s, CH), 26.19 (s, CH_2), 22.68 (s, CH_2), 21.77 (s, CH_2), 10.58 (s, CH_3), 9.78 (s, CH_3), 9.60 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 42.5 (virt. t, $^2J_{P-P}$ = 50 Hz), - 11.1 (dd, $^2J_{P-P}$ = 47 Hz, $^2J_{P-P}$ = 45 Hz), -15.4 (dd, $^2J_{P-P}$ = 45 Hz, $^2J_{P-P}$ = 46 Hz) -143.8 (h, J_{P-F} = 708 Hz, PF_6) ppm. M.S: ES-MS: *m/e* 511.2461 amu (100% $[M]^{\cdot+}$). IR : 2959 s, 2897 s, 2297 s (ν_{PH}), 1968 w, 1455 w, 1094 br, 839 vs. cm^{-1}.

Fac-(triscarbonyl) 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane molybdenum **(4.7)**

To a stirring solution of *fac*–(η^6-1,3,5-trimethylbenzene)molybdenum tricarbonyl (100 mg, 3.3 x 10^{-4} mol in 20 mL toluene) was added 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane (96 mg) with stirring. The yellow coloured solution was stirred under an atmosphere of nitrogen at room temperature for ca. 12 h, after which time a darker precipitate had formed. The yellow solution was filtered, and the solvent distilled off *in vacuo*. The residue was redissolved in petrol, and cooled to –35 °C, whereupon crystalline fac-(triscarbonyl) 4-(1R,2S,5R-menthyl)-1,4,7-triphosphaheptane molybdenum separated and isolated by filtration. Yield = 100 mg (68%).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 4.71 (d, $^1J_{H\text{-}P}$ = 370 Hz, P-H, 1H), δ 4.35 (d, $^1J_{H\text{-}P}$ = 377 Hz, P-H, 1H), δ 3.90 (d, $^1J_{H\text{-}P}$ = 381 Hz, P-H, 1H), δ 3.63 (d, $^1J_{P\text{-}H}$ = 380 Hz, P-H, 1 H), δ 1.00-2.20 (m 18 H), δ 0.88 (d, $^3J_{H\text{-}H}$ = 7 Hz, CH_3, 3 H), δ 0.79 (d, $^3J_{H\text{-}H}$ = 8 Hz, CH_3, 3 H), δ 0.71 (d, $^3J_{H\text{-}H}$ = 7 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 222.81 (s, CO), δ 46.14 (s, CH), δ 40.86 (d, $^2J_{P\text{-}C}$ = 13 Hz, CH), δ 37.71, (s, CH_2), δ 34.29 (m, CH_2), δ 33.55 (d, $^2J_{P\text{-}C}$ = 13 Hz, CH), δ 28.70 (d, J = 5 Hz, CH_2), δ 27.06 (s, CH), δ 26.11 (m, CH_2), δ 24.75 (d, 10 Hz, CH_2), δ 21.23, δ 20.95 (s, CH_3), δ 18.00 (m, CH_2), δ 15.64 (s, CH_3), δ 13.56 (m, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 96.2 (s) δ -50.1 (d, $^2J_{P\text{-}P}$ = 20 Hz), δ -51.6 (d, $^2J_{P\text{-}P}$ = 23 Hz) ppm. M.S: ES-MS: *m/e* 472.29 amu ($[M]^{\cdot+}$).IR :2948, 2871 (υ_{CH}) 2336, 2359 cm^{-1} s, (ν_{PH}), 1862, 1949 cm^{-1} s, (ν_{CO}). *Anal.* Calc. For $C_{17}H_{31}P_3O_3Mo$: C, 43.23; H, 6.62. Found: C,43.56; H,6.53.

Fac-(triscarbonyl) 4-(1R,2S,5R-menthy)l-1,4,7-triphosphanonane molybdenum **(4.8)**.

To a stirring solution of fac–(η^6-1,3,5-trimethylbenzene)molybdenum tricarbonyl (100 mg, 3.3 x 10^{-4} mol in 20 mL toluene)was added **4.2** (110 mg). After stirring for ca. 12 h, a dark, insoluble precipitate had formed, which was separated from the solution by filtration. **4.8** was isolated from a concentrated toluene solution at -35 °C as yellow crystals. Yield = 110 mg (64%).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 4.25 (br d, $^1J_{H\text{-}P}$ = 340 Hz, P-H, 1H), 4.01 (br d, $^1J_{H\text{-}P}$ = 345 Hz, P-H, 1H), 3.60 (br d, $^1J_{H\text{-}P}$ = 343 Hz, P-H, 1H), 3.42 (br d, $^1J_{P\text{-}H}$ = 338 Hz, P-H, 1H), 1.38 (m), 1.29 (m), 1.28 (m), 0.86 (d, $^3J_{H\text{-}H}$ = 10 Hz, CH_3, 3 H), 0.71 (d, $^3J_{H\text{-}H}$ = 12 Hz, CH_3, 3 H), 0.15 (d, $^3J_{H\text{-}H}$ = 11 Hz, CH_3, 3 H) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 221.60 (s, CO), 43.85 (d, J = 19 Hz, CH_2), 32.90 (m, CH_2), 27.27, (m, CH_2), 23.61 (m, CH_2), 21.76 (m, CH), 20.30 (s, CH_3), 19.10 (s, CH_3), 14.37 (m, CH_2) ppm. ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 9.27 (virt. t, $^2J_{P\text{-}P}$ = 30 Hz), -73.8 (dd, $^2J_{P\text{-}P}$ = 26 Hz, $^2J_{P\text{-}P}$ = 24 Hz), -75.4 (dd, $^2J_{P\text{-}P}$ = 25 Hz, $^2J_{P\text{-}P}$ = 26 Hz) ppm. M.S: ES-MS: *m/e* 497.0945 amu (100%, $[M]^{\cdot+}$). IR: 2963 vs (υ_{CH}),2359, 2341 br (ν_{PH}), 1949 , 1880 s, (ν_{CO}), 1724 w, 1432 w, 1077 vs cm^{-1}.

4.9 References

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Appendix

Appendix-i

Crystal data and structure refinement for $Cr(CO)_3(SiMe_3PC_2H_4)_3$

Table 1.

Empirical formula	C18 H39 Cr O3 P3 Si3
Formula weight	532.67
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.875(2) A alpha = 90 deg. b = 14.883(3) A beta = 96.86(3) deg. c = 17.718(4) A gamma = 90 deg.
Volume	2847.2(10) A^3
Z, Calculated density	4, 1.243 Mg/m^3
Absorption coefficient	0.712 mm^-1
F(000)	1128
Crystal size	0.30 x 0.08 x 0.06 mm
Theta range for data collection	3.12 to 27.00 deg.
Limiting indices	-13<=h<=13, -19<=k<=19, -22<=l<=22
Reflections collected / unique	11429 / 6157 [R(int) = 0.0354]
Completeness to theta =	27.00 99.0 %
Absorption correction	Multi scan
Max. and min. transmission	sortav 0.923 and 0.756
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6157 / 16 / 273
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0788
R indices (all data)	R1 = 0.0596, wR2 = 0.0857
Largest diff. peak and hole	0.414 and -0.371 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for asPGE15.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cr(1)	6131(1)	3002(1)	2350(1)	24(1)
P(1)	7061(1)	3968(1)	1504(1)	27(1)
Si(1)	7550(1)	3488(1)	364(1)	32(1)
O(1)	8651(2)	2175(1)	2734(1)	41(1)
C(1)	7683(2)	2509(2)	2595(1)	29(1)
P(2)	6460(1)	4045(1)	3370(1)	29(1)
Si(2)	7864(1)	3815(1)	4401(1)	33(1)
O(2)	5145(2)	1706(1)	3430(1)	50(1)
C(2)	5512(2)	2223(2)	3018(1)	33(1)
P(3)	4143(1)	3615(1)	1973(1)	28(1)
Si(3)	2376(1)	3039(1)	2320(1)	48(1)
O(3)	5547(2)	1551(1)	1185(1)	52(1)
C(3)	5785(2)	2135(2)	1617(1)	34(1)
C(4)	6927(2)	5197(2)	1341(2)	40(1)
C(5)	8137(2)	4900(2)	1766(2)	41(1)
C(6)	8655(2)	4273(2)	-25(1)	44(1)
C(7)	8265(3)	2352(2)	489(1)	47(1)
C(8)	6049(2)	3445(2)	-266(1)	44(1)
C(9)	6269(3)	5273(2)	3371(2)	57(1)
C(10)	5310(3)	4779(2)	3731(2)	56(1)

C(11)	7659(3)	2645(2)	4723(1)	47(1)
C(12)	7617(3)	4615(2)	5180(1)	51(1)
C(13)	9420(2)	3988(2)	4093(2)	51(1)
C(14)	3697(2)	4790(2)	1740(1)	37(1)
C(15)	3641(2)	4181(2)	1064(1)	37(1)
C(17)	2317(3)	1829(2)	2075(2)	79(1)
C(18)	2452(3)	3202(3)	3359(2)	78(1)
C(16A)	1023(6)	3472(8)	1691(6)	52(2)
C(16)	999(6)	3775(7)	1967(7)	49(3)

Table 3. Bond lengths [A] and angles [deg] for asPGE15.

Cr(1)-C(3)	1.837(2)
Cr(1)-C(2)	1.841(2)
Cr(1)-C(1)	1.844(2)
Cr(1)-P(3)	2.3677(8)
Cr(1)-P(2)	2.3779(8)
Cr(1)-P(1)	2.3868(8)
P(1)-C(5)	1.838(2)
P(1)-C(4)	1.855(2)
P(1)-Si(1)	2.2648(10)
Si(1)-C(7)	1.863(3)
Si(1)-C(8)	1.865(3)
Si(1)-C(6)	1.865(3)
O(1)-C(1)	1.163(3)
P(2)-C(10)	1.833(3)
P(2)-C(9)	1.840(3)
P(2)-Si(2)	2.2621(11)
Si(2)-C(11)	1.854(3)
Si(2)-C(13)	1.858(3)
Si(2)-C(12)	1.865(3)
O(2)-C(2)	1.164(3)
P(3)-C(15)	1.842(2)
P(3)-C(14)	1.849(2)
P(3)-Si(3)	2.2564(10)
Si(3)-C(18)	1.849(3)
Si(3)-C(16A)	1.852(6)
Si(3)-C(17)	1.852(4)

Si(3)-C(16)	1.900(7)
O(3)-C(3)	1.167(3)
C(4)-C(5)	1.503(3)
C(9)-C(10)	1.482(4)
C(14)-C(15)	1.498(3)

C(3)-Cr(1)-C(2)	87.30(10)
C(3)-Cr(1)-C(1)	89.54(10)
C(2)-Cr(1)-C(1)	89.56(10)
C(3)-Cr(1)-P(3)	88.20(8)
C(2)-Cr(1)-P(3)	91.87(8)
C(1)-Cr(1)-P(3)	177.26(7)
C(3)-Cr(1)-P(2)	174.55(8)
C(2)-Cr(1)-P(2)	87.40(8)
C(1)-Cr(1)-P(2)	91.69(7)
P(3)-Cr(1)-P(2)	90.70(3)
C(3)-Cr(1)-P(1)	92.64(8)
C(2)-Cr(1)-P(1)	176.29(8)
C(1)-Cr(1)-P(1)	86.73(7)
P(3)-Cr(1)-P(1)	91.83(3)
P(2)-Cr(1)-P(1)	92.73(3)
C(5)-P(1)-C(4)	48.02(11)
C(5)-P(1)-Si(1)	104.63(9)
C(4)-P(1)-Si(1)	101.21(9)
C(5)-P(1)-Cr(1)	126.94(9)
C(4)-P(1)-Cr(1)	131.33(9)
Si(1)-P(1)-Cr(1)	122.16(3)
C(7)-Si(1)-C(8)	111.23(13)
C(7)-Si(1)-C(6)	109.54(12)
C(8)-Si(1)-C(6)	110.91(12)

C(7)-Si(1)-P(1)	108.63(8)
C(8)-Si(1)-P(1)	105.21(9)
C(6)-Si(1)-P(1)	111.24(10)
O(1)-C(1)-Cr(1)	177.7(2)
C(10)-P(2)-C(9)	47.60(14)
C(10)-P(2)-Si(2)	103.37(9)
C(9)-P(2)-Si(2)	102.43(9)
C(10)-P(2)-Cr(1)	127.42(9)
C(9)-P(2)-Cr(1)	129.95(9)
Si(2)-P(2)-Cr(1)	122.77(3)
C(11)-Si(2)-C(13)	111.55(13)
C(11)-Si(2)-C(12)	109.83(13)
C(13)-Si(2)-C(12)	110.25(14)
C(11)-Si(2)-P(2)	107.21(9)
C(13)-Si(2)-P(2)	106.98(9)
C(12)-Si(2)-P(2)	110.95(9)
O(2)-C(2)-Cr(1)	177.5(2)
C(15)-P(3)-C(14)	47.90(10)
C(15)-P(3)-Si(3)	103.84(9)
C(14)-P(3)-Si(3)	102.19(9)
C(15)-P(3)-Cr(1)	126.03(9)
C(14)-P(3)-Cr(1)	129.34(9)
Si(3)-P(3)-Cr(1)	123.74(4)
C(18)-Si(3)-C(16A)	119.4(4)
C(18)-Si(3)-C(17)	110.94(17)
C(16A)-Si(3)-C(17)	101.2(4)
C(18)-Si(3)-C(16)	101.1(4)
C(16A)-Si(3)-C(16)	20.4(2)
C(17)-Si(3)-C(16)	118.7(4)
C(18)-Si(3)-P(3)	106.47(12)

C(16A)-Si(3)-P(3)	110.2(2)
C(17)-Si(3)-P(3)	108.18(12)
C(16)-Si(3)-P(3)	110.8(2)
O(3)-C(3)-Cr(1)	176.0(2)
C(5)-C(4)-P(1)	65.40(13)
C(4)-C(5)-P(1)	66.59(13)
C(10)-C(9)-P(2)	65.96(15)
C(9)-C(10)-P(2)	66.44(15)
C(15)-C(14)-P(3)	65.80(13)
C(14)-C(15)-P(3)	66.29(12)

Appendix-ii

Crystal data and structure refinement for $[Cp^*Fe(DPPB)(HPC_2H_4)]PF_6$

Table 1.

Empirical formula	C42.50 H45 Cl F6 Fe P4	
Formula weight	884.97	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0950(2) Å	a= 75.5430(10)°.
	b = 10.4720(2) Å	b= 83.9150(10)°.
	c = 19.6770(5) Å	g = 85.2320(10)°.
Volume	1999.46(7) $Å^3$	
Z	2	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	914	
Crystal size	0.30 x 0.15 x 0.11 mm^3	
Theta range for data collection	2.50 to 27.48°.	
Index ranges	-12<=h<=13, -13<=k<=13, -25<=l<=25	
Reflections collected	14646	
Independent reflections	9111 [R(int) = 0.0471]	
Completeness to theta = 27.48°	99.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9306 and 0.8258	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9111 / 18 / 543	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1209	
R indices (all data)	R1 = 0.0960, wR2 = 0.1371	
Largest diff. peak and hole	0.587 and -0.632 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for pge0806. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4564(3)	1114(3)	8393(2)	22(1)
C(2)	5203(3)	1516(3)	8919(2)	24(1)
C(3)	4399(3)	2566(3)	9114(2)	23(1)
C(4)	3250(3)	2809(3)	8720(2)	22(1)
C(5)	3340(3)	1897(3)	8288(2)	21(1)
C(6)	5026(3)	-45(3)	8098(2)	32(1)
C(7)	6389(3)	818(4)	9279(2)	34(1)
C(8)	4586(4)	3125(4)	9731(2)	32(1)
C(9)	2014(3)	3632(4)	8874(2)	31(1)
C(10)	2224(3)	1631(3)	7905(2)	27(1)
C(11)	5144(4)	2831(3)	6301(2)	28(1)
C(12)	4386(5)	1776(4)	6315(2)	48(1)
C(13)	4843(6)	846(4)	5928(2)	60(1)
C(14)	6035(6)	996(5)	5511(2)	61(2)
C(15)	6780(5)	2048(5)	5482(2)	53(1)
C(16)	6360(4)	2947(4)	5883(2)	40(1)
C(17)	2926(3)	4530(3)	6603(2)	27(1)
C(18)	2595(4)	4546(5)	5932(2)	45(1)
C(19)	1398(4)	5170(6)	5697(2)	64(2)
C(20)	536(4)	5776(5)	6126(3)	59(1)
C(21)	840(4)	5752(4)	6793(3)	45(1)
C(22)	2026(3)	5118(4)	7034(2)	31(1)
C(23)	5537(3)	5378(3)	6542(2)	20(1)
C(24)	5738(4)	5999(4)	5830(2)	30(1)
C(25)	6539(4)	7058(4)	5608(2)	38(1)

C(26)	7127(4)	7527(4)	6092(2)	33(1)
C(27)	6883(3)	6963(3)	6807(2)	26(1)
C(28)	6081(3)	5893(3)	7036(2)	19(1)
C(29)	6830(3)	5480(3)	8466(2)	21(1)
C(30)	7075(3)	6770(3)	8477(2)	24(1)
C(31)	8122(3)	7008(4)	8824(2)	29(1)
C(32)	8915(3)	5961(4)	9172(2)	33(1)
C(33)	8656(3)	4684(4)	9185(2)	28(1)
C(34)	7617(3)	4443(3)	8832(2)	24(1)
C(35)	4196(3)	6371(3)	8133(2)	20(1)
C(36)	3496(3)	7186(3)	7591(2)	26(1)
C(37)	2411(4)	7999(4)	7749(2)	34(1)
C(38)	2014(3)	8038(4)	8440(2)	33(1)
C(39)	2728(3)	7271(4)	8975(2)	31(1)
C(40)	3799(3)	6449(3)	8822(2)	25(1)
C(41)	8564(4)	3265(4)	7265(2)	47(1)
C(42)	8681(4)	2116(4)	7891(2)	43(1)
P(1)	4579(1)	3905(1)	6897(1)	20(1)
P(2)	5521(1)	5147(1)	7959(1)	18(1)
P(3)	7003(1)	2493(1)	7598(1)	28(1)
Fe(1)	5008(1)	3117(1)	8010(1)	18(1)
P(4)	0	0	0	23(1)
F(1)	-416(2)	-344(3)	-690(1)	58(1)
F(2)	542(2)	-1491(2)	283(2)	56(1)
F(3)	1443(2)	331(2)	-378(1)	47(1)
P(5)	10394(3)	10363(3)	5945(2)	47(1)
F(4)	9407(5)	10005(6)	5448(3)	81(2)
F(5)	11118(10)	8956(6)	6063(5)	180(5)
F(6)	9386(10)	9872(12)	6598(4)	240(10)
F(7)	11428(6)	10833(8)	5285(3)	119(3)
F(8)	9711(8)	11799(6)	5820(5)	171(6)
F(9)	11371(7)	10716(8)	6436(5)	96(3)
C(43)	9898(15)	9968(14)	6079(5)	91(6)
Cl(1)	10831(5)	11351(5)	6040(2)	111(2)
Cl(2)	9175(2)	9393(3)	6938(2)	54(1)

Table 3. Bond lengths [Å] and angles [°] for pge0806.

C(1)-C(5)	1.429(4)
C(1)-C(2)	1.439(5)
C(1)-C(6)	1.493(5)
C(1)-Fe(1)	2.113(3)
C(2)-C(3)	1.419(5)
C(2)-C(7)	1.498(5)
C(2)-Fe(1)	2.138(3)
C(3)-C(4)	1.434(5)
C(3)-C(8)	1.506(5)
C(3)-Fe(1)	2.141(3)
C(4)-C(5)	1.421(5)
C(4)-C(9)	1.505(4)
C(4)-Fe(1)	2.134(3)
C(5)-C(10)	1.501(4)
C(5)-Fe(1)	2.140(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.389(5)
C(11)-C(16)	1.400(5)
C(11)-P(1)	1.836(3)

C(12)-C(13)	1.401(6)
C(12)-H(12)	0.9500
C(13)-C(14)	1.379(7)
C(13)-H(13)	0.9500
C(14)-C(15)	1.371(7)
C(14)-H(14)	0.9500
C(15)-C(16)	1.387(5)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-C(22)	1.389(5)
C(17)-C(18)	1.392(5)
C(17)-P(1)	1.839(3)
C(18)-C(19)	1.391(6)
C(18)-H(18)	0.9500
C(19)-C(20)	1.376(7)
C(19)-H(19)	0.9500
C(20)-C(21)	1.373(6)
C(20)-H(20)	0.9500
C(21)-C(22)	1.389(5)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.391(5)
C(23)-C(28)	1.401(4)
C(23)-P(1)	1.836(3)
C(24)-C(25)	1.381(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.380(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.386(5)
C(26)-H(26)	0.9500
C(27)-C(28)	1.391(4)
C(27)-H(27)	0.9500
C(28)-P(2)	1.837(3)
C(29)-C(34)	1.385(5)
C(29)-C(30)	1.400(5)

C(29)-P(2)	1.842(3)
C(30)-C(31)	1.389(5)
C(30)-H(30)	0.9500
C(31)-C(32)	1.381(5)
C(31)-H(31)	0.9500
C(32)-C(33)	1.378(5)
C(32)-H(32)	0.9500
C(33)-C(34)	1.390(5)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(40)	1.393(4)
C(35)-C(36)	1.404(5)
C(35)-P(2)	1.840(3)
C(36)-C(37)	1.388(5)
C(36)-H(36)	0.9500
C(37)-C(38)	1.385(5)
C(37)-H(37)	0.9500
C(38)-C(39)	1.384(5)
C(38)-H(38)	0.9500
C(39)-C(40)	1.381(5)
C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
C(41)-C(42)	1.499(6)
C(41)-P(3)	1.815(4)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(42)-P(3)	1.828(4)
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
P(1)-Fe(1)	2.2147(9)
P(2)-Fe(1)	2.2051(9)
P(3)-Fe(1)	2.2003(10)
P(3)-H(3)	1.0000
P(4)-F(3)#1	1.5874(19)
P(4)-F(3)	1.5874(19)

P(4)-F(2)#1	1.593(2)
P(4)-F(2)	1.593(2)
P(4)-F(1)#1	1.594(2)
P(4)-F(1)	1.594(2)
P(5)-F(6)	1.558(6)
P(5)-F(5)	1.564(7)
P(5)-F(8)	1.574(6)
P(5)-F(9)	1.575(6)
P(5)-F(7)	1.581(5)
P(5)-F(4)	1.595(5)
C(43)-Cl(2)	1.749(9)
C(43)-Cl(1)	1.774(8)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900

C(5)-C(1)-C(2)	107.7(3)
C(5)-C(1)-C(6)	127.0(3)
C(2)-C(1)-C(6)	124.7(3)
C(5)-C(1)-Fe(1)	71.41(18)
C(2)-C(1)-Fe(1)	71.19(18)
C(6)-C(1)-Fe(1)	129.5(2)
C(3)-C(2)-C(1)	107.9(3)
C(3)-C(2)-C(7)	125.5(3)
C(1)-C(2)-C(7)	126.0(3)
C(3)-C(2)-Fe(1)	70.75(18)
C(1)-C(2)-Fe(1)	69.26(18)
C(7)-C(2)-Fe(1)	132.6(2)
C(2)-C(3)-C(4)	108.1(3)
C(2)-C(3)-C(8)	125.0(3)
C(4)-C(3)-C(8)	125.9(3)
C(2)-C(3)-Fe(1)	70.54(18)
C(4)-C(3)-Fe(1)	70.12(17)
C(8)-C(3)-Fe(1)	134.2(2)
C(5)-C(4)-C(3)	108.1(3)
C(5)-C(4)-C(9)	125.1(3)

C(3)-C(4)-C(9)	125.0(3)
C(5)-C(4)-Fe(1)	70.83(17)
C(3)-C(4)-Fe(1)	70.69(17)
C(9)-C(4)-Fe(1)	135.8(2)
C(4)-C(5)-C(1)	108.1(3)
C(4)-C(5)-C(10)	125.0(3)
C(1)-C(5)-C(10)	125.8(3)
C(4)-C(5)-Fe(1)	70.34(17)
C(1)-C(5)-Fe(1)	69.33(17)
C(10)-C(5)-Fe(1)	135.0(2)
C(12)-C(11)-C(16)	118.1(3)
C(12)-C(11)-P(1)	118.2(3)
C(16)-C(11)-P(1)	123.3(3)
C(11)-C(12)-C(13)	120.6(4)
C(11)-C(12)-H(12)	119.7
C(13)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	120.0(4)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	120.0(4)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.4(4)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-C(11)	120.8(4)
C(15)-C(16)-H(16)	119.6
C(11)-C(16)-H(16)	119.6
C(22)-C(17)-C(18)	118.6(3)
C(22)-C(17)-P(1)	119.3(3)
C(18)-C(17)-P(1)	121.8(3)
C(19)-C(18)-C(17)	120.2(4)
C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(20)-C(19)-C(18)	120.3(4)

C(20)-C(19)-H(19) 119.9
C(18)-C(19)-H(19) 119.9
C(21)-C(20)-C(19) 120.2(4)
C(21)-C(20)-H(20) 119.9
C(19)-C(20)-H(20) 119.9
C(20)-C(21)-C(22) 119.9(4)
C(20)-C(21)-H(21) 120.1
C(22)-C(21)-H(21) 120.1
C(17)-C(22)-C(21) 120.8(4)
C(17)-C(22)-H(22) 119.6
C(21)-C(22)-H(22) 119.6
C(24)-C(23)-C(28) 119.3(3)
C(24)-C(23)-P(1) 124.4(3)
C(28)-C(23)-P(1) 116.3(2)
C(25)-C(24)-C(23) 120.4(3)
C(25)-C(24)-H(24) 119.8
C(23)-C(24)-H(24) 119.8
C(26)-C(25)-C(24) 120.3(3)
C(26)-C(25)-H(25) 119.9
C(24)-C(25)-H(25) 119.9
C(25)-C(26)-C(27) 120.1(3)
C(25)-C(26)-H(26) 119.9
C(27)-C(26)-H(26) 119.9
C(26)-C(27)-C(28) 120.0(3)
C(26)-C(27)-H(27) 120.0
C(28)-C(27)-H(27) 120.0
C(27)-C(28)-C(23) 119.7(3)
C(27)-C(28)-P(2) 125.3(3)
C(23)-C(28)-P(2) 114.7(2)
C(34)-C(29)-C(30) 118.7(3)
C(34)-C(29)-P(2) 119.9(3)
C(30)-C(29)-P(2) 121.4(2)
C(31)-C(30)-C(29) 120.6(3)
C(31)-C(30)-H(30) 119.7
C(29)-C(30)-H(30) 119.7

C(32)-C(31)-C(30) 119.7(3)
C(32)-C(31)-H(31) 120.1
C(30)-C(31)-H(31) 120.1
C(33)-C(32)-C(31) 120.3(3)
C(33)-C(32)-H(32) 119.9
C(31)-C(32)-H(32) 119.9
C(32)-C(33)-C(34) 120.2(3)
C(32)-C(33)-H(33) 119.9
C(34)-C(33)-H(33) 119.9
C(29)-C(34)-C(33) 120.5(3)
C(29)-C(34)-H(34) 119.7
C(33)-C(34)-H(34) 119.7
C(40)-C(35)-C(36) 117.9(3)
C(40)-C(35)-P(2) 120.2(3)
C(36)-C(35)-P(2) 1 21.8(2)
C(37)-C(36)-C(35) 120.2(3)
C(37)-C(36)-H(36) 119.9
C(35)-C(36)-H(36) 119.9
C(38)-C(37)-C(36) 120.8(4)
C(38)-C(37)-H(37) 119.6
C(36)-C(37)-H(37) 119.6
C(39)-C(38)-C(37) 119.2(3)
C(39)-C(38)-H(38) 120.4
C(37)-C(38)-H(38) 120.4
C(40)-C(39)-C(38) 120.2(3)
C(40)-C(39)-H(39) 119.9
C(38)-C(39)-H(39) 119.9
C(39)-C(40)-C(35) 121.5(3)
C(39)-C(40)-H(40) 119.3
C(35)-C(40)-H(40) 119.3
C(42)-C(41)-P(3) 6 6.2(2)
C(42)-C(41)-H(41A) 117.1
P(3)-C(41)-H(41A) 117.1
C(42)-C(41)-H(41B) 117.1
P(3)-C(41)-H(41B) 117.1

C(41)-C(42)-P(3) 65.2(2)
C(41)-C(42)-H(42A) 117.2
P(3)-C(42)-H(42A) 117.2
C(41)-C(42)-H(42B) 117.2
P(3)-C(42)-H(42B) 117.2
C(11)-P(1)-C(23) 103.74(16)
C(11)-P(1)-C(17) 101.63(16)
C(23)-P(1)-C(17) 100.82(15)
C(11)-P(1)-Fe(1) 115.75(11)
C(23)-P(1)-Fe(1) 107.38(11)
C(17)-P(1)-Fe(1) 124.85(11)
C(28)-P(2)-C(35) 100.95(14)
C(28)-P(2)-C(29) 104.50(14)
C(35)-P(2)-C(29) 100.57(14)
C(28)-P(2)-Fe(1) 106.95(11)
C(35)-P(2)-Fe(1) 119.52(10)
C(29)-P(2)-Fe(1) 121.69(11)
C(41)-P(3)-C(42) 48.61(19)
C(41)-P(3)-Fe(1) 136.43(15)
C(42)-P(3)-Fe(1) 138.34(15)
C(41)-P(3)-H(3) 107.2
C(42)-P(3)-H(3) 107.2
Fe(1)-P(3)-H(3) 107.2
C(1)-Fe(1)-C(4) 65.80(12)
C(1)-Fe(1)-C(2) 39.55(13)
C(4)-Fe(1)-C(2) 65.42(12)
C(1)-Fe(1)-C(5) 39.26(12)
C(4)-Fe(1)-C(5) 38.83(12)
C(2)-Fe(1)-C(5) 65.54(12)
C(1)-Fe(1)-C(3) 65.79(13)
C(4)-Fe(1)-C(3) 39.19(12)
C(2)-Fe(1)-C(3) 38.72(13)
C(5)-Fe(1)-C(3) 65.34(12)
C(1)-Fe(1)-P(3) 89.60(9)
C(4)-Fe(1)-P(3) 152.56(9)

C(2)-Fe(1)-P(3)	88.01(9)
C(5)-Fe(1)-P(3)	124.83(9)
C(3)-Fe(1)-P(3)	120.75(10)
C(1)-Fe(1)-P(2)	162.26(10)
C(4)-Fe(1)-P(2)	1 05.14(9)
C(2)-Fe(1)-P(2)	123.35(10)
C(5)-Fe(1)-P(2)	140.19(9)
C(3)-Fe(1)-P(2)	97.36(9)
P(3)-Fe(1)-P(2)	94.96(4)
C(1)-Fe(1)-P(1)	112.24(10)
C(4)-Fe(1)-P(1)	113.13(9)
C(2)-Fe(1)-P(1)	151.34(10)
C(5)-Fe(1)-P(1)	95.02(9)
C(3)-Fe(1)-P(1)	151.96(9)
P(3)-Fe(1)-P(1)	86.62(4)
P(2)-Fe(1)-P(1)	85.18(3)
F(3)#1-P(4)-F(3)	180.0(3)
F(3)#1-P(4)-F(2)#	188.88(12)
F(3)-P(4)-F(2)#1	91.12(12)
F(3)#1-P(4)-F(2)	91.12(12)
F(3)-P(4)-F(2)	88.88(12)
F(2)#1-P(4)-F(2)	180.0(3)
F(3)#1-P(4)-F(1)#	190.21(13)
F(3)-P(4)-F(1)#1	89.79(13)
F(2)#1-P(4)-F(1)#1	90.19(14)
F(2)-P(4)-F(1)#1	89.81(14)
F(3)#1-P(4)-F(1)	89.79(13)
F(3)-P(4)-F(1)	90.21(13)
F(2)#1-P(4)-F(1)	89.81(14)
F(2)-P(4)-F(1)	90.19(14)
F(1)#1-P(4)-F(1)	180.00(17)
F(6)-P(5)-F(5)	90.5(5)
F(6)-P(5)-F(8)	90.9(5)
F(5)-P(5)-F(8)	178.1(5)
F(6)-P(5)-F(9)	90.1(5)

F(5)-P(5)-F(9)	88.4(4)
F(8)-P(5)-F(9)	90.4(4)
F(6)-P(5)-F(7)	178.9(5)
F(5)-P(5)-F(7)	88.4(4)
F(8)-P(5)-F(7)	90.2(4)
F(9)-P(5)-F(7)	90.0(4)
F(6)-P(5)-F(4)	90.0(4)
F(5)-P(5)-F(4)	91.5(4)
F(8)-P(5)-F(4)	89.7(3)
F(9)-P(5)-F(4)	179.9(5)
F(7)-P(5)-F(4)	89.9(3)
Cl(2)-C(43)-Cl(1)	109.3(5)
Cl(2)-C(43)-H(43A)	109.8
Cl(1)-C(43)-H(43A)	109.8
Cl(2)-C(43)-H(43B)	109.8
Cl(1)-C(43)-H(43B)	109.8

Appendix-iii

Crystal data and structure refinement for[$Mn(CO)_3$(trans CHXN)(PhP(allyl)$_2$)]PF_6
Table 1.

Empirical formula	C22 H31 Cl2 F6 Mn N2 O3 P2	
Formula weight	673.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.2290(2) Å	a= 72.1450(10)°.
	b = 14.4430(3) Å	b= 73.3360(10)°.
	c = 16.8230(4) Å	g = 72.4180(10)°.
Volume	3064.40(11) $Å^3$	
Z	4	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	0.772 mm^{-1}	
F(000)	1376	
Crystal size	0.40 x 0.30 x 0.15 mm^3	
Theta range for data collection	2.23 to 27.55°.	
Index ranges	-18<=h<=18, -18<=k<=18, -21<=l<=20	
Reflections collected	21717	
Independent reflections	13925 [R(int) = 0.0415]	
Completeness to theta = 27.55°	98.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8930 and 0.7476	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13925 / 135 / 761	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1680	
R indices (all data)	R1 = 0.1156, wR2 = 0.1930	
Extinction coefficient	0.0056(8)	
Largest diff. peak and hole	1.260 and -0.621 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pge0907. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3364(3)	9111(3)	1298(3)	32(1)
C(2)	2382(3)	8912(3)	1274(3)	31(1)
C(3)	1462(3)	9551(3)	1738(3)	39(1)
C(4)	1546(3)	9476(3)	2651(3)	46(1)
C(5)	2540(3)	9696(3)	2641(3)	42(1)
C(6)	3439(3)	9007(3)	2210(3)	37(1)
C(7)	3556(3)	5823(3)	1385(3)	37(1)
C(8)	5185(3)	6441(3)	656(3)	35(1)
C(9)	4327(3)	6582(3)	2145(3)	37(1)
C(10)	2168(3)	7761(3)	-228(3)	33(1)
C(11)	1737(3)	8707(3)	-665(3)	44(1)
C(12)	699(4)	9006(4)	-608(4)	56(1)
C(13)	88(4)	8364(4)	-131(4)	59(1)
C(14)	512(3)	7427(4)	305(3)	54(1)
C(15)	1538(3)	7123(3)	266(3)	40(1)
C(16)	4094(3)	8260(3)	-1100(3)	36(1)
C(17)	5227(3)	7961(4)	-1235(3)	40(1)
C(18)	5784(4)	8486(4)	-1169(3)	50(1)
C(19)	3897(3)	6227(3)	-657(3)	40(1)
C(20)	3639(4)	6404(4)	-1493(3)	50(1)
C(21)	4290(5)	6363(5)	-2214(4)	71(2)
C(22)	7642(3)	5943(3)	3602(3)	35(1)
C(23)	8763(3)	5652(3)	3593(3)	41(1)
C(24)	9416(3)	5633(4)	2708(3)	50(1)
C(25)	9139(4)	4931(4)	2340(4)	63(2)
C(26)	8028(4)	5240(4)	2301(3)	54(1)
C(27)	7356(3)	5297(3)	3179(3)	44(1)
C(28)	7351(4)	9051(4)	3177(3)	45(1)
C(29)	9014(4)	8058(4)	2572(3)	47(1)
C(30)	8783(4)	8423(4)	3968(3)	52(1)

C(31)	5813(3)	7328(3)	4943(3)	34(1)
C(32)	5619(3)	6419(3)	5474(3)	39(1)
C(33)	4813(4)	6094(4)	5424(3)	49(1)
C(34)	4211(4)	6654(5)	4854(4)	58(1)
C(35)	4391(4)	7565(4)	4335(3)	54(1)
C(36)	5189(3)	7894(4)	4369(3)	43(1)
C(37)	6366(4)	8986(3)	5137(3)	43(1)
C(38)	5578(4)	9007(4)	5942(3)	45(1)
C(39)	5618(5)	9338(4)	6570(4)	61(1)
C(40)	7346(3)	6965(4)	5884(3)	44(1)
C(41)	8291(10)	7133(12)	6001(15)	60(5)
C(42)	8276(10)	7620(11)	6557(8)	91(5)
C(41A)	8102(13)	7426(14)	6003(18)	43(5)
C(42A)	8978(13)	6818(13)	6114(11)	83(6)
F(1)	2503(3)	5602(3)	3288(2)	84(1)
F(2)	1071(3)	6797(3)	3284(3)	105(2)
F(3)	1110(2)	5350(2)	4314(2)	62(1)
F(4)	993(3)	6764(3)	4627(3)	104(2)
F(5)	2437(2)	5576(2)	4630(2)	70(1)
F(6)	2392(2)	7034(2)	3609(2)	52(1)
F(7)	6392(2)	7713(2)	1055(3)	88(1)
F(8)	5950(2)	9400(2)	610(2)	48(1)
F(9)	7442(3)	8502(3)	-35(2)	71(1)
F(10)	7440(2)	9459(2)	766(3)	76(1)
F(11)	7868(2)	7779(2)	1238(2)	46(1)
F(12)	6395(2)	8665(3)	1869(2)	86(1)
Mn(1)	3911(1)	6993(1)	1125(1)	29(1)
Mn(2)	8104(1)	7834(1)	3583(1)	37(1)
N(1)	4205(2)	8406(2)	876(2)	32(1)
N(2)	2472(2)	7807(2)	1609(2)	29(1)
N(3)	7394(3)	7036(3)	3180(2)	35(1)
N(4)	8948(3)	6364(3)	3980(2)	41(1)
O(1)	3368(3)	5056(2)	1552(2)	53(1)
O(2)	6003(2)	6066(2)	385(2)	49(1)
O(3)	4662(2)	6227(3)	2737(2)	50(1)

O(4)	6931(3)	9847(3)	2896(2)	61(1)
O(5)	9578(3)	8308(3)	1954(2)	63(1)
O(6)	9215(3)	8838(3)	4164(3)	71(1)
P(1)	3508(1)	7344(1)	-216(1)	30(1)
P(2)	6919(1)	7742(1)	4900(1)	35(1)
P(3)	1754(1)	6193(1)	3965(1)	41(1)
P(4)	6910(1)	8589(1)	923(1)	33(1)
Cl(1)	1337(2)	5010(3)	9976(3)	83(1)
Cl(2)	1744(4)	3519(5)	11381(3)	172(3)
C(43)	1548(8)	3693(3)	10346(4)	79(3)
Cl(1A)	1167(11)	4647(8)	10047(7)	159(5)
Cl(2A)	1148(6)	2939(6)	11293(4)	116(3)
C(43A)	1982(9)	3477(13)	10386(14)	114(6)
Cl(3)	7327(6)	1600(7)	3755(6)	183(4)
Cl(4)	8997(8)	2315(7)	2295(7)	214(4)
C(44)	8308(10)	1389(10)	2858(8)	102(5)
Cl(3A)	8617(15)	950(14)	4886(10)	430(10)
Cl(4A)	8992(12)	1915(11)	3215(10)	351(7)
C(44A)	7966(10)	1610(30)	4051(14)	245(10)

Table 3. Bond lengths [Å] and angles [°] for pge0907.

C(1)-N(1)	1.481(5)
C(1)-C(2)	1.524(5)
C(1)-C(6)	1.527(6)
C(2)-N(2)	1.500(5)
C(2)-C(3)	1.516(6)
C(3)-C(4)	1.542(7)
C(4)-C(5)	1.535(6)
C(5)-C(6)	1.515(6)
C(7)-O(1)	1.149(5)
C(7)-Mn(1)	1.800(4)
C(8)-O(2)	1.150(5)
C(8)-Mn(1)	1.799(4)
C(9)-O(3)	1.139(5)
C(9)-Mn(1)	1.841(5)
C(10)-C(11)	1.385(6)
C(10)-C(15)	1.395(6)
C(10)-P(1)	1.823(4)
C(11)-C(12)	1.391(6)
C(12)-C(13)	1.374(7)
C(13)-C(14)	1.373(7)
C(14)-C(15)	1.380(6)
C(16)-C(17)	1.505(6)
C(16)-P(1)	1.845(4)
C(17)-C(18)	1.298(6)
C(19)-C(20)	1.481(7)
C(19)-P(1)	1.849(4)
C(20)-C(21)	1.304(8)
C(22)-N(3)	1.497(5)
C(22)-C(23)	1.519(6)
C(22)-C(27)	1.531(6)
C(23)-N(4)	1.490(6)
C(23)-C(24)	1.515(7)
C(24)-C(25)	1.528(8)

C(25)-C(26)	1.523(8)
C(26)-C(27)	1.522(7)
C(28)-O(4)	1.148(6)
C(28)-Mn(2)	1.802(5)
C(29)-O(5)	1.148(5)
C(29)-Mn(2)	1.824(5)
C(30)-O(6)	1.144(6)
C(30)-Mn(2)	1.808(6)
C(31)-C(32)	1.399(6)
C(31)-C(36)	1.399(6)
C(31)-P(2)	1.821(4)
C(32)-C(33)	1.397(6)
C(33)-C(34)	1.373(8)
C(34)-C(35)	1.390(8)
C(35)-C(36)	1.378(6)
C(37)-C(38)	1.491(7)
C(37)-P(2)	1.846(5)
C(38)-C(39)	1.308(7)
C(40)-C(41)	1.512(9)
C(40)-P(2)	1.842(4)
C(41)-C(42)	1.324(10)
C(41A)-C(42A)	1.316(10)
F(1)-P(3)	1.584(4)
F(2)-P(3)	1.591(3)
F(3)-P(3)	1.610(3)
F(4)-P(3)	1.558(4)
F(5)-P(3)	1.574(3)
F(6)-P(3)	1.603(3)
F(7)-P(4)	1.579(3)
F(8)-P(4)	1.607(3)
F(9)-P(4)	1.598(3)
F(10)-P(4)	1.572(3)
F(11)-P(4)	1.606(3)
F(12)-P(4)	1.571(3)
Mn(1)-N(1)	2.099(3)

Mn(1)-N(2)	2.101(3)
Mn(1)-P(1)	2.3543(13)
Mn(2)-N(3)	2.094(4)
Mn(2)-N(4)	2.109(4)
Mn(2)-P(2)	2.3632(13)
Cl(1)-C(43)	1.7697(11)
Cl(2)-C(43)	1.7703(11)
Cl(1A)-C(43A)	1.7698(11)
Cl(2A)-C(43A)	1.7699(11)
Cl(3)-C(44)	1.7701(11)
Cl(4)-C(44)	1.7695(11)
Cl(3A)-C(44A)	1.7698(11)
Cl(4A)-C(44A)	1.7701(11)

N(1)-C(1)-C(2)	107.5(3)
N(1)-C(1)-C(6)	111.7(3)
C(2)-C(1)-C(6)	111.8(3)
N(2)-C(2)-C(3)	114.4(3)
N(2)-C(2)-C(1)	106.9(3)
C(3)-C(2)-C(1)	112.4(3)
C(2)-C(3)-C(4)	112.1(3)
C(5)-C(4)-C(3)	111.0(4)
C(6)-C(5)-C(4)	111.1(4)
C(5)-C(6)-C(1)	110.5(4)
O(1)-C(7)-Mn(1)	177.3(4)
O(2)-C(8)-Mn(1)	177.4(4)
O(3)-C(9)-Mn(1)	171.4(4)
C(11)-C(10)-C(15)	118.4(4)
C(11)-C(10)-P(1)	122.9(3)
C(15)-C(10)-P(1)	118.6(3)
C(10)-C(11)-C(12)	120.3(4)
C(13)-C(12)-C(11)	120.7(5)
C(14)-C(13)-C(12)	119.2(4)
C(13)-C(14)-C(15)	120.8(4)
C(14)-C(15)-C(10)	120.5(4)

C(17)-C(16)-P(1)	111.3(3)
C(18)-C(17)-C(16)	125.1(5)
C(20)-C(19)-P(1)	114.6(3)
C(21)-C(20)-C(19)	125.2(5)
N(3)-C(22)-C(23)	106.6(3)
N(3)-C(22)-C(27)	113.2(4)
C(23)-C(22)-C(27)	112.0(4)
N(4)-C(23)-C(24)	112.9(4)
N(4)-C(23)-C(22)	106.6(4)
C(24)-C(23)-C(22)	112.8(4)
C(23)-C(24)-C(25)	109.5(4)
C(26)-C(25)-C(24)	111.9(4)
C(27)-C(26)-C(25)	111.0(4)
C(26)-C(27)-C(22)	112.7(4)
O(4)-C(28)-Mn(2)	175.4(4)
O(5)-C(29)-Mn(2)	171.7(5)
O(6)-C(30)-Mn(2)	175.8(5)
C(32)-C(31)-C(36)	118.9(4)
C(32)-C(31)-P(2)	122.1(3)
C(36)-C(31)-P(2)	118.7(3)
C(33)-C(32)-C(31)	119.8(4)
C(34)-C(33)-C(32)	120.7(5)
C(33)-C(34)-C(35)	119.7(4)
C(36)-C(35)-C(34)	120.4(5)
C(35)-C(36)-C(31)	120.5(4)
C(38)-C(37)-P(2)	115.3(3)
C(39)-C(38)-C(37)	124.7(5)
C(41)-C(40)-P(2)	115.2(9)
C(42)-C(41)-C(40)	122.8(13)
C(8)-Mn(1)-C(7)	91.31(19)
C(8)-Mn(1)-C(9)	86.44(19)
C(7)-Mn(1)-C(9)	88.29(19)
C(8)-Mn(1)-N(1)	93.41(16)
C(7)-Mn(1)-N(1)	175.27(16)
C(9)-Mn(1)-N(1)	91.61(17)

C(8)-Mn(1)-N(2)	172.98(16)
C(7)-Mn(1)-N(2)	95.60(16)
C(9)-Mn(1)-N(2)	94.98(16)
N(1)-Mn(1)-N(2)	79.70(12)
C(8)-Mn(1)-P(1)	88.10(14)
C(7)-Mn(1)-P(1)	87.90(14)
C(9)-Mn(1)-P(1)	173.27(14)
N(1)-Mn(1)-P(1)	92.65(10)
N(2)-Mn(1)-P(1)	90.92(10)
C(28)-Mn(2)-C(30)	89.3(2)
C(28)-Mn(2)-C(29)	86.4(2)
C(30)-Mn(2)-C(29)	85.8(2)
C(28)-Mn(2)-N(3)	95.54(18)
C(30)-Mn(2)-N(3)	175.15(19)
C(29)-Mn(2)-N(3)	94.53(19)
C(28)-Mn(2)-N(4)	174.9(2)
C(30)-Mn(2)-N(4)	95.47(19)
C(29)-Mn(2)-N(4)	92.15(19)
N(3)-Mn(2)-N(4)	79.68(14)
C(28)-Mn(2)-P(2)	88.91(15)
C(30)-Mn(2)-P(2)	89.01(16)
C(29)-Mn(2)-P(2)	173.02(16)
N(3)-Mn(2)-P(2)	91.03(10)
N(4)-Mn(2)-P(2)	93.00(11)
C(1)-N(1)-Mn(1)	113.0(2)
C(2)-N(2)-Mn(1)	111.3(2)
C(22)-N(3)-Mn(2)	111.4(3)
C(23)-N(4)-Mn(2)	111.8(3)
C(10)-P(1)-C(16)	104.62(19)
C(10)-P(1)-C(19)	102.1(2)
C(16)-P(1)-C(19)	102.4(2)
C(10)-P(1)-Mn(1)	115.76(14)
C(16)-P(1)-Mn(1)	117.48(15)
C(19)-P(1)-Mn(1)	112.53(15)
C(31)-P(2)-C(40)	103.84(19)

C(31)-P(2)-C(37)	102.8(2)
C(40)-P(2)-C(37)	103.1(2)
C(31)-P(2)-Mn(2)	114.97(14)
C(40)-P(2)-Mn(2)	118.76(16)
C(37)-P(2)-Mn(2)	111.51(15)
F(4)-P(3)-F(5)	91.5(2)
F(4)-P(3)-F(1)	178.3(2)
F(5)-P(3)-F(1)	89.4(2)
F(4)-P(3)-F(2)	89.5(3)
F(5)-P(3)-F(2)	178.8(3)
F(1)-P(3)-F(2)	89.6(3)
F(4)-P(3)-F(6)	91.81(19)
F(5)-P(3)-F(6)	91.18(15)
F(1)-P(3)-F(6)	89.54(17)
F(2)-P(3)-F(6)	89.39(16)
F(4)-P(3)-F(3)	88.35(19)
F(5)-P(3)-F(3)	89.28(16)
F(1)-P(3)-F(3)	90.29(18)
F(2)-P(3)-F(3)	90.15(16)
F(6)-P(3)-F(3)	179.51(18)
F(12)-P(4)-F(10)	92.0(2)
F(12)-P(4)-F(7)	89.6(2)
F(10)-P(4)-F(7)	178.4(2)
F(12)-P(4)-F(9)	179.4(2)
F(10)-P(4)-F(9)	88.2(2)
F(7)-P(4)-F(9)	90.3(2)
F(12)-P(4)-F(11)	90.56(16)
F(10)-P(4)-F(11)	90.47(16)
F(7)-P(4)-F(11)	89.51(15)
F(9)-P(4)-F(11)	88.88(16)
F(12)-P(4)-F(8)	89.33(16)
F(10)-P(4)-F(8)	89.55(16)
F(7)-P(4)-F(8)	90.47(15)
F(9)-P(4)-F(8)	91.22(16)
F(11)-P(4)-F(8)	179.9(2)

Appendix-iv

Publication in support of this thesis.

1-Trimethylsilylphosphirane as a ligand and as a stable masked reagent for phosphirane†‡

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1-Trimethylsilylphosphirane, $C_2H_4PSiMe_3$, has been prepared on a multi gram scale from $P(SiMe_3)_3$ *via* $ClCH_2CH_2P(SiMe_3)_2$. $C_2H_4PSiMe_3$ is readily susceptible to protonolysis forming the thermally unstable parent phosphirane, C_2H_4PH, in good yields. Reaction of $C_2H_4PSiMe_3$ with *fac*-$M(CO)_3(CH_3CN)_3$ (M = Cr, Mo) or $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)](PF_6)$ give rise to *fac*-$M(CO)_3(C_2H_4PSiMe_3)_3$ and $[Fe(\eta^5\text{-}C_5H_5)(C_2H_4PSiMe_3)_3](PF_6)$ respectively. Protonolysis of the free or coordinated 1-trimethylsilylphosphirane readily causes P–Si cleavage to give rise to the parent C_2H_4PH or the respective complexes, *fac*-$M(CO)_3(C_2H_4PH)_3$ and *fac*-$[Fe(\eta^5\text{-}C_5H_5)(C_2H_4PH)_3](PF_6)$ *in situ*. All new complexes are characterised by analytical and spectroscopic methods and the X-ray crystal structures of *fac*-$Cr(CO)_3(C_2H_4PSiMe_3)_3$ and *fac*-$Mo(CO)_3(C_2H_4PH)_3$ have also been determined.

Introduction

The smallest saturated monophosphorus heterocycle, the 3-membered phosphirane, is a potentially useful synthon for the formation of larger cyclic, acyclic and polymeric phosphorus containing compounds. The C_2H_4PH parent has been prepared by several methods, notably the reaction of disodium phosphide with 1,2-dihaloethane at low temperature.[1] These syntheses are, however, capricious with variable yields and the isolation of the compound can be frustrated by its thermal instability; phosphirane is reported to decompose during 24 h at 25 °C (when neat) to a mixture of ethyl phosphine, ethene and unidentified viscous products.[1] As a result, the chemistry of phosphirane remains underdeveloped with very few metal complexes being reported.[2] Stable phosphiranes are achieved when bulky alkyl or aryl substituents are introduced at the phosphorus. Thus 1-phenylphosphirane,[3] 1-mesitylphosphirane[4] and 1-*tert*-butylphosphirane[5] are distillable liquids and the coordination chemistry of these ligands has been explored by a number of groups including those of Kubiak,[5] Wild,[6] and Mathey.[2] In addition, Grützmacher has developed the chemistry of more complex phosphiranes that include a P–N function.[7]

We have a long-standing interest in phosphorus ligand synthesis as well as small ring triphosphamacrocycles and have synthesised a series of cyclo-P_3R_3 derivatives from 9aneP_3R_3 to 12aneP_3R_3 by metal-template methods.[8] These procedures are, however, demanding and require several steps for completion; in addition, the desirable 9-membered derivatives are yet to be obtained as the uncoordinated phosphines. The development of more efficient routes to such macrocycles through template systems that allow access to the free ligands remains a major goal in our laboratories. Wild envisaged using phosphiranes as precursors for metal-directed cyclotrimerisation in 1996, and he prepared a number of facial tris-(1-phenylphosphirane) complexes for this purpose.[6] The intention was to promote cyclotrimerisation through a series of phosphirane ring-opening reactions achieved *via* the nucleophilic attack of coordinated phosphides at the carbon atoms of neighbouring phosphirane ligands. This, however, was not possible with the *fac*-$Mo(CO)_3(C_2H_4PPh)_3$ and $[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PPh)_3]^+$ complexes reported because the choice of 1-phenylphosphirane as the precursor precluded easy access to the phosphide. The generation of the necessary metal-bound $C_2H_4P^-$ anion from coordinated C_2H_4PR requires R to be removable, preferably under relatively mild conditions. The obvious choice for R is hydrogen as in the parent phosphirane, although the susceptibility of P–Si bonds to protonolysis makes $C_2H_4PSiMe_3$ an attractive candidate. To this end we have developed the synthesis of the stable 1-trimethylsilylphosphirane, $C_2H_4PSiMe_3$, on a multi-gram scale and investigated its coordination chemistry with the potential macrocyclic template metal systems *fac*-$M(CO)_3(L)_3$ (M = Mo, Cr) and $[(\eta^5\text{-}C_5H_5)Fe(L_3)]^+$ (L = CH_3CN or $1/3C_6H_6$). 1-Trimethylsilylphosphirane is thermally stable, decomposing when neat at above 150 °C and it is an excellent source of C_2H_4PH through *in situ* protonolysis. In this paper, we detail the results of this synthetic study and some aspects of the coordination chemistry of the phosphiranes prepared.

Results and discussion

Unlike the analogous oxygen and nitrogen 3-membered heterocycles, the chemistry of phosphirane has been poorly explored. This is, in part, due to the unstable nature of the compound. Our interest in triphosphamacrocyles led us to seek a more manageable source of phosphirane in order to exploit its potential as a synthetic intermediate in macrocyclic chemistry. The facility with which P–Si bonds undergo protonolysis to give P–H functions makes trimethylsilyl-protected phosphorus derivatives ideal precursors for the preparation of secondary and primary phosphines. Thus, we have sought to use 1-trimethylsilylphosphirane, $C_2H_4PSiMe_3$, as a precursor to the parent phosphirane, C_2H_4PH. Surprisingly,

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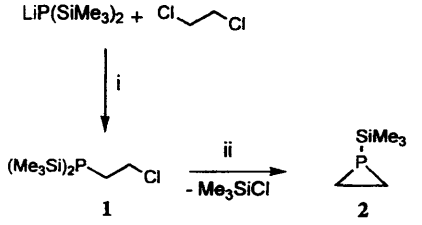
† Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

‡ CCDC reference numbers 663023 and 663024. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715327a

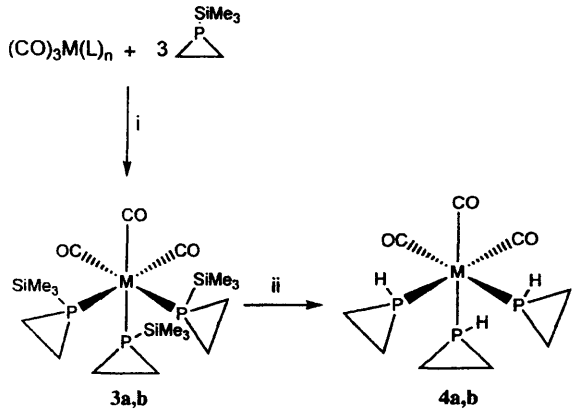
the only report of $C_2H_4PSiMe_3$ in the literature concerns the formation of the ligand at a Mo(0) centre from coordinated HPC_2H_4;[2] although phosphiranes stabilised with bulky groups at P are well established,[3-6] uncoordinated $C_2H_4PSiMe_3$ remains unknown.

The synthesis of $C_2H_4PSiMe_3$, **2**, from $(Me_3Si)_3P$ is highlighted in Scheme 1. The precursor compound $(Me_3Si)_2PCH_2CH_2Cl$, **1**, is prepared by the addition of $(SiMe_3)_2PLi$ to 1,2-dichloroethane in petroleum ether at room temperature. $^{31}P\{^1H\}$ NMR analysis of the reaction mixture showed a singlet at δ_P −175.0 ppm assignable to **1** in addition to a minor peak (<10%) at δ_P −318.3 ppm for the $C_2H_4PSiMe_3$ phosphacycle. The ring-closure to give $C_2H_4PSiMe_3$ is effected upon heating **1** to 100 °C to expel Me_3SiCl. The resultant crude $C_2H_4PSiMe_3$ was distilled at 40 °C (10 mm Hg) to give the phosphirane, **2**, in 82% yield. It is noteworthy that no significant decomposition was observed when neat $C_2H_4PSiMe_3$ was heated at 150 °C for 1 h. The phosphine, **2**, has a ^{31}P chemical shift of −318.3 ppm, showing the usual upfield shift for phosphorus constrained in a 3-membered ring. The ^1H NMR spectrum consists of a complex multiplet at δ_H 1.06 ppm for the four ring hydrogens and a doublet at δ_H 0.02 ppm ($^3J_{H\,P}$ = 4.0 Hz) for the methyl hydrogens. The methyl carbons appear as a doublet ($^2J_{C\,P}$ = 10.0 Hz) at δ_C 0.05 ppm in the $^{13}C\{^1H\}$ NMR spectrum with the methylene carbons in the ring being observed as a doublet at δ_C 5.9 ppm with an absolute $^1J_{C\,P}$ value of 41.6 Hz; all these observations accord with those for other phosphirane species.[9]



Scheme 1 Conditions: (i) hexane, 20 °C; (ii) 100 °C.

Addition of 3.5 mol equivalents of **2** to toluene solutions of (η^6-1,3,5-trimethylbenzene)$Mo(CO)_3$ or *fac*-$Cr(CO)_3(MeCN)_3$ gave the corresponding *fac*-$M(CO)_3(\mathbf{2})_3$ complexes in quantitative yield (Scheme 2).



Scheme 2 M = Mo, L = 1,3,5-trimethylbenzene, n = 1; M = Cr, L = CH_3CN, n = 3. Conditions: (i) toluene, 20 °C; (ii) toluene/methanol, 20 °C.

The complexes were readily recrystallised from toluene at low temperature to give colourless crystals of *fac*-$Mo(CO)_3(\mathbf{2})_3$, **3a**, and bright yellow crystals of *fac*-$Cr(CO)_3(\mathbf{2})_3$, **3b**. The crystal structure of the Cr complex, **3b** was determined and is shown in Fig. 1. The complex has the expected pseudo-octahedral structure with C_3 symmetry in the solid state. All the interligand bond angles are close to the idealised 90° as anticipated. The average Cr–P bond distance of 2.377 Å is somewhat longer than the average values of 2.348, 2.430 and 2.344 Å observed for *fac*-$Cr(CO)_3(PH_3)_3$,[10] *fac*-$Cr(CO)_3(PEt_3)_3$,[11] and *fac*-$Cr(CO)_3(H_2PC(Me)CH_2)_3$,[12] respectively. No direct comparison can be made with other Cr(0) phosphirane complexes as none have been structurally characterised, but the mean C–C and P–C bond lengths of 1.496 Å and 1.844 Å are within the ranges seen for other structurally characterised metal complexes of phosphiranes, as are the C–P–C and C–C–P angles which average 47.86 and 66.08° respectively.[2,5,6,9]

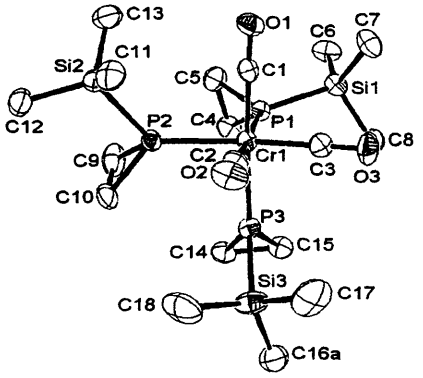


Fig. 1 ORTEP view of the complex $Cr(CO)_3(C_2H_4PSiMe_3)_3$, **3b**, ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): Cr1–P1, 2.3868(8); Cr1–P2, 2.3779(8); Cr1–P3, 2.3677(8); Cr1–C1, 1.844(2); Cr1–C2, 1.841(2); Cr1–C3, 1.837(2); C1–Cr1–C2, 89.56(10); C1–Cr1–C3, 89.54(10); C2–Cr1–C3, 87.30(10); P1–Cr1–P2, 92.73(3); P1–Cr1–P3, 91.83(3); P2–Cr1–P3, 90.70(3); P1–Cr1–C2, 176.29(8); P2–Cr1–C3, 174.55(8); P3–Cr1–C1, 177.26(7).

The complexes **3a** and **3b** show the characteristic downfield coordination shift in their $^{31}P\{^1H\}$ NMR spectra with singlets being observed at δ_P −245.9 (**3a**) and −219.6 ppm (**3b**), respectively. The $^{31}P\{^1H\}$ NMR spectrum of the $Mo(CO)_3(C_2H_4PSiMe_3)_3$ complex also shows a six-line pattern (approximate relative total intensity 15%) arising from the ^{95}Mo in the sample ($^1J_{P\text{-}Mo}$ = 115.6 Hz). The ^1H NMR spectra of the two complexes are very similar with the CH_2 multiplet shifted upfield to 0.85 ppm for the Cr species and 0.90 ppm for the Mo complex relative to the free ligand with the methyl hydrogens being observed as singlets at 0.23 (**3a**) and 0.21 ppm (**3b**) respectively. Unlike the simple doublets seen for the CH_3 and CH_2 carbons in the $^{13}C\{^1H\}$ NMR spectrum for the uncoordinated $C_2H_4PSiMe_3$, the signals for both the methyl and methylene carbons are multiplets in the spectra of the Cr and Mo complexes; a feature noted by Wild and coworkers for the analogous molybdenum complex of 1-phenylphosphirane.[6] These observations may reflect the magnetic inequivalence of the two carbon atoms of the phosphirane ring. The carbonyl resonance is observed as a doublet of triplets in the $^{13}C\{^1H\}$ NMR spectrum of *fac*-$Mo(CO)_3(C_2H_4PSiMe_3)_3$ with a *trans* $^2J_{C\,P}$ coupling constant

$Mo(CO)_3(C_2H_4PPh)_3$[6] are 2090, 1945 and 1950 cm^{-1}, respectively, suggesting that the $C_2H_4PSiMe_3$ ligand is a strong σ-donor and weak π-acceptor. Other measures of σ-donating/π-accepting ability include the observation of one-bond metal–phosphorus coupling constants.[14] The $^1J_{P\text{-}Mo(95)}$ coupling constant for **3a** (115.6 Hz) is appreciably smaller than the value of 143.5 Hz observed by Wild for *fac*-$Mo(CO)_3(C_2H_4PPh)_3$.[6] The dependence of the magnitude of the $^1J_{P\text{-}W}$ coupling constant on the nature of R in complexes of the type $W(CO)_5(PR_3)$ has been more extensively studied[14] with strongly electron-withdrawing groups on phosphorus giving the largest values of $^1J_{P\text{-}W}$.[5,15] In order to examine further the electronic properties of $C_2H_4PSiMe_3$, the complex $W(CO)_5(C_2H_4PSiMe_3)$ was prepared from $W(CO)_5(THF)$ and desilylated *in situ* to the known $W(CO)_5(C_2H_4PH)$, **5**.[2] The value of 207 Hz for $^1J_{P\text{-}W}$ in $W(CO)_5(C_2H_4PSiMe_3)$ compares with that of 202.9 Hz for $W(CO)_5\{(Me_3C)_2PSiMe_3\}$[16] but is lower than in related phosphirane complexes such as $W(CO)_5(C_2H_4PCl)$,[2] $W(CO)_5(C_2H_4PH)$[2] and $W(CO)_5(C_2H_4PCMe_3)$[5] where $^1J_{P\text{-}W}$ values of 303, 254 and 244 Hz, respectively, are observed. This low $^1J_{P\text{-}W}$ value reflects the poor π-acidity of **2**, which appears to behave as a net donor to the metal centre. All data for compound **5** are in agreement with the published data.[2]

The complexes **4a** and **4b** containing tris-coordinated secondary phosphirane were readily obtained upon treatment of toluene solutions of **3a** and **3b** with MeOH. The desilylation process is monitored by $^{31}P\{^1H\}$ NMR spectroscopy as observed for the conversion of **3b** to **4b**. As the intensity of the peak for **3b** decreases growth of a doublet at δ_P −220.0, and triplet at −192.8 ppm ($J_{P\text{-}P}$ = 41 Hz) attributable to an A_2B pattern assigned to the first intermediate $Cr(CO)_3(C_2H_4PSiMe_3)_2(C_2H_4PH)$ precedes the growth of a second A_2B pattern [δ_P −219.6 (t, $J_{P\text{-}P}$ = 41 Hz), and −191.3 (d) ppm] assigned to the second intermediate, $Cr(CO)_3(C_2H_4PSiMe_3)(C_2H_4PH)_2$ and finally a resonance due to the product **4b** (δ_P −190.9) predominates. The desilylation is slow under ambient conditions, taking up to 5 days for completion. The resultant yellow $Cr(CO)_3(C_2H_4PH)_3$ (**4b**) complex was crystallised from petroleum ether at low temperature. The $^{31}P\{^1H\}$ NMR spectrum of **4b** consists of a singlet at δ_P −190.2 ppm which splits into a doublet of multiplets in the ^{31}P NMR spectrum with $^1J_{P\text{-}H}$ = 318 Hz. The ^1H NMR spectrum contains two separate multiplets for the hydrogens of the ring methylenes and a doublet of multiplets ($^1J_{H\text{-}P}$ = 318 Hz) for the P–H protons. As observed for the complexes **3a** and **3b**, the signal for the CH_2 groups is a multiplet in the $^{13}C\{^1H\}$ NMR spectrum of **4b** and the CO resonances appear as a multiplet. The infrared spectrum recorded as a Nujol mull showed a single $\nu_{(PH)}$ stretch at 2319 cm^{-1} and two major ν_{CO} stretches at 1959 and 1881 cm^{-1}; these carbonyl bands were seen at 1949 and 1862 cm^{-1} *in solution* (CH_2Cl_2). The $\nu_{(CO)}$ stretches are shifted significantly (to higher wavenumber) compared to those for **2b** suggesting an appreciable difference in

observed for the analogous silylated complex **3a** su
π-acidity of the C_2H_4PH ligand compared to C_2
deduction is further supported on examination
spectra of **4a**. When recorded as a Nujol mull,
shows a single peak for the $\nu_{(PH)}$ stretch at 2340 cm
$\nu_{(CO)}$ stretches at 1968 and 1887 cm^{-1}. Two minor c
were also observed in the solid-state at 1952
In order to remove any reduction of symmetry
in the crystalline state, the infrared spectrum
dichloromethane solution where only the expecte
were observed at 1959 and 1873 cm^{-1}. As fo
species, the carbonyl stretches are shifted to hig
in the molybdenum complex of C_2H_4PH comp
$C_2H_4PSiMe_3$. The spectroscopic data for **4a** is c
that of *fac*-$Mo(CO)_3(C_2H_4PPh)_3$[6] suggesting th
similar ligand properties to 1-phenylphosphiran
suitable for X-ray crystallography were obtained f
disiloxane solution upon cooling to −35 °C. The
complex with pertinent metric data is shown in Fi
Mo–P bond length of 2.496 Å is the same (with
error) as that of the related *fac*-$Mo(CO)_3(C_2H$
(2.495 Å)[6] as are most other structural featu
the close relation between the donor propert
and C_2H_4PPh consistent with the spectroscop
their molybdenum(0) complexes. It should be no
et al. first mentioned *fac*-$Mo(CO)_3(C_2H_4PH)_3$ b
these authors gave no data regarding the charac
complex.[2]

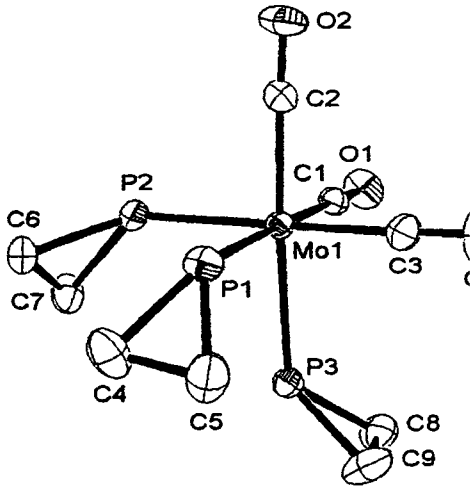
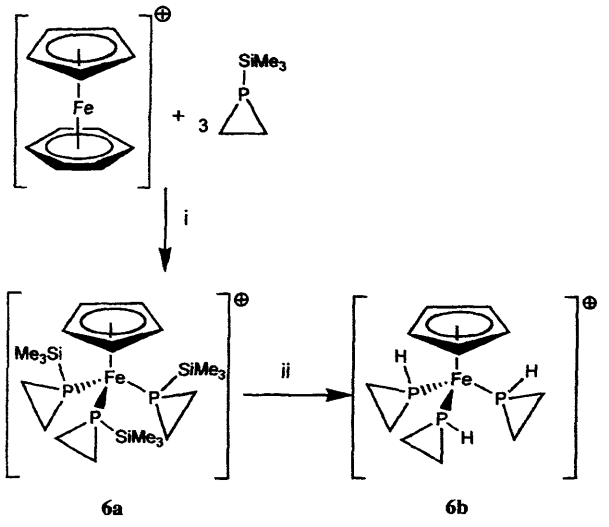


Fig. 2 ORTEP view of the complex $Mo(CO)_3(C_2H_4P$ drawn at 50% probability. Selected bond lengths (Å Mo1–P1, 2.4936(10); Mo1–P2, 2.5017(11); Mo1–P3, 2.4 1.978(4); Mo1–C2, 1.989(4); Mo1–C3, 1.968(4); C1–M C1–Mo1–C3, 89.42(16); C2–Mo1–C3, 87.89(16); P1–M P1–Mo1–P3, 89.13(3); P2–Mo1–P3, 91.82(4); P1–Mo P2–Mo1–C3, 179.10(11); P3–Mo1–C2, 176.32(12).

In these facially coordinated tris-phosphirane complexes, cyclo-oligomerisation to macrocyclic products requires attack of a coordinated phosphide at one of the carbon atoms of a neighbouring phosphirane ligand. A critical component for the success or otherwise of such a strategy relates to the non-bonded P···C distances. The closest non-bonded P···C contact in the crystal structure of **4a** is 3.989 Å and, while accepting that this is probably not the shortest possible distance between a phosphorus and one of the carbon centres at an adjacent phosphirane, this separation is likely to be too great for attack of a coordinated phosphide nucleophile at a neighbouring carbon in these molybdenum systems. By contrast, the shortest non-bonded P···C separation in **3b** is 3.657 Å while in the $[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PPh)_3]^+$ complex of Wild *et al.* it is only 3.599 Å.[6] It is likely then that the smaller Cr(0) and Fe(II) systems should be more amenable in any subsequent template-based cyclisations.

The iron(II) analogue **6a** was prepared (Scheme 3) in a similar manner to that of the zerovalent metals reported above. Addition of 3.5 mol equivalents of **2** to a dichloromethane solution of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6$ gave the $[\eta^5\text{-}C_5H_5)Fe(C_2H_4PSiMe_3)_3]PF_6$ complex as an orange–yellow solid in quantitative yield. The complex shows a sharp singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ_P −205.6 ppm, corresponding to the coordinated 1-trimethylsilylphosphirane in addition to the septet at δ_P −143.2 ppm due to the PF_6^- counterion ($^1J_{P,F} = 712$ Hz). Attempts to isolate and fully characterise this complex were frustrated by the ready desilylation of one or more of the $C_2H_4PSiMe_3$ ligands, even when every precaution had been taken to exclude water from the system. Evidence for the desilylation came from $^{31}P\{^1H\}$ NMR analysis in solution where the presence of the intermediate species $[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PSiMe_3)_2(C_2H_4PH)]^+ (PF_6)^-$ was identified by a triplet at δ_P −164.2 ppm and a doublet at δ_P −203.1 ppm during attempted work-up.



Scheme 3 Conditions: (i) CH_2Cl_2, sunlight, (ii) CH_2Cl_2/MeOH.

Protonolysis of **6a** was achieved readily on addition of MeOH to a dichloromethane solution of the complex. Unlike the Cr and Mo species that took several days for total desilylation, complete loss of the trimethylsilyl groups occurred within minutes at RT for **6a**. The $[(\eta^5\text{-}C_5H_5)Fe(C_2H_4PH)_3]PF_6$ complex, **6b**, was readily recrystallised from MeOH to afford brick-red crystals. The ^1H NMR spectrum of **6b** recorded in CD_3NO_2 consists of two multiplets for the non-equivalent CH_2 ring protons at δ_H 0.88 ppm and 1.39 ppm. A poorly resolved quartet is observed at δ_H 4.45 ppm due to the cyclopentadienyl protons, as well as a doublet of multiplets at δ_H 1.08 ppm for the P–H protons of the secondary phosphines. The $^{13}C\{^1H\}$ NMR spectrum of **6b** shows the ring carbons as an unresolved multiplet at δ_C 0.0 ppm. The carbons of the cyclopentadienyl ring appear as a singlet at δ_C 76.5 ppm. The infrared spectrum of **6b** recorded as a KBr disk shows two $\nu_{(P\text{-}H)}$ stretches at 2344 cm^{-1}. Identification of **6b** was unequivocally confirmed by it mass spectrum (TOF-MS, ES$^+$), which afforded the molecular ion at $m/z = 301.03$.

Phosphirane was readily prepared as a solution in toluene or other unreactive organic solvent by treatment of 1-trimethylsilylphosphirane with an alcohol. Complete removal of the trimethylsilyl group from $C_2H_4PSiMe_3$ was achieved within minutes of adding MeOH to toluene solutions of $C_2H_4PSiMe_3$ (~1 M in phosphirane) and the relatively dilute solutions of C_2H_4PH thus prepared were stable to decomposition at room temperature showing no noticeable deterioration (assessed by ^{31}P NMR spectroscopy) after several weeks at RT. The ^1H and $^{13}C\{^1H\}$ NMR spectra for a sample of C_2H_4PH prepared in C_6D_6 agree exactly with published data, however the $^{31}P\{^1H\}$ NMR chemical shift we observe for the phosphirane does not. The solutions of C_2H_4PH prepared from $C_2H_4PSiMe_3$ (either in deuterated or protic solvents) show a singlet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta_P = -309$ ppm, some 32 ppm downfield of the reported chemical shift of $\delta_P = 341$ ppm.[17] The chemical shifts of R_2PH species are usually downfield of the related R_2PSiMe_3 compounds and our phosphiranes follow this trend. The ^{31}P spectrum recorded at 121.7 MHz shows an apparent doublet of triplets with a $^1J_{P\text{-}H}$ of 160.0 Hz and a $^2J_{P\text{-}H}$ of 16.7 Hz. These patterns are largely in agreement with the values determined by Goldwhite and coworkers[17] although the small $^2J_{P\text{-}H}$ couplings noted by these researchers were not apparent in our spectra: no attempt was made to simulate the spectra as, apart from the discrepancy in the ^{31}P chemical shift, the ^{31}P and ^1H NMR spectra of C_2H_4PH have been well characterised.[17]

Experimental

Methods and materials

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. Metal precursor complexes $(\eta^6\text{-}1,3,5\text{-trimethylbenzene})Mo(CO)_3$,[18] *fac*-$Cr(CO)_3(MeCN)_3$,[19] and $[(\eta^5\text{-}C_5H_5)Fe(\text{-}(\eta^6\text{-}C_6H_6)](PF_6)$[20] were prepared by literature methods. All other chemicals were obtained commercially, and used as received. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane ($\delta = 0$ ppm). Unless stated otherwise, infrared spectra were recorded as Nujol mulls on a

Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd., UK.[21]

Syntheses

1-Trimethylsilylphosphirane (2). A solution of $LiP(SiMe_3)_2$ (4.65 g, 25.2 mmol, prepared from $P(SiMe_3)_3$) in 40 : 60 petroleum ether (50 ml) was added dropwise to a stirred solution of 1,2-dichloroethane (2.38 ml, 30.2 mmol) in 40 : 60 petroleum ether (50 ml) in a manner similar to that previously described.[22] After stirring for 12 h, the mixture was filtered and the volatile materials were removed from the filtrate under reduced pressure. The crude $(MeSi)_2PCH_2CH_2Cl$, **1**, was transferred to a distillation apparatus and heated slowly to 100 °C to expel Me_3SiCl. After the removal of the trimethylchlorosilane was complete, the resultant oily residue was distilled at 40 °C (10 mm Hg) to give **2** as a clear, very slightly yellow liquid. Yield = 2.6 g (77%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ −318.3 ppm. ^1H NMR (C_6D_6, 500 MHz) δ 1.06 (m, 4H), 0.02 (d, 4.0 Hz, 9H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 5.95 (d, 41.5 Hz, CH_2), 0.04 (d, 10.0 Hz, CH_3) ppm.

***Fac*-Mo(CO)$_3$($C_2H_4PSiMe_3$)$_3$ (3a).** To a solution of (η^6-1,3,5-trimethylbenzene)Mo(CO)$_3$ (114 mg, 0.38 mmol) in toluene (10 ml) was added a solution of **2** (175 mg, 3.5 mol equiv.) as a 10% w/v solution in toluene. The solution was stirred at RT overnight and the solvents subsequently removed *in vacuo*. The pale yellow solid was crystallised from 40 : 60 petroleum ether at −35 °C as tan crystals. Yield = 175 mg (80%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ −245.9 (s with satellites, $^1J_{P\text{-}Mo(95)}$ = 115.6 Hz) ppm. ^1H NMR (C_6D_6, 500 MHz) δ 0.72 (m, 12H), 0.23 (s, 27H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 218.5 (m, *C*O), 7.05 (m, CH_2), 0.02 (m, CH_3) ppm. IR (Nujol): 1923 vs, 1821 vs cm^{-1} (ν_{CO}). Anal.: calc for $C_{18}H_{39}O_3P_3Si_3Mo$: C, 37.49; H, 6.82%. Found: C, 37.4; H, 6.8%. ES-MS: *m/e* 579 amu ([M]•$^+$).

***Fac*-Cr(CO)$_3$($C_2H_4PSiMe_3$)$_3$ (3b).** To a slurry of *fac*-Cr(CO)$_3$(MeCN)$_3$ (100 mg, 0.39 mmol) in toluene (8 ml) was added a solution of **2** (179 mg, 3.5 mol equiv.) as a 10% w/v solution in toluene. Any undissolved starting complex was immediately solubilised on addition of the phosphirane. The solution was stirred at RT overnight, filtered and the solvents subsequently removed in *vacuo*. The remaining solid was crystallised from 40/60 petroleum ether at −35 °C as bright yellow crystals. Yield = 180 mg (87%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ −219.6 (s) ppm. ^1H NMR (C_6D_6, 500 MHz) δ 0.75 (m, 12H), 0.12 (s, 27H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 230.1 (m, *C*O), 6.10 (m, CH_2), 0.01 (m, CH_3) ppm. IR (Nujol): 1917 vs, 1815 vs cm^{-1} (ν_{CO}). Anal.: calc for $C_{18}H_{39}O_3P_3Si_3Cr$: C, 40.59; H, 7.38%. Found: C, 39.9; H, 7.1%. ES-MS: *m/z* 533 amu ([M]•$^+$).

***Fac*-Mo(CO)$_3$(C_2H_4PH)$_3$ (4a).** A solution of C_2H_4PH in toluene was prepared by the addition of MeOH (0.2 ml) to a stock solution of **2** (10% w/v solution in toluene containing 154 mg, 1.16 mmol, of **2**). The resultant solution of C_2H_4PH was then added to a solution of (η^6-1,3,5-trimethylbenzene)Mo(CO)$_3$ (100 mg, 0.33 mmol) in toluene (10 ml). The solution was stirred at room temperature overnight and the solvents subsequently removed in *vacuo*. The pale solid was crystallised from 40/60 petroleum ether at −35 °C as colourless crystals. Crystals suitable for single crystal X-ray analysis were grown from a solution of the complex in hexamethyldisiloxane at −35 °C. Yield = 80 mg (67%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ −225.9 (s with satellites, $^1J_{P\text{-}Mo(95)}$ = 143.2 Hz) ppm. ^1H NMR (C_6D_6, 500 MHz) δ 0.82 (dm, $^1J_{H\text{-}P}$ 319 Hz, 3H), 0.73 (m, 6H), 0.42 (m, 6H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 215.5 (m, *C*O), 2.05 (m, CH_2) ppm. IR (Nujol): 2340 w (ν_{PH}), 1968 vs, 1887 vs cm^{-1} (ν_{CO}). Anal.: calc for $C_9H_{15}O_3P_3Mo$: C, 30.02; H, 4.20%. Found: C, 29.8; H, 4.3%. ES-MS: *m/z* 360 amu ([M]•$^+$).

***Fac*-Cr(CO)$_3$(C_2H_4PH)$_3$ (4b).** To a solution of **3b** (100 mg, 0.19 mmol) in toluene (8 ml) was added MeOH (0.1 ml, excess) and the solution stirred at RT for 72 h. All volatile materials were removed *in vacuo* and yellow **4b** was crystallised from petroleum ether at −35 °C. Yield = 54 mg (90%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ −190.2 (s) ppm. ^1H NMR (C_6D_6, 500 MHz) δ 1.09 (dm, $^1J_{H\text{-}P}$ 315 Hz, 3H, 0.82 (m, 6H), 0.52 (m, 6H) ppm. $^{13}C\{^1H\}$ DEPT NMR (C_6D_6, 125.8 MHz) δ 226.5 (m, *C*O), 0.03 (m, CH_2) ppm. IR (Nujol): 2319 w (ν_{PH}), 1959 vs, 1881 vs cm^{-1} (ν_{CO}). Anal.: calc for $C_9H_{15}O_3P_3Cr$: C, 34.19; H, 4.78%. Found: C, 34.1; H, 4.8%. ES-MS: *m/e* 317 amu ([M]•$^+$).

W(CO)$_5$(C_2H_4PH) (5). To a solution of W(CO)$_5$(THF) (prepared *in situ* by overnight UV photolysis of a solution of tungsten hexacarbonyl, 184 mg, 0.52 mmol, in 110 ml of THF) was added a solution of **2** (90 mg, 0.68 mmol) in toluene. The solution was stirred overnight at room temperature and a $^{31}P\{^1H\}$ NMR spectrum of the mixture was obtained. This showed the presence of two peaks at −273.0 and −253.8 ppm assignable to W(CO)$_5$($C_2H_4PSiMe_3$) and W(CO)$_5$(C_2H_4PH) respectively. An excess of MeOH (0.2 ml) was added to convert the remaining W(CO)$_5$($C_2H_4PSiMe_3$) to W(CO)$_5$(C_2H_4PH). The conversion was complete after 24 h of continued stirring at room temperature. The volatile materials were removed *in vacuo* and the dark residue extracted into 40 : 60 petroleum ether (2 × 10 ml). After concentrating to a small volume, **5** was crystallised as a white solid at −35 °C. Yield = 95 mg (47%). All spectroscopic and analytical data were as previously reported.[2]

***Fac*-[(η^5-C_5H_5)Fe(C_2H_4PH)$_3$](PF$_6$) (6b).** To a dark yellow solution of [(η^5-C_5H_5)Fe(η^6-C_6H_6)](PF$_6$) (100 mg, 2.91 × 10^{-4} mol) in dichloromethane (20 mL), was added a solution of **2** (3.5 equivalents, 1 mmol, 132 mg), and the mixture stirred in sunlight (12 h) after which time the colour had become dark red. Methanol (1 mL) was added, and the solution was allowed to stir for a further 4 h. The product was isolated by removal of the volatile solvents under reduced pressure, and recrystallised readily from MeOH at −35 °C. Yield = 97 mg (75%). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121.7 MHz) δ −170.0 (s) δ −143.2 ppm (m). ^1H NMR (CD_3NO_2 500 MHz) δ 4.45 (q, Cp 5H) δ 1.08 (d m P–H, 3H), δ 0.80, δ 1.39, δ 0.88 ppm (m, CH_2, 12H). $^{13}C\{^1H\}$ DEPT NMR (CD_3NO_2, 125.8 MHz) δ 76.5 (s, Cp), δ 0.0 ppm (m, CH_2). IR (KBr): 2344 cm^{-1} d, (ν_{PH}). *Anal*: calc for [(η^5-C_5H_5)Fe(HPC_2H_4)$_3$](PF$_6$): C, 29.62; H, 4.52. Found: C, 29.1; H, 4.4. ES-MS: *m/z* 301.03 amu ([M]•$^+$).

Preparation of C_2H_4PH *in situ*

To a stirred solution of $C_2H_4PSiMe_3$ in toluene (10 ml of a 10% w/v solution) was added MeOH (0.5 ml) at room temperature. $^{31}P\{^1H\}$ NMR analysis of the solution showed complete conversion of **2** to C_2H_4PH within minutes, as indicated by the presence of a

Table 1 Crystallographic data for compounds **3b** and **4a**‡

Compound	**3b**	**4a**
Empirical formula	$C_{18}H_{39}O_3P_3Si_3Cr$	$C_9H_{15}O_3P_3Mo$
Formula weight	532.67	360.06
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/c$
a/Å	10.875(2)	12.5870(4)
b/Å	14.883(3)	8.2520(3)
c/Å	17.718(4)	13.8730(6)
β/°	96.86(3)	92.499(1)
U/Å^3	2847.2(10)	1439.59(9)
Z	4	4
D_c/Mg m^{-3}	1.243	1.661
$F(000)$	1128	720
θ range/°	3.12 to 27.00	2.94 to 27.46
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-22 \le l \le 22$	$-16 \le h \le 16$, $-10 \le k \le 10$, $-17 \le l \le 18$
Reflections: Collected	11 429	20 472
Reflections: Independent	6157	3278
R_{int}	0.0354	0.1391
Data/restraints/parameters	6157/16/273	3278/0/145
Goof (on F^2)	1.009	1.082
Final $R1$, $wR2$ $[I>2\sigma(I)]$	0.0399, 0.0788	0.0434, 0.0977
(all data)	0.0596, 0.0857	0.0543, 0.1027
Largest diff. peak and hole/e Å^{-3}	0.414 and −0.371	0.594 and −1.160

single peak at −309 ppm that appeared as a doublet of multiplets in the ^{31}P NMR spectrum. ^{1}H and ^{13}C NMR spectra obtained following addition of MeOD to a C_6D_6 solution of **2** on an NMR scale confirmed the formation of C_2H_4PH (as the sole phosphorus containing product) and Me_3SiOMe; the spectra were in full agreement with those published previously.[17]

Crystallography

All single crystal X-ray data was collected at 150 K on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), equipped with an Oxford Cryostream cooling apparatus. Crystallographic data is collected in Table 1. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV.[23] Structure solution was achieved by Patterson methods (Dirdiff-99 program system[24]) and refined by full-matrix least-squares on F^2 (SHELXL-97[25]) with all non hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. For compound **3b**, one methyl group was disordered and was successfully modelled with a two-site occupancy of 51% and 49%, the former being shown in Fig. 1. Molecular structures in the figures were drawn with ORTEP 3.0 for Windows (version 1.08).[26]

Conclusions

1-Trimethylsilylphosphirane is a readily prepared, thermally stable phosphirane that is a versatile synthon allowing access to phosphirane chemistry. 1-Trimethylsilylphosphirane forms readily accessible coordination compounds with d^6 organometallic species within which the P–Si bond remains susceptible to protolysis giving rise to parent phosphirane complexes cleanly and in good yield. We are currently exploring further aspects of the coordination chemistry of $C_2H_4PSiMe_3$ and C_2H_4PH and their application in synthesis.

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