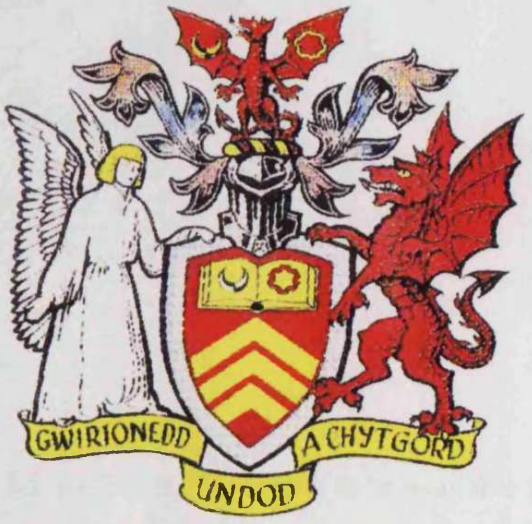
New Aspects Of Low Co-ordination Phosphorus Chemistry

By

Markus Brym



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Die Wiſſenſchaft fängt eingentlich erſt da an,
intereſſant zu werden, wo ſie aufhört.

- Justus von Liebig -
(1803 - 1873)

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ABSTRACT

The work presented in this thesis revolves around one main theme: the chemistry of low co-ordinated phosphorus. The work is divided into six chapters. Chapter one is a general introduction and gives a brief review of the basic properties of group 15 elements. The double bond rule is introduced as well as the concept of low co-ordination and how low co-ordinate main group species can be stabilised using bulky substituents and / or delocalisation of electrons.

Chapter two describes the reaction of Vaska's Compound, $[IrCl(CO)(PPh_3)_2]$, with the phosphavinyl Grignard reagent Z-$[CyP=C(Bu^t)Mg(OEt_2)Cl]$ to yield the novel iridaphosphirene $[Ir\{=C(Bu^t)P(Cy)\}(CO)(PPh_3)_2]$. Its reactivity towards a number of reagents such as protic reagents and chalcogens has been investigated. Furthermore, its auration, argentation and mercuration reactions have been investigated. In all these cases, reaction occurs at the phosphorus centre of the 3-membered ring and not at the metal centre. The protonated complexes, $[Ir\{=C(Bu^t)P(H)(Cy)\}(CO)(PPh_3)_2][X]$, (X = $CF_3CO_2^-$, $CF_3SO_3^-$, BF_4^-), showed an irreversible 1,2-hydrogen shift to yield a cationic iridium(I)-phosphaalkene complex, $[Ir(CO)(PPh_3)_2\{\eta^1\text{-}P(Cy)=C(H)(Bu^t)\}][X]$. The phosphaalkene could be liberated from the metal complex. In addition, a stereospecific synthetic route to E-phosphaalkenes has been described.

Chapter three describes the preparation and characterisation of the first diphosphaalkyne, $[P\equiv CC(C_6H_4)_3CC\equiv P]$. Additionally its reactivity is discussed and investigated. These preliminary studies have shown that its reactivity mimics that of known mono-phosphaalkynes.

Chapter four describes the chemistry of a triphosphacyclohexadienyl anion. In its reactions with a variety of transition and main group metal halides, "decomposition" to the 2,4,5-tri-*tert*-butyl-1,3-diphospholyl anion was often observed. Some main group metal complexes such as $[Tl(\eta^5\text{-}P_2C_3Bu^t_3)]$ and the tetraphosphametallocenes $[M(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ (M = Sn, Pb) have been prepared and structurally characterised. The fluxional behaviour of the latter two has been investigated by low temperature $^{31}P\{^1H\}$ NMR spectroscopy.

Chapter five describes the preparation of several crystalline and air stable triptycene group 15 chlorides, $[HC(C_6H_4)_3CECl_2]$ (E = P, As, Sb, Bi), and hydride compounds, $[HC(C_6H_4)_3CEH_2]$ (E = As, Sb).

Chapter six describes miscellaneous results obtained during these investigations; some revolve around several iridium compounds, *e.g.* ortho-metallated Vaska's compound, $[IrHCl(CO)(PPh_3)\{\eta^2\text{-}PPh_2(C_6H_4)\}]$, others around group 15 formamidinate and phenolate compounds, and others around ruthenium phosphaalkenyl chemistry.

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ABBREVITATIONS

Å	Angstrom units, 10^{-10} m
Ad	Adamantyl
anal.	Analysis
Ar	A general aromatic substituent
Bbt	2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl
bp	Boiling point
br.	Broad
Bu^n	Normal butyl
Bu^t	Tertiary butyl
ca.	Approximately
calc.	Calculated value
cf.	Compare with
cm	10^{-2} m
COD	1,5-Cyclooctadiene
COT	Cyclooctatetraene
Cp	Cyclopentadienyl
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
Ct	Centroid
Cy	Cyclohexyl
Cy^P	Cyclopentyl
d	Doublet
DBU	1,8-Diazabicyclo[5.4.0]undecene-7
DCM	Dichloromethane
dd	Doublet of doublets
dec.	Decomposes
δ (Delta)	Chemical shift in ppm
DFT	Density functional theory
Diglyme	Diethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_2CH_3$
DME	1,2-Dimethoxyethane (monoglyme)

DMSO	Dimethyl sulfoxide
e	Electron
E	A general non-metal
EI/CI	Electron impact / chemical ionisation
Et	Ethyl
Fiso	N-N'-Di(2,6-diisopropylphenyl)formamidinate
g	Grams
η^n	Hapticity, through n atoms
HFiso	N,N'-Bis-(2,6-diisopropyl-phenyl)-formamidine
HOMO	Highest occupied molecular orbital
Hz	Hertz, s^{-1}
IR	Infrared
L	A general ligand
λ^n	Indicates a non-standard bonding number
LSIMS	Liquid secondary ion mass spectrometry
LUMO	Lowest unoccupied molecular orbital
M	A general metal or concentration in moles per litre
m.	Multiplet
M^+	Molecular ion
μ	Symbol for bridging ligands
Me	Methyl
Mes	1,3,5-Trimethylphenyl
Mes*	1,3,5-Tri-*tert*-butylphenyl
ml	Millilitres
MO	Molecular orbital
mp.	Melting point
MW	Molecular weight
NBD	Norbornadiene
NBS	N-Bromsuccinimide
$^nJ_{xy}$	Coupling constant between nuclei X and Y, over n bonds in hertz
nm	10^{-9} m
NMR	Nuclear magnetic resonance

OTf	Triflate anion
Ph	Phenyl
ppm	Parts per million
Pr^i	Isopropyl
Pr^n	Normal propyl
q	Quartet
R	A general non-aromatic organic substituent
s	Singlet
Tbt	2,4,6-Tris(bis(trimethylsilyl)methyl)phenyl
Tetraglyme	Tetraethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_4CH_3$
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
TLC	Thin layer chromatography
TMEDA	N,N,N'N'-tetramethylethane-1,2-diamine
Tp'	$[HB(3,5\text{-}Me_2C_3HN_2)_3]$
tr.	Triplet
tript	Triptycene; 9,10-dihydro-9,10[1'2']benzenoanthracene
υ	Frequency
unres.	Unresolved
UV	Ultra violet
X	Halide

Chapter One

1 General introduction

1.1 The group 15 elements

1.1.1 Background

Group 15 of the periodic table consists of nitrogen, phosphorus, arsenic, antimony and bismuth. The elements of this group have the general electron configuration ns^2np^3. The physical properties of this group vary widely since nitrogen is a gas, and the other elements are solids of an increasingly metallic character upon descending the group. Nitrogen in its elemental form is a diatomic gas formed from a nitrogen nitrogen triple bond. Two stable isotopes of nitrogen are known, ^{14}N with an abundance of 99.63 % and ^{15}N with an abundance of 0.37 %. ^{15}N with a nuclear spin of ½ can be used in NMR experiments.

Phosphorus occurs in four different modifications, there are three crystalline and one amorphous modification. The white, violet and black modifications are crystalline, whilst red phosphorus is amorphous. The most common and reactive allotrope is white phosphorus. In contrast to nitrogen, phosphorus consists of tetrahedral P_4 units. This can be understood by considering the relative strengths of the triple and single bonds of these two elements. Nitrogen prefers a triple bond since it has more than three times the energy of a single-bond, whereas for phosphorus the triple-bond energy is less than three times the single-bond energy and so allotropes having three single bonds per phosphorus atom are more stable than those with a triple bond.[1] Furthermore, the covalent radius of nitrogen is anomalously small which makes it easier to form multiple bonds.

E (N≡N) / kJ per mol of N	946	E (P≡P) / kJ per mol of P	490
E (>N-N<) / kJ per mol of N	159	E (>P-P<) / kJ per mol of P	200
Ratio	5.95	Ratio	2.45

Table 1.1 Relative bond strengths of nitrogen and phosphorus

White phosphorus is pyrophoric and burns in air with a bright flame. Red phosphorus is obtained from heating white phosphorus, and is much denser with a higher melting point. Black phosphorus is the most thermodynamically stable allotrope and has a well-defined polymeric structure. Only one stable isotope is known, $^{31}_{15}P$, therefore its atomic weight is known with extreme accuracy: 30.973762.[2] Six radioactive isotopes are known, of which ^{32}P is by far the most important. It finds use in tracer and mechanistic studies as well as in medicine. ^{31}P has a nuclear spin quantum number of ½; as a result it is much used in NMR spectroscopy.[2]

Arsenic, antimony and bismuth exist in several allotropic forms though the allotropy is not as extensive as in phosphorus. The most stable form of arsenic is the rhombohedral form, the grey or "metallic" arsenic. In the vapour phase at 800 °C arsenic consists of tetrahedral As_4 molecules, above 1700 °C, as As_2 molecules. By rapid condensation of arsenic vapour with liquid nitrogen yellow arsenic can be obtained. Arsenic is considered a semi metal or metalloid. In compounds arsenic can be anionic like a non metal, *e.g.* metal arsenide, or cationic polarised, *e.g.* arsenic oxide. The same is true for the next group member antimony. Bismuth on the other hand only shows metallic character, so it only appears in nature in the cationic form. The common modification of antimony is the rhombohedral form, grey or metallic antimony. The crystal structure is analogous to that of grey arsenic. The Sb_4 molecule is only stable in the gas or liquid phase; on condensation the polymeric amorphous form is obtained. The rhombohedral structure of grey or metallic bismuth is identical to grey arsenic and grey antimony. Like antimony vapour, bismuth vapour consists of Bi_2 and Bi_4 molecules. The isolation of Bi_4 by rapid condensation with liquid nitrogen does not yield a metastable form.

Arsenic has only one stable isotope, $^{77}_{33}As$, while antimony consists of two stable isotopes, $^{121}_{51}Sb$ (57.3 %) and $^{123}_{51}Sb$ (42.7 %). The heaviest stable isotope of any element is the only stable bismuth isotope $^{209}_{83}Bi$; all nuclides beyond it are radioactive.[1]

	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electron Configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10}4s^2 4p^3$	$[Kr]4d^{10}5s^2 5p^3$	$[Xe]4f^{14}5d^{10}6s^2 6p^3$
Electronegativity					
Pauling	3.04	2.19	2.18	2.05	2.02
Allfred Rochow	3.07	2.06	2.20	1.82	1.67
Melting point / K	63.3	317.3	1090.0	903.9	544.4
Density / $kg \cdot m^{-3}$	1.2506	1820 (white)	5780	6691	9747
Resistivity / $\mu\Omega$ cm	-	-	33.3 (α)	41.7 (α)	120 (α)
Σ 1^{st} ionisation energies / MJ mol^{-1}	8.835	5.825	5.481	4.872	4.779
Covalent radii / nm	0.070	0.110	0.121	0.141	0.146

Table 1.2 Selected properties of the group 15 elements [1-5]

1.1.2 The inert pair effect

The inert pair effect is often observed in many main group element compounds, a classic example would be the difference in the stability of the oxidation states of carbon and lead; *i.e.* Carbon prefers the +4 oxidation state while lead favours the +2 state. Commonly the principle of hybridisation is used to describe bonding. In order for hybridisation to take place, the orbitals mixing must be of similar energy. Upon descending a group the energy gap between s and p orbitals increases, this makes hybridisation less favourable. Using group 14 elements to highlight this, it is often observed that four valent carbon is described by invoking the presence of sp^3 hybrid orbitals, in the case of lead this is far less common. Relativistic effects are considered to play a role for heavier elements in the contraction of s orbitals and thus the inert pair effect.[6, 7]

The inert pair effect is also observed in the first and second main groups, *e.g.* sodium is observed as Na^- with a suitable, complex cation. Calcium forms, with suitable complexing agents, compounds with a zero valent metal centre, *e.g.* $Ca(NH_3)_6$. In both cases the result is a filled s-shell.[2] The inert pair effect can be defined as the resistance of a pair of s electrons to participate in covalent bond formation.[8]

1.1.3 The double bond rule and low co-ordination chemistry

A situation in which the co-ordination number of an element in a compound is less than its common valency, thereby implying the presence of a multiple bond, is the best definition of a low co-ordination compound. Low co-ordination states in compounds containing first row elements are extremely common. Bonds such as C=C, C=O, C=N, C≡C and C≡N represent some of the most important functional groups in organic chemistry.

The chemistry of compounds featuring multiple bonds between the heavier main group elements has attracted attention in recent years.[9] The so-called "classical double bond rule"[10] predicted only stable compounds with double bonds within the elements of the second row (hereby hydrogen and helium are considered as first row

elements). It was believed that due to a large distance between the elements and poor overlap of the valence p orbitals, such bonding should not be possible for the heavier elements. This was supported by a number of unsuccessful attempts to synthesize such compounds. A classical example is the "phosphabenzene" of *Köhler* and *Michaelis*. They reported the formation of diphenyldiphosphene, Ph-P=P-Ph, in a condensation reaction of $PhPCl_2$ and $PhPH_2$.[11] Later it was shown by molecular weight measurements and then by X-ray crystallography that this product was a mixture of oligomers of "phosphabenzene" (i.e. $(PhP)_5$ and $(PhP)_6$).[12, 13]

Ehrlich described the chemotherapeutic drug "Salvarsan" with a monomeric diarsene structure (**1**),[14, 15] but again X-ray crystallography later revealed its oligomeric character.[16] In 1950 *Mulliken* challenged the double bond rule in a report that detailed computational evidence based on experimental bond distances and orbital overlap.[17] It was shown that bond distances did not significantly alter when heavier elements were used instead of second row elements (hereby hydrogen and helium are considered as first row elements). It was proposed by *Mulliken* that the real basis for the double bond rule was that there was a greater difference between σ and π bond strengths for the heavier elements and the formation of two σ bonds was preferable to one π bond.

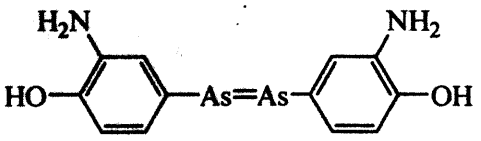
In the 1960's further doubt was cast on the reliability of the so-called double bond rule. During investigations carried out by *Gier* in which phosphine (PH_3) was passed through an electric arc between graphite electrodes, phosphaacetylene (HC≡P) was produced as a gas, stable only at low temperatures.[18] The reaction with anhydrous HCl, which afforded CH_3PCl_2 as the sole product, was further evidence for the proposed structure. An intensified search for the synthesis of stable compounds of this type was initiated by this discovery.

It was resonance stabilisation that yielded the first compound stable at room temperature to have a two co-ordinate phosphorus centre, a phosphenium cation (**2**).[19] This type of stabilisation also allowed the preparation of the complete series of heteroarenes C_5H_5E (E = N, P, As, Sb, Bi).[20] This field was established by *Märkl* in 1966 with the synthesis of 2,4,6-triphenylphosphabenzene (**3**).[21]

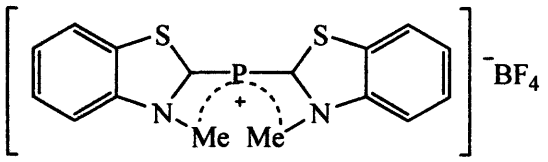
The first compound to be synthesised and isolated in which the possibility of multiple bonding between two heavier main group elements was evident, was

$[Sn\{CH(SiMe_3)_2\}_2]_2$ (**4**).[22, 23] This compound was prepared by *Davidson* and *Lappert* in 1973. It is monomeric in solution, but shows a double bond in the solid state. The crystal structure showed that the tin-tin distance was only slightly (0.03 Å) shorter then the tin-tin distance in elemental tin.[24, 25]

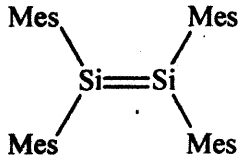
To prepare low co-ordinate main group element compounds, the multiple bonds have to be kinetically protected. Such protection can be achieved for example by introduction of sufficiently large substituents. This is necessary to avoid oligomerization of these reactive species. The introduction of bulky substituents led to the first synthesis of a disilene (**5**)[26] and a diphosphene (**6**)[27] in 1981.



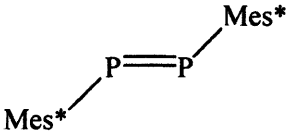
(**1**)



(**2**)



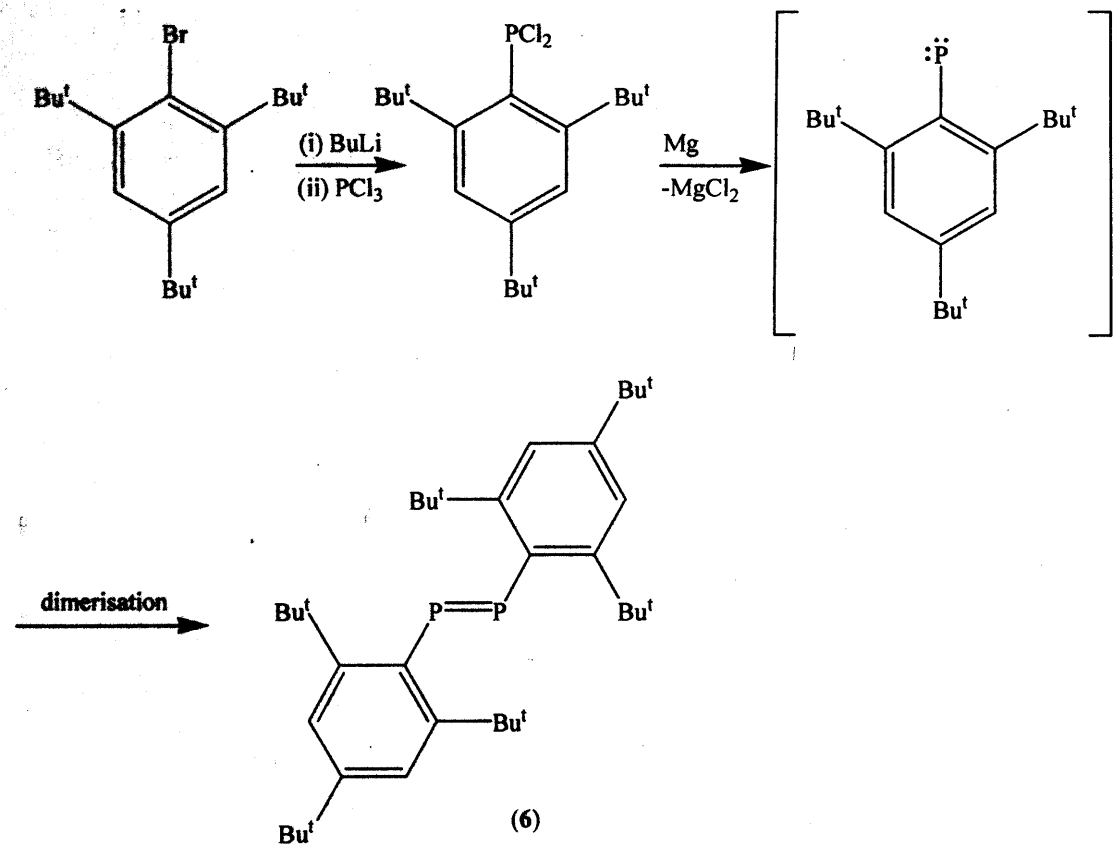
(**5**)



(**6**)

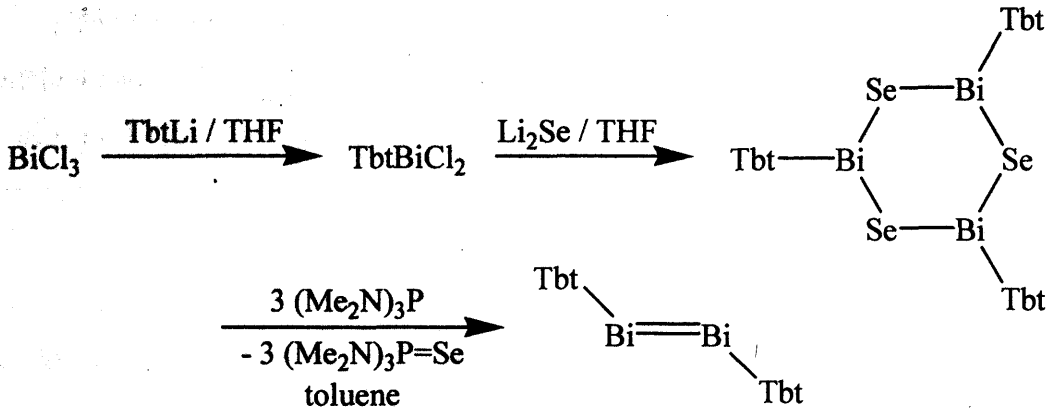
Figure 1.1 Examples of low co-ordination group 15 compounds

The diphosphene (**6**) was obtained by *Yoshifuji et al.* by the reduction of (2,4,6-tri-*tert*-butylphenyl)phosphorus dichloride with elemental magnesium (Scheme 1.1). From the isolation of this product it was clear that low co-ordination phosphorus compounds were able to exist under normal conditions because (**6**) was found to be air and moisture stable and had a high decomposition temperature.



Scheme 1.1 Synthesis of a diphosphene by *Yoshifuji*

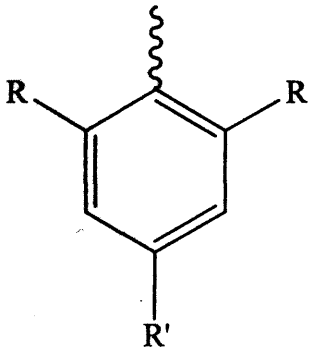
By the use of even bulkier substituents *Power et al.* have been able to prepare a homologous series of element dipnictenes, R-E=E-R (E = P, As, Sb, Bi).[28] The first bismuth-bismuth double bond was, however, reported for compound (**7**), 16 years after the diphosphene (**6**). In 1997 *Tokitoh et al.* succeeded by taking advantage of the bulky group, Tbt (2,4,6-tris(bis(trimethylsilyl)methyl)phenyl) (Scheme 1.2).[29] Compound (**7**) contained the first example of a multiple bond between sixth row elements.



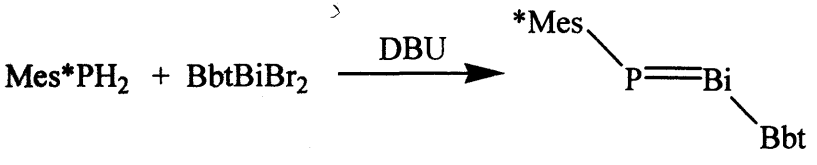
(7)

Scheme 1.2 Synthesis of a stable dibismuthene

The synthesis of the first phosphorus bismuth double bond was also accomplished by kinetic stabilisation using steric protection (Scheme 1.3).[30] Compound (**8**) was prepared by the condensation reaction of $BbtBiBr_2$ and Mes^*PH_2. It is the first example of a stable compound containing a double bond between third and sixth row main group elements.



Mes* R = R' = Bu^t
Tbt R = R' = $CH(SiMe_3)_2$
Bbt R = $CH(SiMe_3)_2$, R' = $C(SiMe_3)_3$



(**8**)

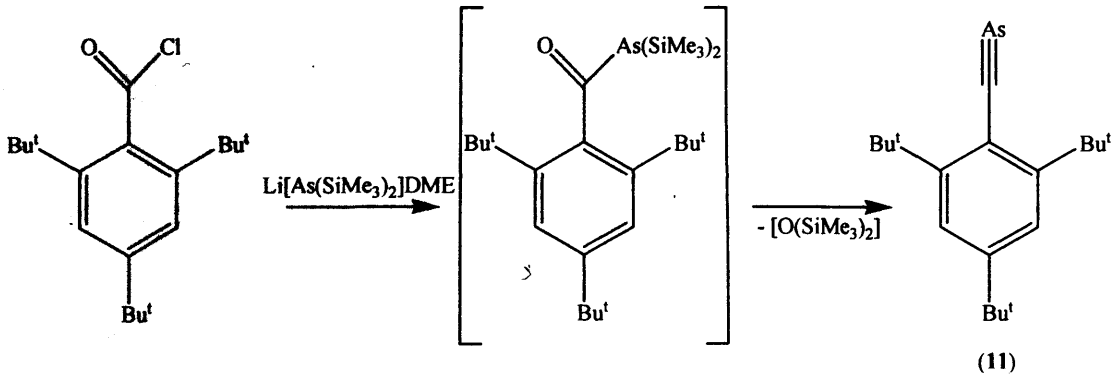
Scheme 1.3 Synthesis of a phosphabismuthene

The first example of a compound with a localised acyclic phosphorus carbon double bond was the phosphaalkene $(Me_3Si)P=C(Bu^t)(OSiMe_3)$ (**9**), reported by *Becker* in 1976. The double bond is kinetically stabilised by the presence of a sterically encumbered substituent.[31]

The preparation of compounds containing localised phosphorus carbon triple bonds has also been achieved by the use of encumbered substituents. The first example to be stable at room temperature was $P\equiv CBu^t$ (**10**). This was prepared by the catalytic elimination of hexamethyldisiloxane from (**9**) as reported by *Becker* in 1981.[32] The colourless liquid is remarkably stable and opened the new field of phosphaalkyne chemistry. Many more phosphaalkynes have subsequently been reported and characterised. Several reviews of their chemistry have been published.[33-35]

These compounds have developed from being chemical curiosities to versatile and widely utilised starting materials for the preparation of organophosphorus cage, heterocyclic and acyclic compounds, phospha-organometallics and co-ordination complexes which display a variety of phosphaalkyne ligation modes.[33-37]

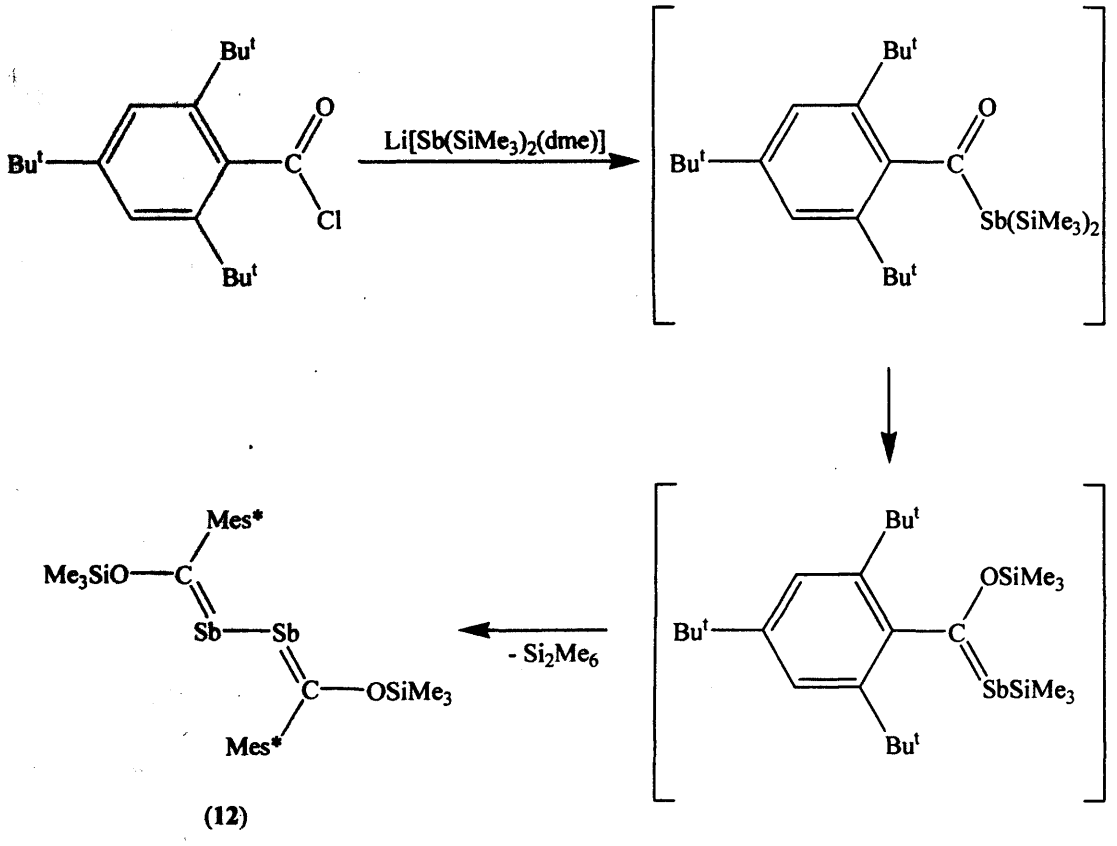
Multiple bonds involving the heavier group 15 elements are less common. The only known arsaalkyne to be stable at room temperature, Mes*C≡As (**11**), was synthesised by *Märkl et al.*[38] (Scheme 1.4)



(**11**)

Scheme 1.4 Synthesis of an arsaalkyne by *Märkl*

The preparation of a distibabutadiene (**13**) has been reported by *Nixon et al.* It was prepared by the reaction of Mes*COCl with $Li[Sb(SiMe_3)_2(DME)]$.[39] (Scheme 1.5) This is a closely related reaction to the preparation of phosphaalkynes and the arsaalkyne (**11**). But in contrast to the reaction described in Scheme 1.4, where the elimination of hexamethyldisiloxane yields the arsaalkyne, comparable stibaalkyne formation was not observed in their work. Instead the elimination of hexamethyldisilane in a coupling reaction yielded the 2,3-distibabutadiene (**12**).



(12)

Scheme 1.5 Synthesis and proposed mechanism for the formation of the distibabutadiene (12)

To date, there have been no reports concerning stibaalkynes or bismaalkynes.

1.2 References

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Chapter Two

2 Preparation and reactivity of an iridaphosphirene

2.1 Introduction

2.1.1 Grignard reagents

The most commonly handled organo-magnesium complexes are Grignard reagents. This is due to their easy preparation and synthetic versatility. They were first prepared by Victor Grignard (1871 - 1935) in 1900.[1] Further studies on the synthetic utility of Grignard reagents won him the Nobel prize for chemistry in 1912.

The main synthetic routes to Grignard reagents are the direct insertion of elemental magnesium into an alkyl or aryl halide in solvents such as diethyl ether or tetrahydrofuran (Scheme 2.1).[2]

$$Mg^0 + RX \xrightarrow{\text{ether}} RMgX$$

R = alkyl or aryl group, X = halide

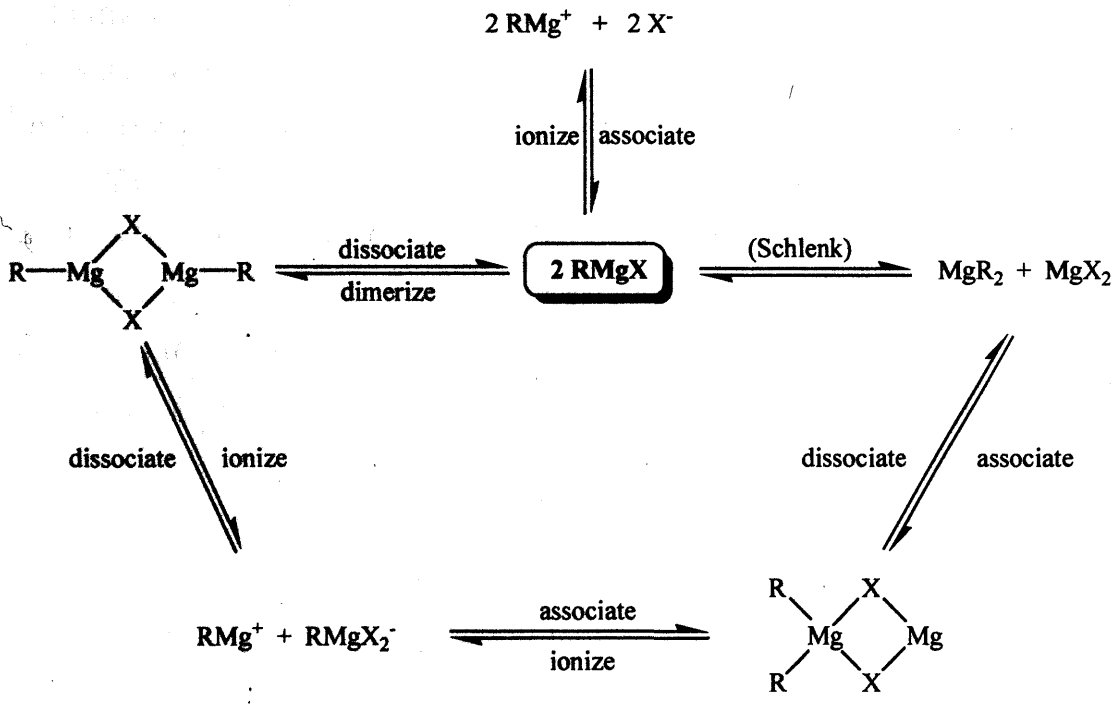
Scheme 2.1 Synthesis of Grignard reagents from elemental magnesium

Grignard reagents are mainly prepared and utilized in solution. Their formulation in solution has always been a source of uncertainty.[3] It now seems established that they contain a variety of chemical species interlinked by mobile equilibria, the positions of which depend on at least five factors:

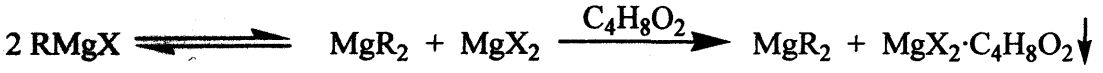
i) steric and electronic nature of the R group
ii) nature of the halogen
iii) nature of the solvent
iv) concentration
v) temperature

The most discussed feature of Grignard reagents in solution is the Schlenk equilibrium (Scheme 2.2).[4] Evidence for this and other equilibria comes from a variety of techniques such as vibrational spectroscopy, NMR spectroscopy,

molecular weight determinations, radio isotopic exchange using ^{28}Mg and electrical conductivity.[5] The Schlenk-equilibrium can be displaced in some cases by the addition of complexing agents such as 1,4-dioxane or crown ethers. The addition of 1,4-dioxane to an ethereal solution of a Grignard reagent causes precipitation of the magnesium halide; leaving a solution of MgR_2 (Scheme 2.3).[6]



Scheme 2.2 Equilibria exhibited by Grignard reagents



Scheme 2.3 Shift of the Schlenk equilibrium by magnesium complexation with 1,4-dioxane

The range of applications of Grignard reagents is now enormous and some examples of the extraordinary versatility of organomagnesium compounds can be found in nearly every chemistry text book.[7-9]

2.1.2 Phosphaalkenes

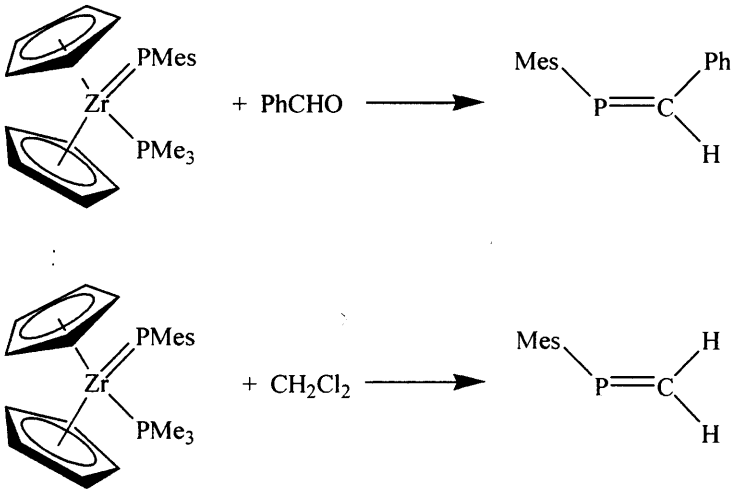
Phosphaalkenes are tervalent phosphorus compounds with a double bond between phosphorus and carbon. The earliest compounds containing a phosphorus-carbon double bond were reported by *Dimroth* and *Hoffmann* in the 1960's.[10, 11] The first thermally stable acyclic compound featuring a phosphorus-carbon double bond was prepared by *Becker* in 1976.[12] The system incorporated bulky substituents which gave it the necessary kinetic stability.

Unstable phosphaalkenes can be prepared by using high temperature pyrolysis of Me_2PH, $MePCl_2$ and CF_3PH_2 by 1,2 elimination reactions.[13-16] Other preparative routes for the formation of phosphaalkenes include 1,2 elimination reactions from suitable precursors with bases such as Et_3N, DBU, hexamethyldisilazine or metals such as lithium or sodium (*e.g.* Scheme 2.4).[17]

$$MesP(Cl)C(H)Ph_2 \xrightarrow[DBU\cdot HCl]{DBU} MesP{=}CPh_2$$

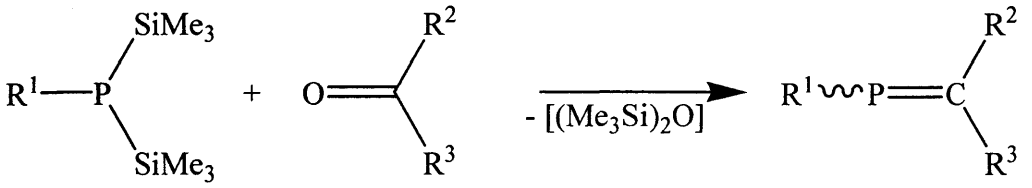
Scheme 2.4 An example of phosphaalkene formation *via* a 1,2-elimination reaction

Phosphaalkenes can also be obtained from transition metal complexes, for example in the reaction of terminal phosphinidene complexes with carbonyl compounds or dichloromethane (Scheme 2.5).[18-20]



Scheme 2.5 Examples of phosphaalkene synthesis from transition metal complexes

The most common and also the most simple route to phosphaalkenes is *via* condensation reactions (Scheme 2.6).[21-23]



R^1 = alkyl or aryl
R^2 = H
R^3 = Me_2N, Ph

Scheme 2.6 Phosphaalkene formation by condensation reactions

The phosphorus carbon double bond length has been established for several phosphaalkenes, the mean value being 1.708 Å.[24] This is significantly shorter than a phosphorus carbon single bond (1.85 Å). In addition, a comparison of π ionisation energies for $X=CH_2$ (X = CH_2, NH, PH) has indicated a closer similarity between carbon and phosphorus containing species then their nitrogen analogues.[25] Although the P=C bond has a lower strength than its carbon or nitrogen analogues, the P=C π system is more comparable to C=C than C=N in its conjugative interactions.[26-28] Calculations show that the lone pair on the phosphorus centre in phosphaalkenes will have some tendency to become involved in bonding to metal centres and this has been confirmed by thermodynamic data.[29] There are now five types of complexes known containing phosphaalkene ligands (Figure 2.1).[30] The structural integrity of the phosphaalkene ligand is largely retained in the complex types **A** to **E**.

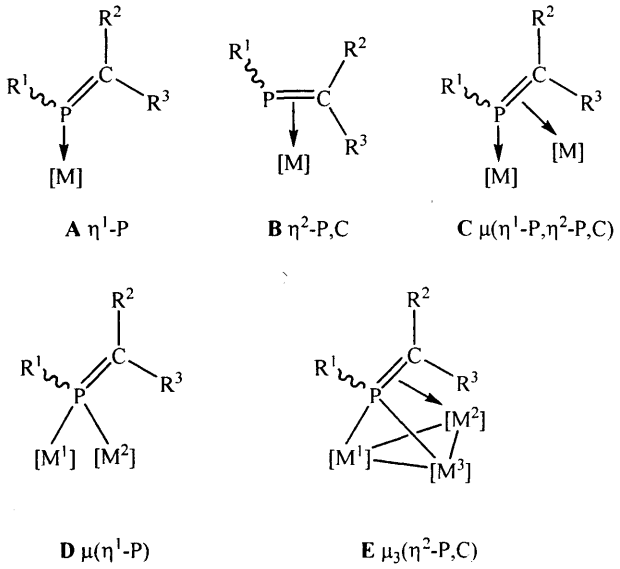


Figure 2.1 Basic phosphaalkene-transition metal co-ordination modes

2.1.3 Metallophosphaalkenes

In metallophosphaalkenes one or more substituents, R, on the phosphaalkene are replaced by a transition or main group metal fragment.[31] Hereby, five basically different types of compounds, **I - V,** can be differentiated.

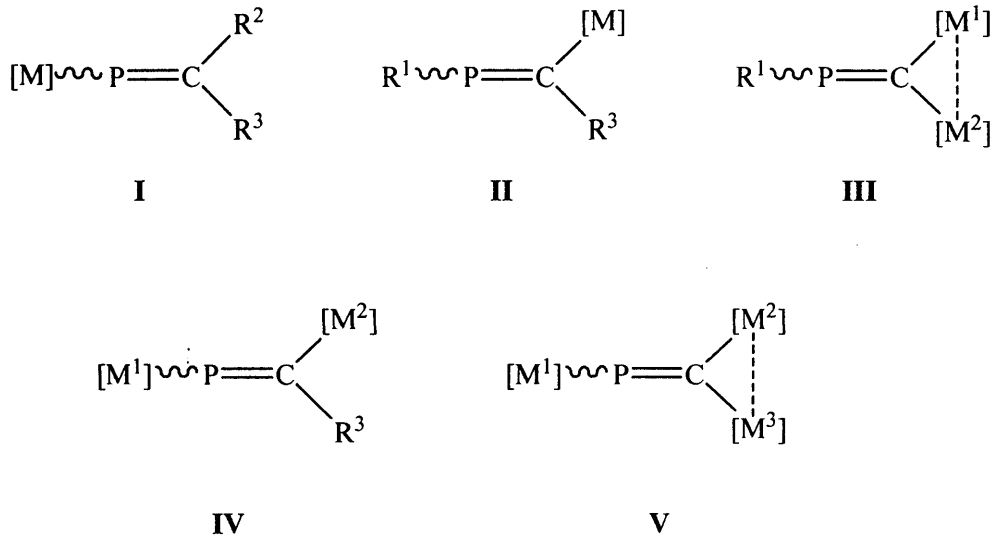


Figure 2.2 Basic type of metallophosphaalkenes

Many metallophosphaalkenes of type **I - IV** have been reported, the vast majority of which are type **I** and **II**, while representatives of type **V** still remain elusive.[32] Metallophosphaalkenes can be subdivided into P-metallophosphaalkenes and C-metallophosphaalkenes.

2.1.3.1 P-metallophosphaalkenes

Three general routes (a-c) are available for the synthesis of P-metallophosphaalkenes (Figure 2.3). In route (a), the P=C bond is constructed from precursors such as metallophosphanes. In route (b) a metal-phosphorus bond is formed between a P-functionalized phosphaalkene and an appropriate metal complex. In route (c) phosphaalkynes are reduced within the co-ordination sphere of a transition metal complex.[31]

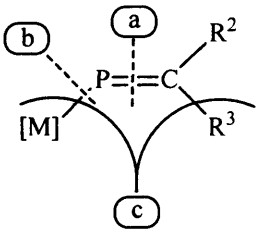
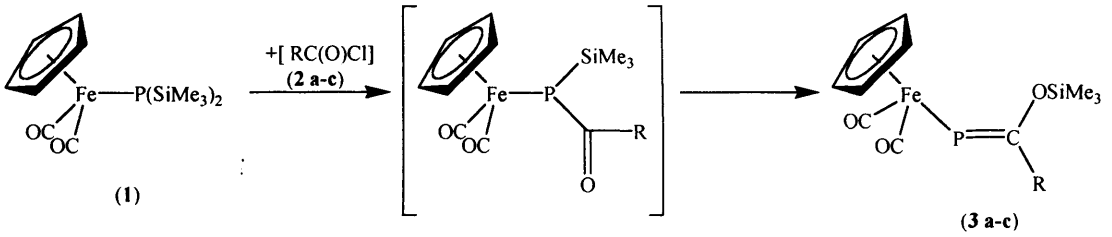


Figure 2.3 General routes to P-metallophosphaalkenes

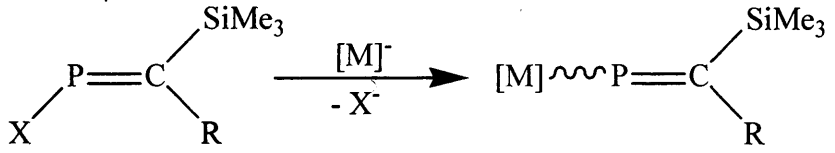
The reaction of metallodisilylphosphane (**1**) with acid chlorides (**2 a-c**) yielded the first P-metallophosphaalkenes (**3 a-c**) by route (a) (Scheme 2.7).[33, 34] Compounds (**3 a-c**) are type **I** metallophosphaalkenes. However this is not a general synthetic pathway as variation of the acid chloride substituent afforded varied products, for example $[Cp^*(CO)_2Fe\text{-}P(SiMe_3)_2]$ reacts with (**2 c**) to yield the diacylphosphido complex $[Cp^*(CO)_2Fe\text{-}P\{C(Bu^t)=O\}_2]$.[35]



a) R = Mes, b) R = Ph, c) R = Bu^t

Scheme 2.7 Synthesis of the first P-metallophosphaalkenes

An efficient method for the synthesis of P-metallophosphaalkenes by route (b) utilizes the reaction of halogeno(methylene)phosphanes with carbonylmetalate ions.[36-38]



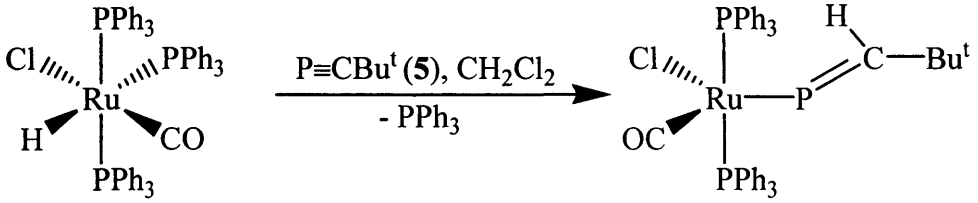
M = $[Cp(CO)_nZ]$ or $[Cp^*(CO)_nZ]$

Z = Mo or W, R = $SiMe_3$ or Ph, X = Cl or Br, n = 3

Z = Fe, R = $SiMe_3$ or Ph, X = Cl or Br, n = 2

Scheme 2.8 Synthesis of P-metallophosphaalkenes from carbonylmetalates and halogenophosphaalkenes

Access to P-metallophosphaalkenes by route (c) is based upon the 1,2-addition of suitable transition metal complexes across the PC triple bond of phosphaalkynes. During the reaction of the hydridoruthenium complex (**4**) with $P{\equiv}CBu^t$ (**5**) in a CH_2Cl_2 solution, the orange-red rutheniophosphaalkene (**6**) was formed in 92 % yield by a regioselective cis-addition (Scheme 2.9).[39]

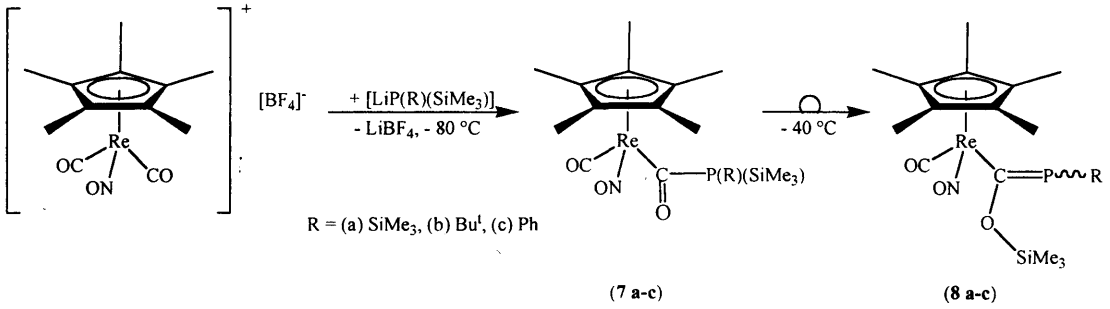


(**4**) (**6**)

Scheme 2.9 Formation of a rutheniophosphaalkene

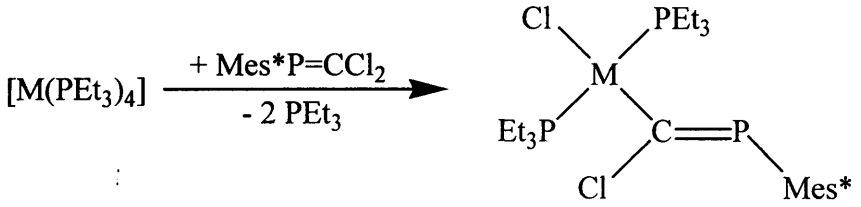
2.1.3.2 C-metallophosphaalkenes

The addition of lithiosilylphosphanes to the carbonylrhenium cation $[Cp^*Re(CO)_2(NO)]^+$ at - 80 °C in diethyl ether yielded the first C-metallaphosphaalkenes of type **II**. The initially formed complexes (**7 a-c**) can be seen in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures but these rearrange above - 40 °C to give the desired complexes (**8 a-c**) (Scheme 2.10).[40, 41]



Scheme 2.10 Synthesis of the first C-metallophosphaalkenes

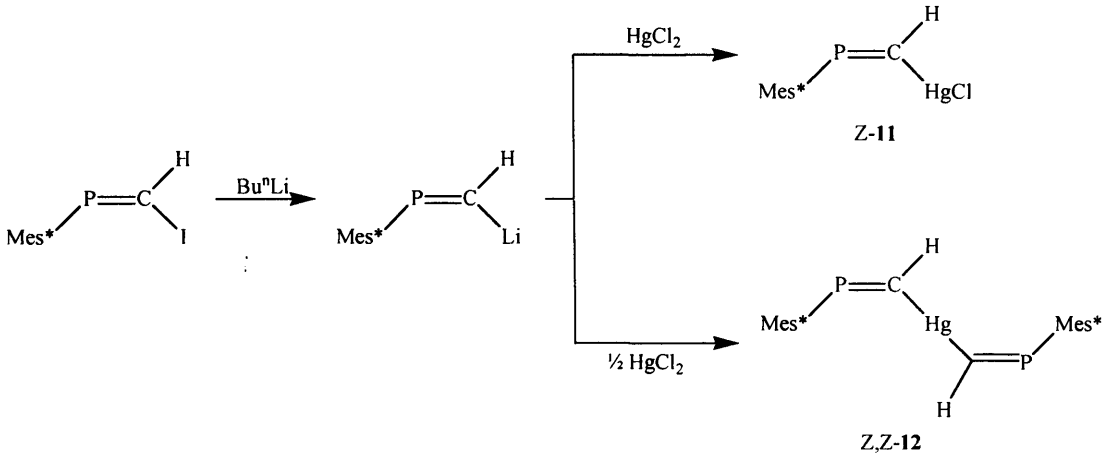
Two research groups have succeeded in the preparation of C-metallophosphaalkenes from phosphaalkenes which have halide functions on the methylene carbon atom.[42-44] The oxidative addition of $Mes^*P{=}CCl_2$ to $M(PEt_3)_4$, (M = Pt, Pd) yielded the trans-configured compounds (**9**) and (**10**) (Figure 2.11).[44]



(**9**) M = Pt
(**10**) M = Pd

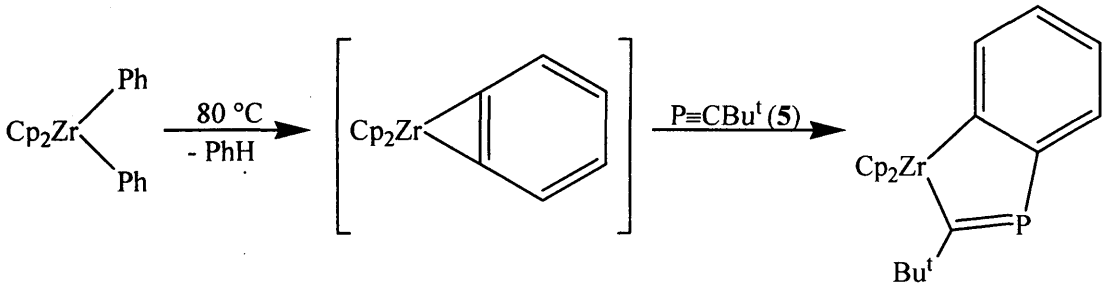
Scheme 2.11 Preparation of C-palladio- and C-platiniophosphaalkenes

Treatment of the organolithium compound (Z)-Mes*P=CHLi with one equivalent of mercury dichloride gave a mercuriophosphaalkene (**11**), while treatment with only half an equivalent of mercury dichloride resulted in the bisphosphaalkenyl derivate (**12**), both *via* salt elimination reactions (Scheme 2.12).[42]



Scheme 2.12 Synthesis of C-mercuriophosphaalkenes

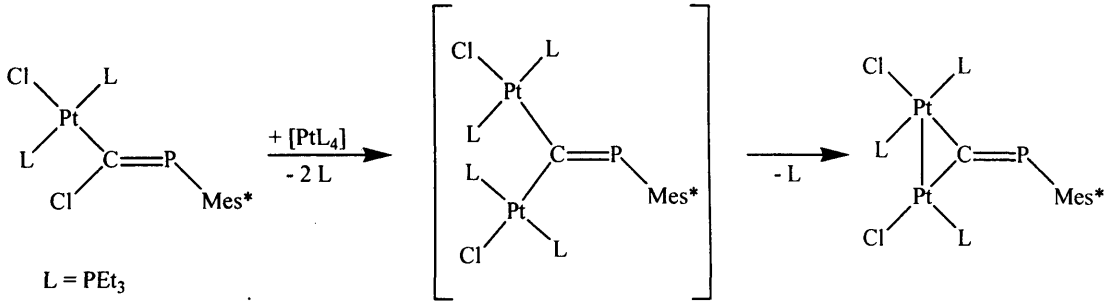
Another way to prepare C-metallophosphaalkenes is by the reaction of phosphaalkynes with transition- or main group metal compounds. These reactions often lead to the formation of metallaheterocycles featuring C-metallophosphaalkene fragments.[43] For example, when (**5**) is reacted with diphenyl zirconocene in n-hexane at 80 °C for several hours, the zirconiophosphaalkene (**14**) is obtained. The η^2-dehydrobenzene complex (**13**) was postulated as an intermediate in this reaction (Scheme 2.13).[45] It is noteworthy that an analogous titanium complex has also been reported.[46]



(13) (14)

Scheme 2.13 Preparation of a C-zirconiophosphaalkene from a phosphaalkyne

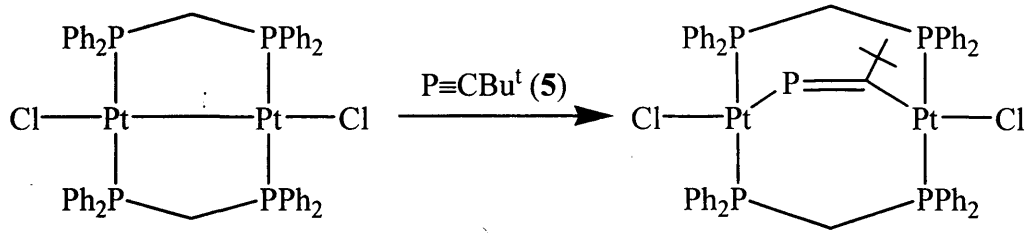
The first example of a type **III** metallophosphaalkene was reported by *Angelici et al.* in 1991.[44] The oxidative addition of $[Pt(PEt_3)_4]$ to the C-metallophosphaalkene (**9**) led to the formation of (**16**) in 65 % yield (Scheme 2.14).



(9) (15) (16)

Scheme 2.14 Synthesis of C,C-diplatiniophosphaalkenes (type III)

In another synthetic route, the addition of (**5**) to the diplatinum complex (**17**) yielded the first example of a type **IV** metallophosphaalkene, (**18**) (Scheme 2.15).[47]



(17) (18)

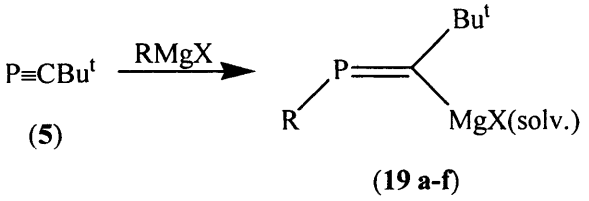
Scheme 2.15 Synthesis of a type IV metallophosphaalkene

One type of C-metallophosphaalkene are phosphavinyl Grignard reagents which are of emerging value in organophosphorus chemistry as versatile synthetic reagents.

2.1.4 Phosphavinyl Grignard reagents

The wide range of applications of vinyl Grignard reagents and the analogy between low co-ordinate phosphorus systems and their hydrocarbon counterparts led *Jones et al.* to expect a similar synthetic utility for phosphavinyl Grignard reagents.[48] Only a handful of such reagents were reported previous to their work, *e.g.* [Mes*P=C(X)MgBr] (X = halide, $SiMe_3$, Mes* = 2,4,6-$(Bu^t)_3C_6H_2$), all of which are substituted at the phosphorus centre with the bulky supermesityl group.[49, 50]

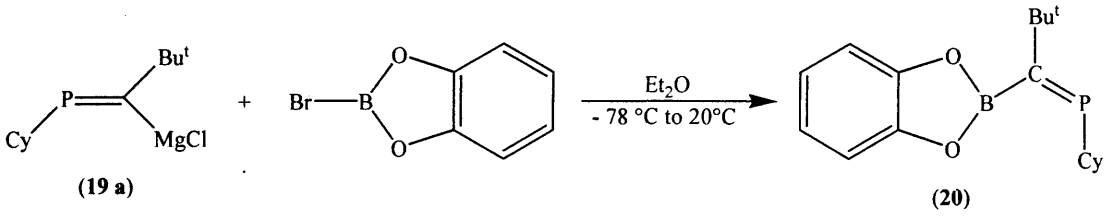
The reactions of $P{\equiv}CBu^t$ (**5**) with one equivalent of RMgX led to the formation of thermally stable phosphavinyl Grignard reagents in high yield (Scheme 2.16).[48, 51] The addition of the Grignard reagent to (**5**) is regio- and stereo-selective. NMR spectroscopy revealed only one isomer in solution, which X-ray crystallography suggested was the (Z)-isomer.



Scheme 2.16 Synthesis of some phosphavinyl Grignard reagents

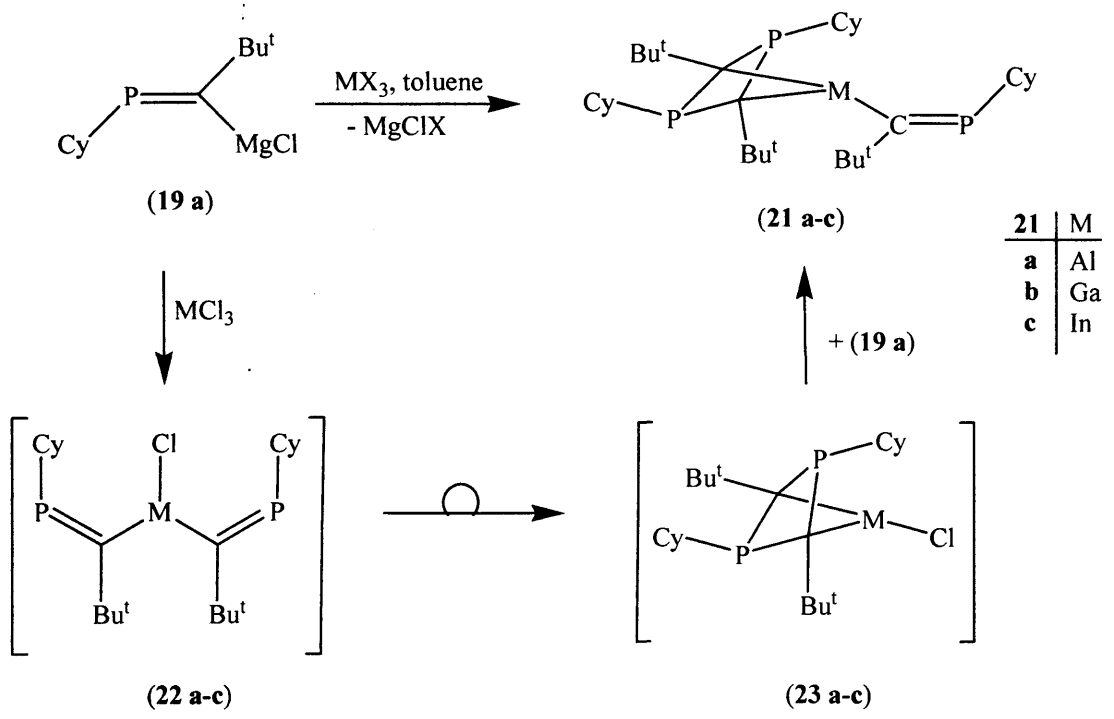
19	R	X	solv
a	Cy	Cl	Et_2O
b	Cy^P	Cl	Et_2O
c	Et	Br	Et_2O
d	Mes	Br	Et_2O
e	Pr^i	Cl	Et_2O
f	Bu^t	Br	THF

Phosphavinyl Grignard reagents have been found to be excellent precursors for a series of novel group 13 and group 14-metallophosphaalkenes *via* transmetalation processes. The use of vinyl boronic-acids and -esters in transition metal catalyzed C-C bond forming reactions, such as the Suzuki-cross coupling, is well established. It was obvious to envisage the preparation of the phosphavinyl equivalents of these boronic esters as building blocks in organophosphorus synthesis. To this end, bromocatecholborane was treated with one equivalent of Z-[CyP=C(Bu^t)Mg(OEt_2)Cl] (**19 a**), which cleanly afforded compound (**20**) as a waxy solid. Sublimation afforded analytically pure samples of the borylated phosphaalkene (Scheme 2.17).[52]



Scheme 2.17 Formation of a borylated phosphaalkene

In contrast, novel diphospha-metallobicyclo[1.1.1]pentane derivates (**21 a-c**) were prepared, unexpectedly, when (**19 a**) was reacted with group 13 halides in an attempt to prepare a series of homoleptic triphosphavinyl-group 13 compounds (Scheme 2.18).[53]

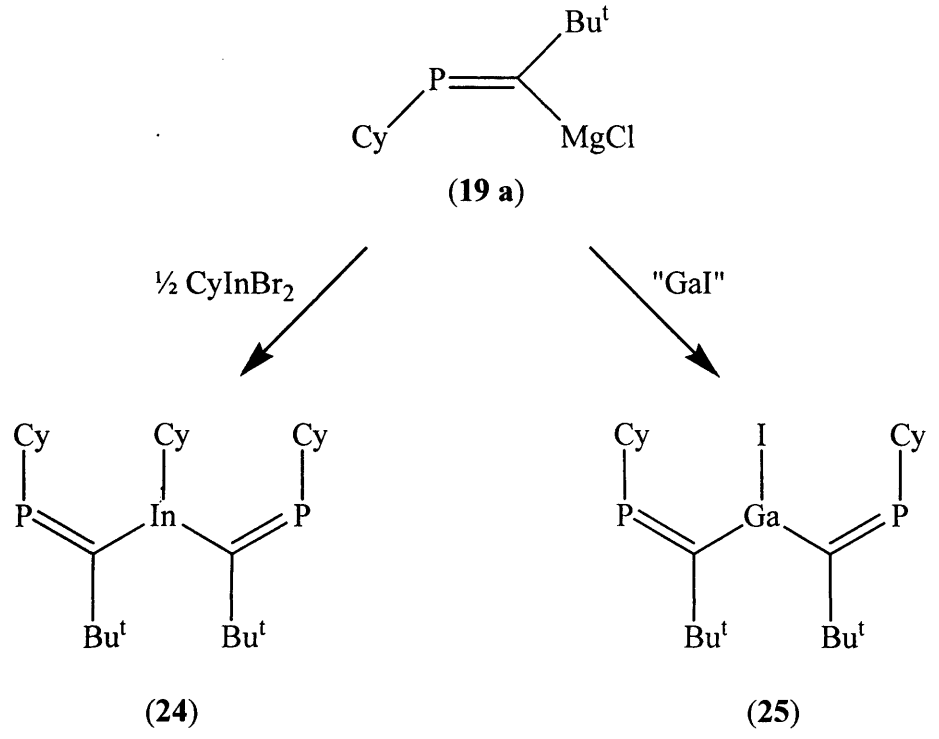


Scheme 2.18 Reaction of Z-[CyP=C(Bu^t)Mg(OEt$_2$)Cl] (19 a) with group 13 halides

No spectroscopic evidence for intermediates were observed in these reactions, but it is believed that the metal halide initially reacted with two equivalents of (**19 a**) to give the intermediates (**22 a-c**), which then underwent intramolecular phosphavinyl coupling reactions to yield (**23 a-c**). The reaction of (**23 a-c**) with a third equivalent of (**19 a**) resulted in the formation of (**21 a-c**).

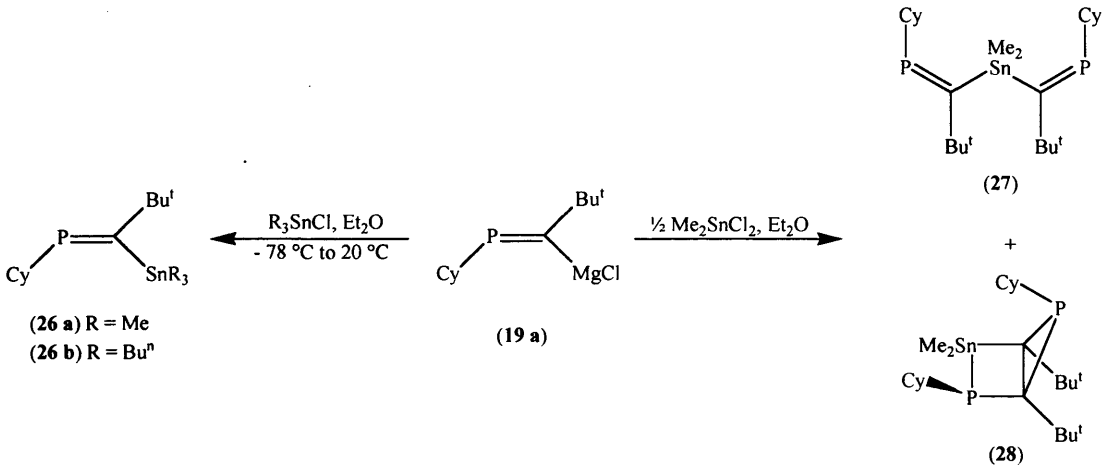
Treatment of two equivalents of (**19 a**) with *in situ* generated $CyInBr_2$ in toluene afforded the bis(phosphaalkenyl)indium derivative (**24**). Compound (**24**) is thermally stable and was obtained in 40 % yield (Scheme 2.19). Presumably the

bulky cyclohexyl group prevented the type of cyclization reactions, encountered in the formation of (**22 a-c**).[53] The reaction of (**19 a**) with "GaI" resulted in a similar compound to (**24**) (Scheme 2.19). The corresponding monohalides, InCl and TlCl, did not show such behaviour. In both cases the reaction of (**19 a**) led to metal deposition and high yield formation of the 2,4-diphosphabicyclobutane $Cy_2P_2C_2Bu^t$ *via* oxidative coupling reactions. It is noteworthy that (**25**) does not react with an extra equivalent of (**19 a**) to give a (**21 b**).[52]

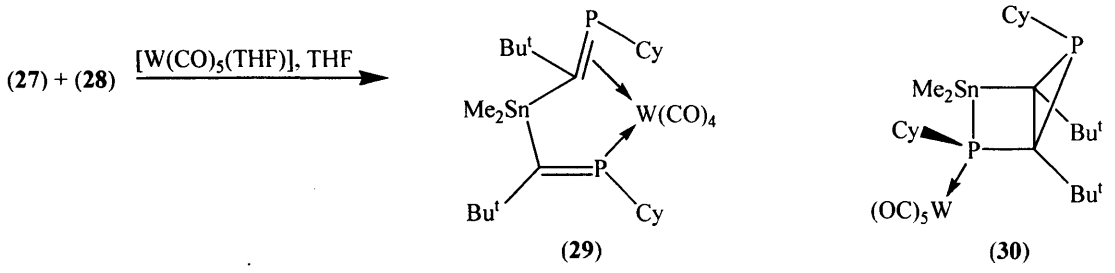


Scheme 2.19 Reaction of Z-[CyP=C(Bu^t)Mg(OEt$_2$)Cl] (19 a) with group 13 halide compounds

When (**19 a**) was treated with trimethyl- or tributyl-chlorostannane in diethyl ether at - 78 °C, the straightforward formation of the stannylated phosphaalkenes (**26 a-b**) occurred (Scheme 2.20). In contrast, compounds (**27**) and (**28**) were formed as an inseparable mixture when two equivalents of (**19 a**) were reacted with $SnMe_2Cl_2$ in diethyl ether. Treatment of this mixture with an excess of [$W(CO)_5$THF] in THF yielded an orange crystalline bis(phosphavinyl)tin complex (**29**) and a yellow diphosphastannabicyclopentane complex (**30**) after chromatographic workup (Scheme 2.21).[54]

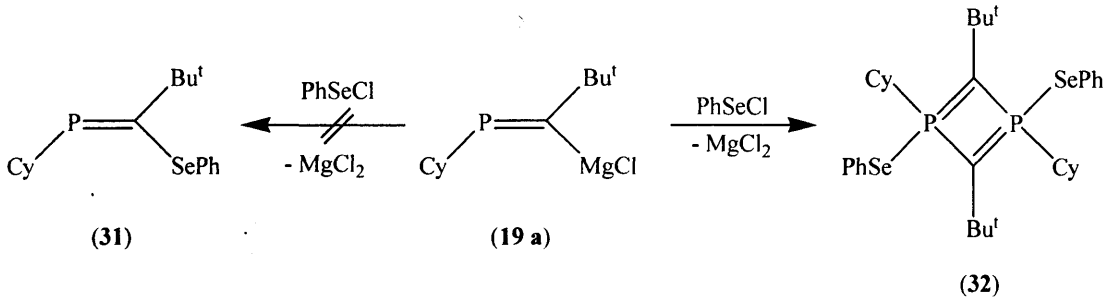


Scheme 2.20 Reaction of a phosphavinyl Grignard reagent with R_3SnCl and Me_2SnCl_2



Scheme 2.21 Tungsten carbonyl complexes of (27) and (28)

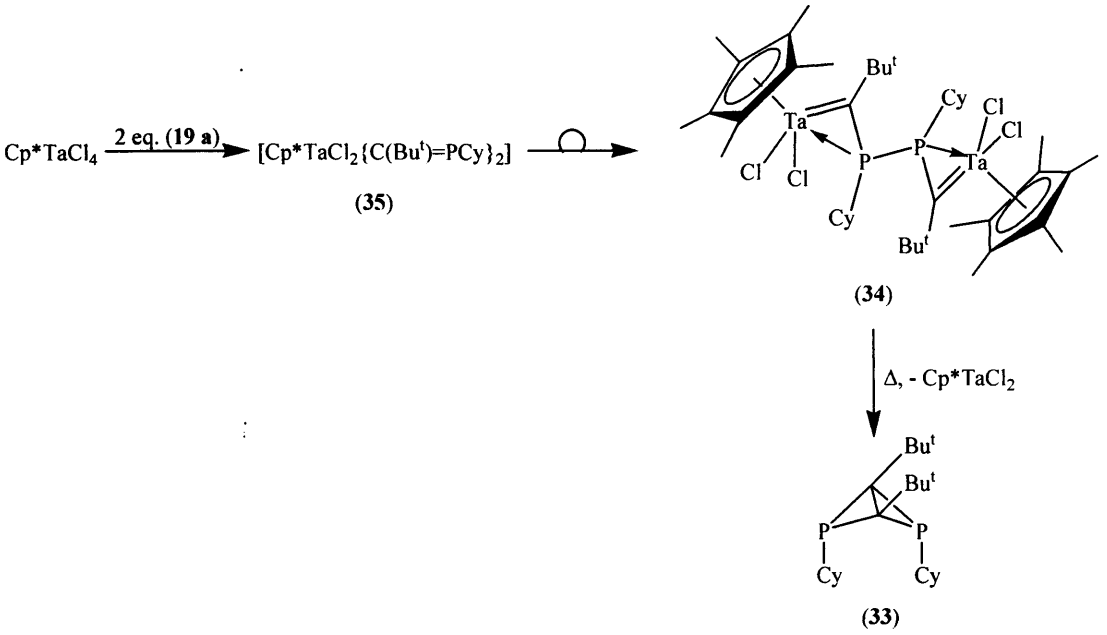
The 1:1 reaction of (**19 a**) with PhSeCl in diethyl ether did not afford the anticipated (Z)-phosphaalkenyl compound (Z)-[PhSe{C(Bu^t)=PCy}] (**31**) but instead the 1,3-λ^5,λ^5-diphosphete (**32**) in a high yield. It is thought that (**31**) was initially formed, as evidenced by a singlet observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at δ 320 ppm. Compound (**31**) then underwent a 1,2 selenyl shift to give a short lived λ^5-phosphaalkyne [Cy(PhSe)P≡CBu^t] which underwent a spontaneous [2+2] cycloaddition to give (**32**) (Scheme 2.22).[52]



Scheme 2.22 Reaction of Z-[CyP=C(Bu^t)Mg(OEt_2)Cl] (19 a) with PhSeCl

2.1 Introduction

Treatment of a slurry of Cp^*TaCl_4 with two equivalents of (**19 a**) resulted in a deep blue-green solution which changed colour to brown upon warming to room temperature. The product isolated from this reaction was the bicyclic compound (**33**) which resulted from an oxidative coupling process. The blue-green intermediate (**34**) could be isolated when the reaction mixture was kept below - 30 °C. It was assumed that the C-metallophosphaalkene (**35**) was formed as initial product. The reaction mechanism was proposed to involve a series of redox reactions and rearrangements to give the radical $[Cp^*TaCl_2\{=C(Bu^t)\text{-}P\text{-}Cy\}]\cdot$, which dimerized to give (**33**).[55]

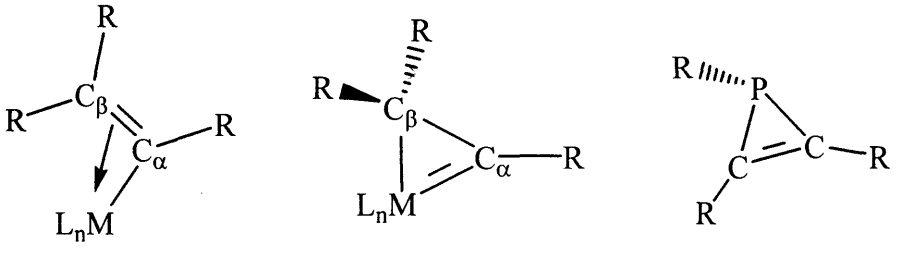


Scheme 2.23 Reaction of (19 a) with Cp^*TaCl_4

2.1.5 Metallocyclopropenes and phosphirenes

The $[\eta^2\text{-}\{C(R)=CR_2\}]^-$ ligand has been alternately described as an η^2-vinyl ligand or as an η^2-alkenyl ligand. Its resulting complexes can been called either η^2-vinyl (**36**) or 1-metallacyclopropene complexes (**37**).[56] Both names adequately describe the η^2-$CRCR_2$ ligand but the η^2-vinyl seems less helpful in understanding the bonding and structure of the complex. A "vinyl-group" implies a geometry in which the two vinyl carbons and their four attached groups lie in the same plane. It also leads to the expectation that a short C=C distance, similar to alkenes should be observed. The term "1-metallacyclopropene" implies the η^2-$CRCR_2$ ligand having a metal-carbon double bond to the monosubstituted carbon and a metal-carbon single bond to the disubstituted carbon[57]. This is based on structural evidence, *viz.* shortness of the M-C_α bond and the fact that the M-C_α-R fragment is often almost perpendicular to the R-C_β-R fragment; spectroscopic evidence, viz. the C_α centre resonates at very low field and the C_β centre at much higher field in the ^{13}C NMR spectra of these complexes; and theoretical evidence, *viz.* the results of DFT studies.[57] However, there have been a small number of complexes reported which contain close to planar vinyl ligands that are weakly η^2-co-ordinated to the metal centre.[58]

The first example of a phosphirene, generalized in Figure 2.4 as (**38**), was reported by *Marinetti* and *Mathey* by an unambiguous synthesis in 1982.[59] Several structural studies of the phosphirene ring have been carried out and have shown that the heterocycles are characterised by a small CPC intracyclic angle in the range of 42 - 46 °. As a result the ^{31}P nucleus of phosphirenes tends to resonate at high fields.[60]



(**36**) (**37**) (**38**)

Figure 2.4 Generalized η^2-vinyl-, 1-metalla-cyclopropene, phosphirene units

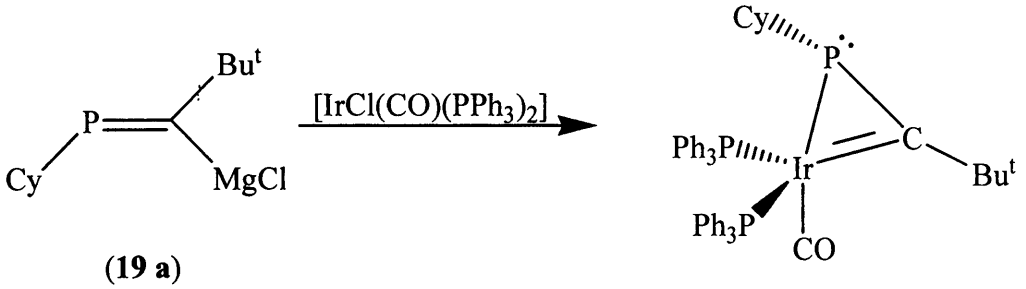
2.2 Research Proposal

As shown in Scheme 2.23, the reaction of (**19 a**) with Cp^*TaCl_4, yielded an isolable intermediate (**34**) which can be viewed as a 4e-λ^3-diphosphinocarbene complex or alternatively as an η^2-4e-λ^5-diphosphaalkyne complex. Compound (**34**), however, is thermally unstable in solutions above - 50 °C. It was the object of the work described in this chapter to extend these findings by investigating the reactivity of (**19 a**) towards transition metal precursors with the metal centre in a low oxidation state. It was thought these would be suited to the preparation of more stable complexes derived from (**19 a**) that would not be open to oxidative coupling reactions. Such a precursor is Vaska's compound, $[IrCl(CO)(PPh_3)_2]$, the reactivity of which with (**19 a**) was to be investigated.

2.3 Results and Discussion

2.3.1 Preparation of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39)

When [IrCl(CO)(PPh$_3$)$_2$] was reacted with one equivalent of (**19 a**) a moderate yield of (**39**) resulted (51 %) after recrystallisation from toluene (Scheme 2.24). This work was conducted in cooperation with A. F. Richards.



(**19 a**) (**39**)

Scheme 2.24 Preparation of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39)

Compound (**39**) can be considered as an 18-electron complex containing a three-membered iridaphosphirene ring in which the iridium centre is co-ordinated by a 3e-η^2-phosphidocarbene ligand. An alternative formulation for this ligand would have it acting as a 3e-η^2-phosphavinyl fragment within a Ir-C=P three-membered ring but the spectroscopic and crystallographic evidence suggests this is not the case. Crystallographically authenticated metallaphosphirene complexes with the phosphorus centre in the +3 oxidation state are rare but, unlike (**39**), those that have been reported are all derived from the earlier transition metals, *e.g.* [Cp(CO)$_2$W=C(Ph)-P(Ph){η^1-W(CO)$_5$}] (**40**)[61] and [Tp'(CO)$_2$W=C(H)-PC(NEt$_2$)$_2$][SO$_3$CF$_3$], Tp' = [HB(3,5-Me$_2$C$_3$HN$_2$)$_3$] (**41**).[62] Interestingly, the three-membered ring within (**39**) is related to those in (**34**) and related complexes, *e.g.* [Cp*H$_2$Ta{=C(H)-PMe$_2$}(PMe$_3$)],[63] but in those cases the carbene ligands are 4e - donors.

The spectroscopic data for (**39**) support its proposed structure. Its ^{31}P{^{1}H} NMR spectrum exhibits a signal at high field (δ - 157.2 ppm, *cf.* - 188.7 ppm for (**40**)) that corresponds to the iridaphosphirene P-centre and is coupled to both PPh$_3$ phosphorus atoms ($^2J_{PP}$ = 22 and 66 Hz). If the compound existed as an η^2-phosphavinyl complex this signal would be expected to appear at considerably lower

field. In addition, the carbenic carbon centre resonates at very low field (δ 331.5 ppm) in the expected region for metallaphosphirenes (*cf.* δ 266.3 ppm for (**40**)). The IR spectrum of (**39**) displays a single strong CO stretching absorption at 1954 cm^{-1} and its APCI mass spectrum exhibits a molecular ion peak. The molecular structure of (**39**) is depicted in (Figure 2.5).

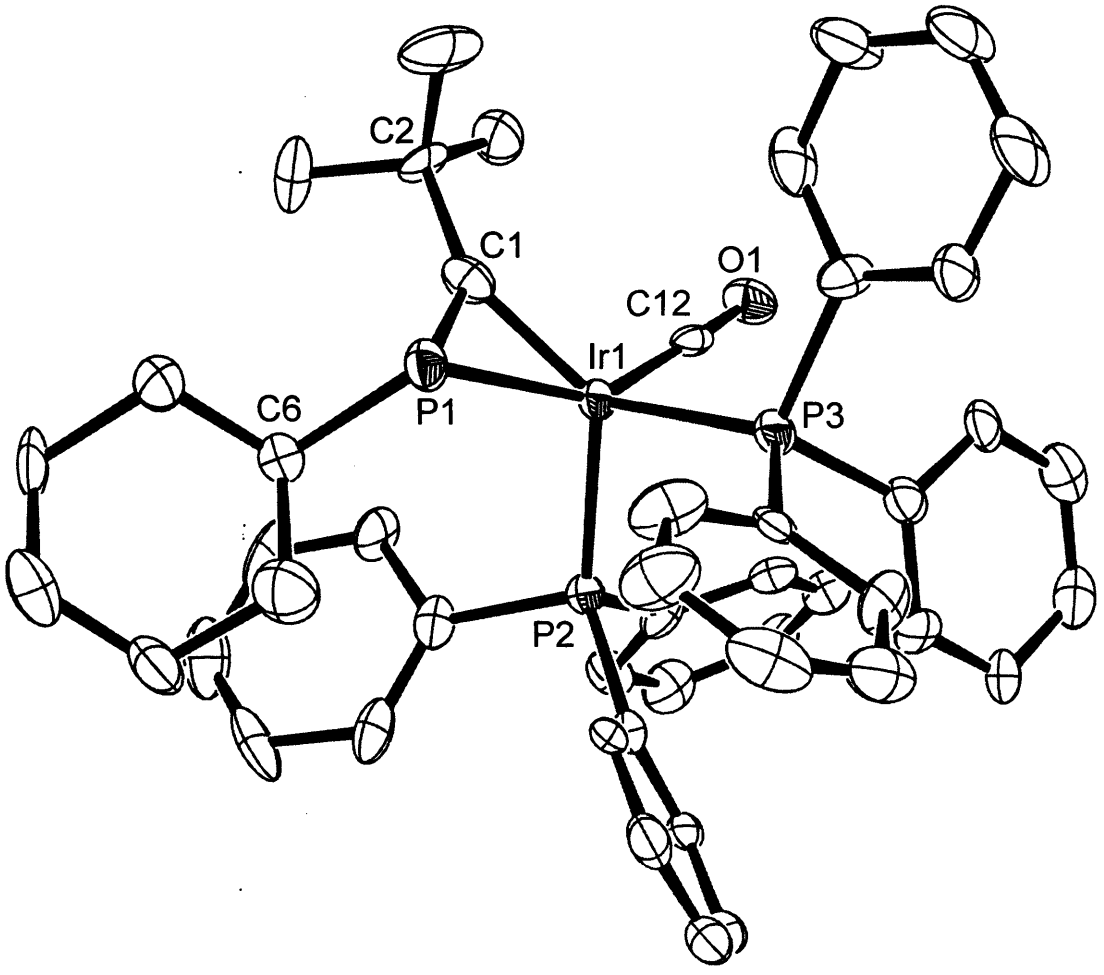


Figure 2.5 Molecular structure of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39)

Selected bond lengths (Å) and angles (°): Ir(1)-C(12) 1.867(13), Ir(1)-C(1) 1.918(14), Ir(1)-P(2) 2.342(3), Ir(1)-P(3) 2.386(3), Ir(1)-P(1) 2.442(3), P(1)-C(1) 1.753(13), O(1)-C(12) 1.176(15); C(12)-Ir(1)-C(1) 104.4(5), C(12)-Ir(1)-P(2) 93.7(4), C(1)-Ir(1)-P(2) 127.5(4), C(12)-Ir(1)-P(3) 92.7(4), C(1)-Ir(1)-P(3) 128.2(4), P(2)-Ir(1)-P(3) 98.93(12), C(12)-Ir(1)-P(1) 149.1(4), C(1)-Ir(1)-P(1) 45.5(4), P(2)-Ir(1)-P(1) 110.33(11), P(3)-Ir(1)-P(1) 102.11(11), C(1)-P(1)-Ir(1) 51.3(4), P(1)-C(1)-Ir(1) 83.3(6).

The monomeric molecule is chiral and crystallises as a racemic mixture of enantiomerically pure crystals. The iridium centre is best described as having a heavily distorted trigonal bipyramidal geometry with the carbonyl ligand and P(1) in the axial positions and C(1), P(2) and P(3) in the equatorial sites. Although the P(1)-C(1) bond length is short [1.753(13) Å] for a single bonded interaction, it is similar to that in (**40**) [1.775(8) Å] and intracyclic P-C bond lengths in phosphirene complexes, *e.g.* 1.78 Å average in $[PtCl_2(PEt_3)\{\eta^1\text{-}P(Ph)C(Ph)C(Ph)\}]$.[64] Similarly, the Ir-C(1) distance of 1.918(14) Å is longer than Ir-CO interactions but close to the mean for all other crystallographically determined Ir-C double bonds, 1.918 Å.[24] This, combined with the fact that P(1) has a distorted pyramidal co-ordination environment with a stereochemically active lone pair, [C(2)-C(1)-P(1)-C(6) torsion angle - 77.9°], leaves little doubt that the formulation of (**39**) as a phosphidocarbene complex is correct.

Compound (**39**) is air stable in the solid state, but sensitive in solution. When a solution of (**39**) is exposed to air for several hours, it decomposed to several phosphorus containing products. An APCI mass spectrum of this mixture showed, next to many other products, a possible molecular ion peak for a dioxygen adduct of (**39**). The possibility of reacting $2e^-$-donors (L) with (**39**) in order to convert it to an $18e^-$ terminal phosphavinyl complex, $[Ir(CO)(PPh_3)_2(L)\{\eta^1\text{-}C(Bu^t)=PCy\}]$, was given. Therefore, reactions with a range of donor reagents have been conducted but with no real success, other than an unusual rearrangement reaction with carbon monoxide (see section 2.3.5). Reactions of (**39**) with electrophiles proved more fruitful and are discussed in the next sections.

2.3.2 Reactions of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with protic agents and methyl iodide

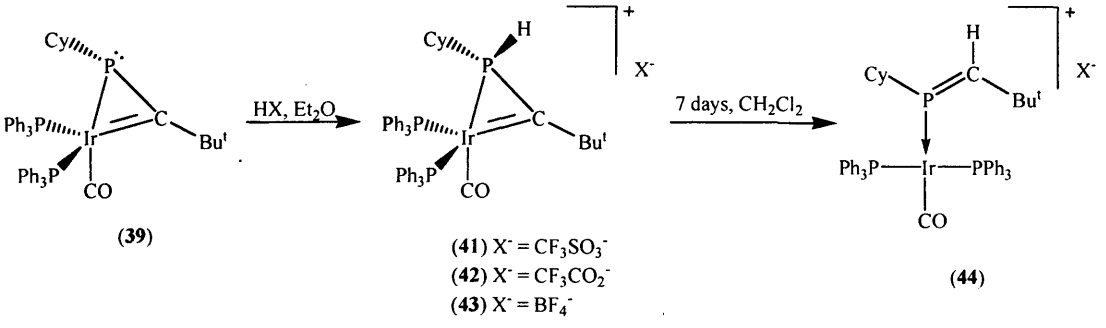
Treatment of metallocyclopropenes, (**37**), with protic reagents can lead to protonation of the metal, C_α or C_β sites depending on the metal and/or vinyl substituents employed.[56] If an analogy is drawn with (**39**), its reaction with protic reagents, HX, could potentially lead to protonation at

(i) the metal centre to give an η^1-phosphavinyl complex, [Ir^{III}{η^1-C(Bu^t)=P(Cy)}(CO)HX(PPh$_3$)$_2$]

(ii) the C_α centre to give a phosphaalkene complex, [Ir^I(CO)(PPh$_3$)$_2${η^1-P(Cy)=C(H)(Bu^t)}]X

(iii) the phosphavinyl P-centre to give a λ^5-iridaphosphirenium complex, [Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$]X, X = anion.

To investigate these possibilities the reaction of (**39**) with several acids has been investigated and in all cases moderate yields of the iridaphosphirenium salts, (**41 - 43**), resulted (Scheme 2.25).



(**39**)

(**41**) X$^-$ = $CF_3SO_3^-$
(**42**) X$^-$ = $CF_3CO_2^-$
(**43**) X$^-$ = BF_4^-

(**44**)

Scheme 2.25 Reaction of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with protic agents

These proved to be thermally stable in the solid state and all exist as ion separated salts. As a result, the spectroscopic data for the three complexes are similar. Most informative of these is their $^{31}P\{^1H\}$ NMR spectra which display high field virtual triplet resonances (*ca.* δ - 140 ppm) which lie *ca.* 20 ppm to lower field of the iridaphosphirene resonance in (**39**), as would be expected upon protonation of

the heterocyclic phosphorus centre. In addition, the IR spectra of (**41** - **43**) revealed shifts to higher frequency (ca. 50 cm^{-1}) for the CO stretching absorptions in these complexes compared to that in (**39**) (1954 cm^{-1}). This, again, is not surprising considering that in the former complexes the CO ligands are associated with cationic moieties. X-ray crystal structure analyses of (**41**) and (**42**) were carried out and in both the geometry of the phosphirenium moiety is very similar. In addition, the structures of both cations are strikingly similar to that of their neutral precursor, (**39**).

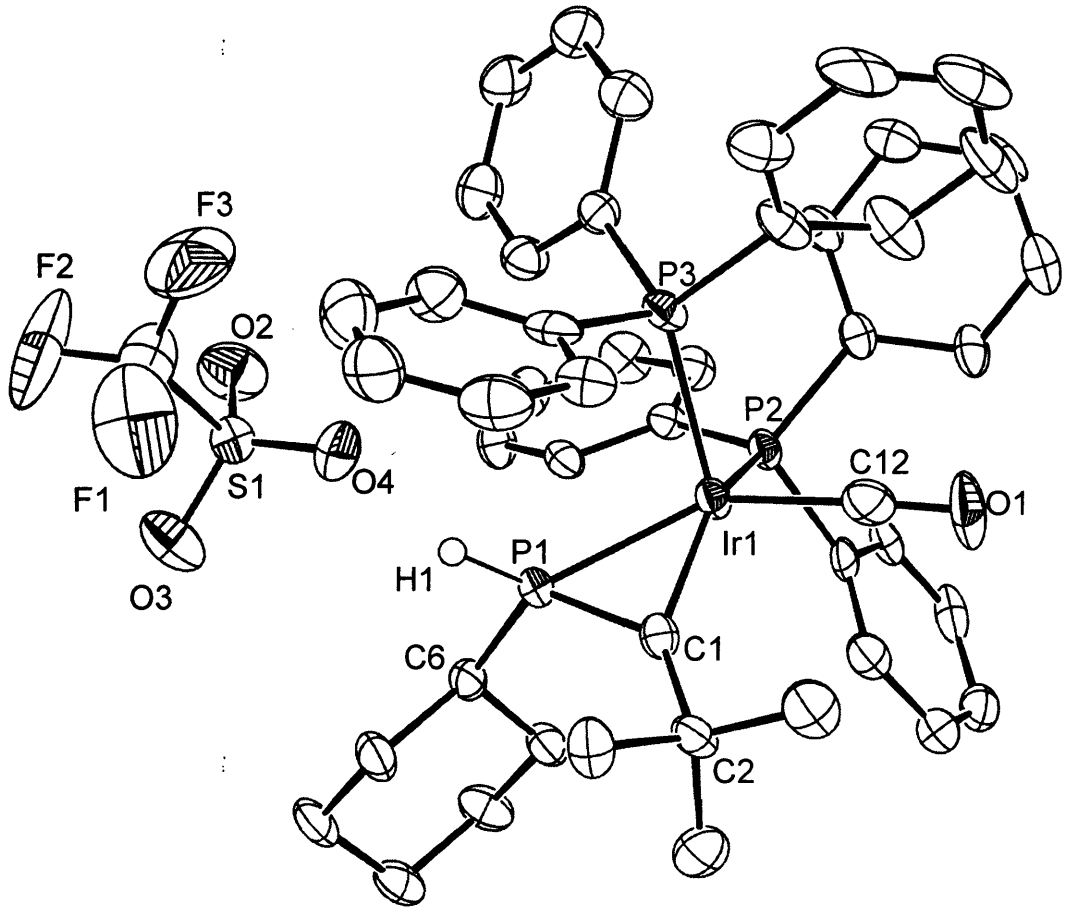


Figure 2.6 Molecular structure of $[Ir\{=C(Bu^t)P(H)(Cy)\}(CO)(PPh_3)_2][SO_3CF_3]$ (41)

Selected bond lengths (Å) and angles (°): Ir(1)-C(1) 1.934(8), Ir(1)-P(1) 2.3186(19), Ir(1)-P(2) 2.384(2), Ir(1)-P(3) 2.347(2), Ir(1)-C(12) 1.873(9), P(1)-C(1) 1.735(8), P(1)-H(1) 1.31(7), P(1)-C(6) 1.828(8), C(12)-O(1) 1.169(10), C(1)-C(2) 1.512(11), C(12)-Ir(1)-C(1) 100.0(3), C(12)-Ir(1)-P(1) 147.1(2), C(1)-Ir(1)-P(1) 47.1(2), C(12)-Ir(1)-P(3) 98.8(3), C(1)-Ir(1)-P(3) 119.8(2), P(1)-Ir(1)-P(3) 100.27(7), C(12)-Ir(1)-P(2) 88.4(3), C(1)-Ir(1)-P(2) 138.3(2), P(1)-Ir(1)-P(2) 114.81(7), P(3)-Ir(1)-P(2)

98.67(7), C(1)-P(1)-C(6) 119.5(4), C(1)-P(1)-Ir(1) 54.7(3), C(2)-C(1)-P(1) 138.1(6), P(1)-C(1)-Ir(1) 78.2(3).

The iridium centre of (**41**) can be considered as having a heavily distorted trigonal bipyramidal geometry with the carbonyl ligand and P(1) taking up the axial sites and C(1), P(2) and P(3) in the equatorial positions. The P(1)-C(1) interaction [1.734(8) Å] is short for a single P-C bond but not significantly shorter than the corresponding bond in (**39**), [1.753(13) Å]. In addition, the Ir(1)-C(1) distance [1.934(8) Å] is longer than in (**39**) [1.918(14) Å] but still in the normal range for localised Ir-C double bonds,[65] whilst the P(1)-Ir(1) bond length [2.3186(19) Å] is significantly shorter than the analogous distance in (**39**) [2.442(3) Å]. This difference can be explained by the electron poor nature of the phosphirenium phosphorus centre in cationic (**41**) relative to the phosphirene phosphorus centre in neutral (**39**). The fact that the C(6)P(1)C(1)C(2) torsion angle is 63.6° confirms that (**41**) should be considered as an iridaphosphirenium complex rather than a protonated η^2-phosphavinyl complex.

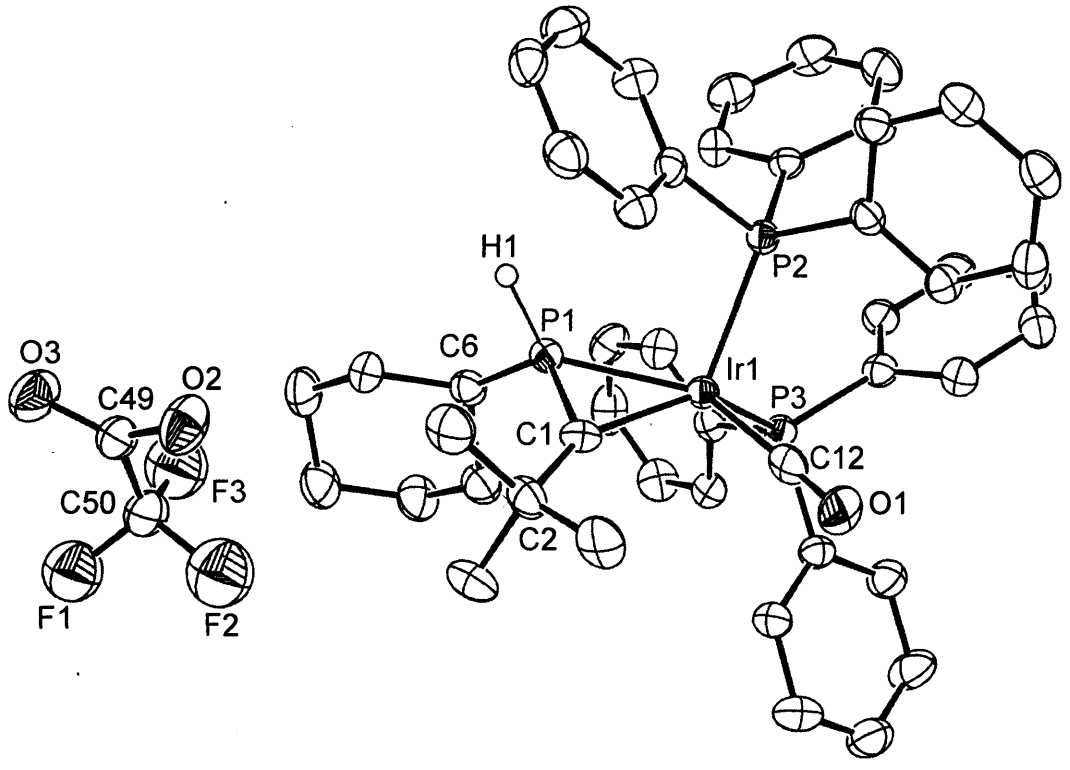


Figure 2.7 Molecular structure of [Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][CF$_3$CO$_2$] (42)

Selected bond lengths (Å) and angles (°): Ir(1)-C(12) 1.887(7), Ir(1)-C(1) 1.931(7), Ir(1)-P(1) 2.3119(17), Ir(1)-P(2) 2.3597(17), Ir(1)-P(3) 2.3671(17), P(1)-C(1) 1.750(6), P(1)-C(6) 1.830(7), O(1)-C(12) 1.143(8), C(1)-C(2) 1.510(9), C(12)-Ir(1)-C(1) 99.0(3), C(12)-Ir(1)-P(1) 146.62(19), C(1)-Ir(1)-P(1) 47.68(19), C(12)-Ir(1)-P(2) 99.0(2), C(1)-Ir(1)-P(2) 122.59(19), P(1)-Ir(1)-P(2) 99.70(6), C(12)-Ir(1)-P(3) 93.3(2), C(1)-Ir(1)-P(3) 132.81(19), P(1)-Ir(1)-P(3) 110.39(6), P(2)-Ir(1)-P(3) 99.83(6), C(1)-P(1)-C(6) 122.5(3), C(1)-P(1)-Ir(1) 54.7(2), C(6)-P(1)-Ir(1) 135.4(2), C(2)-C(1)-P(1) 135.0(5), C(2)-C(1)-Ir(1) 147.1(5), P(1)-C(1)-Ir(1) 77.7(3).

Very similar observations have been made for (**42**), though this crystallised with one molecule each of toluene and CF_3CO_2H per asymmetric unit. The geometrical features of the cation are close to those for (**41**) and will not be discussed here in detail. The molecular structure is depicted in Figure 2.7. The C(6)-P(1)-C(1)-C(2) torsion angles 59.2° in (**42**), compared to 63.6° in (**41**), indicating the formulation of the complex as an iridaphosphirenium complex. Very comparable geometrical trends have been observed in metallacyclopropene complexes,[56] which theoretical studies suggest arise from a degree of isolobality between the C2 fragment of the 3-membered ring and $4e^-$ donor alkyne ligands.[57]

Although (**41** - **43**) are thermally very stable in the solid state, in dichloromethane solutions they are less so and quantitatively and irreversibly rearrange *via* 1,2-hydrogen migrations to give the cationic Ir(I)-phosphaalkene complexes, (**44**) (Scheme 2.25), over one week. This suggest that complexes (**41** - **43**) are the kinetic products in the protonation reactions of (**39**), while (**44**) is the thermodynamic product.

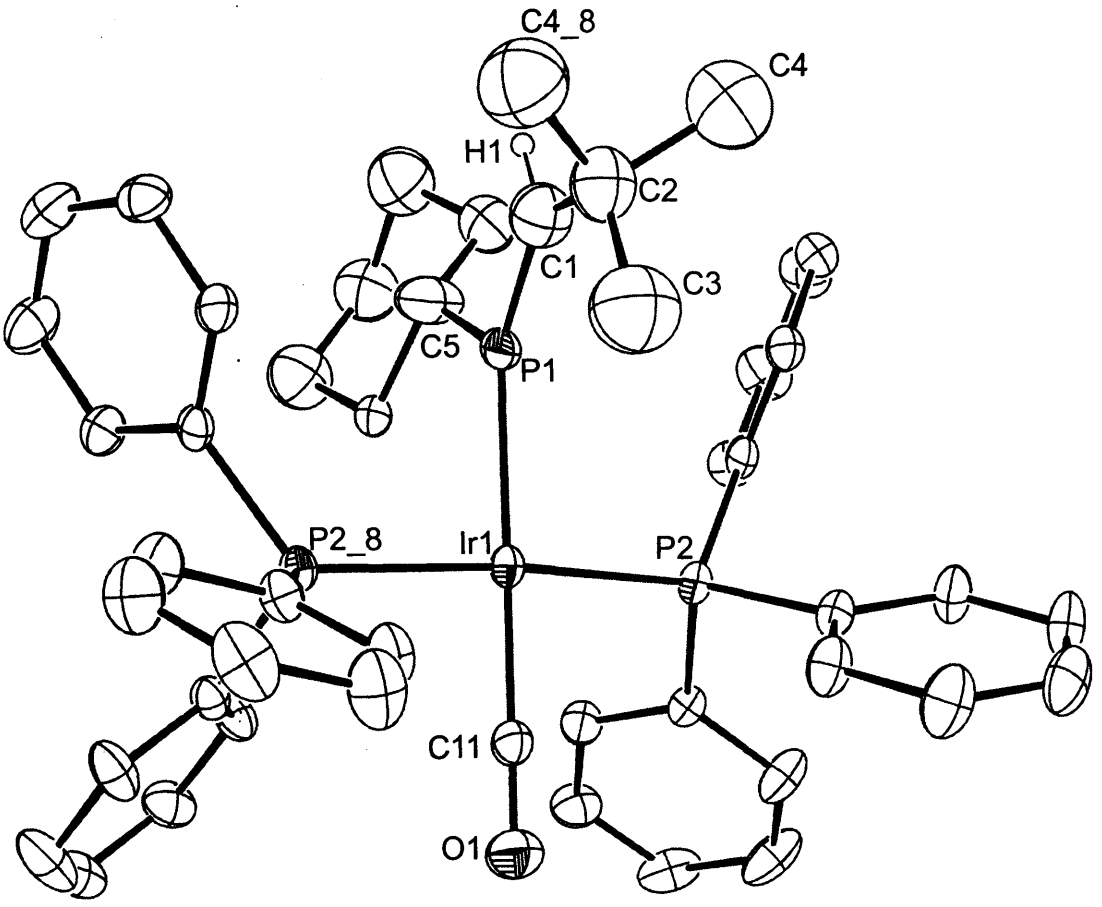


Figure 2.8 Structure of the cationic component of $[Ir(CO)(PPh_3)_2\{\eta^1\text{-}P(Cy)=C(H)(Bu^t)\}][BF_4]$ (44)

Selected bond lengths (Å) and angles (°): Ir(1)-P(1) 2.328(3), Ir(1)-C(11) 1.859(9), Ir(1)-P(2) 2.3365(15), P(1)-C(1) 1.607(14), P(1)-C(5) 1.998(18), C(1)-C(2) 1.408(19), C(11)-Ir(1)-P(1) 179.7(3), C(11)-Ir(1)-P(2) 87.81(4), P(1)-Ir(1)-P(2) 92.20(4), P(2)-Ir(1)-P(2_8) 173.22(7), C(1)-P(1)-Ir(1) 139.0(6), C(5)-P(1)-Ir(1) 116.2(4), P(1)-C(1)-C(2) 131.4(13), Symmetry operation: x, - y + ½, z.

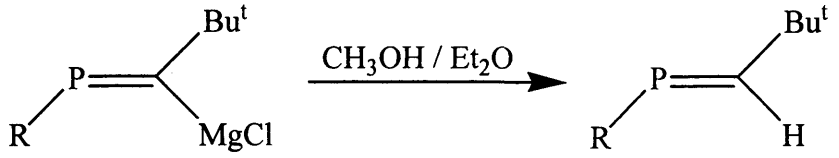
It is noteworthy that similar but reversible 1,2-hydrogen shifts between the two carbon centres in metallocyclopropenes, *e.g.* [Cp*Re(CO)$_2${=C(H)(Ph)C(*o*-tolyl)}], have been observed.[57] In addition, and in a related fashion to the formation of the phosphaalkene complexes, (**44**), protonation of metallocyclopropenes can occur at the C_α centre and lead to the formation of free alkenes.[66] The spectroscopic data for (**44**), X = BF_4^-, are consistent with its proposed structure. Of note is its $^{31}P\{^1H\}$ NMR spectrum which displays an AB_2 pattern, the doublet signal of which

(δ 15.4 ppm) corresponds to the chemically equivalent PPh_3 ligands whilst the triplet signal occurs at low field (δ 222.4 ppm) in the normal region for η^1-co-ordinated phosphaalkenes. The coupling between the two signals (51 Hz) suggests a *cis*-relationship between the phosphaalkene and the two phosphine ligands.

The structure of the cationic component of (**44**), X = BF_4^-, is depicted in Figure 2.8. The molecule sits on a crystallographic mirror plane which contains the phosphaalkene ligand and thus its cyclohexyl substituent is necessarily disordered. There are no close contacts between the cation and the BF_4^- anion, and the 16e$^-$ iridium centre has a slightly distorted square planar geometry. Both the P(1) and C(1) centres have trigonal planar geometries and the distance between these centres [1.607(14) Å] is normal for a localised P-C double bond.[65]

In order to generate the free phosphaalkene, [CyP=C(H)(Bu^t)], (**45**), from (**44**), X = BF_4^-, CO gas was passed through a dichloromethane solution of the phosphaalkene complex over five minutes. An examination of the $^{31}P\{^1H\}$ NMR spectrum of the product mixture revealed that (**45**)[67] had been quantitatively displaced from the cation of (**44**), as evidenced by the appearance of a singlet resonance at δ 257.8 ppm. The by-product in this reaction was found to be the previously reported compound, $[Ir(CO)_3(PPh_3)_2][BF_4]$.[68]

It was found that (**45**) can alternatively be prepared by the reaction of (**19 a**) with degassed and dried methanol (Scheme 2.26). Compound (**45**) exhibits a low field singlet at δ 257.8 ppm in its $^{31}P\{^1H\}$ NMR spectrum, whilst a characteristic vinylic proton signal at δ 8.64 ppm was observed in its ^1H NMR spectrum ($^2J_{PH}$ = 24.8 Hz). Those values are in good agreement with an earlier published phosphaalkene, *Z*-[Bu^t-C(H)=PBu^n], which exhibits a singlet in its $^{31}P\{^1H\}$ NMR spectrum at δ 243 ppm and its vinylic proton gives rise to a doublet ($^2J_{PH}$ = 25 Hz) at δ 8.65 ppm in the ^1H NMR spectrum.[69] Considering the stereochemistry of (**19 a**) it is not unexpected for (**45**) to acquire *E*-stereochemistry upon its formation. The assignment of this stereochemistry is supported by the size of the $^2J_{PH}$ coupling which is in the characteristic range for *E*-phosphaalkenes, according to the "*cis*-rule".[70]

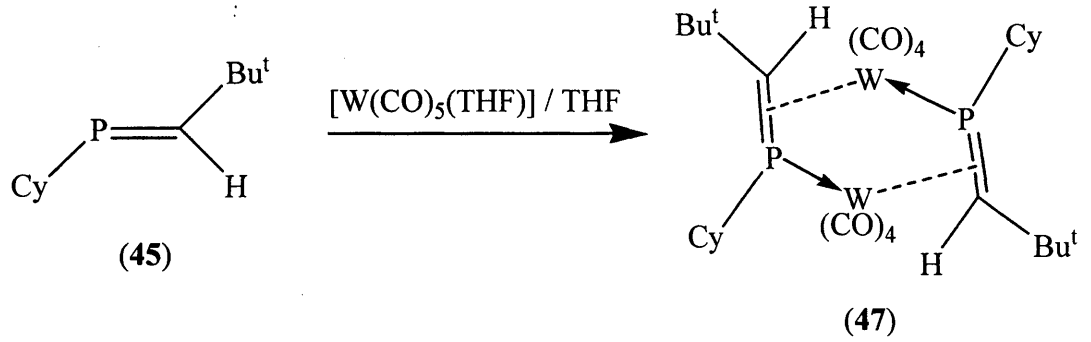


(**19 a**) R = Cy
(**19 d**) R = Mes

(**45**) R = Cy
(**46**) R = Mes

Scheme 2.26 Reaction of phosphavinyl Grignard reagents with MeOH

To show the generality of this reaction, (**19 d**) was reacted with dry and degassed methanol. This led to a high yield of the *E*-phosphaalkene (**46**). The vinylic proton was observed as a doublet in the ^{1}H NMR spectrum at δ 8.43 ppm ($^2J_{PH}$ = 25.3 Hz), whilst the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 228.4 ppm. Both (**45**) and (**46**) are oils, so it was attempted to form a crystalline complex of (**45**) *via* its treatment with [W(CO)$_5$(THF)] (Scheme 2.27).



(**45**)

(**47**)

Scheme 2.27 Reaction of E-[CyP=C(H)Bu^t] (45) with [W(CO)$_5$(THF)]

This led to a mixture of phosphorus containing products. It was possible to isolate one complex (**47**) out of this mixture but, unfortunately, the yield was very low (< 1 %). Because of this it could not be spectroscopically characterised but its X-ray crystal structure was obtained.

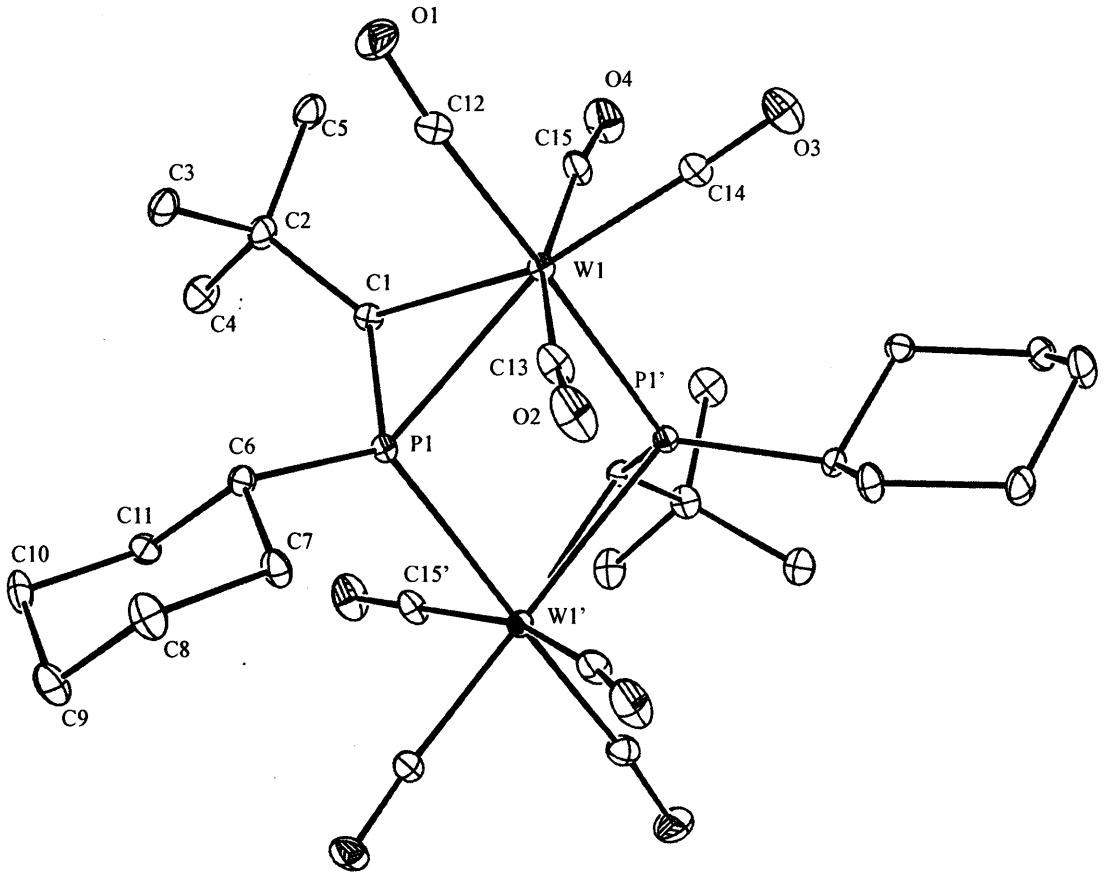


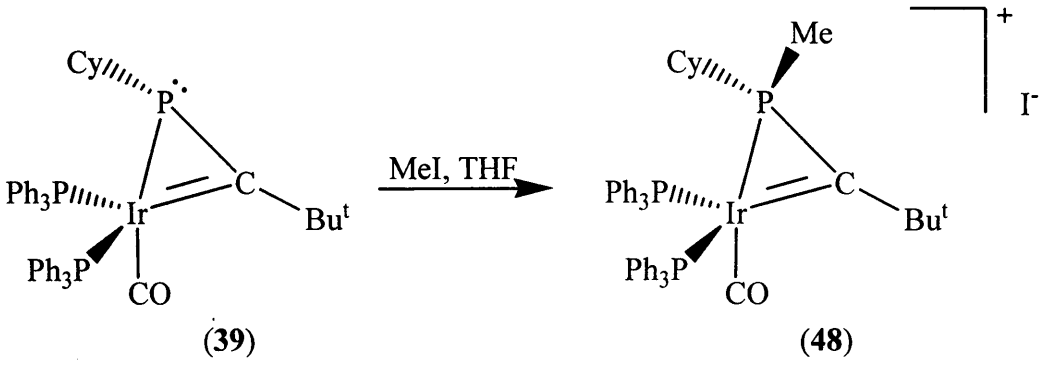
Figure 2.9 Molecular structure of $[\{(CO)_4W\}_2\{\mu\text{-}\eta^1,\eta^2\text{-}P(Cy)=C(Bu^t)\}_2]$ (47)

Selected bond length (Å) and angles (°): P(1)-C(1) 1.749(6), P(1)-W(1) 2.5689(16), C(1)-W(1) 2.457(6), P(1)-W(10) 2.546(2), C(2)-C(1)-P(1) 133.5(4), C(2)-C(1)-W(1) 125.9(4), P(1)-C(1)-W(1) 73.1(2) W(10)-P(1)-W(1) 104.59(6), Symmetry operation: - x, y, - z + ½.

The molecular structure of (**47**) shows it to be dimeric with each phosphaalkene ligand co-ordinated to two $[W(CO)_4]$ fragments through both an η^1-P interaction [P(1)-W(1'), 2.546(2) Å] and a longer η^2-P=C interaction [P(1)-W(1), 2.5689(16) Å; C(1)-W(1), 2.457 Å]. As is normally the case with η^2-phosphaalkene ligation[54] the P=C bond in (**47**) has undergone an elongation from the normal uncoordinated bond length range to 1.749(6) Å, *cf.* the P=C bond in *Z*-$[CyP=C(Bu^t)C(H)(OH)Ph]$[67] [1.682 Å avge.]. It is also noteworthy that the co-ordinated phosphaalkene possesses *Z*-stereochemistry as opposed to the *E*-stereochemistry of the free ligand. Such phosphaalkene isomerisations upon co-

ordination to a metal fragment are not without precedent[54] and arise from the relatively weak nature of the π-component of the P=C bond.

A further electrophile, MeI, was also reacted with (**39**) and this did not lead to oxidative addition of the methyl fragment to the iridium centre but to methylation of the phosphorus centre in the 3-membered ring to give (**48**) in high yield (Scheme 2.28).



(**39**) (**48**)

Scheme 2.28 Reaction of $[Ir(PPh_3)_2(CO)\{C(Bu^t)P(Cy)\}]$ (39) with MeI

The $^{31}P\{^1H\}$ NMR spectrum of (**48**) shows a virtual triplet at significantly lower field (δ - 125.5 ppm) than for (**39**), but characteristic of a metallophosphirene. The ^{13}C NMR spectrum of (**48**) displays a low field signal at δ 330.4 ppm corresponding to the carbon centre double bonded to iridium.

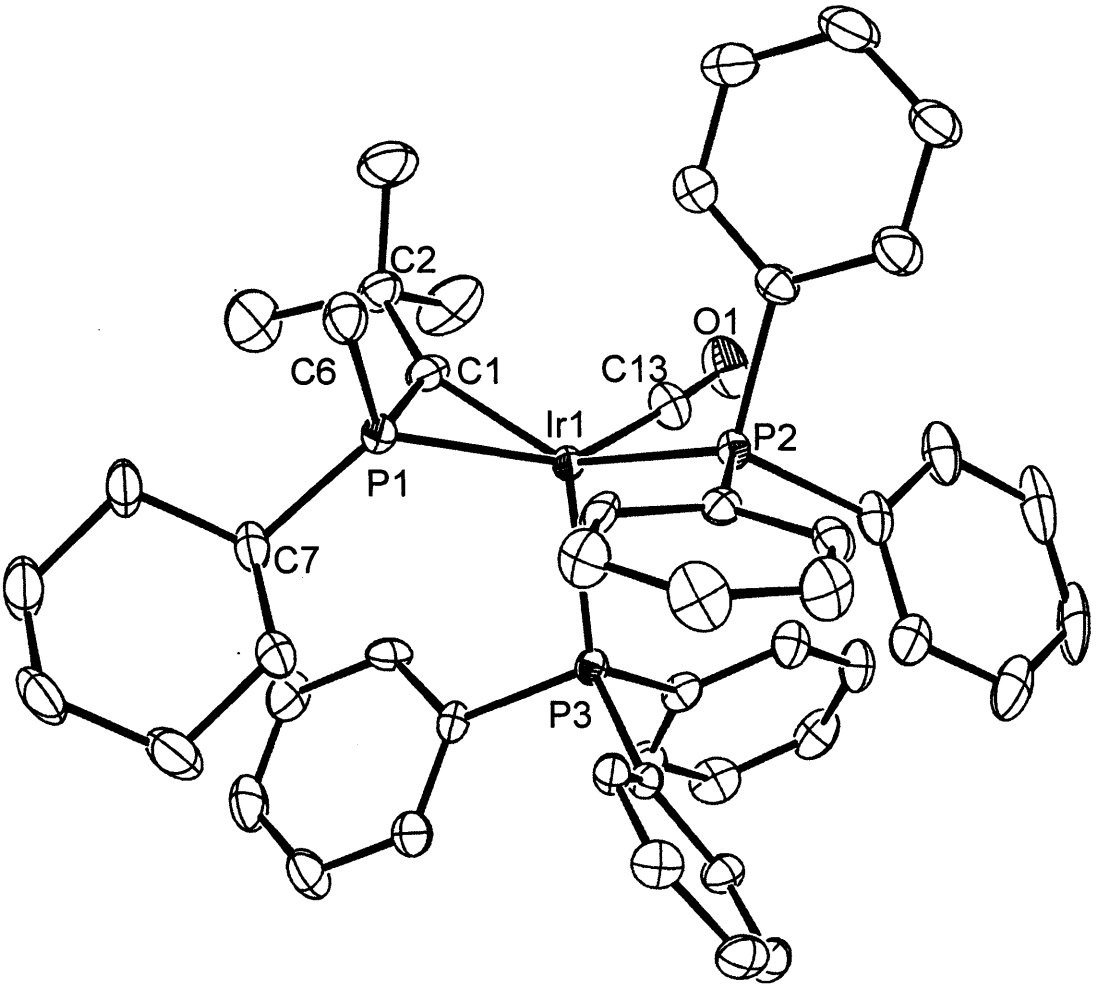


Figure 2.10 Structure of the cationic component of [Ir{=C(Bu^t)P(Me)(Cy)}(CO)(PPh$_3$)$_2$]I (48)

Selected bond lengths (Å) and angles (°): Ir(1)-C(1) 1.932(4), Ir(1)-P(1) 2.3280(11), Ir(1)-P(2) 2.3903(11), Ir(1)-P(3) 2.3630(13), Ir(1)-C(13) 1.888(5), P(1)-C(1) 1.738(5), P(1)-C(6) 1.821(5), P(1)-C(7) 1.845(5), C(13)-O(1) 1.138(5), C(1)-C(2) 1.521(6), C(13)-Ir(1)-C(1) 98.7(2), C(13)-Ir(1)-P(1) 144.71(15), C(1)-Ir(1)-P(1) 47.03(14), C(13)-Ir(1)-P(3) 96.16(15), C(1)-Ir(1)-P(3) 122.96(13), P(1)-Ir(1)-P(3) 109.44(4), C(13)-Ir(1)-P(2) 89.11(14), C(1)-Ir(1)-P(2) 137.78(13), P(1)-Ir(1)-P(2) 110.64(4), P(3)-Ir(1)-P(2) 96.97(4), C(1)-P(1)-C(6) 115.0(2), C(1)-P(1)-C(7) 119.7(2), C(1)-P(1)-Ir(1) 54.43(15), C(2)-C(1)-P(1) 137.7(4), P(1)-C(1)-Ir(1) 78.54(18).

The structure of the cation of (**48**) shows similar geometries to those observed for (**39**), (**41**) and (**42**). Moreover, the P(1)-C(1) bond length [1.738(5) Å] and Ir(1)-

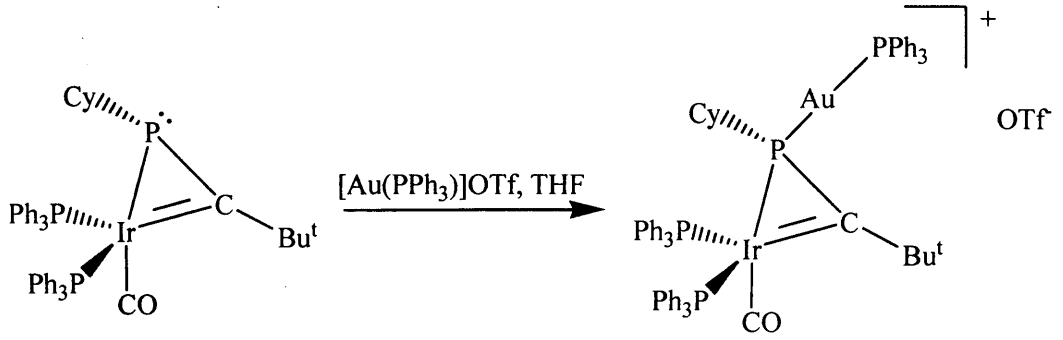
C(1) distance are close to those in (**39**), (**41**) and (**42**), while the Ir(1)-P(1) interaction [2.3280(11) Å] is comparable with that in (**41**) and (**42**) but significantly shorter than in (**39**), as would be expected. It is worth noting that (**48**) is indefinitely stable in solution and therefore does not undergo a 1,2-methyl migration similar to the 1,2-hydrogen migrations that occur for (**41 - 43**).

2.3.3 Reactions of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with group 11 and 12 compounds

On the basis of the isolobal analogy with H^+, the $[Au(PR_3)]^+$ fragment has been referred to as the "cluster chemist's proton".[71] Given that [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) is readily protonated, it was decided to explore this analogy with respect to the iridaphosphirene. Abstraction of the chloride ligand from [AuCl(PPh$_3$)] at low temperature using silver triflate resulted in the *in situ* generation of [Au(PPh$_3$)]OTf (OTf = $CF_3SO_3^-$) which was filtered into a tetrahydrofuran solution of complex (**39**). After stirring the reaction mixture for 18 hours at room temperature, work-up yielded (**49**) as an orange crystalline solid (Scheme 2.29). It is noteworthy that (**49**) showed no signs of rearrangements, similar to those observed for (**41**) - (**43**), when a dichloromethane or toluene solution of it was stored at room temperature for several days.

The $^{31}P\{^1H\}$ NMR spectrum of this complex proved highly diagnostic as it exhibits a low field resonance at δ 41.4 ppm for the [Au(PPh$_3$)] moiety showing coupling to the phosphorus nuclei of both the iridaphosphirene ($^2J_{PP}$ = 341 Hz) and iridium-bonded triphenylphosphine ligands ($^4J_{PP}$ = 30 and 7 Hz). The iridaphosphirene phosphorus also shows a coupling to the three inequivalent PPh_3 ligands as a doublet of pseudotriplets at δ - 117.2 ppm ($^2J_{PP}$ = 341 Hz, $^2J_{PP}$ = 30 Hz). In addition, the presence of the triflate counter-anion was indicated by a singlet in the ^{19}F NMR spectrum of the complex at δ - 77.0 ppm. The small shift in υ(CO) absorption in the solid state infrared spectrum to 1974 cm^{-1} for (**49**) from 1980 cm^{-1} in the neutral precursor (**50**) suggests that the positive charge on the complex is mainly associated with the gold(I) center. The ES mass spectrum of (**49**) shows a molecular ion peak for the cation, $[M\text{-}CF_3SO_3]^+$, with 50 % relative intensity and a

correct elemental analysis was obtained. Single crystals of complex (**49**) were obtained and a structural analysis carried out. This confirmed the formulation as [Ir{=C(Bu^t)P[Au(PPh$_3$)](Cy)}(CO)(PPh$_3$)$_2$]OTf (**49**) and showed the triflate counter-anion to have no interaction with the cation. The molecular structure of the cationic component is shown in Figure 2.11.



(**39**) (**49**)

Scheme 2.29 Reaction of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with [Au(PPh$_3$)]OTf

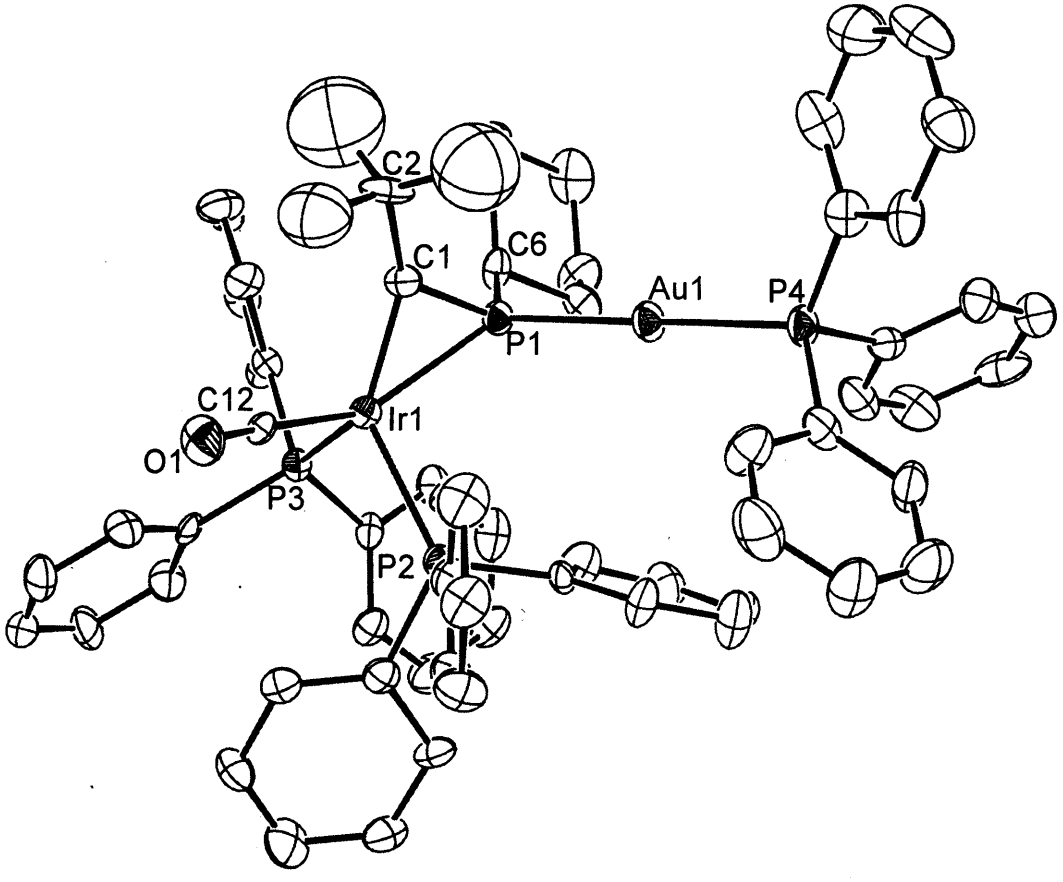


Figure 2.11 Structure of the cationic component of [Ir{=C(Bu^t)P[Au(PPh$_3$)](Cy)}(CO)(PPh$_3$)$_2$]SO$_3$CF$_3$ (49)

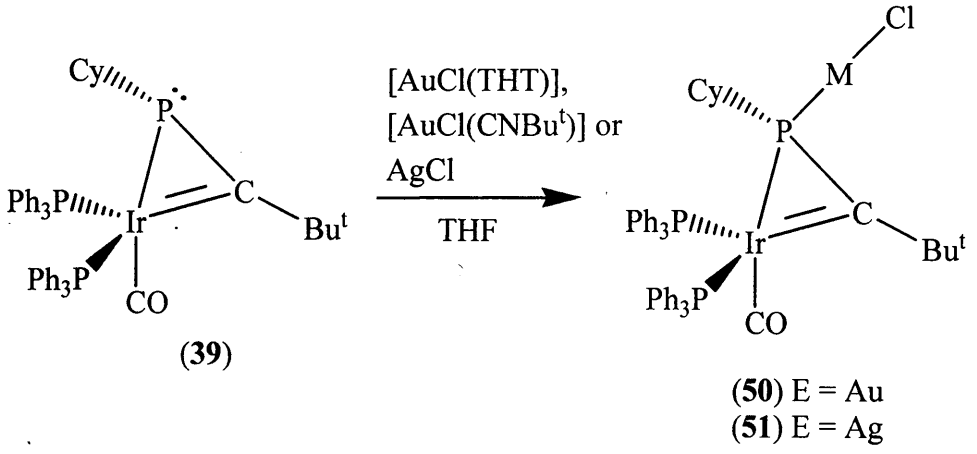
Selected bond length (Å) and angles (°): Au(1)-P(4) 2.299(3), Au(1)-P(1) 2.308(3), Ir(1)-C(12) 1.870(10), Ir(1)-C(1) 1.916(10), Ir(1)-P(1) 2.352(3), Ir(1)-P(2) 2.353(3), Ir(1)-P(3) 2.391(3), P(1)-C(1) 1.768(10), O(1)-C(12) 1.143(12), P(4)-Au(1)-P(1) 179.12(11), C(12)-Ir(1)-C(1) 98.7(4), C(12)-Ir(1)-P(1) 144.9(3), C(1)-Ir(1)-P(1) 47.6(3), C(12)-Ir(1)-P(2) 93.5(3), C(1)-Ir(1)-P(2) 129.7(3), P(1)-Ir(1)-P(2) 101.91(9), C(12)-Ir(1)-P(3) 102.5(3), C(1)-Ir(1)-P(3) 126.6(3), P(1)-Ir(1)-P(3) 106.53(10), P(2)-Ir(1)-P(3) 97.35(10), C(1)-P(1)-Ir(1) 53.1(3), P(1)-C(1)-Ir(1) 79.3(4).

Compound (**49**) crystallises as orange crystals in a monoclinic space group together with 2 molecules of toluene in the asymmetric unit. The structure of the cation is similar to that of its neutral precursor. The iridium centre of (**49**) can be considered as having a heavily distorted trigonal bipyramidal geometry with the carbonyl ligand and P(1) taking up the axial sites and C(1), P(2) and P(3) in the equatorial positions. The P(1)-C(1) interaction [1.768(10) Å] is not significantly different than the corresponding bonds in (**39**), [1.753(13) Å] or (**41**) [1.734(8) Å]. The Ir(1)-C(1) distance [1.916(10) Å] is the same as in (**39**) [1.918(14) Å] but shorter than that in (**41**) [1.934(8) Å]. The Ir(1)-P(1) bond length [2.352(3) Å] is increased in comparison with the methylated compound (**48**) [2.3280(11) Å]. The C(6)-P(1)-C(1)-C(2) torsion angle was found to be 86.5° and is greater than the torsion angles between the cyclohexyl and *tert*-butyl substituents observed in other compounds discussed here which range from 73.4 to 86.5°. This is presumably a result of the bulky triphenylphosphine ligand attached to the gold centre. The P(1)-Au(1)-P(4) angle was found to be 179.12(11)° and the Au(1)-P(1) distance is 2.308(3) Å, while the Au(1)-P(4) bond length was determined as 2.299(3) Å.

In order to broaden the investigation of the co-ordinating abilities of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$], (**39**), to include other electrophilic metal fragments, the complex was treated with an equimolar quantity of [AuCl(THT)] (THT = tetrahydrothiophene). This reaction was expected to result in displacement of the sulfur donor by the lone pair of the heterocycle phosphorus. This proved to be the case with the product [Ir{=C(Bu^t)P[Au(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (**50**) being isolated in good yield (Scheme 2.30). It is noteworthy that reaction of [AuCl(CNBu^t)] with (**39**) also led to the isolation of complex (**50**), but in lower yield. Such displacement of an

isocyanide ligand from gold(I) complexes is not uncommon and has been mentioned in recent reports.[72-74]

The $^{31}P\{^{1}H\}$ NMR spectrum of (**50**) suggests that the *cis*-disposition of the triphenylphosphine ligands in the iridaphosphirene starting material is retained in the gold complex, as evidenced by two overlapping doublet resonances (pseudotriplets) at δ 13.9 and 9.5 ppm with a mutual coupling of 24 Hz. In addition, the aurated phosphorus center gives rise to an unresolved multiplet resonance at δ - 129.4 ppm in this spectrum. Attempts to obtain further resolution of the PAuCl signal in the $^{31}P\{^{1}H\}$ NMR spectrum of (**50**) by variable temperature $^{31}P\{^{1}H\}$ NMR studies failed. The shift of the phosphirene P-signal by approximately 28 ppm to lower field compared to the corresponding feature in (**39**), indicates a decrease in shielding of this phosphorus center upon co-ordination. Moreover, the increase of the υ(CO) absorption from 1954 cm^{-1} for (**39**) to 1980 cm^{-1} for (**50**) indicates a subtle decrease in electron density at the metal center as a result of co-ordination to the gold fragment. A molecular ion peak was seen in the mass spectrum of (**50**) and the accurate mass of the $[M]^+$ and $[M\text{-}Cl]^+$ ions were determined using LSIMS mass spectrometry. Furthermore, the overall composition of the complex was confirmed by microanalysis. Crystals of complex (**50**) suitable for X-ray analysis were grown by slow diffusion of a dichloromethane solution of the complex into hexane. The molecular structure of (**50**) is depicted in Figure 2.12.



(**39**)

(**50**) E = Au
(**51**) E = Ag

Scheme 2.30 Reaction of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with [AuCl(THT)], [AuCl(CNBu^t)] and AgCl

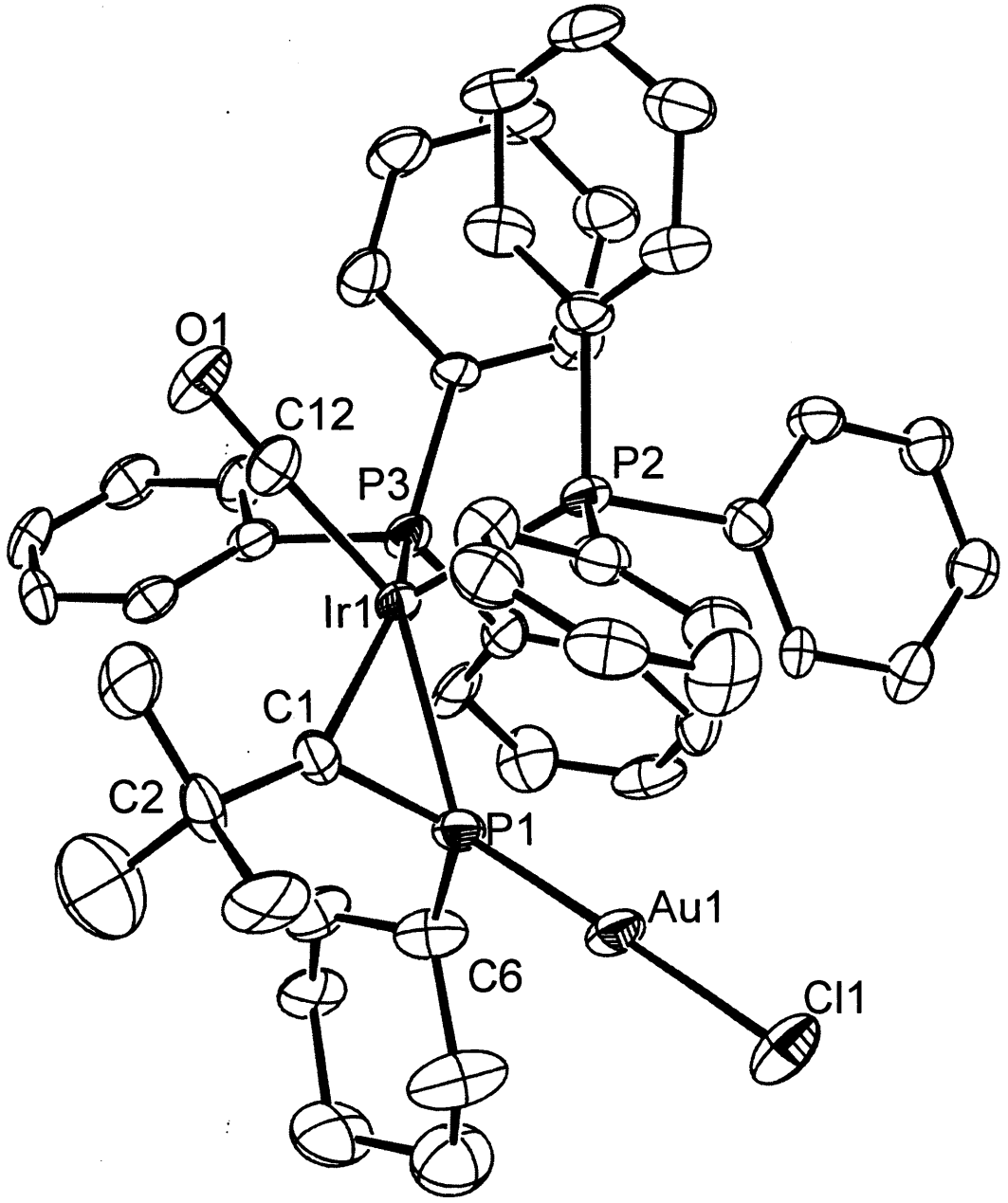


Figure 2.12 Molecular structure of [Ir{=C(Bu^t)P[Au(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (50)

Selected bond length (Å) and angles (°): Au(1)-P(1) 2.255(2), Au(1)-Cl(1) 2.300(2), Ir(1)-C(12) 1.882(9), Ir(1)-C(1) 1.909(9), Ir(1)-P(1) 2.356(2), Ir(1)-P(3) 2.358(2), Ir(1)-P(2) 2.359(2), P(1)-C(1) 1.753(9), P(1)-C(6) 1.888(10), O(1)-C(12) 1.150(10), P(1)-Au(1)-Cl(1) 177.40(9), C(12)-Ir(1)-C(1) 101.7(4), C(12)-Ir(1)-P(1) 148.8(3), C(1)-Ir(1)-P(1) 47.1(3), C(12)-Ir(1)-P(3) 91.7(3), C(1)-Ir(1)-P(3) 131.1(3), P(1)-Ir(1)-P(3) 109.04(8), C(12)-Ir(1)-P(2) 96.2(3), C(1)-Ir(1)-P(2) 122.0(3), P(1)-Ir(1)-

P(2) 101.47(8), P(3)-Ir(1)-P(2) 102.53(8), C(1)-P(1)-Ir(1) 52.9(3), P(1)-C(1)-Ir(1) 79.9(3).

Compound (**50**) was found to crystallise in the monoclinic space group P2(1)/c. The geometrical features are very similar to those for (**49**) and the iridium centre can be considered as having a heavily distorted trigonal bipyramidal geometry with the carbonyl ligand and P(1) taking up the axial sites, whilst C(1), P(2) and P(3) are in the equatorial positions. The P(1)-C(1) bond was found to be 1.753(9) Å and is not significantly different than the corresponding bond in (**39**), [1.753(13) Å]. The Ir(1)-C(1) distance [1.909(9) Å] is also very close to the Ir(1)-C(1) bond length found in (**39**) [1.918(14) Å]. The Ir(1)-P(1) bond length [2.356(2) Å] is similar to that observed for (**49**) [2.352(3) Å] while its C(6)-P(1)-C(1)-C(2) torsion angle was found to be 80.7°. The geometry at gold is close to linear [P(1)-Au(1)-Cl(1) 177.4(9)°] and the Au(1)-P(1) distance was found to be 2.255(2) Å. Finally, the Au(1)-Cl(1) bond length [2.300(2) Å] is in the normal range.[65]

Considerable confusion is seen in textbooks and periodic tables about the relative sizes of silver and gold. Values quoted for the covalent or ionic radii of the metals are either equal or larger for gold than silver.[4, 8] Some recent theoretical calculations, including relativistic effects, consistently predict that gold should be significantly smaller than silver, a phenomenon which is generally referred to as the "relativistic contraction".[75-77]

Schmidbaur et al. made an experimental attempt to settle this simple question in 1996.[78] The most straightforward approach would be a comparison of metal-to-ligand bond lengths. The experimental approach should give unambiguous results if several criteria are met, for example:

i) the same ligand and counterions,
ii) the same co-ordination number and geometry,
iii) an isomorphous crystal lattice,
iv) equal experimental conditions.

Schmidbaur et al. found those criteria fulfilled in $[\{(Mes)_3P\}_2M]BF_4$ (M = Au, Ag) and accurate single-crystal work showed that gold (I) is indeed significantly smaller then silver (I), by almost 0.1 Å.[78]

We saw the possibility to prepare the silver analogue of (**50**) to confirm *Schmidbaur's* findings. With this in mind, a solution of (**39**) was treated with an equimolar quantity of silver chloride. Due to the well-known light sensitivity of silver compounds, the reaction was conducted in the dark. Unlike the experiments detailed above, no discernable reaction was observed after one day and so the reagents were allowed to react over an extended period (*ca.* one week). Ultimately, a good yield of the silver analogue of complex (**50**), *viz.* $[Ir\{=C(Bu^t)P[Ag(Cl)](Cy)\}(CO)(PPh_3)_2]$ (**51**), was obtained (Scheme 2.30).

The spectroscopic data for this complex are similar to those for the gold complex, (**50**), with the exception of a higher field iridaphosphirene phosphorus resonance at δ - 152.0 ppm in its $^{31}P\{^1H\}$ NMR spectrum. Additionally this signal displays a one bond coupling of 702 Hz to the spin active $^{107,109}Ag$ (I = ½) nuclei. The infrared spectrum of (**51**) showed the CO stretching absorption at 1976 cm^{-1}, while the ES mass spectrum exhibits a molecular ion peak. Subsequent accurate mass spectrometry confirmed the formulation of (**51**). Once again, suitable single crystals were grown and a structural study undertaken. This allowed a direct comparison to be made between the isomorphous structures of the gold and silver complexes. The molecular structure of (**51**) is depicted in Figure 2.13.

Compound (**51**) was found to be isostructural and isomorphous to (**50**) and fulfilled all criteria given by *Schmidbaur.*[78] The geometry at silver is slightly more bent than in (**50**) but still close to linear [P(1)-Ag(1)-Cl(1) 172.41(4)°] and the Ag(1)-P(1) distance was found to be 2.3522(13) Å which is indeed larger by almost 0.1 Å than the Au(1)-P(1) distance in (**50**), which was determined with 2.255(2) Å. These finding are in good agreement with the "relativistic contraction" predicted and confirmed by *Schmidbaur et al.*[78]

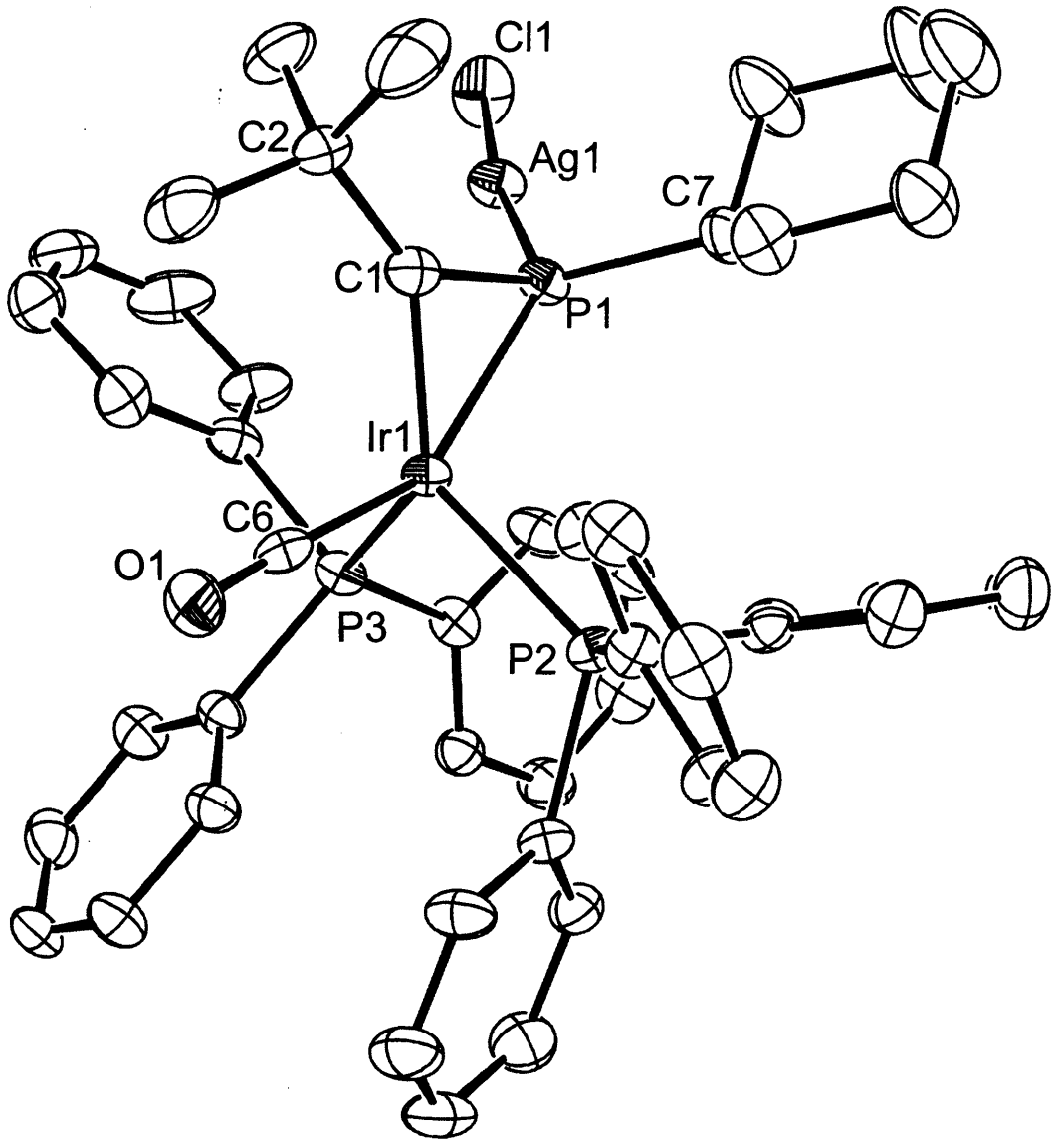
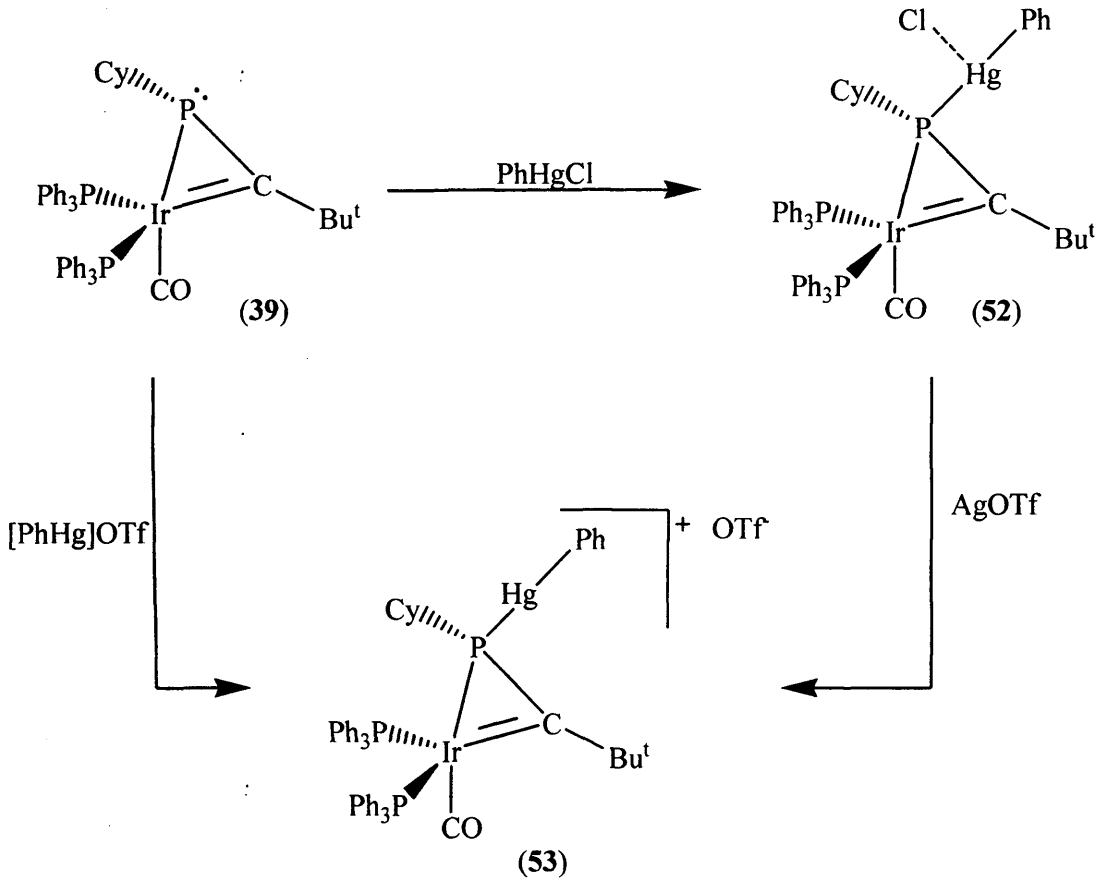


Figure 2.13 Molecular structure of [Ir{=C(Bu^t)P[Ag(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (51)

Selected bond length (Å) and angles (°): Ir(1)-C(6) 1.884(4), Ir(1)-C(1) 1.916(3), Ir(1)-P(3) 2.3572(10), Ir(1)-P(2) 2.3574(10), Ir(1)-P(1) 2.3721(11), Ag(1)-Cl(1) 2.3242(13), Ag(1)-P(1) 2.3522(13), P(1)-C(1) 1.770(4), P(1)-C(7) 1.868(4), O(1)-C(6) 1.148(4), C(6)-Ir(1)-C(1) 102.94(15), C(6)-Ir(1)-P(3) 96.76(11), C(1)-Ir(1)-P(3) 120.35(10), C(6)-Ir(1)-P(2) 91.19(11), C(1)-Ir(1)-P(2) 131.93(10), P(3)-Ir(1)-P(2) 102.77(4), C(6)-Ir(1)-P(1) 150.20(11), C(1)-Ir(1)-P(1) 47.29(11), P(3)-Ir(1)-P(1) 98.77(4), P(2)-Ir(1)-P(1) 109.82(4), Cl(1)-Ag(1)-P(1) 172.41(4), C(1)-P(1)-Ir(1) 52.71(12), P(1)-C(1)-Ir(1) 80.00(14).

Recent work on the synthetically versatile ruthenium-phosphavinyl complexes, $[Ru\{P{=}C(H)Bu^t\}Cl(CA)(PPh_3)_2]$ (A = O, S), showed that organomercury halide reagents can add across the Ru-P bond to provide complexes of the form $[Ru\{P(HgR){=}C(H)Bu^t\}Cl(X)(CA)(PPh_3)_2]$ (R = Me, Ph, ferrocenyl, Cl; X = Cl, I).[71, 79] This prompted us to investigate the reactivity of $[Ir\{{=}C(Bu^t)P(Cy)\}(CO)(PPh_3)_2]$ (**39**) towards phenylmercury chloride.

Stirring a solution containing a 1:1 mixture of the reagents (**39**) and PhHgCl, initially at - 78 °C and then at room temperature, for a period of 3 hours led to the formation of $[Ir\{{=}C(Bu^t)P[Hg(Ph)](Cy)\}(CO)(PPh_3)_2]Cl$ (**52**) in a 77 % yield (Scheme 2.31). In this case, the $^{31}P\{^1H\}$ NMR spectrum of the complex was found to be less diagnostic than those of (**49 - 51**) as the resonances at δ 14.0, 7.3 and - 112.0 ppm all appeared as broadened multiplets. Unfortunately, variable temperature $^{31}P\{^1H\}$ NMR studies did not lead to greater resolution of any of these signals. The ^1H NMR data for the complex support its proposed formulation, as does its elemental analysis and mass spectrum (LSIMS) which displays a molecular ion at *m/z* = 1205. The carbonyl stretching absorption was found at 1986 cm^{-1} in the IR spectrum. In a C_6D_6 solution the compound gradually decomposes leading to crystallization of $[IrCl(CO)(PPh_3)_2]$ and deposition of elemental mercury. A singlet observed at δ 255.0 ppm in the $^{31}P\{^1H\}$ spectrum of the decomposition mixture was tentatively assigned to the phosphaalkene, $[(Cy)P{=}C(Ph)Bu^t]$. A mass spectrum was also obtained on this compound and showed a correlation between the observed isotopic abundances and their simulated values for the molecular ion of this phosphaalkene. This decomposition is similar to that observed for compounds (**41**) - (**43**) which gave (**45**), a phosphaalkene that showed a chemical shift of δ 257.8 ppm in its $^{31}P\{^1H\}$ NMR spectrum.



Scheme 2.31 Preparation of (52) and (53)

A structural investigation of complex (**52**) revealed the chloride to have a weak "T-shaped" interaction with the mercury centre. This is depicted in the molecular structure of the complex shown in Figure 2.14. The geometry at the iridium centre can be considered as distorted trigonal bipyramidal, similar to the precursor (**39**). The P(1)-C(1) interaction [1.751(6) Å] is not significantly different than the corresponding bond in (**39**), [1.753(13) Å], while the Ir(1)-C(1) distance [1.923(6) Å] is slightly longer than in (**39**) [1.918(14) Å]. The C(6)-P(1)-C(1)-C(2) torsion angle was found to be 73.4°.

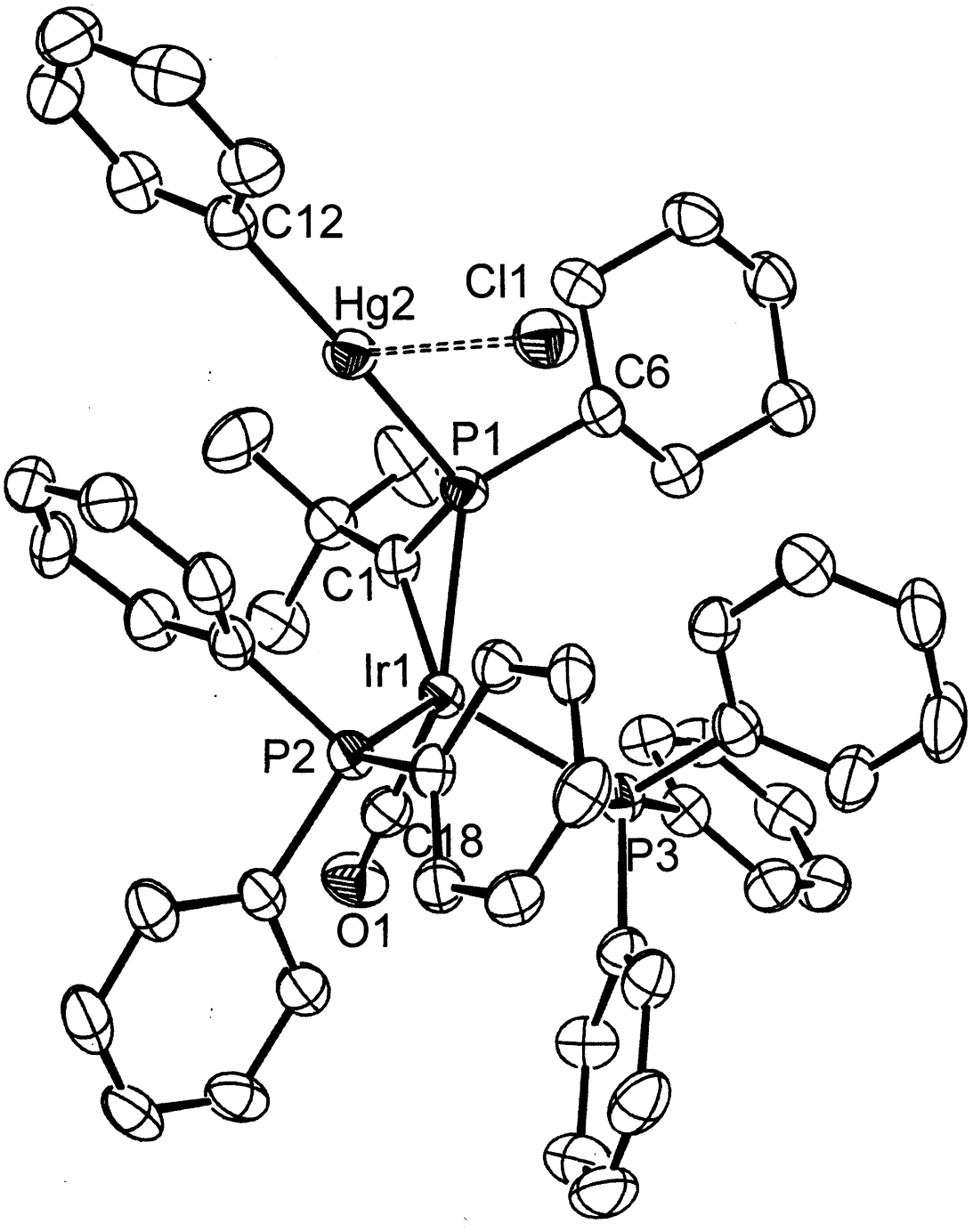


Figure 2.14 Molecular structure of [Ir{=C(Bu^t)P[Hg(Ph)](Cy)}(CO)(PPh$_3$)$_2$]Cl (52)

Selected bond length (Å) and angles (°): Hg(2)-C(12) 2.083(6), Hg(2)-P(1) 2.4037(18), Hg(2)-Cl(1) 2.7959(17), Ir(1)-C(18) 1.875(6), Ir(1)-C(1) 1.923(6), Ir(1)-P(2) 2.3576(16), Ir(1)-P(1) 2.3629(17), Ir(1)-P(3) 2.3805(19), P(1)-C(1) 1.751(6), O(1)-C(18) 1.167(7), C(12)-Hg(2)-P(1) 168.17(18), C(12)-Hg(2)-Cl(1) 100.81(18),

P(1)-Hg(2)-Cl(1) 89.67(6), C(18)-Ir(1)-C(1) 99.8(2), C(18)-Ir(1)-P(2) 99.11(19), C(1)-Ir(1)-P(2) 123.87(19), C(18)-Ir(1)-P(1) 146.69(18), C(1)-Ir(1)-P(1) 46.84(18), P(2)-Ir(1)-P(1) 101.49(6), C(18)-Ir(1)-P(3) 90.81(19), C(1)-Ir(1)-P(3) 133.20(18), P(2)-Ir(1)-P(3) 98.63(6), P(1)-Ir(1)-P(3) 111.45(6), C(1)-P(1)-Ir(1) 53.3(2), P(1)-C(1)-Ir(1) 79.9(2).

It was found that the chloride of (**52**) could be abstracted by treatment of the complex with AgOTf to give [Ir{=C(Bu^t)P[Hg(Ph)](Cy)}(CO)(PPh$_3$)$_2$]OTf (**53**) (Scheme 2.31). The same complex could be prepared by a more direct route using the *in situ* preparation of [HgPh]OTf and its subsequent reaction with [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**). The ^{31}P{^{1}H} NMR spectrum of (**53**) is better resolved than that of (**52**) and shows resonances of the expected multiplicity at δ 12.6, 7.4 and - 109.1 ppm. The υ(CO) absorption in the solid state infrared spectrum occurs at 2000 cm^{-1}, a small (14 cm^{-1}) increase in frequency compared to [Ir{=C(Bu^t)P[Hg(Ph)](Cy)}(CO)(PPh$_3$)$_2$]Cl (**52**). This may suggest that the positive charge is not solely resident on the mercury but may be shared with the iridium center. Single crystals of complex (**53**) were obtained by cooling a toluene solution of the complex. A structural study was carried out and the structure of its cation is shown in Figure 2.15.

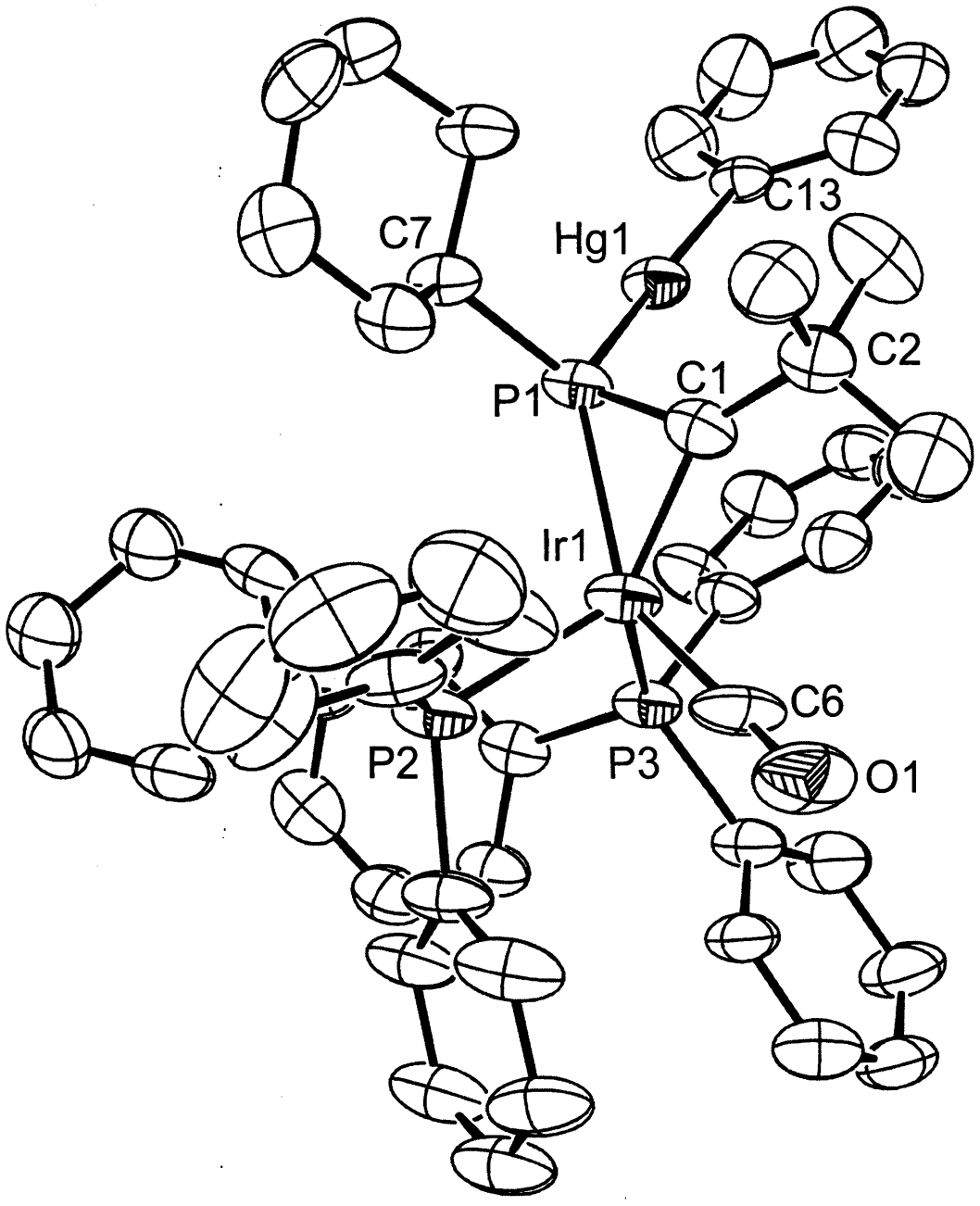


Figure 2.15 Structure of the cationic component of [Ir{=C(Bu^t)P[Hg(Ph)](Cy)}(CO)(PPh_3)$_2$][SO_3CF_3] (53)

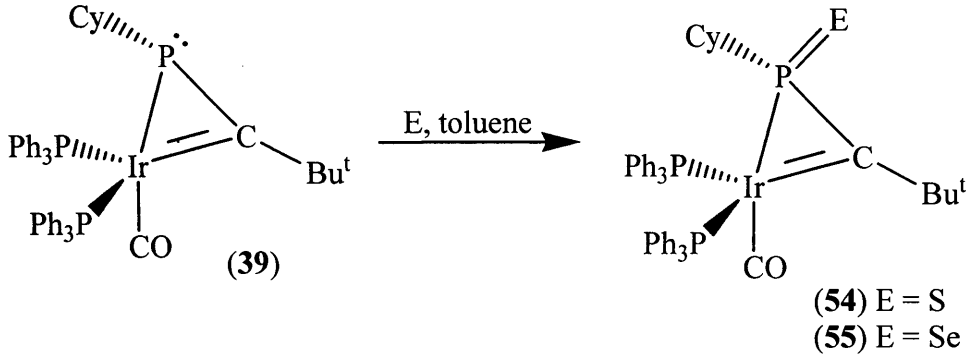
Selected bond length (Å) and angles (°): Hg(1)-C(13) 2.105(9), Hg(1)-P(1) 2.405(3), Ir(1)-C(6) 1.901(12), Ir(1)-C(1) 1.928(9), Ir(1)-P(3) 2.355(3), Ir(1)-P(1) 2.356(2), Ir(1)-P(2) 2.393(3), P(1)-C(1) 1.755(11), O(1)-C(6) 1.112(13), C(13)-Hg(1)-P(1) 169.0(3), C(6)-Ir(1)-C(1) 99.1(5), C(6)-Ir(1)-P(3) 97.3(4), C(1)-Ir(1)-P(3) 125.0(3), C(6)-Ir(1)-P(1) 146.2(3), C(1)-Ir(1)-P(1) 47.1(3), P(3)-Ir(1)-P(1) 102.38(9), C(6)-

Ir(1)-P(2) 91.9(4), C(1)-Ir(1)-P(2) 133.5(3), P(3)-Ir(1)-P(2) 97.64(9), P(1)-Ir(1)-P(2) 112.17(10), C(1)-P(1)-Ir(1) 53.5(3), P(1)-C(1)-Ir(1) 79.4(4).

Compound (**53**) crystallises in the monoclinic space group P2(1)/c. The iridium centre shows the same trigonal bipyramidal geometry observed in the other iridium compounds, (**39**) or (**52**). Crystallographically investigated mercury-phosphorus bonds are relatively rare and it was only in 1988 that the first structurally characterized complex of mercury(II) containing a phosphorus ligand was reported, *viz.* $[(Ph_3P)HgPh]NO_3$.[80] The P-Hg bond length in this complex is 2.431(2) Å which is slightly longer than in the structures of (**52**) [2.4037(18) Å] and (**53**) [2.405(3) Å]. However, the Hg-C bond lengths for the compounds $[(Ph_3P)HgPh]NO_3$ [2.090(5) Å], (**52**) [2.083(6) Å] and (**53**) [2.105(9) Å] are all in the same range and are very similar to that for PhHgCl itself [2.044(9) Å].[17] The Hg(2)-Cl(1) distance of 2.7959(17) Å in (**52**) is greater than the sum of the atomic radii of the elements (2.5 Å) but less than the sum of the van der Waals radii (3.3 Å)[81] and so is best described as a counteranion interaction. The "T-shape" motif in (**52**) [P(1)-Hg(2)-Cl(1) 89.67(6)°, C(12)-Hg(2)-Cl(1) 100.81(18)°] is not uncommon for mercury compounds and has been observed, for example, in the structure of $[Ph_3PHgPh]NO_3$ in which the NO_3^- counteranion has a similar interaction with the cation. Unlike PhHgCl, which has been reported as being exactly linear,[82] compounds (**52**) and (**53**) both show significant deviations from linearity at mercury, P-Hg-C 168.17(18)° and 169.0(3)° respectively, which is presumably due to steric reasons in both complexes. In addition, the Hg···Cl interaction in (**52**) could add to the deviation seen in that compound.

2.3.4 Reactions of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with group 16 elements

The reactivity of (**39**) toward elemental chalcogens, was examined with similar results to its protonation. The reaction of (**39**) with elemental sulfur and selenium leads to oxidation of the phosphirene phosphorus centre to give (**54**) and (**55**) respectively.



Scheme 2.32 Reaction of [Ir(PPh$_3$)$_2$(CO){C(Bu^t)P(Cy)}] (39) with chalcogens

The $^{31}P\{^1H\}$ NMR spectra of (**54**) and (**55**) both show virtual triplet resonances corresponding to the metallophosphirene phosphorus centres at significantly lower field ((**54**) δ -86.1 ppm, (**55**) δ -117.4 ppm) than the related resonances seen for both (**39**) and (**41 - 43**). This observation reflects the relatively electron poor nature of the phosphorus centres in the former compounds. In addition, the ^{13}C NMR spectra of (**54**) and (**55**) display low field signals ((**54**) δ 371.3 ppm, (**55**) δ 341.2 ppm) corresponding to the carbon centres double bonded to iridium.

To confirm the formulation of (**54**), an X-ray crystal structure determination was carried out. The similarities between the spectroscopic data for (**54**) and (**55**), as well as the ion $[MH]^+$ (1008, 100 %) found for (**55**) in its APCI mass spectrum leaves no doubt that the formulation of (**55**) is similar to that of (**54**).

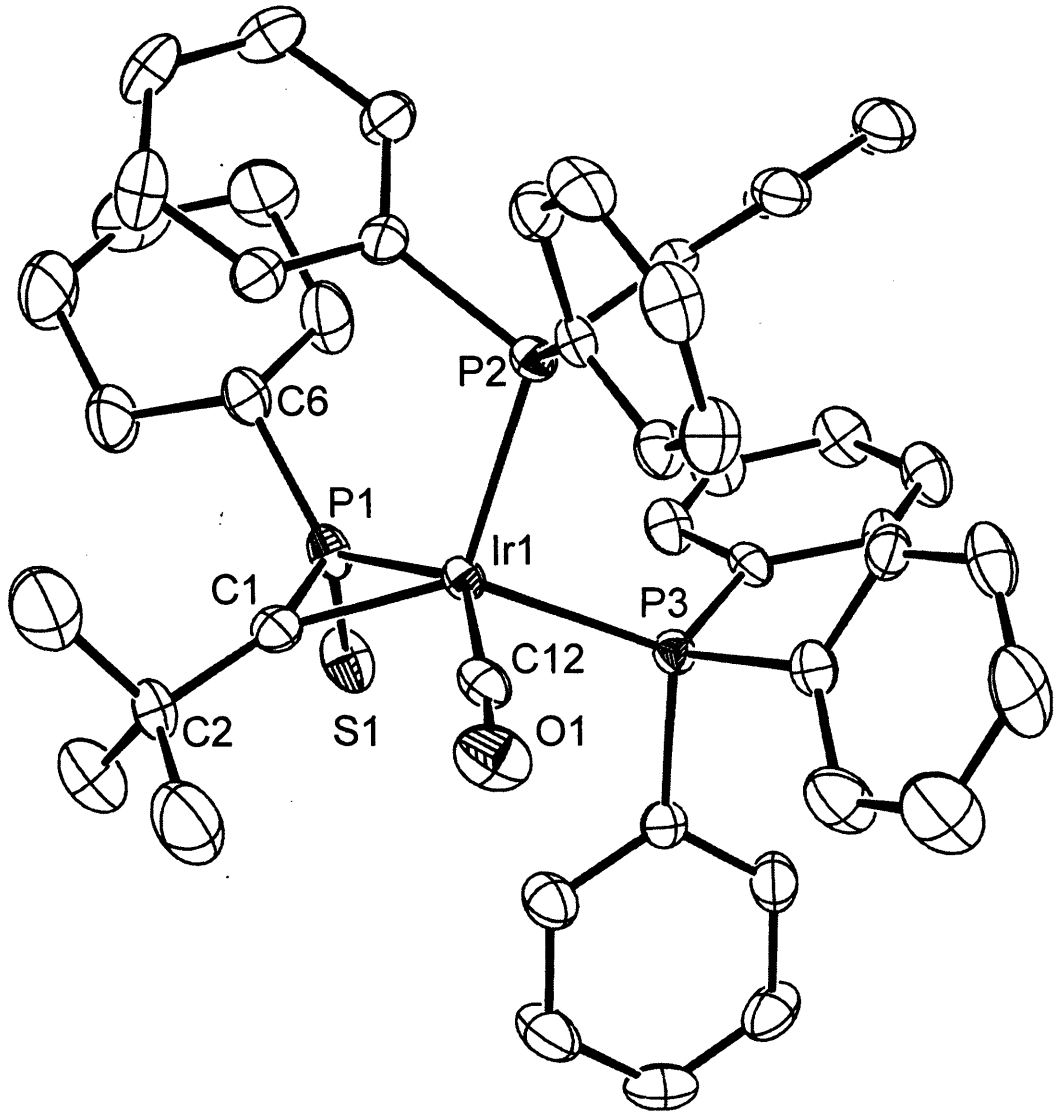
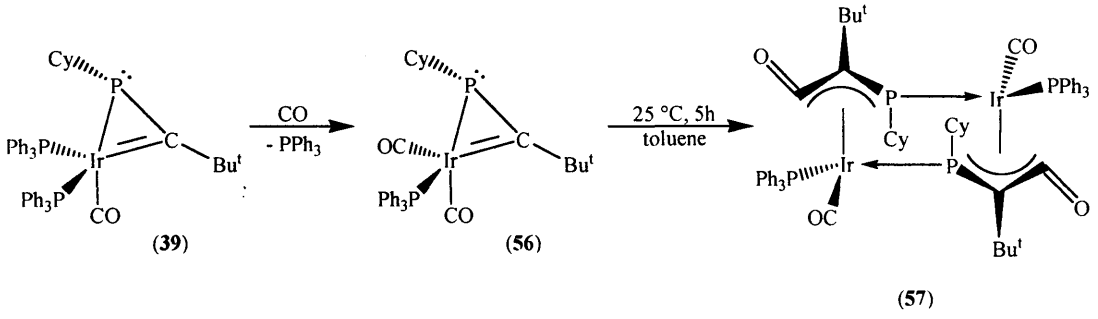


Figure 2.16 Molecular structure of [Ir{=C(Bu^t)P(=S)(Cy)}(CO)(PPh$_3$)$_2$] (54)

The molecular structure of (**54**) (Figure 2.16) shows a geometry at the iridium centre similar to those in (**39**) and (**41** - **43**). Moreover, its P(1)-C(1) bond length [1.746(6) Å] and Ir(1)-C(1) distance [1.945(6) Å] are close to those in (**39**) and the Ir(1)-P(1) interaction [2.3552(17) Å] is comparable to those in (**41** - **43**) but significantly shorter than in (**39**), as would be expected. Finally, the P(1)-S(1) distance in (**54**) [1.992(2) Å] is in the normal range for double bonds between these two elements.[65]

2.3.5 Miscellaneous reactions of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39)

When CO gas was passed through a toluene solution of (**39**), displacement of one PPh_3 ligand and formation of (**56**) occurred (Scheme 2.33). This was confirmed by the $^{31}P\{^1H\}$ NMR spectrum of the complex in which the signal corresponding to the phosphido centre (δ - 152.3 ppm) has shifted only slightly down field from that in (**39**) but is now coupled to only one PPh_3 ligand ($^2J_{PP}$ = 79 Hz). In addition, the IR spectrum of (**56**) shows two strong CO stretching absorptions (1977, 1949 cm^{-1}). Compound (**56**) is thermally stable in the solid state but in toluene or ethereal solutions decomposes over several hours to give many phosphorus containing products. One of these products, (**57**), could be isolated in very low yield (< 1 %) but unfortunately it was not possible to obtain any data on this compound other than its X-ray crystal structure (Figure 2.17).



Scheme 2.33 Reaction of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (39) with CO

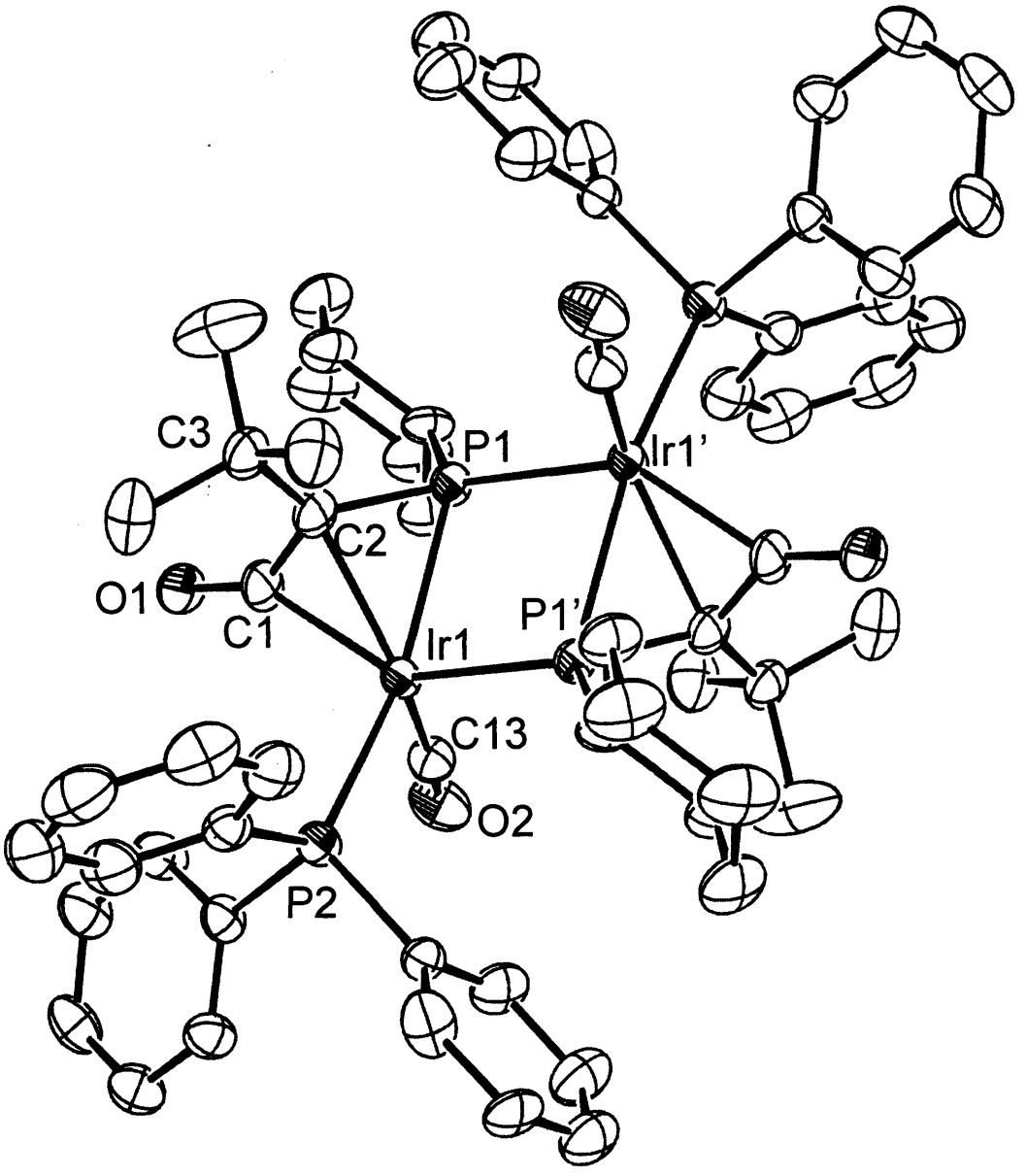


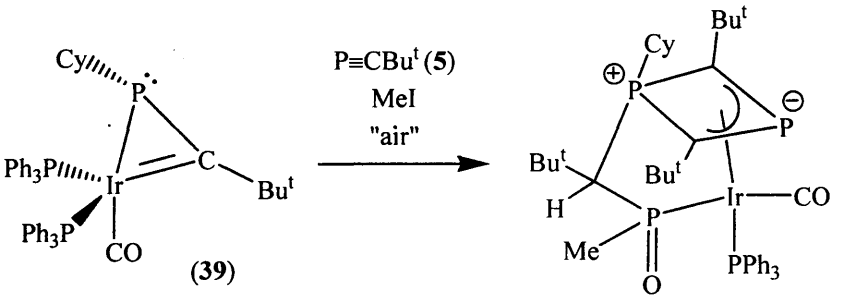
Figure 2.17 Molecular structure of $[Ir(PPh_3)(CO)_2\{C(Bu^t)P(Cy)\}]_2$ (57)

Selected bond lengths (Å) and angles (°): Ir(1)-C(13) 1.889(7), Ir(1)-C(1) 2.018(7), Ir(1)-C(2) 2.209(7), Ir(1)-P(2) 2.3481(19), Ir(1)-P(1) 2.3769(19), Ir(1)-P(1) 2.4550(17), P(1)-C(2) 1.800(8), O(1)-C(1) 1.213(8), C(1)-C(2) 1.433(11); C(1)-C(2)-P(1) 104.0(5), O(1)-C(1)-C(2) 139.7(8), C(2)-P(1)-C(7) 109.1(3), C(2)-P(1)-Ir(1) 122.1(2), Ir(1)-C(1)-O(1) 142.7(7), Ir(1)-P(1)-C(7) 116.9(2). Symmetry operation: ' = -x, -y + 1, -z.

Compound (**57**) demonstrates the ability of the phosphidocarbene ligand in (**56**) to undergo a facile intramolecular C-C bond forming reaction with one of its carbonyl ligands. This has given rise to a complex in which the generated oxo-η^3-phosphaallylic ligand adopts an *anti*-configuration, thus allowing its P-lone pair to intermolecularly donate to an Ir centre to give the observed 18e$^-$-dimeric structure for (**57**). There is only one other crystallographically characterised example of an oxo-phosphaallylic complex, [Cp*Fe(CO){η^3-O=CC(H)P[C(H)(SiMe$_3$)$_2$]}] (**58**), which was isolated as both its *syn*- and *anti*-isomers.[83] In (**57**), the phosphaallylic ligand appears to be largely delocalised (as is the case in (**58**)) with both the P(1)-C(2) [1.800(8) Å] and C(1)-C(2) [1.433(11) Å] bond lengths lying between the norms for double and single bonded interactions.[65] The bond lengths from this ligand to Ir(1) confirm its η^3-mode of attachment and the C(1)-O(1) bond length [1.213(8) Å] is strongly suggestive of a localised double bond.

When (**39**) was reacted with (**5**) and subsequently with MeI a variety of phosphorus containing products were formed. Out of those only one, an unexpected phosphaalkyne coupled product, (**59**), was isolated in a very low yield. Unfortunately due to the low yield, no data other than the crystal structure (Figure 2.18) could be obtained. The mechanism of formation is unknown at present.

The structure shows that two molecules of (**5**) underwent a cycloaddition reaction with the phosphidocarbene ligand of (**39**) and the addition of a methyl group to one of the phosphorus centres has also occurred. Furthermore, one atom of oxygen, presumably from aerial oxygen, is attached to the methylated phosphorus atom. During the reaction the loss of one triphenylphosphine ligand occurs. The two fragments C(4)-C(1)-P(1) and C(18)-C(3)-P(3) originate from (**5**). The C(1)-P(1), C(3)-P(2) and C(3)-P(3) bonds were determined to be 1.845, 1.861 and 1.868 Å respectively, which are in the expected range for phosphorus-carbon single bonds.[65]



Scheme 2.34 Reaction of [Ir(PPh$_3$)$_2$(CO){C(Bu^t)P(Cy)}] (39) with P≡CBu^t (5) and MeI

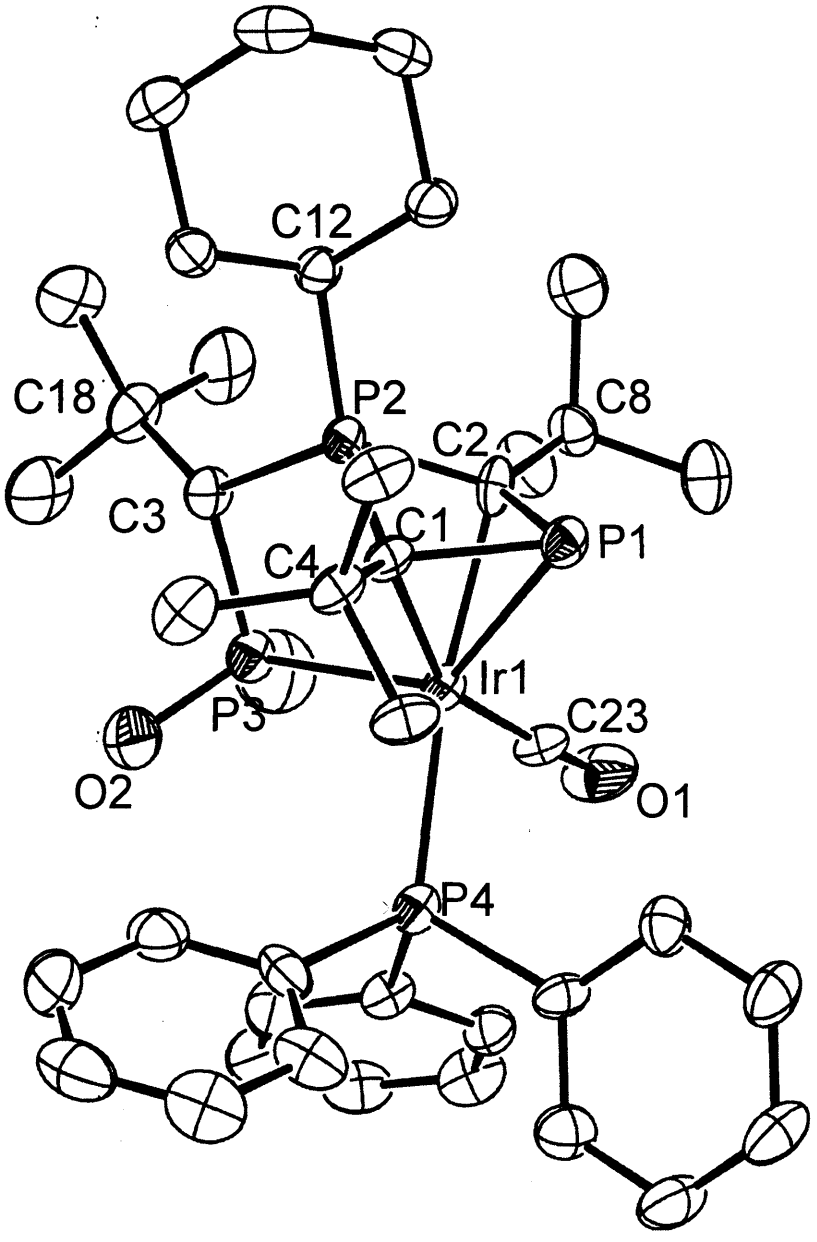


Figure 2.18 Molecular structure of (59)

Selected bond length (Å) and angles (°): Ir(1)-C(23) 1.863(7), Ir(1)-C(2) 2.195(7), Ir(1)-C(1) 2.235(6), Ir(1)-P(3) 2.3418(19), Ir(1)-P(1) 2.364(2), Ir(1)-P(4) 2.371(2), P(1)-C(1) 1.845(7), P(1)-C(2) 1.852(7), P(2)-C(1) 1.803(6), P(2)-C(2) 1.814(6), P(2)-C(12) 1.840(6), P(2)-C(3) 1.861(6), P(3)-O(2) 1.530(6), P(3)-C(22) 1.791(11), P(3)-C(3) 1.868(7), O(1)-C(23) 1.157(8), C(1)-C(4) 1.522(9), C(23)-Ir(1)-C(2) 96.1(3), C(23)-Ir(1)-C(1)157.1(3), C(2)-Ir(1)-C(1) 65.1(2), C(23)-Ir(1)-P(3)102.7(2), C(2)-Ir(1)-P(3) 92.30(17), C(1)-Ir(1)-P(3) 91.55(16), C(23)-Ir(1)-P(1)110.7(2), C(2)-Ir(1)-P(1) 47.78(17), C(1)-Ir(1)-P(1) 47.20(17), P(3)-Ir(1)-P(1) 128.99(6), C(23)-Ir(1)-P(4) 85.6(2), C(2)-Ir(1)-P(4) 169.25(16), C(1)-Ir(1)-P(4) 110.42(17), P(3)-Ir(1)-P(4) 97.67(7), P(1)-Ir(1)-P(4) 121.73(6), C(1)-P(1)-C(2) 80.3(3), C(1)-P(1)-Ir(1) 62.74(19), C(2)-P(1)-Ir(1) 61.3(2), C(1)-P(2)-C(2) 82.4(3), C(1)-P(2)-C(12) 117.2(3), C(2)-P(2)-C(12) 119.7(3), C(1)-P(2)-C(3) 112.0(3), C(2)-P(2)-C(3) 113.9(3), C(12)-P(2)-C(3) 109.4(3), O(2)-P(3)-C(22) 102.3(4), O(2)-P(3)-C(3) 106.1(3), C(22)-P(3)-C(3) 113.4(4), O(2)-P(3)-Ir(1) 124.4(2), C(22)-P(3)-Ir(1)108.6(4), C(3)-P(3)-Ir(1) 102.4(2),

2.4 Conclusion

The development of a facile synthetic route to the first example of an iridaphosphirene has been reported. Furthermore, the reactivity of this iridaphosphirene toward a variety of electrophiles has been investigated. In all cases reaction occurred at the phosphorus centre of the three membered ring and not at the metal centre. With the protonated complexes (**41 - 43**) an irreversible 1,2-hydrogen shift is observed to yield a cationic iridium(I)-phosphaalkene complex. From this, the phosphaalkene could be liberated by treatment with CO gas. In addition, a stereospecific synthetic route to E-phosphaalkenes has been described. Furthermore, the reactivity of (**39**) towards electrophilic fragments of gold, silver and mercury, which leads to an unprecedented range of aurated, argentated and mercurated iridaphosphirene complexes, has been described. The comprehensive structural characterisation of these species reveals that only the Ir-P bond length within the Ir-C-P triangular unit of these complexes changes significantly on binding to a secondary metal fragment. Due to the structural characterisation of isostructural and isomorphous silver and gold complexes, a direct comparison of the relative sizes of silver and gold has been possible.

2.5 Experimental

For general experimental procedures refer to appendix I. The complexes [AuCl(CNBu^t)],[84] [AuCl(THT)][85] and [AuCl(PPh_3)][86] were prepared according to published procedures. [$W(CO)_5$THF] was prepared by irradiating a THF solution of [$W(CO)_6$] in a UV apparatus for 16 h.[87] Other chemicals were commercially available and were purified, when necessary, according to published literature procedures.[88] ^{13}C NMR spectra of (**41** - **43**) and (**49** - **53**) were complicated by overlapping multiplets in the aliphatic and aromatic regions and these signals could not be confidently assigned.

[Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (39)

To a cold (- 78 °C) suspension of [Ir(PPh_3)$_2$(CO)Cl] (0.25 g, 0.23 mmol) in toluene (15 cm^3) was added a solution of (**19 a**) (0.10 g, 0.32 mmol) in toluene (5 cm^3) dropwise. This was allowed to warm to room temperature and stirred for 48 h. The solvent was removed *in vacuo* and the red brown residue washed with hexane and extracted with toluene (20 cm^3). Concentration, addition of hexane till first precipitation and slow cooling to - 30 °C resulted in red brown crystals of (**39**).
(yield 51 %); mp 170 - 174 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K) δ 0.72 - 2.11 (m, 11H, Cy), 1.77 (s, 9H, Bu^t), 6.73 - 7.77 (m, 30H, ArH); ^{13}C NMR (101.6 MHz, C_6D_6, 300 K) δ 27.9 (m, CCH_3), 31.5 (m, CH), 33.6 (d, CH_2, $^2J_{PC}$ = 18 Hz), 34.2 (d, CH_2, $^3J_{PC}$ = 11Hz), 36.4 (s, CH_2), 50.9 (m, CCH_3), 134.0 (d, m-ArC, $^3J_{PC}$ = 10 Hz), 134.5 (d, o-ArC, $^2J_{PC}$ = 13 Hz), 135.0 (s, p-ArC), 137.3 (m, ipso-ArC), 187.6 (dd, CO, $^2J_{PC}$ = 17 and 5 Hz), 331.5 (m, Ir=C); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 300 K) δ -157.2 (dd, Ir=CP, $^2J_{PP}$ = 22 and 66 Hz), 2.2 (dd, PPh_3, $^2J_{PP}$ = 22 and 66 Hz), 16.0 (v. tr., PPh_3, $^2J_{PP}$ = 22 and 22 Hz); MS APCI: m/z (%) 929 (MH^+, 15), 263 (PPh_3H^+, 100); IR (Nujol) ν/cm^{-1} 699 (m), 745 (m), 1091 (m), 1377 (m), 1434 (s), 1460 (s), 1954 (s, CO str.), 2924 (br); Found: C, 46.67; H, 7.11; $C_{48}H_{50}OP_3Ir$ requires: C, 47.0; H, 7.10 %.

[Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][SO$_3$CF$_3$] (41)

To a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (0.10 g, 0.11 mmol) in diethyl ether (10 cm^3) was added HSO$_3$CF$_3$ (0.12 mmol) in diethyl ether (5 cm^3) at - 78 °C over 5 min. The resulting solution was warmed to room temperature, stirred for 4 hours after which the volatiles were removed *in vacuo*. The residue was washed with hexane, dissolved in CH_2Cl_2 (1 cm^3) and layered with hexane to afford orange prisms of (**41**) overnight.

(0.06 g, 52 %); mp 183 - 185 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 0.70 - 2.03 (m, 11H, Cy), 1.52 (s, 9H, Bu^t), 7.02 - 7.53 (m, 30H, ArH), PH resonance not observed; ^{31}P{^{1}H} NMR (121.7 MHz, CD_2Cl_2, 300 K): δ - 142.7 (v.t., Ir=CP, $^2J_{PP}$ = 32 Hz), 8.0 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz), 9.6 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz); MS FAB (Noba matrix): *m/z* (%) 900 [M$^+$ - (CO + CF_3SO_3), 70 %]; IR (Nujol) υ/cm^{-1}: 2003 (s, CO str.), 2350 (m, PH str.).

[Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][CF$_3$CO$_2$] (42)

To a cold (- 78 °C) solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (0.1 g, 0.1 mmol) in toluene (10 cm^3) was added a solution of CF_3COOH in toluene (1.0 cm^3, 0.1 mmol). This was stirred for 5 minutes, then allowed to warm to room temperature and stirred for 3 hours. Concentration of the mother liquor and cooling to - 35 °C resulted in red-orange crystals of (**42**).

(yield 0.06 g, 60 %); mp 73 - 75 °C; ^{1}H NMR (400 MHz, C_7D_8, 300 K): δ 0.70 - 2.03 (m, 11H, Cy), 1.47 (s, 9H, Bu^t), 7.02 - 7.87 (m, 30H, ArH), PH resonance not observed; ^{31}P{^{1}H} NMR (121.7 MHz, C_7D_8, 300 K): δ - 139.2 (v.t., Ir=CP, $^2J_{PP}$ = 32 Hz), 5.70 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz), 13.2 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz); MS FAB (Noba matrix): *m/z* (%) 930 [M$^+$ - CF_3CO_2 100 %]; IR (Nujol) υ/cm^{-1}: 2013 (s, CO str.), 2340 (m, PH str.).

[Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][BF$_4$] (43)

To a cold (- 78 °C) suspension of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (0.1 g, 0.1 mmol) in ether (10 cm^3) was added a solution of HBF_4 in Et_2O (16 μl, 54 w.t. % in Et_2O, 0.1 mmol). This was stirred for 5 minutes, then allowed to warm to room

temperature and stirred for 1 hour. An orange precipitate was observed. The solvent was removed *in vacuo*. The precipitate was washed with hexane and toluene, yielding (**43**) as orange powder.

(0.05 g, 50 %); mp 169 - 171 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 0.79 - 1.87 (m, 11H, Cy), 1.53 (s, 9H, Bu^t), 6.99 - 7.67 (m, 30H, ArH), PH resonance not observed; $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2, 300 K): δ - 142.9 (v.t., Ir=CP, $^2J_{PP}$ = 32 Hz), 8.20 (v.t., PPh_3, $^2J_{PP}$ = 32 Hz), 9.43 (v.t., PPh_3, $^2J_{PP}$ = 32 Hz); MS FAB (Noba matrix): *m/z* (%) 930 (M^+ - 25 %) ; IR (Nujol) υ/cm^{-1}: 2014 (s, CO str.), 2370 (m, PH str.).

[Ir(CO)(PPh$_3$)$_2${η^1-P(Cy)=C(H)(Bu^t)}][BF$_4$] (44)

A solution of [Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][BF$_4$] (**43**) (0.03 g, 0.03 mmol) in CH_2Cl_2 (2 cm^3) was allowed to stand at 25 °C for 7 days after which time it was layered with hexane (10 cm^3) to yield orange prisms of (**44**) overnight.

(0.028 g, 93 %); mp 183 - 185 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 0.70 - 2.04 (m, 11H, Cy), 0.82 (s, 9H, Bu^t), 7.23 - 7.58 (m, 30H, ArH), 7.65 (d, 1H, P=CH, $^2J_{PH}$ = 23 Hz); $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2, 300 K): δ 15.2 (d, 2 PPh_3, $^2J_{PP}$ = 51 Hz), 222.4 (t, P=C, $^2J_{PP}$ = 51 Hz); MS FAB (Noba matrix): *m/z* (%) 745 [Ir(CO)(PPh$_3$)$_2^+$, 40], 715 [Ir(PPh$_3$)$_2^+$, 55], 263 [PPh_3H^+, 100]; IR (Nujol) υ/cm^{-1}: 2006 (s, CO str.).

***E*-[CyP=C(H)Bu^t] (45)**

To a solution of (**19 a**) (0.50 g, 1.58 mmol) in diethyl ether (20 cm^3) at 25 °C was added methanol (0.20 cm^3, 4.74 mmol) to give the immediate formation of a white precipitate. The suspension was filtered and volatiles were removed in vacuo from the filtrate to yield an oily residue which was extracted into hexane (10 cm^3). The resultant suspension was then filtered and volatiles removed from the filtrate in vacuo. This gave (**45**) as a colourless oil (0.28 g, 96 %), ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 8.64 (d, $^2J_{PH}$ = 24.8 Hz, 1H, P=CH), 2.10 - 1.10 (m, 11H, Cy), 1.15 (d, $^4J_{PH}$ = 1.7 Hz, 9H, CMe_3); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K) δ 257.8 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 198.2 (d, $^1J_{PC}$ = 44.8 Hz, P=*C*), 41.1 (d, $^1J_{PC}$ = 33.2 Hz, Cy), 36.1 (d, $^2J_{PC}$ = 11.9 Hz, *C*Me$_3$), 32.3 (d, $^2J_{PC}$ = 9.1 Hz, Cy), 30.8 (s, C*Me$_3$*),

30.5 (d, $^3J_{PC}$ = 12.2 Hz, Cy), 26.0 (s, Cy); MS APCI m/z 185 (M^+, 25 %); IR (Nujol) υ/cm^{-1}: 1448 (s), 1358 (m), 1258 (m), 1167 (m), 1117 (m), 1017 (m), 936 (w), 886 (w), 846 (w), 801 (w).

***E*-[MesP=C(H)Bu^t] (46)**

A similar procedure to the preparation of (**45**) was employed.

Colourless oil (yield 88 %), ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 8.43 (d, $^2J_{PH}$ = 25.3 Hz, 1H, P=CH), 7.15 (s, 2H, ArH), 2.31 (s, 6H, Me), 2.13 (s, 3H, Me), 1.15 (d, $^4J_{PH}$ = 2.2 Hz, 9H, CMe_3); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K) δ 228.4 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 203.3 (d, $^1J_{PC}$ = 43.8 Hz, P=*C*), 186.7 (d, $^1J_{PC}$ = 51.9 Hz, Ar), 140.0 (d, $^2J_{PC}$ = 5.8 Hz, Ar), 137.6 (s, Ar), 128.7 (s, Ar), 38.9 (d, $^2J_{PC}$ = 13.8 Hz, *C*Me_3), 30.1 (d, $^3J_{PC}$ = 10.8 Hz, C*Me*$_3$), 23.0 (d, $^3J_{PC}$ = 9.2 Hz, Me), 20.9 (s, Me); MS APCI m/z (%) 221 (M^+, 17 %), 151 ([M^+-CHBu^t], 100 %); IR (Nujol) υ/cm^{-1}: 1604 (m), 1458 (s), 1358 (m), 1258 (m), 1102 (m), 1031 (m), 871 (w), 845 (w), 806 (w).

[{(CO)$_4$W}$_2${μ-η^1,η^2-P(Cy)=C(Bu^t)}$_2$] (47)

To a solution of [W(CO)$_5$THF] (0.3 mmol) in THF (30 cm^3) was added a solution of E-CyP=C(H)Bu^t (**45**) (0.2 mmol) and the mixture stirred overnight. Volatiles were removed *in vacuo* and the residue extracted with hexane (5 cm^3). The solution was then cooled to - 30 °C to yield orange crystals of (**47**). Yield: (< 1 %)

[Ir{=C(Bu^t)P(Me)(Cy)}(CO)(PPh$_3$)$_2$]I (48)

To a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (0.10 g, 0.11 mmol) in THF (10 cm^3) at - 78 °C was added a solution of methyl iodide in THF (0.5 cm^3 containing 0.12 mmol). The resulting solution was warmed to room temperature, stirred for 4 hours after which time the volatiles were removed *in vacuo*. The residue was washed with hexane, dissolved in DCM (1 cm^3), layered with hexane to afford red prisms of (**48**) overnight.

(yield 0.075 g, 70 %); mp 216 - 218 °C; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.85 - 2.08 (m, 11H, Cy), 1.18 (d, 3H, P-CH_3, $^2J_{PH}$ = 12 Hz), 1.53 (s, 9H, Bu^t), 6.99 - 7.46 (m, 30H, ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K): δ 178.3 (m, CO), 330.4 (m,

Ir=C); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ -121.4 (v.t., Ir=CP, $^2J_{PP}$ = 31 Hz), 4.8 (v.t., PPh_3, $^2J_{PP}$ = 31 Hz), 8.9 (v.t., PPh_3, $^2J_{PP}$ = 31 Hz); Acc. Mass. ES^+: *m/z* (%) calc. for $[M^+-I]$ 943.2948, found 943.2942; IR (Nujol) υ/cm^{-1}: 1992 (s, CO str.); elemental analysis found: C 54.03, H 5.01, $C_{49}H_{53}OP_3Ir$ requires C 55.00, H 4.99.

[Ir{=C(Bu^t)P[Au(PPh$_3$)](Cy)}(CO)(PPh$_3$)$_2$][SO$_3$CF$_3$] (49)

[AuCl(PPh$_3$)] (53 mg, 0.11 mmol) and $AgSO_3CF_3$ (28 mg, 0.11 mmol) were suspended in tetrahydrofuran (10 cm^3) and stirred for 30 min at - 78 °C. This solution was filtered into a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (100 mg, 0.11 mmol) in tetrahydrofuran (10 cm^3), also cooled to - 78 °C. A color change from red to yellow was observed. The solution was allowed to warm to room temperature and stirred for 18 h. All solvent was removed under vacuum and the residue extracted with a minimum volume of toluene. Slow cooling to - 30 °C yielded orange crystals of (**49**).

(74 %, 114 mg). mp. 78 - 80 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.50 - 2.05 (m, 11H, Cy), 1.62 (s, 9H, Bu^t), 6.88 - 7.39 (m, 45H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 41.4 (ddd, Au(PPh_3), $^2J_{PP}$ = 341 Hz, $^4J_{PP}$ = 30 Hz, $^4J_{PP}$ = 7 Hz), 11.9 (overlapping unresolved m., 2 x PPh_3), - 117.2 (d. of pseud. t., IrPCy, $^2J_{PP}$ = 341 Hz, 2 x $^2J_{PP}$ = 30 Hz); $^{19}F\{^1H\}$ NMR (282.8 MHz, C_6D_6, 298 K): δ - 77.0 (s, CF_3SO_3); MS (ES) *m/z* (%): $[M-SO_3CF_3]^+$ (1387.5, 50), $[M-SO_3CF_3-PPh_3]^+$ (1125.4, 100); IR (Nujol) υ/cm^{-1}: 1974; elemental analysis calc. for $C_{67}H_{65}AuF_3IrO_4P_4S{\cdot}2.5(C_7H_8)$: C, 57.5; H, 4.9 %. Found: C, 57.4; H, 4.9 %.

[Ir{=C(Bu^t)P[Au(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (50)

a) [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (100 mg, 0.11 mmol) was dissolved in tetrahydrofuran (10 cm^3) and a solution of [AuCl(THT)] (34 mg, 0.11 mmol) in tetrahydrofuran (5 cm^3) was added at - 78 °C. The reaction was slowly warmed to room temperature and stirred for 20 h in the dark. Volatiles were then removed *in vacuo* and the residue taken up in a minimum volume of dichloromethane. This was layered with hexane resulting in orange crystals of complex (**50**). Yield: 85 mg (73 %). **b)** [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (100 mg, 0.11 mmol) was dissolved in tetrahydrofuran (10 cm^3) and a solution of [AuCl(CNBu^t)] (34 mg, 0.11 mmol) in

tetrahydrofuran (5 cm^3) was added at - 78 °C. The solution was slowly warmed to room temperature and stirred for 18 h in the dark. The solvent was removed under vacuum and the residue dissolved in a minimum volume of dichloromethane. Layering with hexane resulted in orange crystals of (**50**).

(40 %, 46 mg); mp. 198 - 200 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.77 - 1.81 (m, 11H, Cy), 1.63 (s, 9H, Bu^t), 6.79 - 7.87 (m, 30H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 13.9 (pseud. t., PPh_3, $^2J_{PP}$ = 24 Hz), 9.5 (pseud. t., PPh_3, $^2J_{PP}$ = 24 Hz), - 129.4 (br. m., PAuCl); Variable temperature $^{31}P\{^1H\}$ NMR studies did not lead to further resolution of the PAuCl signal; MS (LSIMS) *m/z*: Acc. mass. [M^+] 1160.2052, found 1160.2053, [M-Cl] 1125.2364, found 1125.2354; IR (Nujol) υ/cm^{-1}: 1980 (s, CO str.); elemental analysis calc. for $C_{48}H_{50}AuClIrOP_3$: C, 49.7; H, 4.3 %. Found: C, 50.1; H, 4.5 %.

[Ir{=C(Bu^t)P[Ag(Cl)](Cy)}(CO)(PPh_3)$_2$] (51)

[Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (80 mg, 0.09 mmol) was dissolved in tetrahydrofuran (10 cm^3) and a solution of AgCl (13 mg, 0.09 mmol) in tetrahydrofuran (5 cm^3) was added at - 78 °C. The reaction was slowly warmed to room temperature and stirred for one week in the dark. No discernable color change was observed. Volatiles were then removed *in vacuo* and the residue taken up in a minimum volume of toluene. Slow cooling of this solution to - 30 °C yielded red crystals of (**51**).

(73 %, 90 mg); mp. 205 - 207 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.25 - 1.94 (m, 11H, Cy), 1.64 (s, 9H, Bu^t), 6.83 - 7.39 (m, 30H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 14.6 (br. m., PPh_3), 7.7 (br. m., PPh_3), - 152.0 (d. of br. m., PAgCl, $^1J_{PAg}$ = 702 Hz); MS (LSIMS) *m/z*: Acc. mass. [M-Cl]$^+$ 1035.1749 (^{107}Ag, ^{193}Ir), found 1035.1762; IR (Nujol) υ/cm^{-1}: 1976.

[Ir{=C(Bu^t)P[Hg(Ph)](Cy)}(CO)(PPh_3)$_2$]Cl (52)

A solution of PhHgCl (31 mg, 0.10 mmol) in tetrahydrofuran (10 cm^3) was added to a tetrahydrofuran solution (10 cm^3) of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (96 mg, 0.10 mmol) at - 78 °C. A color change from orange to yellow was observed. The reaction mixture was warmed to room temperature and stirred for 3 h. Volatiles were

removed *in vacuo* and the residue dissolved in dichloromethane (5 cm^3). Hexane was added until precipitation of the product began to occur. The solution was then cooled to - 30 °C to yield orange crystals of (**52**).

(77 %, 93 mg); mp. 114 - 117 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.73 - 2.04 (m, 11H, Cy), 1.54 (s, 9H, Bu^t), 6.80 - 7.61 (m, 35H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 14.0 (br. m., PPh_3), 7.3 (br. m., PPh_3), - 112.0 (br. m., PHgPh); MS (LSIMS) *m/z* (%): 1205.3 (M^+, 20), 943.3 ($[M\text{-}PPh_3]^+$, 100); IR (Nujol) υ/cm^{-1}: 1986 (s, CO str.); elemental analysis calc. for $C_{54}H_{55}ClHgIrOP_3$: C, 52.4; H, 4.5 %. Found: C, 52.2; H, 4.0 %.

[Ir{=C(Bu^t)P[Hg(Ph)](Cy)}(CO)(PPh_3)$_2$][SO_3CF_3] (53)

A solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (75 mg, 0.08 mmol) in tetrahydrofuran (10 cm^3) was treated with a tetrahydrofuran solution (10 cm^3) of [PhHg]OSO_2CF_3 prepared *in situ* from $AgSO_3CF_3$ (21 mg, 0.08 mmol) and PhHgCl (25 mg, 0.08 mmol) at - 78 °C. A color change was observed from red to yellow. The reaction was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue extracted with toluene (5 cm^3). The solution was then cooled to - 30 °C to yield orange crystals of (**53**).

(75 %, 80 mg); mp. 101 - 103 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.29 - 1.75 (m, 11H, Cy), 1.43 (s, 9H, Bu^t), 6.72 - 7.65 (m, 35H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 12.6 (pseud. t., PPh_3, 2 x $^2J_{PP}$ = 30 Hz), 7.4 (pseud. t., PPh_3, 2 x $^2J_{PP}$ = 30 Hz], - 109.1 (pseud. t., PHgPh, 2 x $^2J_{PP}$ = 30 Hz); $^{19}F\{^1H\}$ NMR (282.8 MHz, C_6D_6, 298 K): δ - 77.0 (s, CF_3SO_3); MS (ES) *m/z* (%): 1205.4 (M^+, 100); IR (Nujol) υ/cm^{-1}: 2000 (s, CO str.).

[Ir{=C(Bu^t)P(=S)(Cy)}(CO)(PPh_3)$_2$], (54)

A solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (0.10 g, 0.11 mmol) in toluene (10 cm^3) was added to a solution of sulphur (5 mg, 0.15 mmol) in toluene (10 cm^3) at 25 °C and the resulting solution stirred for 3 hours. Concentration of this solution *in vacuo* to ca. 5 cm^3 and cooling to - 30 °C overnight results in red prisms of (**54**).

(yield 0.074 g, 72 %); mp 104 - 106 °C; ^1H NMR (300 MHz, C_6D_6, 298 K): δ 0.66 - 2.38 (m, 11H, Cy), 1.82 (s, 9H, Bu^t), 7.29 - 7.78 (m, 30H, ArH); ^{13}C NMR (75.6

MHz, CD_2Cl_2, 298 K): δ 183.3 (m, CO), 371.3 (m, Ir=C); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ -86.1 (v.t., Ir=CP, $^2J_{PP}$ = 27 Hz), 9.1 (v.t., PPh_3, $^2J_{PP}$ = 27 Hz), 13.5 (v.t., PPh_3, $^2J_{PP}$ = 27 Hz); MS APCI: *m/z* (%) 961 (MH^+, 75), 263 (PPh_3H^+, 75); IR (Nujol) υ/cm^{-1}: 1983 (s, CO str.).

[Ir{=C(Bu^t)P(=Se)(Cy)}(CO)(PPh_3)$_2$], (55)

To a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (0.1 g, 0.1 mmol) in toluene (10 cm^3) was added selenium powder (0.01 g, 0.13 mmol). This was stirred for 3 hours. The mother liquor was filtered and concentrated. Cooling to - 30 °C afford black prisms of (**55**).

(yield 0.044 g, 40 %); mp 95 - 97 °C; ^1H NMR (300 MHz, C_6D_6, 300 K): δ 0.60 - 2.32 (m, 11H, Cy), 1.86 (s, 9H, Bu^t), 7.00 - 7.95 (m, 30H, ArH); ^{13}C NMR (101.6 MHz, CD_2Cl_2, 300 K): δ 189.8 (m, CO), 341.2 (m, Ir=C); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 300 K): δ - 117.4 (v.t., Ir=CP, $^2J_{PP}$ = 28 Hz, $^1J_{SeP}$ = 653 Hz), 7.1 (v.t., PPh_3, $^2J_{PP}$ = 27 Hz), 14.5 (v.t., PPh_3, $^2J_{PP}$ = 27 Hz); MS APC: *m/z* (%) 1008 (MH^+, 100); IR (Nujol) υ/cm^{-1}: 1974 (s, CO str.).

[Ir{=C(Bu^t)P(Cy)}(CO)$_2$(PPh_3)] (56)

CO gas was bubbled through a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (0.06 g, 0.06 mmol) in toluene (15 cm^3) for 10 min, volatiles were removed *in vacuo* leaving (**56**) as orange powder.

(yield 100 %); mp 170 - 172 °C (dec.). ^1H NMR (400 MHz, C_6D_6, 300 K): δ 0.67 - 2.21 (m, 11H, Cy), 1.48 (s, 9H, Bu^t), 6.67 - 7.57 (m, 15H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 300 K) δ - 152.3 (d, Ir=CP, $^2J_{PP}$ = 79 Hz), 10.2 (d, PPh_3, $^2J_{PP}$ = 79 Hz); MS APCI: m/z (%) 666 ($M\text{-}CO^+$, 22), 262 (PPh_3, 100); IR (Nujol) ν/cm^{-1}: 1977 (s, CO str.), 1949 (s, CO str.).

[Ir(PPh_3)(CO)$_2${C(Bu^t)P(Cy)}]$_2$ (57)

CO gas was bubbled through a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (**39**) (0.06 g, 0.06 mmol) in toluene (15 cm^3) for 30 min, the solution was left under carbon monoxide atmosphere. The Schlenk flask was stored at room temperature overnight. The colour changed from red brown to orange. Crystals suitable for x-ray

diffraction were grown from a toluene solution that had been layered with hexane. Yield (< 1 %).

[Ir(CO)(PPh$_3$){P(O)(CH$_3$)C(H)(Bu^t)P(Cy)[η^3-C(Bu^t)PC(Bu^t)]}] (59)

To a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] (**39**) (0.10 g, 0.11 mmol) in toluene (10 cm^3) was added a solution of P≡CBu^t (**5**) (20 µl, 0.12 mmol) in toluene (10 cm^3) at 25 °C and the resulting solution stirred for 16 hours. An excess of methyl iodide was added and stirring was maintained a further 24 hours, volatiles were removed *in vacuo* and the residue extracted in benzene. After leaving this solution standing for several days at ambient temperature blue crystals of (**59**) were obtained. Yield (< 1 %).

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Chapter Three

3 Preparation and reactivity of a diphosphaalkyne

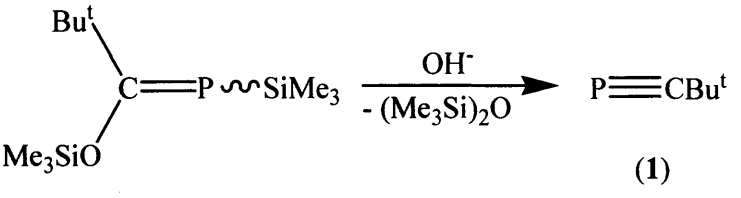
3.1 Introduction

Since the preparation of the first stable phosphaalkyne, P≡CBu^t (**1**), in 1981,[1] these compounds have developed from being chemical curiosities to versatile and widely utilised starting materials for the preparation of organophosphorus cage, heterocyclic and acyclic compounds, phospha-organometallics and co-ordination complexes which display a variety of phosphaalkyne ligation modes.[2-4] The versatility of phosphaalkynes in this respect is largely due to the fact that their chemistry more closely mimics that of alkynes than nitriles. Their importance to organometallic and organophosphorus chemists is perhaps best illustrated by the fact that over 400 publications describing phosphaalkyne chemistry have appeared to date. Despite this, there have been no reports of diphosphaalkynes save for a spectroscopic observation of the transient 1,4-diphosphabutadiyne, P≡C-C≡P (**2**),[5] and the preparation of the partially delocalised alkali metal phosphaethynolate salts, [M(O-C≡P)$_2$], M = Mg, Ca, Sr, Ba.[6] If diphosphaalkynes could be developed they would have enormous potential as building blocks in the formation of organophosphorus polymers, phosphaalkynyl substituted organophosphorus heterocycles and cages, and co-ordination polymers.

3.1.1 Phosphaalkyne chemistry

The first experimental evidence for phosphaalkynes was produced by *Gier* in 1961. He conducted an experiment in which phosphine was subjected to an electric arc struck between two graphite electrodes.[7] Amongst the volatile products condensed at - 196 °C, he could identify P≡CH (**3**), which polymerised above - 130 °C. Evidence for the structure of (**3**) was obtained by a trapping reaction with anhydrous HCl which yielded CH_3PCl_2 as the only product. Over the following

couple of years a number of other unstable phosphaalkynes were identified spectroscopically or by trapping reactions, *e.g.* $P{\equiv}CCH_3$,[8, 9] $P{\equiv}CSiMe_3$,[10] $P{\equiv}CF$.[11] Twenty years after *Giers* initial report, phosphaalkynes still were regarded as chemical curiosities. This changed in 1981 when *Becker et al.* reported the first thermally robust, kinetically stabilized phosphaalkyne, $P{\equiv}CBu^t$ (**1**).[1] This was prepared by a base catalysed *β*-elimination of hexamethyldisiloxane from the phosphaalkene $[(Me_3SiO)(Bu^t)C{=}PSiMe_3]$ (Scheme 3.1).



Scheme 3.1 Synthesis of the first stable phosphaalkyne

Compound (**1**) is a stable colourless liquid, which boils at 61 °C, and is the most widely used of all phosphaalkynes. A high precision low temperature X-ray diffraction study of $P{\equiv}CBu^t$ revealed that the lone pairs are located much closer to the P atom than in the phosphaalkene precursor.[12] The P≡C bond length was found to be 1.548 Å.[13] The HOMO of this phosphaalkyne involves the π-bonding orbitals of the PC triple bond and not the P lone pair, a situation which strongly suggests that phosphaalkynes would be expected to have a chemistry closely related to that of alkynes instead of nitriles.[14, 15] Thus, the P≡C bond in phosphaalkynes is polarised in the sense $P^{\delta+}$-$C^{\delta-}$ and it has been established that in spite of the presence of the P lone pair, protonation of (**1**) occurs exclusively at the carbon centre.[16] Phosphaalkynes have five possible modes of co-ordination to metal centres, (Figure 3.1).

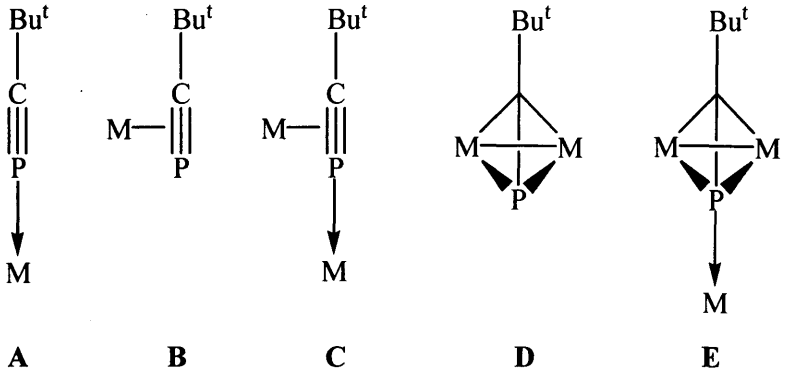
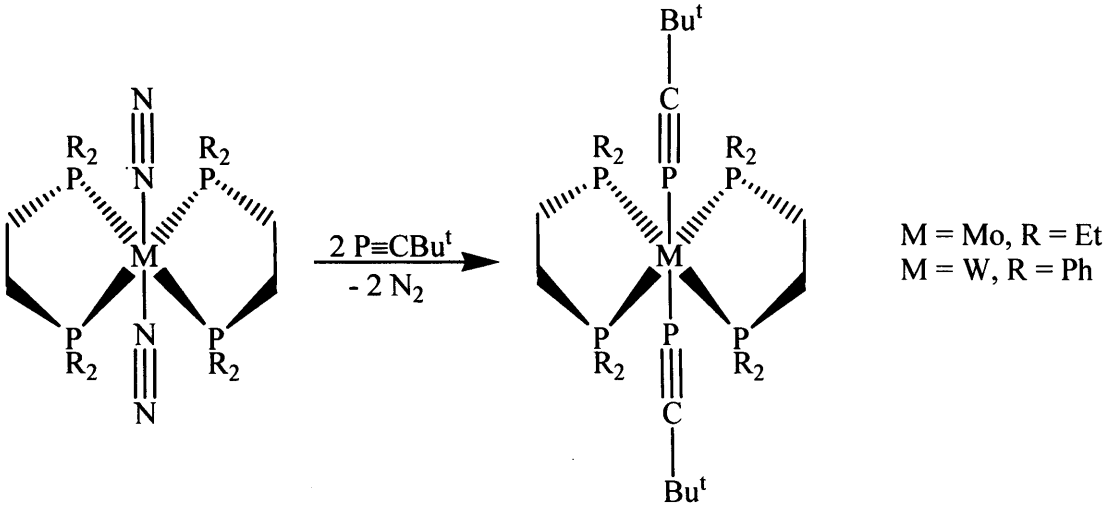


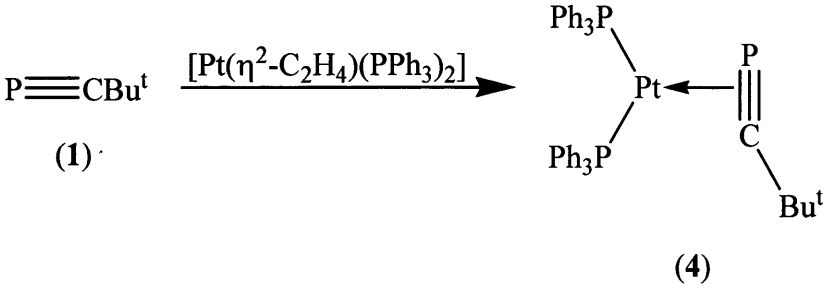
Figure 3.1 Co-ordination modes of phosphaalkynes

Type **A** co-ordination occurs solely *via* the phosphorus lone pair;[17] type **B** involves a side on co-ordination in an η^2 fashion, which is commonly observed for alkyne co-ordination;[18] whereas type **C** is a combination of both **A** and **B** type co-ordination modes. In **D** the phosphaalkyne acts as an η^2 bridge[19] and in **E** the phosphaalkyne acts simultaneously as η^2 bridge and electron pair donor.[20] Phosphaalkyne η^1 co-ordination is the least common, as this requires an end on co-ordination into a sterically hindered pocket which circumvents η^2 co-ordination. Few examples for this have been reported (Scheme 3.2).[17]



Scheme 3.2 Synthesis of η^1 phosphaalkyne complexes

η^2 co-ordination was found in the first phosphaalkyne complex (**4**). The η^2 co-ordination mode was established by ^{31}P NMR spectroscopy and an X-ray diffraction study (Scheme 3.3).[18]

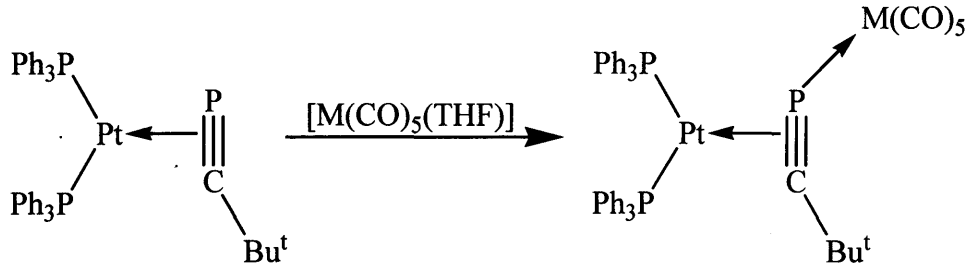


(**1**) (**4**)

Scheme 3.3 Synthesis of the first phosphaalkyne complex $[Pt(PPh_3)_2(\eta^2\text{-}P{\equiv}CBu^t)]$ (4)

This co-ordination mode is consistent with results of photoelectron studies which have shown that the HOMO of phosphaalkynes is the π orbital and that the π-n separation is greater than in nitriles (n = lone pair energy).[14, 21] Thus, phosphaalkynes

are expected to display alkyne like co-ordination chemistry. Examples of type **C** ligation can be found in some group 6 metal pentacarbonyl complexes (Scheme 3.4).



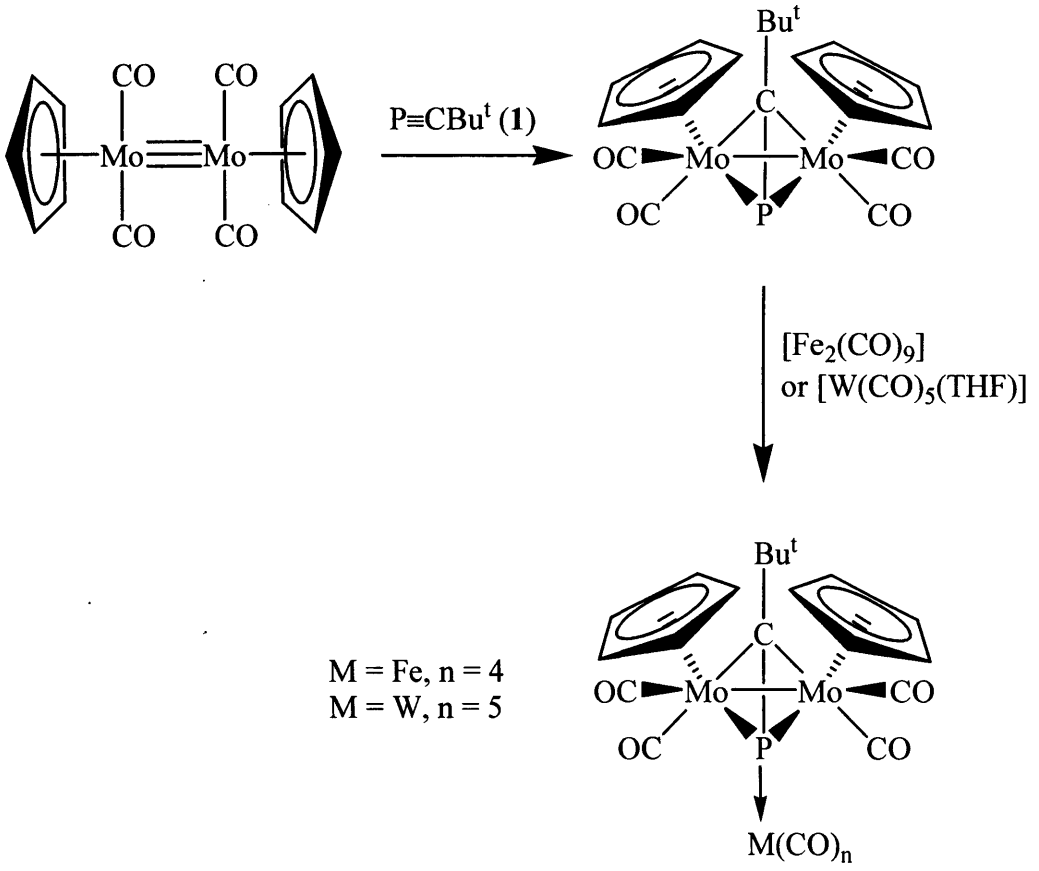
(4)

M = Cr, Mo, W

Scheme 3.4 Synthesis of some η^1:η^2 phosphaalkyne complexes

An interesting general feature of these, and type **B** co-ordination, is the lengthening of the phosphorus carbon triple bond compared to that in the free phosphaalkyne.[12] This is a consequence of donation of π electron density from the phosphaalkyne to the metal and back-bonding of metal d-electron density into the π^*-LUMO of the phosphaalkyne. This causes a reduction in the phosphorus carbon bond order. A reflection of this is the bending of the *tert*-butyl group away from the metal, indicating an increase in the hybridisation of the phosphorus and carbon centres from sp to sp^2. This lengthening of the phosphorus carbon bond in η^2 complexes is in contrast to the phosphorus carbon bond in η^1 complexes which is close to that in the free phosphaalkyne and consistent with bonding through the phosphorus lone pair.

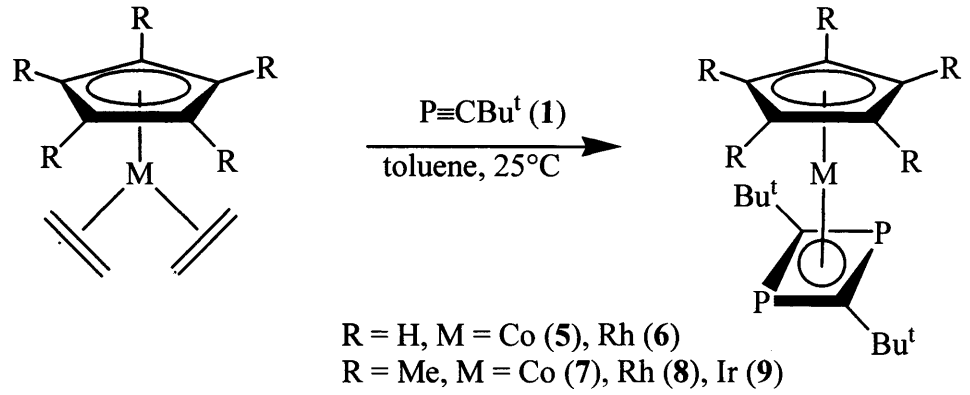
Type **D**[18, 19] and **E**[20, 22] complexes are known in which the phosphaalkyne can be viewed as a four or six electron donor respectively. A typical route to these complexes is shown in Scheme 3.5.



Scheme 3.5 Synthesis of examples of μ-η^2 and μ-η^2:η^1 phosphaalkyne complexes

3.1.2 Metal mediated phosphaalkyne oligomerisations

An interesting feature of phosphaalkynes is their ability to undergo metal mediated cyclooligomerisation[23-25] reactions and in this respect their behaviour is similar to that of alkynes.[26] For example [M(η^5-C$_5$R$_5$)(η^2-C$_2$H$_4$)$_2$] (R = H, M = Co, Rh; R = Me, M = Co, Rh, Ir) reacts with (**1**) to give the 1,3-diphosphacyclobutadiene complexes (**5 - 9**) (Scheme 3.6).[27] It is interesting to note that theoretical studies have predicated head to head dimerisation (to give 1,2-diphosphabicyclobutadienes) is more favourable, but in most experimental studies 1,3-diphosphacyclobutadiene ring formation is preferred, probably due to steric reasons.[27-29]

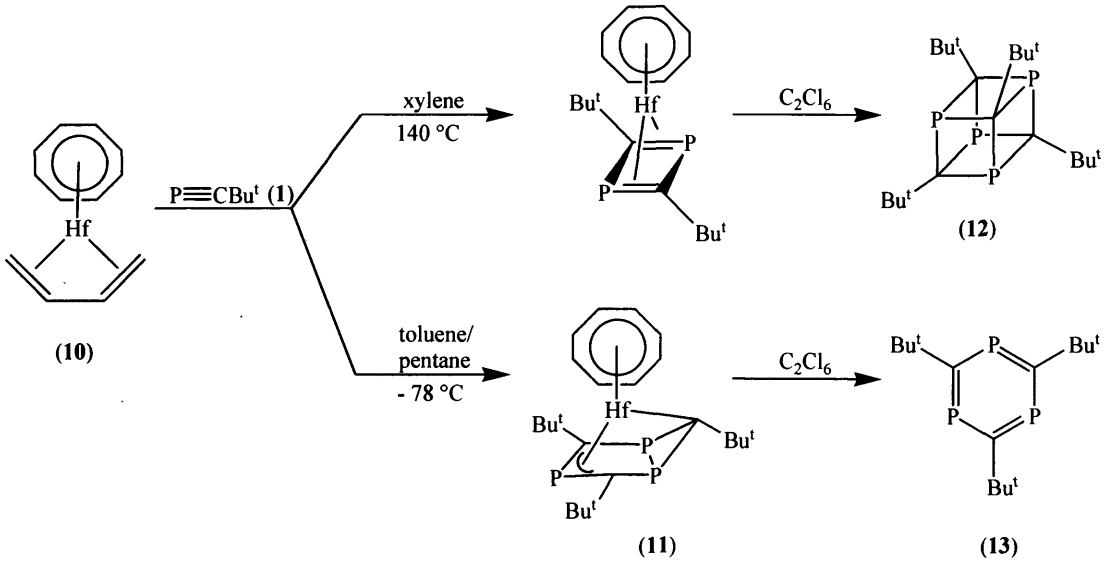


R = H, M = Co (**5**), Rh (**6**)
R = Me, M = Co (**7**), Rh (**8**), Ir (**9**)

Scheme 3.6 Metal mediated cyclodimerisation of a phosphaalkyne

Theoretical and photoelectron studies on (**5**) and [Fe(η^4-1,3-$P_2C_2Bu^t_2$)$(CO)_3$] have indicated that the diphosphacyclobutadiene moiety is bound more strongly than the η^4-cyclobutadiene unit of related hydrocarbon only complexes.[30] The fact that it has been impossible to liberate the diphoshacyclobutadiene fragment from any of the complexes (**5 - 9**) is therefore not surprising.

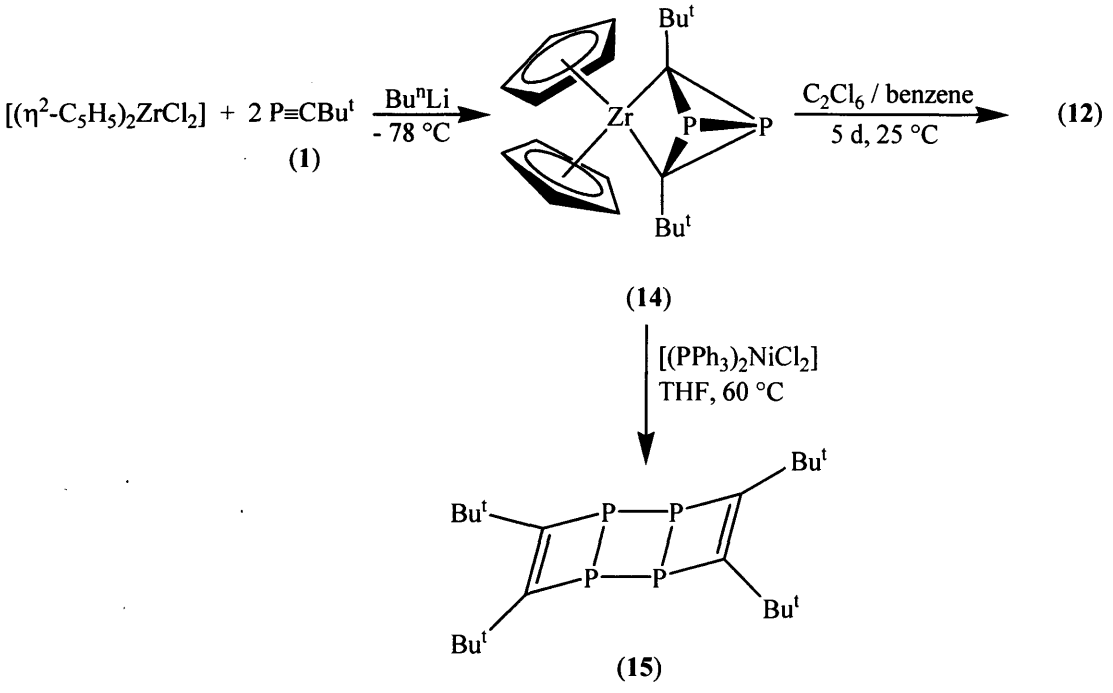
Metal mediated cyclo-, tri- and tetra-merisation reactions of phosphaalkynes have also been reported. Compound (**1**) reacts with [Hf(η^8-COT)(η^4-CH_2=CH-CH=CH_2)] (**10**) at - 78 °C to give complex (**11**) which contains a cyclic trimer of (**1**). When (**11**) is treated with hexachloroethane, 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**13**) is obtained in 53 % yield (Scheme 3.7).[31]



Scheme 3.7 Metal mediated cyclooligomerisations of a phosphaalkyne

The outcomes of these reactions are sensitive to stoichiometry and temperature. For example, compound (**10**) reacts with 2 equivalents of (**1**) to yield a complex containing a COT ligand and a 1,3-diphosphacyclobutadiene fragment which arises from the head to tail dimerisation of two molecules (**1**) at the metal centre. Further treatment with hexachloroethane liberated the 1,3-diphosphacyclobutadiene which undergoes a series of cycloadditions to yield the tetraphosphacubane (**12**) in 34 % yield (Scheme 3.7).[31] It is noteworthy that (**13**) can also be prepared by the cyclotrimerisation of (**1**) mediated by the strong Lewis acid $Bu^tN{=}VCl_3$.[32]

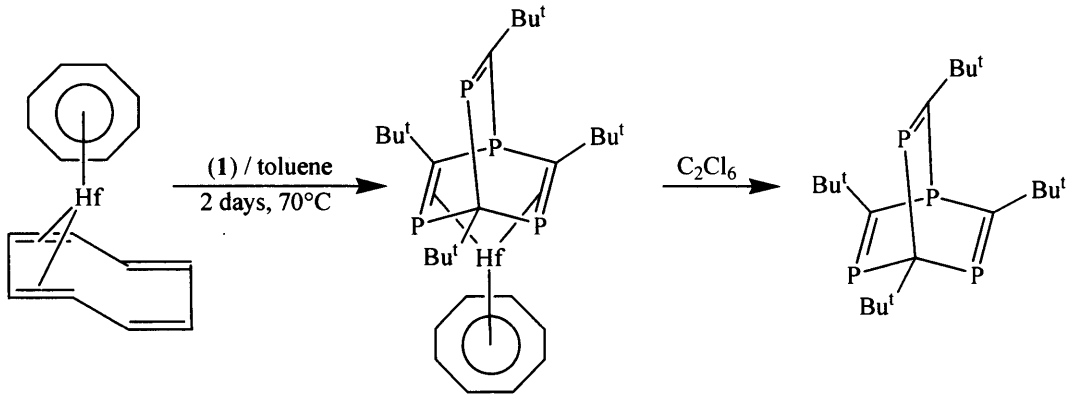
Cyclotetramerisation reactions of phosphaalkynes have been promoted by utilising the zirconium complex (**14**). This was synthesised from the reaction of zirconocene dichloride with (**1**), in the presence of Bu^nLi, in 70 % yield.[33] When (**14**) is treated with hexachlorethane in benzene, (**12**) is formed over 5 days in 70 % yield. Treatment of (**14**) with $[(PPh_3)_2NiCl_2]$ affords a further isomer of (**12**), namely (**15**) in 70 % yield (Scheme 3.8).[34]



Scheme 3.8 Metal mediated phosphaalkyne tetramerisations

A further phosphaalkyne tetramerisation was reported by *Binger et al.* which occurs in the co-ordination sphere of the hafnium complex (**16**). The 1,3,5,7-

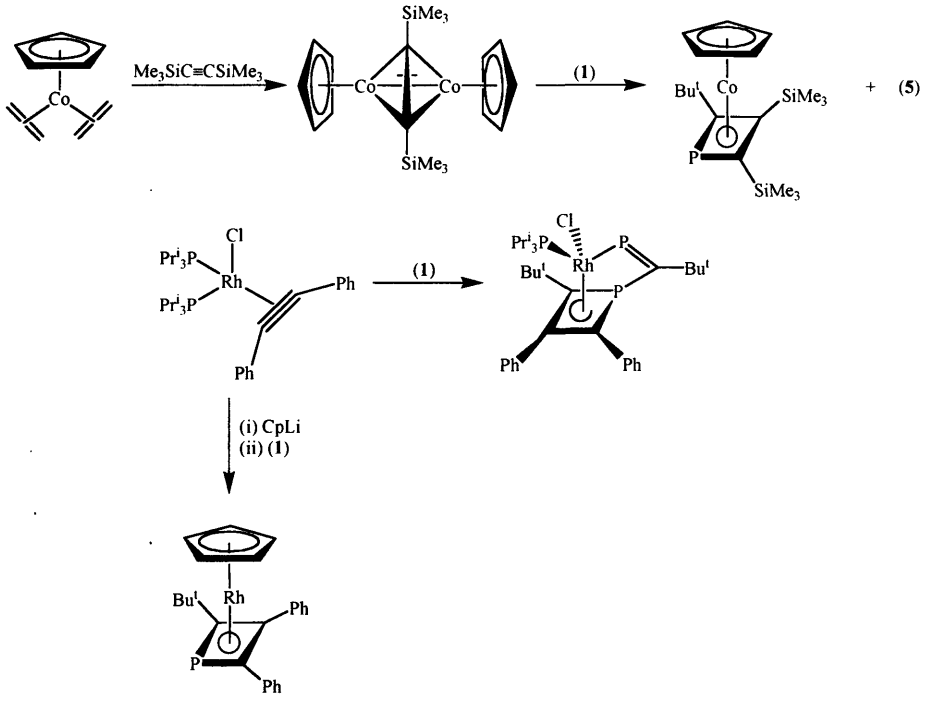
tetraphosphabarralene complex (**17**) was obtained after treatment of (**16**) with (**1**) in 88 % yield. The tetraphosphabarralene ligand (**18**) can be liberated and isolated in 88 % yield upon treatment of (**17**) with hexachloroethane[35] (Scheme 3.9). Compound (**18**) is air sensitive but thermally stable.



(**16**) (**17**) (**18**)

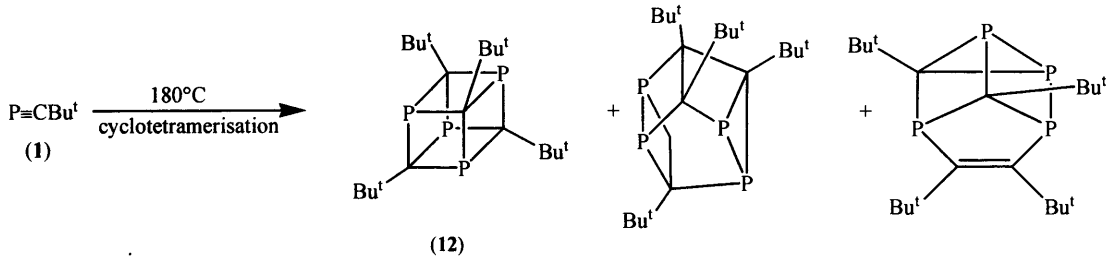
Scheme 3.9 Tetramerisation of a phosphaalkyne

It was *Binger et al.* again, who reported in 1987 and 1991 the cyclodimerisation of a phosphaalkyne with alkynes within the co-ordination sphere of transition metals[36, 37] (Scheme 3.10).



Scheme 3.10 Alkyne-phosphaalkyne dimerisations at transition metal centres

Phosphaalkyne oligomerisations can also be observed in the absence of any metal centre. For example (**1**) reacts at 180 °C in the absence of solvent and metal to a mixture of products which include (**12**)[38] (Scheme 3.11).



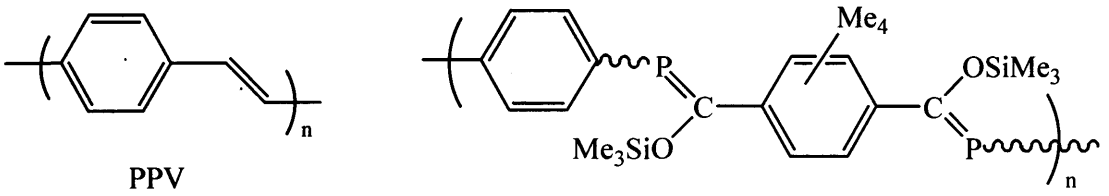
Scheme 3.11 Solvent and metal free oligomerisation of a phosphaalkyne

Studies confirmed that the thermal cyclotetramerization of (**1**) to form (**12**) must involve a [2+2] cycloaddition to yield a 1,3-diphosphacyclobutadiene which then undergoes a [4+2] cycloaddition and a further intramolecular [2+2] cycloaddition to form the cubane compound.[38]

Oligomerisation of (**1**) in the presence of reactive elemental metals has also proved facile when utilising metal vapour synthesis as a technique. Here phosphaalkyne is co-condensed at - 196 °C with metal vapours. Upon warming to 25 °C a variety of novel phosphaorganometallic compounds are often formed.[24, 39-42]

3.1.3 Polymers incorporating group 15 elements

Very recently a π-conjugated macromolecule, poly(*p*-phenylenephosphaalkene) (**19**), was prepared by *Wright* and *Gates.* Compound (**19**) was prepared by a thermally induced polycondensation of the two bifunctional monomers 2,3,5,6-tetramethyl-terephthaloyl dichloride and 1,4-bis-(1,1,1,3,3,3-hexamethyl-disilaphosphan-2-yl)-benzene.[43] This polymeric compound may be regarded as the first phosphorus analogue of the now well known conjugated poly(*p*-phenylenevinylenes) (PPVs), which have drawn attention due to the electroluminescence they often exhibit.[44, 45]



(19)

Figure 3.2 π-conjugated macromolecules

As recently as 2004 further thermally stable phosphaalkene polymers *e.g.* (**20**) and (**21**), were reported by *Smith* and *Protasiewicz* (Figure 3.3).[46] Compound (**21**) is the first example of a polymer featuring multiple bonds between two heavier main group elements along a polymer backbone. This successful stabilization of diphosphene units suggests the possibility of stabilizing other, heavier, E-E multiple bonds in a similar way. In this respect, an analogue of (**21**) having As=As units in the main chain has been prepared by the same group and is currently under investigation.[46]

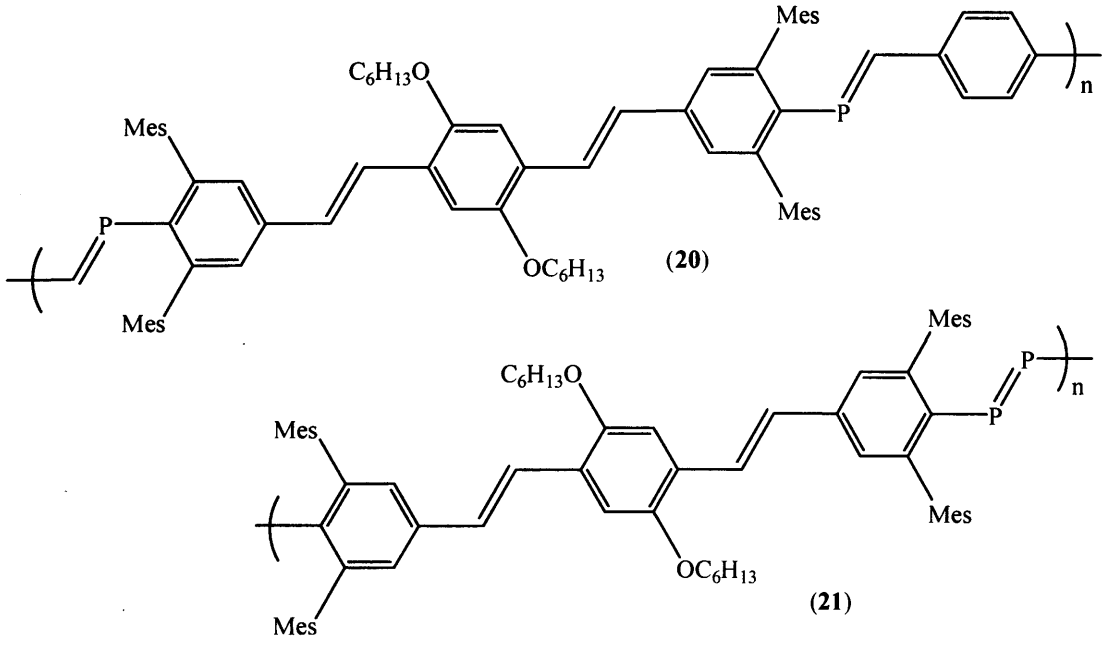


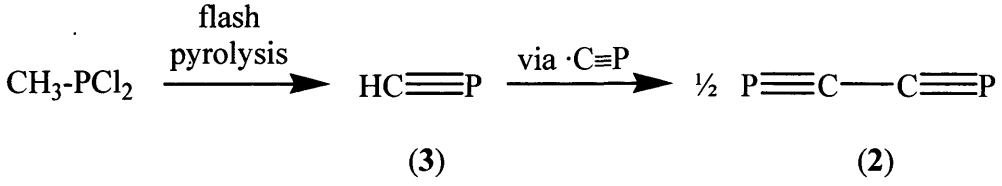
Figure 3.3 Phosphaalkene polymers

The preparation of π-conjugated polymers incorporating phosphorus moities opens the way for the preparation of a wide range of fundamental new materials.[47] The large variety of reactions of phosphaalkynes *e.g.* phosphorus coupling reactions or co-ordination complexes formed in the co-ordination sphere of transition metals,[3,

[25] make diphosphaalkynes potential precursors for phosphorus containing polymers and co-ordination polymers.

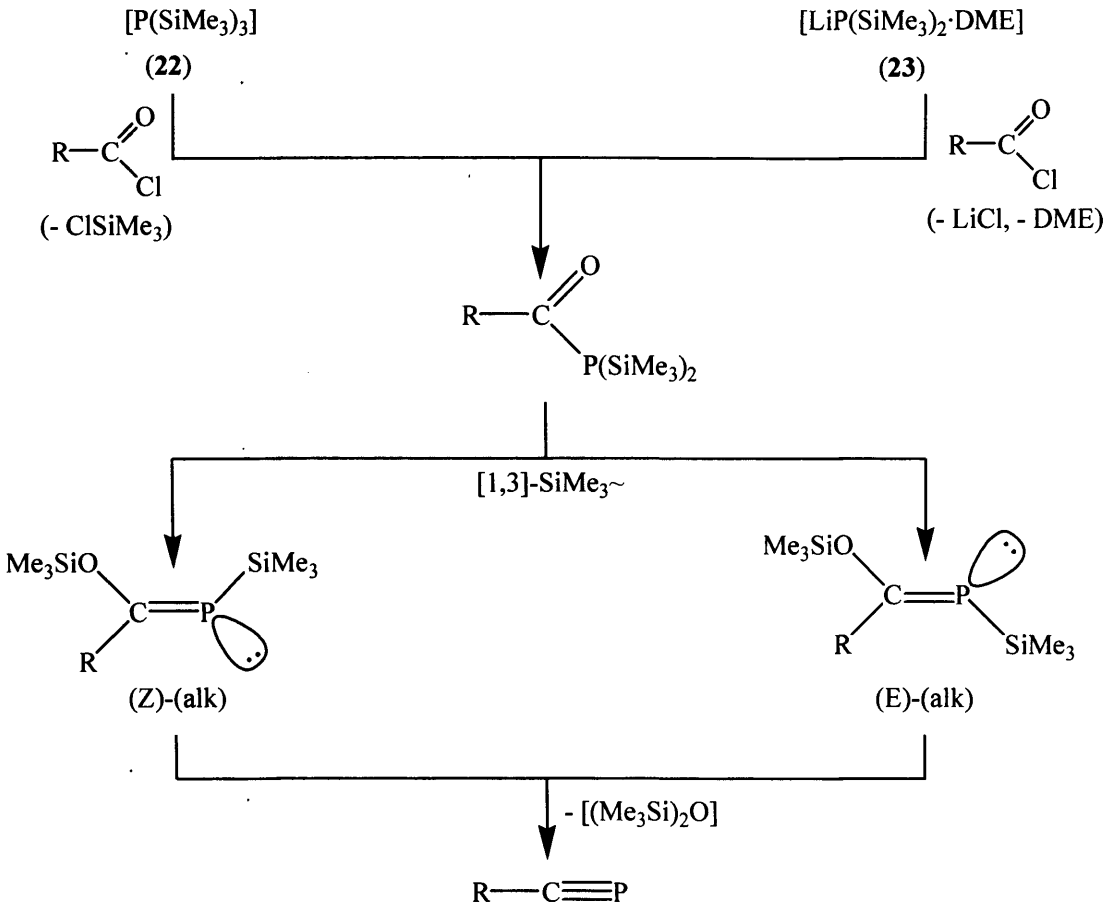
3.1.4 Diphosphaalkyne chemistry

Compound (**2**) was first mentioned by *Smoes et al.* in 1971 when they used mass spectrometry to determine the ionisation energies of carbon phosphorus compounds.[48] In an experimental approach (**2**) was detected as a compound in the equilibrium product mixture from the gaseous elements at temperature above 2000 K.[49] The dechlorination of Cl_2P-C≡C-PCl_2 on a heterogeneous catalyst at 670 °C also yielded (**2**) as a minor product and it was identified by mass spectrometry and photoelectron spectroscopy.[50] Recently theoretical investigations have been carried out by *Bickelhaupt* and *Bickelhaupt* showing that an isolable complex of (**2**) should be feasible.[51] Further spectroscopic evidence for the existence of (**2**) was found by *Brönstrup et al.* in 2000 though in this and all previous studies (**2**) is only stable at very low temperatures.[5] An interesting observation was made upon flash pyrolysis of CH_3-PCl_2. A by-product of this reaction was the 1,4-diphospha-1,3-diyne (**2**). This diyne was trapped as a diazaphosphole by the reaction with a diazoacetate. In this case the formation of (**2**) was explained by a radical cleavage of the CH bond of HC≡P (**3**) and subsequent dimerisation of ·C≡P upon warming of the reaction mixture (Scheme 3.12).[3]



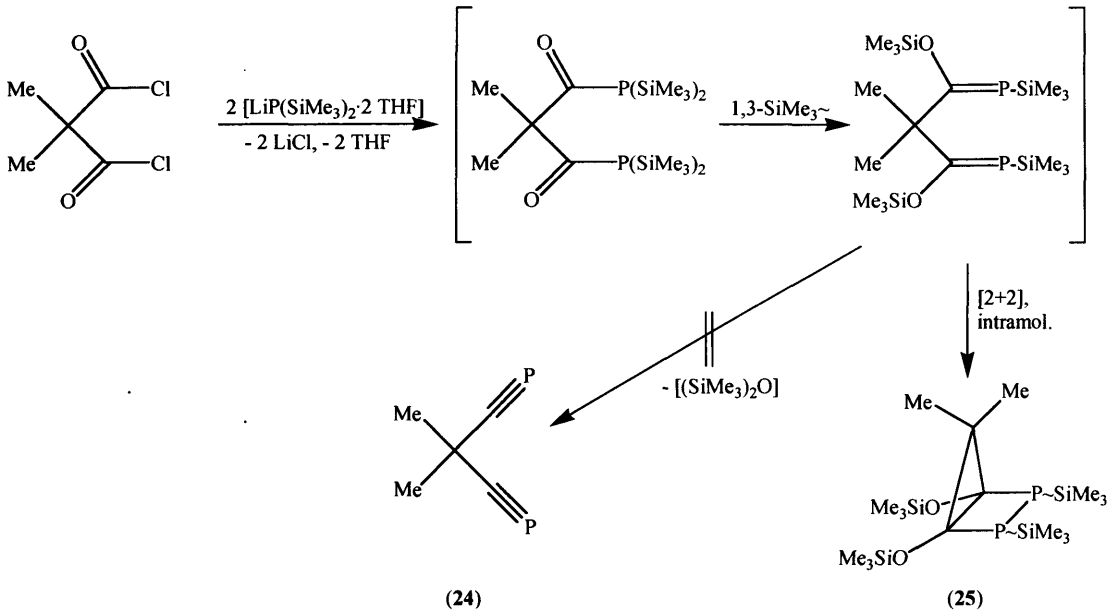
Scheme 3.12 Formation of 1,4-diphospha-1,3-diyne (2)

The base catalysed β-elimination of hexamethyldisiloxane is used in the preparation of kinetically stabilised phosphaalkynes.[3] The starting material for this reactions is tris(trimethylsilyl)phosphane (**22**). When (**22**) is reacted with alkyllithium reagents the lithium phosphide (**23**) is obtained. Both react with acid chlorides to give phosphaalkenes which can subsequently be converted to phosphaalkynes (Scheme 3.13).



Scheme 3.13 Phosphaalkyne preparation by *β*-elimination of hexamethyldisiloxane

This synthetic methodology failed when attempts where made to prepare the diphosphaalkyne (**24**) (Scheme 3.14).[52] Upon an attempt to react dimethylmalonic acid dichloride with the highly reactive lithium-bis(trimethylsilyl)phosphide, $[LiP(SiMe_3)_2(THF)_2]$, an intramolecular [2+2] cycloaddition takes place to yield the 2,3-diphosphabicyclo[2.1.0]pentane (**25**). It was a major objective of this project to synthesise the first example of a disphosphaalkyne and explore its reactivity.



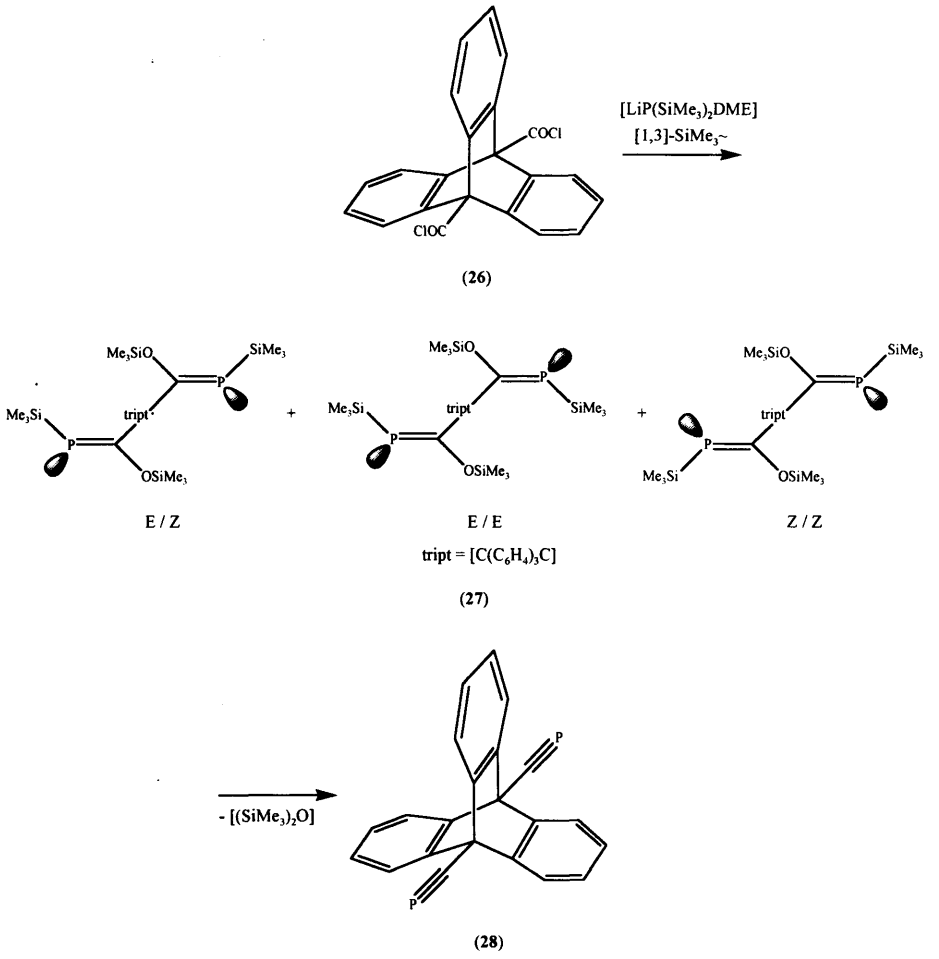
Scheme 3.14 Attempted synthesis of a diphosphaalkyne

3.2 Results and discussion

3.2.1 Preparation of 9,10-bis-phosphanylidynemethyl-triptycene (28)

We realised that in order to prepare a diphosphaalkyne, intramolecular [2+2] cycloaddition reactions must be prevented by separating the two phosphaalkyne functionalities. The triptycenyl unit was thought to be a good candidate. The linear arrangement of the two bridgehead protons in triptycene, which would be replaced with the phosphaalkyne functionalities, and the mirror plane running through the molecule, creating the same chemical environment for both phosphaalkyne functionalities, seemed ideal. It is noteworthy that a mono-phosphaalkyne derived from triptycene has also been already reported by *Märkl* and *Sejpka* in 1985.[53]

The reaction of 9,10-triptycenedicarbonyl chloride (**26**) with 2 equivalents of $[LiP(SiMe_3)_2(DME)]$ (**23**) led to the formation of the new diphosphaalkene, $[(Me_3Si)P{=}C(OSiMe_3)C(C_6H_4)_3CC(OSiMe_3){=}P(SiMe_3)]$ (**27**). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture displayed 4 singlet resonances (δ 148.1, 148.6, 158.5, 159.5 ppm) which is consistent with (**27**) existing as a mixture of its Z,Z-, Z,E- and E,E-isomers. Treatment of (**27**) with a catalytic amount of KOH in DME afforded the diphosphaalkyne, (**28**), in good yield (67 %) as an air and moisture stable solid (Scheme 3.15). Other crystalline phosphaalkynes have been reported with bulky substituents, *e.g.* adamantan-1-ylmethylidyne-phosphane,[54] 9-phosphanylidynemethyl-triptycene[53] and 2,4,6-tri-*tert*-butyl-phenylmethylidyne-phosphane,[55] and all have good air and moisture stability.



Scheme 3.15 Preparation of a diphosphaalkyne

The $^{31}P\{^{1}H\}$ NMR spectrum of (**28**) displays a singlet (δ - 15.7 ppm) in the normal region for phosphaalkynes.[2, 4] In addition, an alkynic carbon resonance appears as a doublet ($^{1}J_{PC}$ = 47.1 Hz) at δ 164.0 ppm in its ^{13}C NMR spectrum. The molecular structure of (**28**) is depicted in (Figure 3.4) and shows it to be monomeric with no intermolecular close contacts. Its P-C bond lengths (1.532 Å avge.) are comparable with those in other phosphaalkynes, *e.g.* 1.548(1) Å in P≡CBu^{t} (**1**),[12] and are consistent with localised triple bonded interactions. It is likely that the linear nature of the molecule and the separation of the two phosphaalkyne functionalities lends stability to the compound because the possibility of intramolecular phosphaalkyne coupling reactions is circumvented.

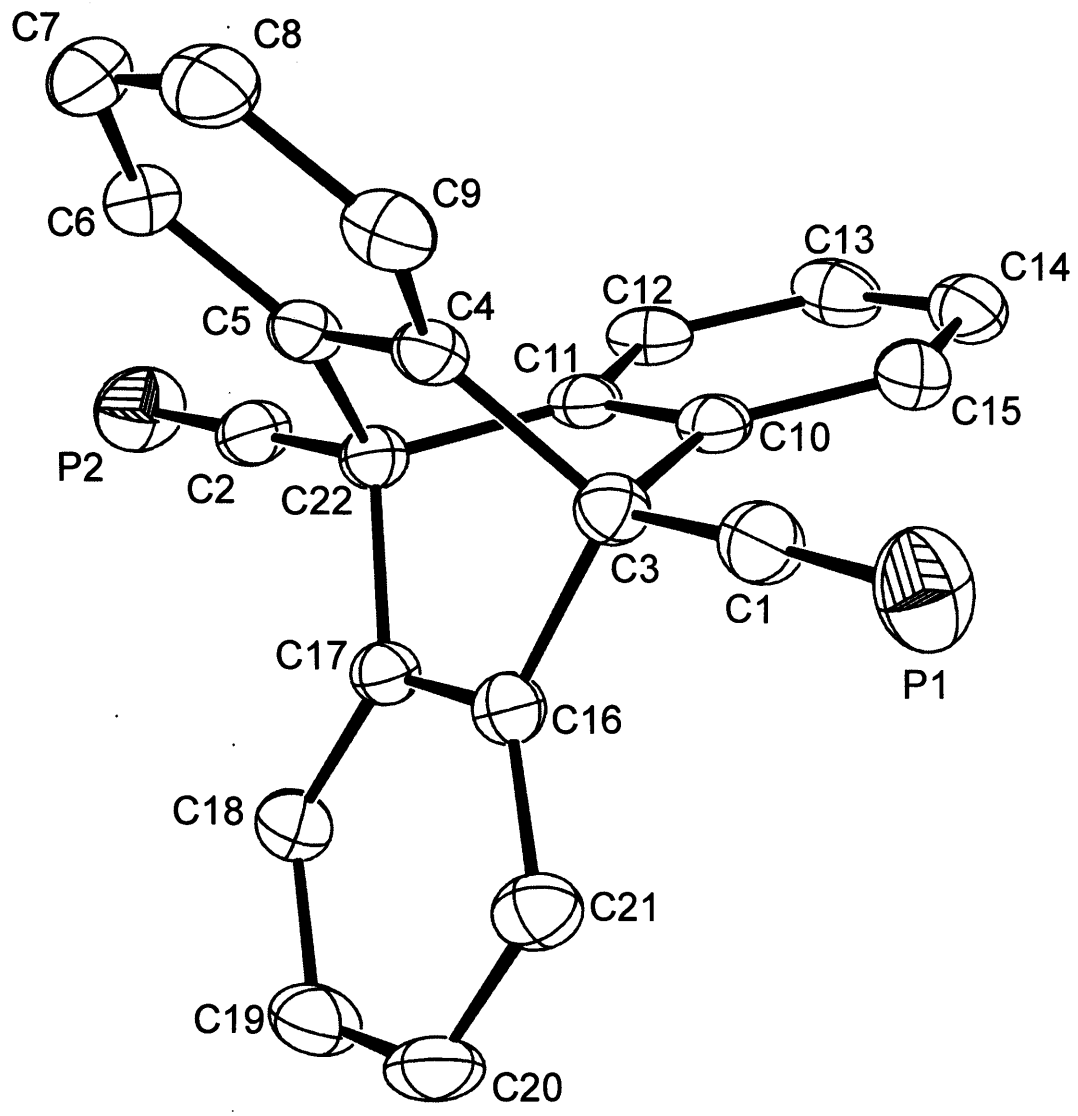
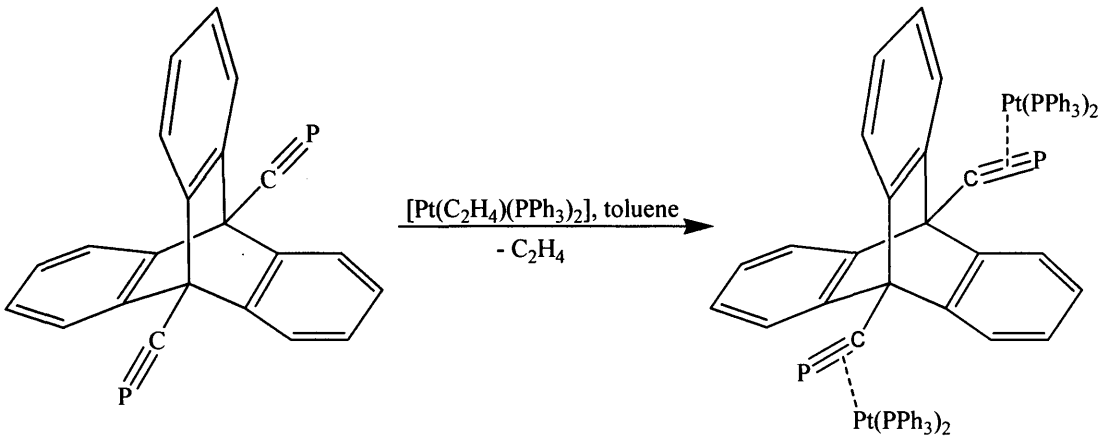


Figure 3.4 Molecular structure of [P≡CC(C_6H_4)$_3$CC≡P] (28)

Selected bond lengths (Å) and angles (°): P(1)-C(1) 1.531(2), P(2)-C(2) 1.533(2), C(1)-C(3) 1.473(3), C(2)-C(22) 1.476(3); C(3)-C(1)-P(1) 177.44(19), C(22)-C(2)-P(2) 179.52(19), C(1)-C(3)-C(16) 113.36(18), C(1)-C(3)-C(10) 113.70(19), C(1)-C(3)-C(4) 113.63(19), C(2)-C(22)-C(5) 113.65(19), C(2)-C(22)-C(11) 113.84(18), C(2)-C(22)-C(17) 113.04(18).

3.2.2 Reactivity of 9,10-bis-phosphanylidynemethyl-triptycene (28)

Efforts have been made to compare the reactivity of (**28**) to that of mono-phosphaalkynes and these have shown it to behave in a similar fashion. Its reaction with two equivalents of $[Pt(C_2H_4)(PPh_3)_2]$ led to ethylene displacement and the high yield (70 %) formation of the bis-platinum(0) co-ordination complex, (**29**) (Scheme 3.16).



(28) **(29)**

Scheme 3.16 Preparation of $[\{(PPh_3)_2Pt\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}P{\equiv}CC(C_6H_4)_3CC{\equiv}P\}]$ (29)

The $^{31}P\{^1H\}$ NMR spectrum of (**29**) is strongly suggestive of a symmetrical complex in which the phosphaalkyne moieties are η^2-bonded to the platinum fragments, as in the related complex, $[Pt(PPh_3)_2(\eta^2\text{-}P{\equiv}CBu^t)]$, (**4**).[18] It exhibits three doublet of doublet resonances; two corresponding to the inequivalent PPh_3 ligands with ^{195}Pt satellites having couplings in the normal range ($^1J_{PtP}$ = 3273 and 3747 Hz), and one at low field [δ 94.9 ppm, *cf.* 56.9 ppm in (**4**)] which displays a very small $^1J_{PtP}$ coupling of 53 Hz, *cf.* 62 Hz in (**4**). The magnitude of this coupling is consistent with the proposed alkyne like η^2-co-ordination of (**29**), and the ca. 110 ppm downfield shift for this resonance upon co-ordination of the phosphaalkyne functionalities points towards significant back-bonding from the Pt centres into the π*-orbitals of the P-C triple bonds.

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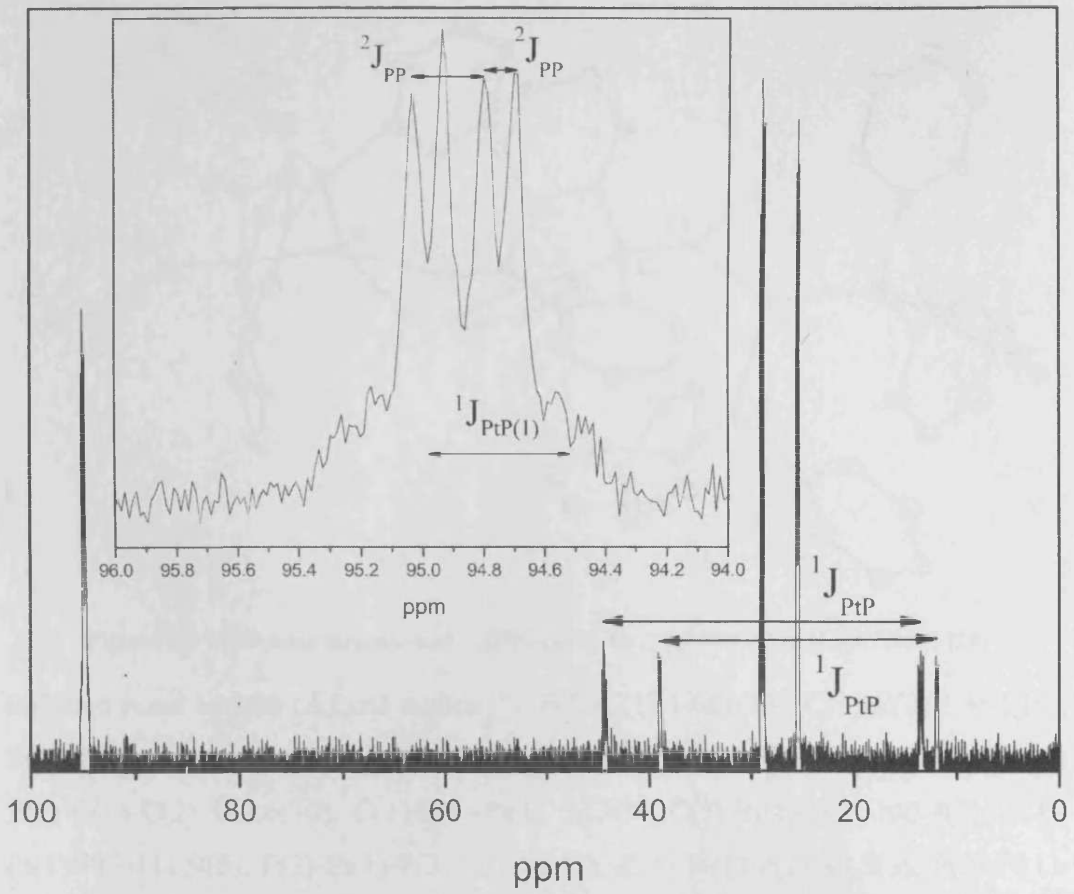


Figure 3.5 $^{31}P\{^1H\}$ **NMR spectrum of** $[\{(PPh_3)_2Pt\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}P{\equiv}CC(C_6H_4)_3CC{\equiv}P\}]$ **(29)**

The X-ray crystal structure of (**29**) was obtained (Figure 3.6) and provides confirmation that (**28**) acts as a bifunctional ligand in this complex. In addition, it shows that the C(1) and P(1) centres have moved towards being sp^2-hybridised upon co-ordination, as the C(1)-P(1) bond length, 1.681(13) Å, *cf.* 1.672(17) Å in (**4**), is 9.8 % longer than the P-C bonds in (**28**) and, indeed, is in the normal P=C bond length range.[2, 4] This combined with the fact that the PCC angles are no longer linear, *viz.* 142.6(10)°, *cf.* 132(2)° in (**4**), provides strong evidence for the proposed backbonding in this complex.

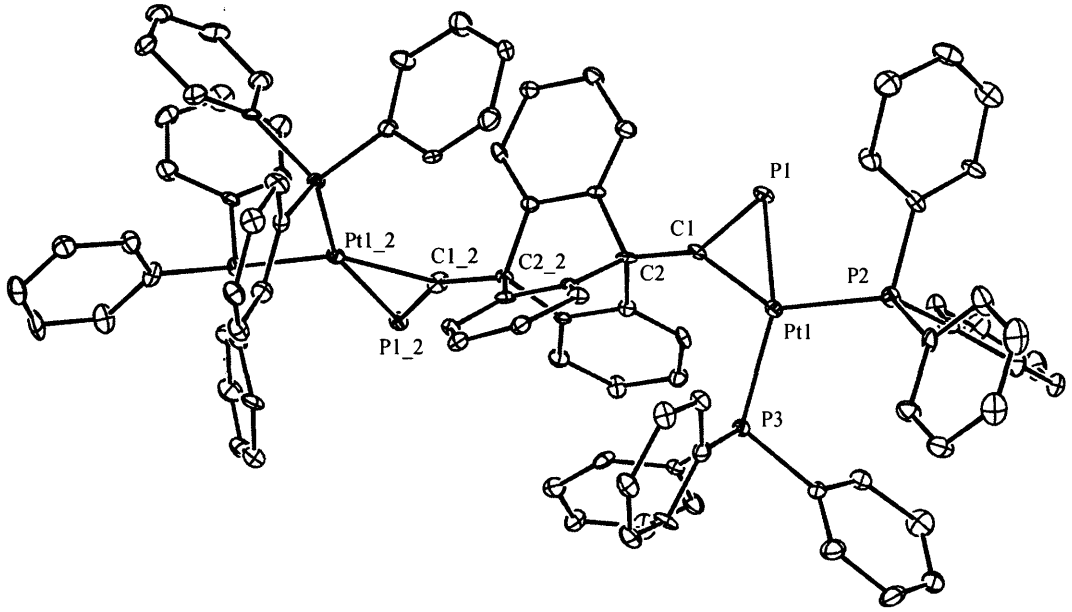
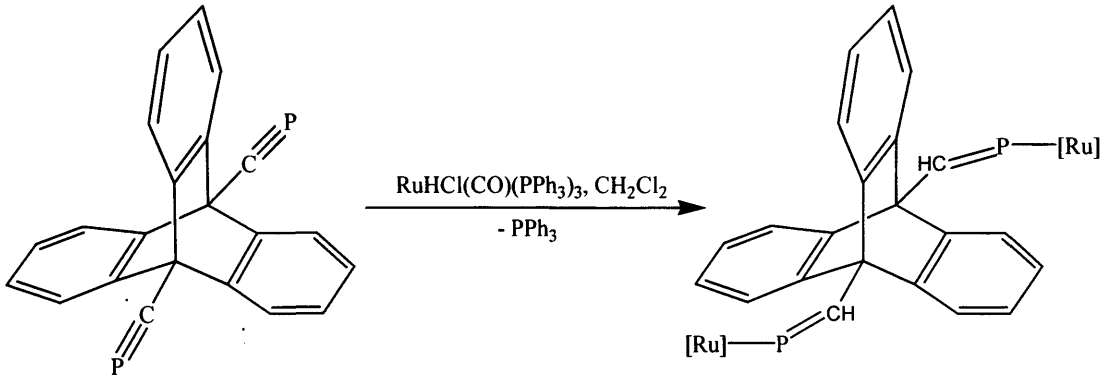


Figure 3.6 Molecular structure of [{$(PPh_3)_2Pt$}$_2${μ-η^2:η^2-P≡CC(C_6H_4)$_3$CC≡P}] (29)

Selected bond lengths (Å) and angles (°): P(1)-C(1) 1.681(13), C(1)-C(2) 1.462(19), Pt(1)-C(1) 2.098(14), Pt(1)-P(2) 2.297(3), Pt(1)-P(3) 2.304(3), Pt(1)-P(1) 2.323(4); P(1)-C(1)-C(2) 142.6(10), C(1)-P(1)-Pt(1) 60.7(5), C(1)-Pt(1)-P(2) 140.4(3), C(1)-Pt(1)-P(3)111.9(3), P(2)-Pt(1)-P(3) 107.36(13), C(1)-Pt(1)-P(1) 44.3(3), P(2)-Pt(1)-P(1) 96.24(13), P(3)-Pt(1)-P(1) 156.21(12). Symmetry operation: - x + 1, y, - z + 3/2.

Previously the facile hydrometallation of mono-phosphaalkynes with [RuHCl(CO)(PPh_3)$_3$][56] was reported and it was shown that the resulting ruthenium-phosphaalkenyl complexes have a diverse and fascinating chemistry.[56, 57] It was reasoned that if similar reactivity were demonstrated by (**28**) then its hydrometallation products may well be useful precursors to a variety of previously inaccessible diphosphaalkenes, metallophosphaalkenes and even unconjugated polyphosphaalkenes. Accordingly, the reaction of (**28**) with two equivalents of [RuHCl(CO)(PPh_3)$_3$] led to the high yield (85 %) formation of the bis-ruthenium phosphaalkenyl complex, (**30**) (Scheme 3.17). Unfortunately, X-ray quality crystals of this complex could not be obtained but all the spectroscopic evidence is compatible with the proposed structure. Its $^{31}P\{^1H\}$ NMR spectrum characteristically exhibits a very low field signal (δ 516.7 ppm) corresponding to the phosphaalkenyl P-centres, and a resonance at δ 39.9 ppm for the equivalent PPh_3 ligands. These

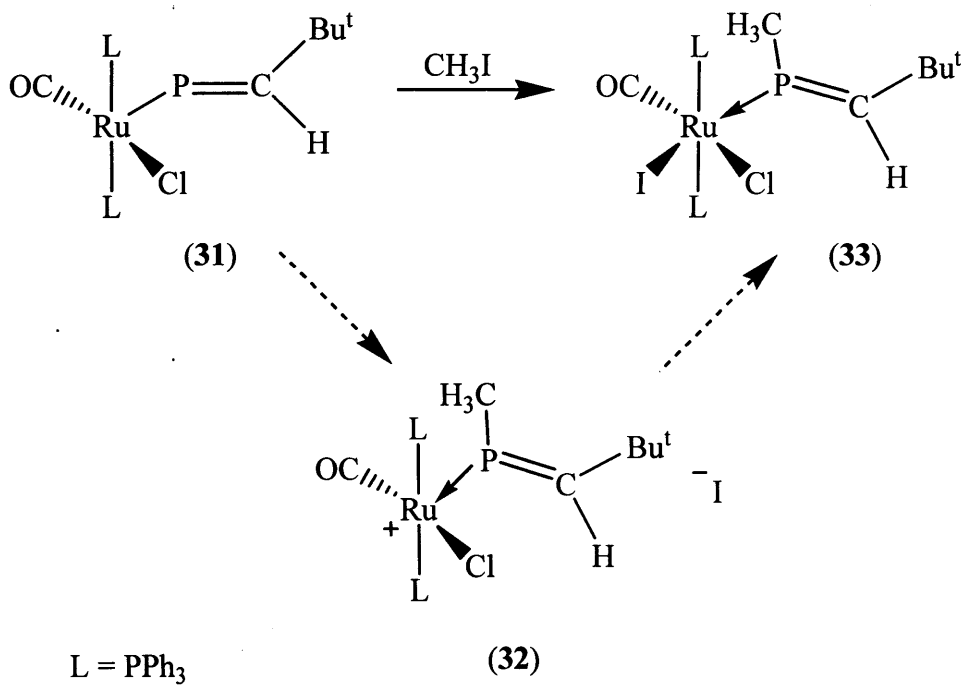
shifts can be compared to those in the related complex, [RuCl-{P=C(H)Bu^t}(CO)(PPh$_3$)$_2$], (**31**) (δ 450.4, 33.9 ppm),[56] though in that complex a $^2J_{PP}$ coupling of 10 Hz was observed, whereas in (**30**) the signals are too broad for any coupling to be resolved. The ^{1}H NMR spectrum of the complex is as expected and exhibits an alkenic proton resonance at δ 7.98 ppm. In addition, a single CO stretching absorption [υ 1924 cm^{-1}, *cf.* 1929 cm^{-1} in (**31**)] can be seen in its infrared spectrum.



(**28**) (**30**)

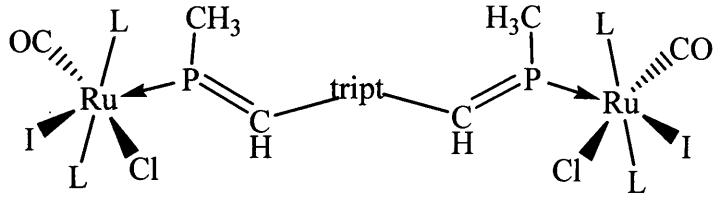
Scheme 3.17 Preparation of [(CO)(PPh$_3$)$_2$ClRu{P=C(H)}C(C$_6$H$_4$)$_3$C{C(H)=P}-Ru(CO)(PPh$_3$)$_2$Cl] (30)

As previously reported, when a solution of [Ru(P=CHBu^t)Cl(CO)(PPh$_3$)$_2$] (**31**) was treated with an excess of methyl iodide, decolourisation and formation of a yellow complex occurred. This was formulated as [Ru(PMe=CHBu^t)Cl(I)(CO)(PPh$_3$)$_2$] (**33**).[58] The proposed mechanism involved an initial nucleophilic displacement of iodide from methyl iodide, which subsequently attacked the ruthenium centre to give (**33**) (Scheme 3.18).



Scheme 3.18 Proposed reaction mechanism for the formation of [Ru{P(Me)=CH(Bu^t)}Cl(I)(CO)(PPh_3)$_2$] (33)

A similar reactivity was expected for (**30**), and upon addition of MeI to a solution of (**30**) in CH_2Cl_2, the colour changed to yellow and the spectroscopic data suggested the formation of (**34**). The $^{31}P\{^1H\}$ NMR spectrum exhibits two broad signals at δ 250 and 4 ppm and the infrared spectrum shows the carbonyl stretch at 1950 cm^{-1}. These values are in good comparison with (**33**) (δ 225.1 and 10.4 ppm, $\upsilon_{(CO)}$ = 1976 cm^{-1}). Despite many attempts it was not possible to obtain single crystals of (**34**) to confirm its proposed structure (Figure 3.7).

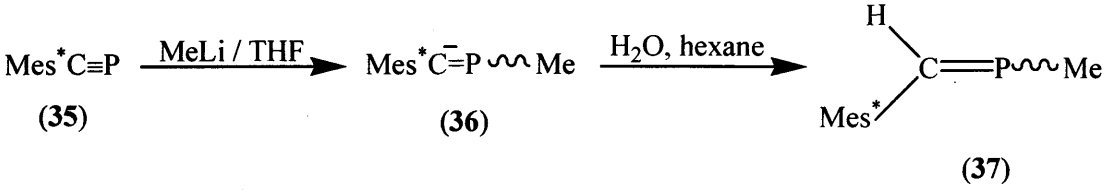


tript = [$C(C_6H_4)_3C$]

(**34**)

Figure 3.7 Proposed structure of [(I)(CO)(PPh_3)$_2$ClRu{P(Me)=(H)C}C(C_6H_4)$_3$C{C(H)=(Me)P}-Ru(I)(CO)(PPh_3)$_2$Cl] (34)

In 1988 *Arif et al.* reported the reaction of a bulky phosphaalkyne, Mes*C≡P (**35**), with MeLi.[59] They observed the formation of a deep purple carbanion (**36**) and upon hydrolysis the formation of the expected phosphaalkene (**37**).

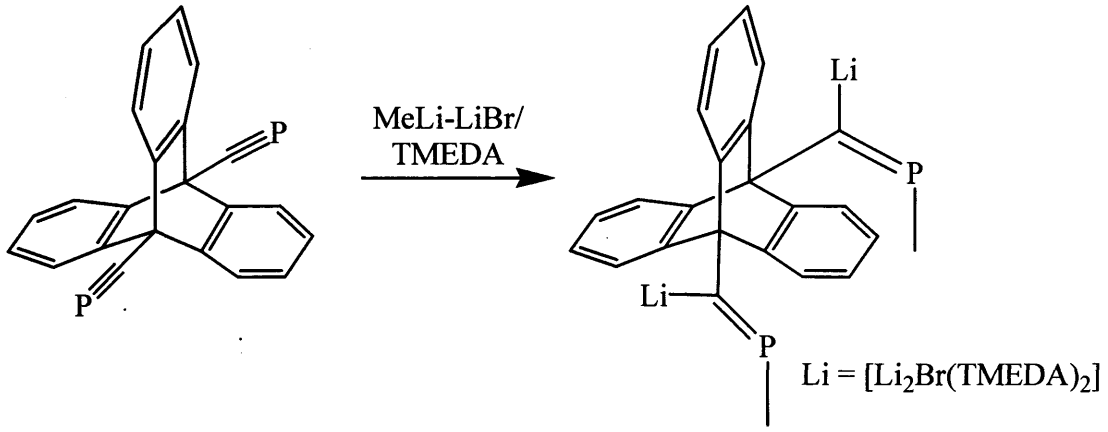


(**35**) (**36**) (**37**)

Scheme 3.19 Phosphaalkene formation

Interestingly no reaction was observed when (**28**) was reacted with MeLi or a MeLi/LiBr mixture, though the reaction with the stronger base, Bu^{t}Li, afforded a mixture of phosphorus containing products of which none could be isolated. This lack of reactivity is probably due to the hindered nature of the phosphaalkyne. When the reaction was carried out with a MeLi/LiBr mixture and TMEDA, facile lithiation of (**28**) took place and (**38**) was formed in moderate yield (Scheme 3.20). These reactions were carried out in collaboration with an Erasmus student visiting the laboratory from Germany, Florian Brodkorb.

The $^{31}P\{^1H\}$ NMR spectrum of (**38**) shows a singlet at δ 248.2 ppm, in the expected region for a phosphaalkene.[4] An unresolved multiplet in the ^1H NMR spectrum at δ 0.28 ppm corresponds to the P bound methyl groups. Compound (**38**) is prepared in about 50 % yield and crystallizes from Et_2O as orange, highly air and moisture sensitive crystals and the molecular structure is shown in Figure 3.8. The P(1)-C(2) bond length [1.662(5) Å] is with in the normal range for phosphorus carbon double bonds.[60] Examination of the structure suggests that the stability of the complex is due to the protection afforded to the carbanionic centres by the bulky [$Li_2Br(TMEDA)_2$] moieties. Presumably, the presence of TMEDA in the reaction mixture increases the nucleophilicity of the MeLi allowing it to react with (**28**). It was shown later that lithium bromide was not necessary in the lithiation step, as similar results have been achieved by the use of MeLi/TMEDA alone, though the lithiumphosphavinyl product is not stable at 25 °C.



(28) **(38)**

Scheme 3.20 Formation of [P(Me)={$Li_2Br(TMEDA)_2$}$CC(C_6H_4)_3CC${$Li_2Br(TMEDA)_2$}=P(Me)] (38)

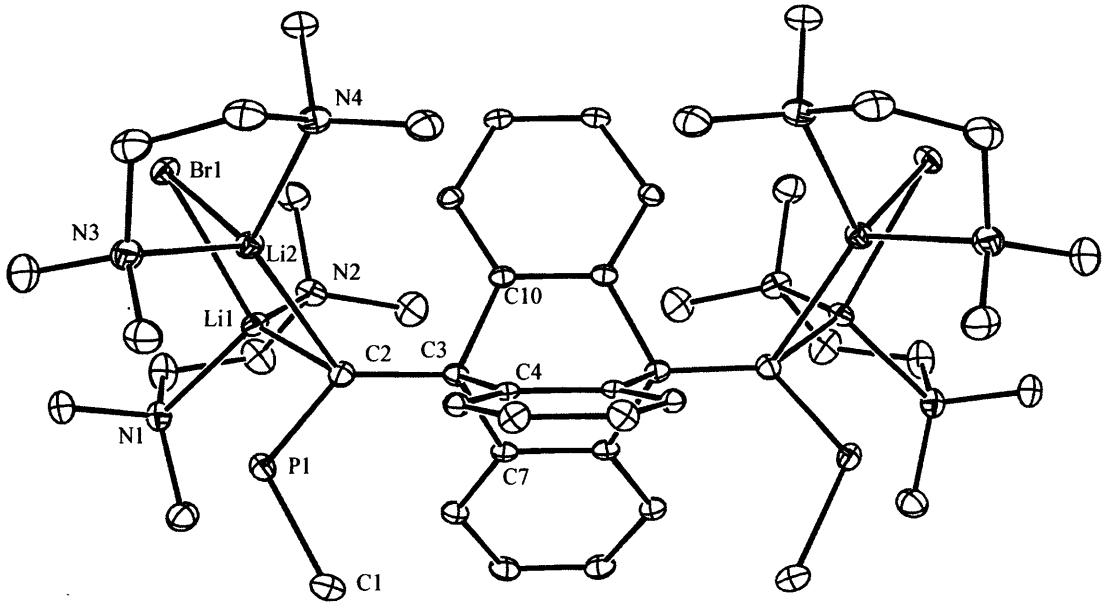
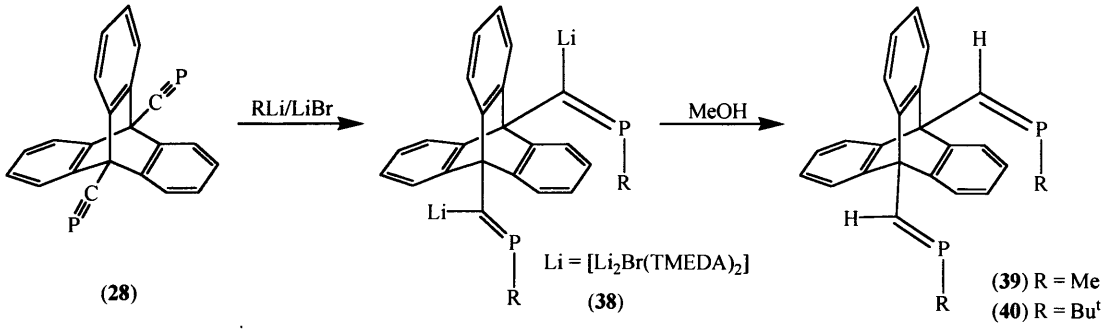


Figure 3.8 Molecular structure of [P(Me)={$Li_2Br(TMEDA)_2$}$CC(C_6H_4)_3CC${$Li_2Br(TMEDA)_2$}=P(Me)] (38)

Selected bond length (Å) and angles (°): P(1)-C(2) 1.662(5), P(1)-C(1) 1.863(6) C(2)-C(3) 1.518(7), C(2)-P(1)-C(1) 114.1(3), C(3)-C(2)-P(1) 127.2(4), C(3)-C(2)-Li(2) 121.9(4), P(1)-C(2)-Li(2) 96.5(3), C(3)-C(2)-Li(1) 123.5(4), P(1)-C(2)-Li(1) 96.3(3), Li(2)-C(2)-Li(1) 79.1(4), Symmetry operation: x, - y + 1½, z.

When (**38**) was quenched with dry, degassed methanol, the corresponding bisphosphavinyltriptycene (**39**) was obtained in 91 % yield (Scheme 3.21). Unfortunately, despite many attempts it was not possible to obtain crystals of this compound suitable for X-ray crystallographic studies. However, the spectroscopic evidence for the formation of (**39**) is consistent with its proposed structure. The $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet at δ 128.4 ppm, which was only observed as an unresolved multiplet in the ^{31}P NMR spectrum.

When (**28**) was treated with Bu^tLi/LiBr/TMEDA, a tertiary butyl substituted lithiated phosphavinyl compound could similarly be prepared. The reactivity of (**28**) towards Bu^tLi was rather low, however, heating in a sealed flask to 50 °C for 2 days was necessary to obtain complete conversion to (**38**) (R = Bu^t) (Scheme 3.21). No attempts were made to isolate the product, but methanol was used to quench the reaction mixture. The $^{31}P\{^{1}H\}$ NMR spectrum of the product, (**40**), shows a singlet at δ 191.0 ppm indicating the presence of phosphaalkene functionalities, similar to (**39**), whilst a characteristic vinylic proton signal at δ 8.62 ppm ($^{2}J_{PH}$ = 7.2 Hz) was observed in its ^{1}H NMR spectrum.



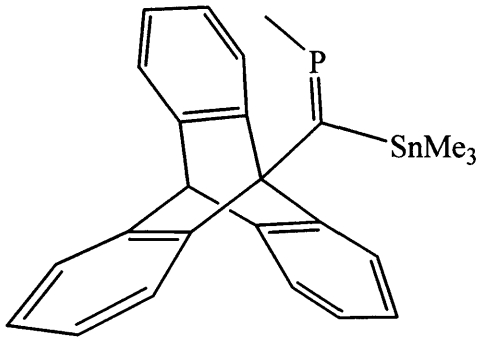
Scheme 3.21 Methanol quenching of a lithiated diphosphaalkyne

We saw the potential of (**38**) to form polymeric compounds and attempted several reactions to prepare phosphorus containing polymers. When (**38**) was treated with Me_2SiCl_2, an insoluble product was formed. A $^{31}P\{^{1}H\}$ NMR spectrum, obtained from the supernatant liquor showed no signals, thus suggesting an insoluble organophosphorus polymeric material had, indeed, been formed. Attempts to characterise the precipitate failed due to its insolubility in all common solvents. A

further reaction of (**38**) with Me_2SnCl_2 was carried out, but again an insoluble product was formed, presumably a polymeric species.

To form a soluble model of the latter polymer, (**38**) was reacted with two equivalents of Me_3SnCl. Unfortunately a reaction product could not be isolated and obtained in a pure form. Multiple signals were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, none of which could be identified.

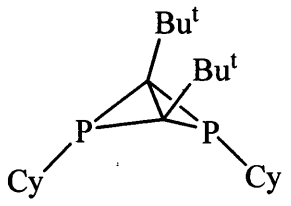
In the hope of a cleaner reaction, the monofunctional phosphaalkyne derived from triptycene, $[HC(C_6H_4)_3CC{\equiv}P]$,[53] was lithiated and reacted with Me_3SnCl. Again the reaction mixture showed multiple signals in its $^{31}P\{^1H\}$ NMR spectrum, but the main product showed a singlet with satellites at δ 320.7 ppm ($^2J_{PSn}$ = 120 Hz) which is believed to originate from (**41**) (Figure 3.9). Compound (**41**) could be isolated only as an orange powder but all attempts to crystallise it proved unsuccessful.



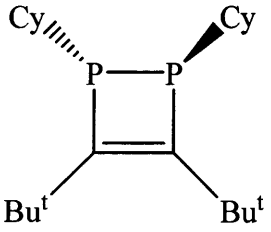
(**41**)

Figure 3.9 Proposed structure of [CH(C$_6$H$_4$)$_3$CC(SnMe$_3$)=P(Me)] (41)

In a further attempt to obtain a phosphorus containing polymer, (**38**) was reacted with $PbCl_2$. It was thought this would lead to a phosphorus containing polymer by an oxidative coupling reaction. Similar coupling reactions have been observed by *Jones et al.* in the reaction of *Z*-[CyP=C(Bu^t)MgCl(OEt$_2$)] (**42**) with $PbCl_2$[61] and Cp^*NbCl_4[62]. The reaction of (**42**) with Cp^*NbCl_4 yielded a mixture of (**43**) and (**44**). Compound (**44**) was identified by a singlet at δ - 52 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture as well as by an X-ray structure determination.



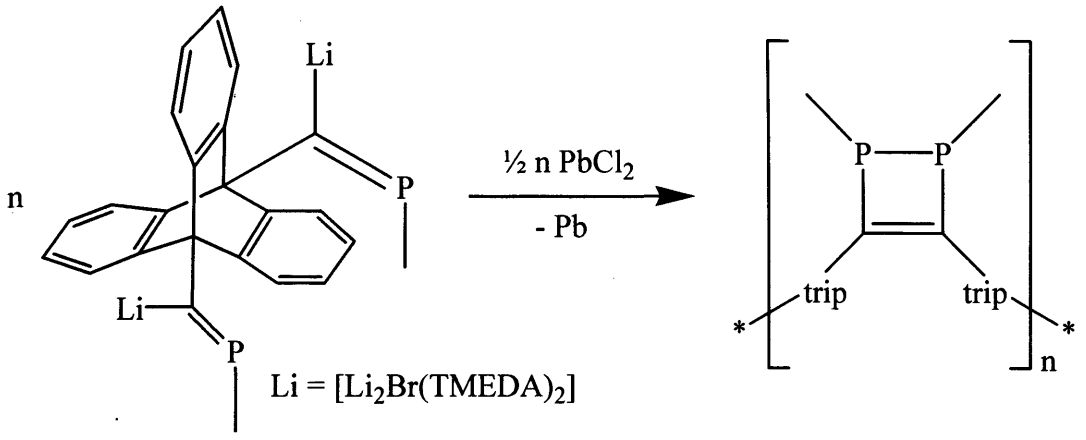
(43)



(44)

Figure 3.10 Products obtained from oxidative coupling reactions of (42)

A $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture of (**38**) and $PbCl_2$ showed a weak singlet at δ - 58.9 ppm. This is close to the resonance observed in (**44**) and is thought to result from the formation of (**45**) (Scheme 3.22). The product, (**45**), does however have very low solubility in all common solvents and so a solid state $^{31}P\{^{1}H\}$ NMR spectrum of the reaction precipitate was carried out. This showed a broad signal around δ - 60 ppm ($\upsilon_{½}$ = 1215 Hz) supporting the suggested structure.



(38) (45)

Scheme 3.22 Proposed formation of $[Me_2P_2C_2(tript)_2]_n$ (45)

3.2.3 Attempted synthesis of further multifunctional phosphaalkynes

In an attempt to prepare further diphosphaalkynes several promising ligand systems have been investigated. Adamantane was used by *Allspach* and *Regitz* in 1986 to prepare the monofunctional adamantane phosphaalkyne, adamantan-1-ylmethylidyne-phosphane (**46**).[54] It was thought that the separation of the phosphaalkyne functionalities by a CH_2 fragment would be sufficient enough to prevent intramolecular coupling reactions, given the likely rigidity of the resulting diphosphaalkyne.

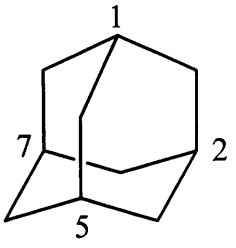
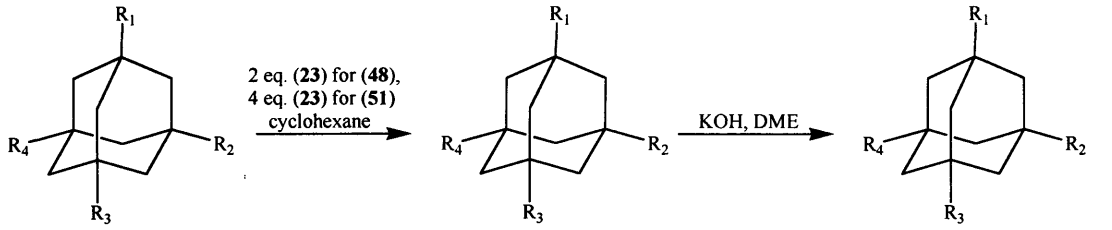


Figure 3.11 Adamantane

Adamantane-1,3-dicarboxylic acid is a commercially available chemical, which can easily be converted to adamantane-1,3-dicarbonyl dichloride (**47**) by refluxing it in thionyl chloride for 16 hours under inert atmosphere.

The reaction of adamantane-1,3-dicarbonyl dichloride (**47**) with 2 equivalents of $[LiP(SiMe_3)_2DME]$ (**23**) was carried out and led to the formation of the diphosphaalkene, (**48**), as mixture of its E and Z-isomers. The $^{31}P\{^1H\}$ NMR spectrum of (**48**) shows two singlets at δ 112 and 113 ppm. Treatment of (**48**) with a catalytic amount of KOH in DME affords the 1,3-bis-phosphanylidynemethyl-adamantane (**49**) (Scheme 3.23). The $^{31}P\{^1H\}$ NMR spectrum of this compound shows a singlet at δ - 69 ppm, which is in good agreement with the known adamantan-1-ylmethylidyne-phosphane, (**46**), which shows a singlet in its $^{31}P\{^1H\}$ NMR spectrum at δ - 66.9 ppm.[54] An infrared spectrum taken on the crude product, (**49**), showed a strong stretch at 1530 cm^{-1} which was assigned to the phosphorus carbon triple bond (*cf.* 1528 cm^{-1} for (**46**)).[54] Unfortunately attempts to isolate (**49**) as pure compound failed and it proved impossible to obtain full spectroscopic data.



(47) $R_1 = R_2 = COCl$, $R_3 = R_4 = H$
(50) $R_1 = R_2 = R_3 = R_4 = COCl$

(48) $R_1 = R_2 = [C(OSiMe_3)=PSiMe_3]$, $R_3 = R_4 = H$
(51) $R_1 = R_2 = R_3 = R_4 = [C(OSiMe_3)=PSiMe_3]$

(49) $R_1 = R_2 = C\equiv P$, $R_3 = R_4 = H$
(52) $R_1 = R_2 = R_3 = R_4\ C\equiv P$

Scheme 3.23 Preparations of di- and tetraphosphaalkynes

An attempt to prepare a tetraphosphaalkyne was made using adamantane-1,3,5,7-tetracarbonyl tetrachloride, (**50**), as a precursor. This was prepared according to literature procedure.[63] The reaction of (**50**) with (**23**) presumably led to the formation of the corresponding tetraphosphaalkene (**51**), displaying two signals at δ 127.6 and 125.9 ppm in its $^{31}P\{^1H\}$ NMR spectrum. Compound (**51**) was treated with a catalytic amount of KOH in DME. The resultant solution showed multiple signals in the $^{31}P\{^1H\}$ NMR spectrum, the major one at δ - 33.5 ppm. This is still in the expected region for phosphaalkynes but not in such good agreement with the known value for (**46**).[54] All attempts to isolate and characterise a pure product have so far failed.

3.3 Conclusion

Polyalkynes are important materials in the preparation of polymeric materials. Due to the fact that phosphaalkyne chemistry resembles the chemistry of alkynes[4] more than the chemistry of related nitriles, there is much potential which waits to be discovered for polyphosphaalkynes, *e.g.* as precursors for phosphorus containing polymers and co-ordination polymers.

We have shown that the synthetic route most widely used in the preparation of phosphaalkynes,[3] *i.e.* the β-elimination of hexamethyldisiloxane, can be used in the preparation of di- or even multifunctional phosphaalkynes if the phosphaalkyne functionalities are separated in the molecule to prevent any intramolecular reactions. Furthermore, it was shown that the reactivity of bifunctional phosphaalkynes resembles the reactivity of known monophosphaalkynes. Further attempts should be made to prepare more multifunctional phosphaalkynes, *e.g.* utilising diadamantane as a spacer, and the chemistry of these species explored.

3.4 Experimental

For general experimental procedures refer to appendix I. $[P(SiMe_3)_3]$ (**22**) and $P{\equiv}CBu^t$ (**1**) were prepared, with slight modification, according to literature procedures.[64] Compound (**26**) was prepared in a multistep synthesis from anthracene with modification to the published literature procedure (see below). Adamantane-1,3-dicarbonyl dichloride (**47**) was prepared from commercially available adamantane-1,3-dicarboxylic acid by refluxing in thionyl chloride for 16 hours under inert atmosphere. Adamantane-1,3,5,7-tetracarbonyl tetrachloride (**50**)[63, 65] was prepared according to the literature procedure. Other chemicals were commercially available and were purified according to published techniques.[66] The interpretation of the ^{13}C NMR spectra of (**29**) and (**30**) proved difficult due to the low solubility of both compounds in standard deuterated solvents and the presence of many overlapping multiplet resonances. Reproducible microanalyses for these two compounds could not be obtained due to the presence of diethyl ether and dichloromethane of crystallisation in (**29**) and (**30**) respectively. Despite this, the available spectroscopic data pointed towards the bulk materials having a purity in excess of 97 %.

9,10-Bis-(chloromethyl)-anthracene[67]

A mixture of dioxane (360 cm^3) and concentrated hydrochloric (60 cm^3) acid was saturated with hydrogen chloride gas (prepared *in situ* by dropwise addition of concentrated H_2SO_4 to NH_4Cl). Anthracene (45 g) and paraformaldehyde (38 g) were added. The mixture was stirred vigorously and heated slowly at reflux for 2 hours, while hydrogen chloride gas was bubbled through the suspension. A colour change to yellow was observed. The hydrogen chloride addition was stopped and reflux was maintained for a further 3 hours. The solution was allowed to cool to ambient temperature overnight without stirring. The resulting yellow solid was isolated by filtration and washed with dioxane (2 x 25 cm^3) to yield 9,10-bis-(chloromethyl)-anthracene (90 %).

mp. 254 - 256 °C.[68]

9,10-Bis(acetoxymethyl) anthracene[69]

A solution of 9,10-bis-(chloromethyl)-anthracene (20 g) and sodium acetate (25 g) in glacial acetic acid (400 cm^3) was heated at reflux for 5 hours. The mixture was cooled to room temperature and yellow crystals were filtered and dried *in vacuo*. mp. 220 °C.

9,10-Bis(hydroxymethyl) triptycene[70]

To a refluxing solution of 9,10-bis(acetoxymethyl)anthracene (24.5 g) and isoamyl nitrite (25 cm^3) in CH_2Cl_2 (400 cm^3) was added a solution of anthranilic acid (13.7 g) in THF (150 cm^3) dropwise over 4 hours. After addition, reflux was maintained for 30 min. The solvent was removed under reduced pressure to leave a brown residue. Diglyme (100 cm^3) and maleic anhydride (8 g) were then added. This mixture was refluxed for one hour. The mixture was then poured into a KOH solution (40 g in 120 cm^3 water and 240 MeOH cm^3). The resulting suspension was boiled for 30 min with stirring and water added until precipitation was complete. The ivory solid was isolated by filtration and washed with water until washings were neutral. Drying under vacuum yielded 22 g of 9,10-bis(hydroxymethyl)triptycene. mp. > 300 °C.

9,10-Triptycenedicarboxylic acid[70]

A mixture of chromium trioxide (8.92 g) and concentrated sulphuric acid (8.0 cm^3) was carefully diluted to 30 cm^3 with water and allowed to cool to room temperature. This solution was slowly added to a suspension of 9,10-bis(hydroxymethyl)triptycene (10.0 g in 380 cm^3 acetone) so that the temperature did not exceed 35 °C. The green mixture was stirred overnight at room temperature. The volume was reduced by half and an equal amount of water was added. Most of the acetone was removed on a rotary evaporator and replaced with water. The formed green powder was isolated by filtration and washed with water until washings were colourless. The filter cake was dissolved in a 10 % KOH solution (150 cm^3), filtered and acidified with 10 % hydrochloric acid. The resulting precipitate was digested on a steam bath for 15 min, isolated by filtration and dried under vacuum at 100 °C for 4 hours, yielding 9.5 g of 9,10-triptycenedicarboxylic acid. mp. > 300 °C, IR (Nujol) υ/cm^{-1}: 1695 (s), 1266 (s).

9,10-Triptycenedicarbonyl chloride (26) [70]

A solution of 5.7 g of 9,10-triptycenedicarboxylic acid in 110 cm^3 of dry dioxane was added dropwise over 3 hours to 40 cm^3 of freshly distilled thionyl chloride under an inert atmosphere. The pale yellow solution was refluxed while stirring for a further 6 hours. After cooling to room temperature, the *volatiles* were removed *in vacuo,* yielding 5.5 g of (**26**) mp. > 300 °C, IR (Nujol) υ/cm^{-1}: 1785 (s), 1058 (s), 1042 (s).

$[(Me_3Si)P=C(OSiMe_3)C(C_6H_4)_3CC(OSiMe_3)=P(SiMe_3)]$ (27)

To a solution of $[LiP(SiMe_3)_2DME]$ (**23**) (1.45 g, 5.2 mmol) in cyclohexane (30 cm^3) was added a suspension of 9,10-triptycene dicarbonyl chloride (**26**) (1.00 g, 2.6 mmol) in cyclohexane (50 cm^3) at 5 °C. An immediate colour change to yellow orange was observed. The suspension was allowed to warm to ambient temperature, stirred overnight and filtered. Volatiles were removed from the filtrate *in vacuo* to yield (**27**) as a pale yellow oil (1.65 g, 95 %). The $^{31}P\{^1H\}$ NMR spectrum of this oil displayed 4 singlet resonances (δ 148.1, 148.6, 158.5, 159.5 ppm) which is consistent with (**27**) existing as a mixture of its Z,Z-, Z,E- and E,E-isomers. No further characterisation of the mixture was attempted and it was used for the synthesis of (**28**).

$[P\equiv CC(C_6H_4)_3CC\equiv P]$ (28)

To a solution of (**27**) (1.65 g, 2.5 mmol) in DME (60 cm^3) was added a catalytic amount of KOH (50 mg) and the resulting mixture stirred for 4 hours. Volatiles were removed from the mixture *in vacuo* and the residue washed with hexane (10 cm^3), extracted into Et_2O (80 cm^3), filtered and the diethyl ether removed from the filtrate *in vacuo.* The resultant residue was dissolved in toluene (20 cm^3) and the solution cooled to - 30 °C overnight to yield (**28**) as colourless crystals.

(0.60 g, 67 %), mp. 263 - 265 °C (dec.); ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.85 - 6.87 (m, 6H, ArH), 7.86 - 7.91 (m, 6H, ArH); $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6, 298 K): δ 51.0 (d, C3*C*, $^2J_{PC}$ = 17.4 Hz), 122.3, 125.9 (s, ArC), 143.0 (d, q, ArC, $^3J_{PC}$ = 4.2 Hz), 164.0 (d, PC, $^1J_{PC}$ = 47.1 Hz); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ -

15.7 (s, P≡C); MS APCI: *m/z* (%) 339 [MH^+, 100]; IR (Nujol) *v*/cm^{-1}: 1555 (m); Acc. mass EI: calc. for M^+ 338.0409, found 338.0411.

[{$(PPh_3)_2Pt$}$_2${μ-η^2:η^2-P≡CC$(C_6H_4)_3$CC≡P}] (29)

To a solution of [$(PPh_3)_2Pt(C_2H_4)$] (100 mg, 0.13 mmol) in toluene (20 cm^3) at - 78 °C was added a solution of (**28**) (23 mg, 0.07 mmol) in toluene (10 cm^3) over 5 min. The resultant solution was allowed to warm to ambient temperature and stirred 4 hours. Volatiles were then removed *in vacuo*, the residue washed with hexane and dissolved in CH_2Cl_2 (10 cm^3). Layering of this solution with diethyl ether resulted in the deposition of cream coloured crystals of (**29**).

(70 %, 87 mg); mp. 251 - 255 °C (dec.); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.39 - 7.18 (m, 60H, PPh_3), 6.54 - 6.58 (m, 6H, ArH), 7.60 - 7.64 (m, 6H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 25.4 (dd, PPh_3, $^2J_{PP}$ = 21 and 11 Hz, $^1J_{PtP}$ = 3273 Hz), 28.9 (dd, PPh_3, $^2J_{PP}$ = 28 and 21 Hz, $^1J_{PtP}$ = 3747 Hz), 94.9 (dd, P≡C, $^2J_{PP}$ = 28 and 11 Hz, $^1J_{PtP}$ = 53 Hz); MS FAB (NOBA) *m/z* (%): 1776 [M^+, 6], 1514 [M^+ - PPh3, 11], 1252 [M^+ - 2 PPh_3, 8], 719 [$Pt(PPh_3)_2^+$, 100], 338 [M^+ - 2 $Pt(PPh_3)_2$, 22]; IR (Nujol) *v*/cm^{-1}: 1260(s), 1091(s), 1021(s), 803(s), 751(m), 690(m).

[$(PPh_3)_2$(CO)ClRu{P=C(H)}C$(C_6H_4)_3$C{C(H)=P}Ru(CO)$(PPh_3)_2$Cl] (30)

To a solution of $RuHCl(CO)(PPh_3)_3$ (200 mg, 0.2 mmol) in CH_2Cl_2 (20 cm^3) at - 78 °C was added a solution of (**28**) (35 mg, 0.1 mmol) in CH_2Cl_2 (10 cm^3) over 5 mins. The resultant solution was allowed to warm to ambient temperature during which time a colour change to deep orange was observed. The solution was then stirred overnight, volatiles removed *in vacuo*, the residue washed twice with hexane (2 x 20 cm^3) and diethyl ether (20 cm^3) to leave (**30**) as an orange microcrystalline solid.

(85 %, 146 mg); mp. 233 - 235 °C; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.88 - 7.59 (m, 72H, ArH), 7.98 (br. m, 2H, CH=P); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 39.9 (br. m, PPh_3), 516.7 (br. m., CH=P); MS FAB (noba) *m/z* (%): 688 [$Ru(PPh_3)_2(CO)Cl^+$, 7], 653 [$Ru(PPh_3)_2(CO)^+$, 11], 625 [$Ru(PPh_3)_2^+$, 10], 263 [PPh_3H^+, 100]; IR (Nujol) *v*/cm^{-1}: 1924 (s, CO str.).

[(I)(PPh$_3$)$_2$(CO)ClRu{P(Me)=(H)C}C(C$_6$H$_4$)$_3$C{C(H)=(Me)P}Ru(I)(CO)(PPh$_3$)$_2$ Cl] (34).

To a suspension of (**30**) (150 mg, 0.09 mmol) in CH_2Cl_2 (30 cm^3) was added methyl iodide (10 µl, 0.16 mmol) at - 78 °C. The solution was allowed to warm to ambient temperature, and stirred overnight. The solvent was removed *in vacuo,* the residue washed with hexane (20 cm^3) and diethyl ether (20 cm^3), to give (**34**) as an orange powder.

(70 %, 126 mg); mp. 185 - 187 °C dec.; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K): δ 2.85 (d, 6H, P-CH$_3$, $^1J_{PH}$ = 13 Hz), 6.60 - 7.67 (m, 72H, ArH), 8.18 - 8.26 (m, 2H, CH=P); ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 4.1 (br. m., PPh_3), 250.5 (br., P=CH); IR (Nujol) υ/cm^{-1}: 1950 (s, CO str.).

[P(Me)={Li$_2$Br(TMEDA)$_2$}CC(C$_6$H$_4$)$_3$CC{Li$_2$Br(TMEDA)$_2$}=P(Me)] (38)

To a solution of (**28**) (0.5 mmol, 170 mg) and TMEDA (0.5 cm^3) in Et_2O (40 cm^3) was added, dropwise, MeLi ·LiBr (1 mmol, 0.7 cm^3, 1.5 M in Et_2O) at - 78 °C. After 30 min at - 78 °C the reaction mixture was allowed to warm to room temperature and stirring was maintained for 1 h. A colour change to orange was observed. Volatiles were removed *in vacuo* and the residue extracted with Et_2O (20 cm^3). Concentration and slow cooling to - 30 °C yielded orange crystals of (**38**).

(96 mg, 50 %), mp. 137 - 139 °C (dec.); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.28 (m, 6H, P-Me), 1.92 (s, 16H, CH_2-TMEDA), 2.16 (s, 48H, CH_3-TMEDA), 7.46 - 7.52 (m, 12H, ArH); ^{31}P{^{1}H}(121.7 MHz, C_6D_6, 298 K): δ 248.2 (s, P=C); IR (Nujol) ν/cm^{-1}: 1603(w), 1372 (s), 1292 (m), 1035 (s), 950 (m), 830 (m).

[P(Me)=(H)CC(C$_6$H$_4$)$_3$CC(H)=P(Me)] (39)

To a solution of (**28**) (0.5 mmol, 170 mg) and TMEDA (0.5 cm^3) in Et_2O (40 cm^3) was added, dropwise, methyllithium as complex with lithium bromide (1.0 mmol, 0.7 cm^3, 1.5 M in Et_2O) at - 78 °C. After 30 min at - 78 °C the reaction mixture was allowed to warm to room temperature and stirring was maintained for 1 h. A colour change to orange was observed. To the resulting solution methanol (1 cm^3, ca. 25 eq.) in Et_2O (10 cm^3) was added at - 78 °C. After 30 min at - 78 °C the reaction mixture was allowed to warm to room temperature, stirring was maintained for 2 h,

yielding a colourless solution. The solvent was removed from this *in vacuo* and the residue extracted with hexane (30 cm^3). Removal of the solvent *in vacuo* yielded (**39**) as a white powder.

(164 mg, 91 %), mp. 84 - 87 °C; $^{31}P\{^1H\}$(121.7 MHz, C_6D_6, 298 K) : δ 128.4 (s, P=C); ^{31}P(121.7 MHz, C_6D_6, 298 K) : δ 128.4 (unres. m., P=C); ^1H NMR (300.5 MHz, C_6D_6 , 298 K): δ 1.86 (m, 6H, Me), 6.90 - 6.95 (m, 6H, ArH), 7.44 - 7.62 (m, 6H, ArH), 8.61 (d, $^2J_{PH}$ = 4 Hz, 2H, P=CH); IR (Nujol) ν/cm^{-1}: 1629 (s), 1282 (s), 1031 (s), 946 (m).

[P(Bu^t)=(H)CC(C_6H_4)$_3$CC(H)=P(Bu^t)] (40)

To a solution of (**28**) in (0.5 mmol, 170 mg) in Et_2O (40 cm^3) was added dropwise a suspension of Bu^{t}Li (3.16 cm^3, 2 mmol), LiBr (180 mg) and TMEDA (0.5 cm^3) in Et_2O (30 cm^3) at - 78 °C. After warming up to room temperature the mixture was heated to 50 °C for 48 h. To the yellow solution was added methanol (1.0 cm^3, 25 eq.) in Et_2O (10 cm^3) at - 78 °C. After stirring at room temperature for 24 hours and removing the solvent *in vacuo*, extraction with hexane (30 cm^3) concentrating and slow cooling yielded light yellow microcrystals of (**40**).

(68 mg, 30 %), mp. 89 - 94 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 1.22 (m, 18H, Bu^t), 6.85 - 6.92 (m, 6H, ArH), 7.69 - 7.90 (m, 6H, ArH), 8.62 (d, $^2J_{PH}$ = 7.2 Hz, 2H, P=CH); $^{31}P\{^1H\}$(121.7 MHz, C_6D_6, 298 K) : δ 191.1 (s, P=C); IR (Nujol) ν/cm^{-1}: 1740 (s), 1354 (s), 1288 (s), 1250(m), 1161(m), 1038 (s), 949 (s), 794 (m), 757 (s).

[CH(C_6H_4)$_3$CC(SnMe$_3$)=P(Me)] (41)

To a solution of 9-phosphaalkyne-triptycene (100 mg, 0.34 mmol) in diethyl ether (20 cm^3) and TMEDA (0.5 cm^3) was added a solution of MeLi in diethyl ether (0.21 cm^3 1.6 M, 0.34 mmol) at - 78 °C dropwise. The solution was slowly warmed to - 20 °C and kept at this temperature for 5 minutes. The orange suspension was cooled back to - 78 °C and a solution of Me_3SnCl (0.067 g, 0.34 mmol) in diethyl ether was added dropwise. The suspension was slowly warmed to ambient temperature and stirring was maintained for 4 hours. The solvent was removed *in vacuo* and the residue extracted twice with hexane (2 x 20 cm^3). Removal of the solvent left an orange powder.

(46 %, 74 mg); mp 105 °C (softens); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.29 (br. m., 9H, Sn-Me), 1.21 (d, 3H, P-Me, $^{2}J_{PH}$ = 5 Hz), 5.18 (s, 1H, C_3CH), 6.83 - 6.87 (m, 6H, ArH), 7.10 - 7.19 (m, 6H, ArH); $^{13}C\{^{1}H\}$ NMR (75.6 MHz, C_6D_6, 298 K): δ 54.9 (s, C_3CH), 124.5 - 127.5 (m, ArC), 144.5 - 146.9 (m, ArC); $^{31}P\{^{1}H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 320.7 (s, P=C, $^{2}J_{PSn}$ = 120 Hz); IR (Nujol) υ/cm^{-1}: 1612 (w), 1260 (s), 1095 (s), 1026 (s), 799 (s), 744 (s).

$[Me_2P_2C_2(tript)_2]_n$ (45)

To a suspension of (**38**) (0.34 mmol) in diethyl ether (30 cm^3) was added a suspension of $PbCl_2$ in diethyl ether (0.28 g, 1.0 mmol) at - 78 °C. This was slowly warmed to ambient temperature and stirred overnight. The colour changed from orange to brown and elemental lead was deposited. Volatiles were removed *in vacuo* and the residue was washed with hexane. The residue proved to be insoluble in all common solvents and could not be separated from the formed lead and residual $PbCl_2$. This made it unfeasible to obtain an accurate yield, but no starting material was observed in the $^{31}P\{^{1}H\}$ NMR spectrum of the supernatant solvent. The brownish powder was characterized by solid state NMR.

mp. > 300 °C; $^{31}P\{^{1}H\}$ solid state NMR: δ - 59 ppm ($\upsilon_{½}$ = 1215 Hz), $^{13}C\{^{1}H\}$ solid state NMR: δ 145.2 ($\upsilon_{½}$ = 1800 Hz), 124.8 ($\upsilon_{½}$ = 1900 Hz), 111.2 ($\upsilon_{½}$ = 500 Hz), 53.6 ($\upsilon_{½}$ = 500 Hz), 45.2 ($\upsilon_{½}$ = 800 Hz), 17.3 ($\upsilon_{½}$ = 1100 Hz); IR (Nujol) υ/cm^{-1}: 1261 (m), 1081 (s), 1029 (s), 951 (m), 866 (m), 785 (m), 753 (m), 722 (m).

$[1,3\text{-}\{(Me_3Si)P{=}C(OSiMe_3)\}_2(Ad)]$ (48)

To a solution of $[LiP(SiMe_3)_2DME]$ (**23**) (0.53 g, 1.9 mmol) in cyclohexane (20 cm^3) was added a suspension of adamantane-1,3-dicarbonyl dichloride (**47**) (0.50 g, 1.9 mmol) in cyclohexane (30 cm^3) at 5 °C. An immediate colour change to yellow orange was observed. The suspension was allowed to warm to ambient temperature, stirred overnight and filtered. Volatiles were removed from the filtrate *in vacuo* to yield (**48**). The $^{31}P\{^{1}H\}$ NMR spectrum displayed 2 singlet resonances (δ 112, 113 ppm). No further characterisation of the mixture was attempted.

[1,3-(P≡C)$_2$(Ad)] (49)

To a solution of (**48**) in DME (30 cm^3) was added a catalytic amount of KOH (50 mg) and the resulting mixture stirred for 16 hours. Volatiles were removed from the mixture *in vacuo* and the residue extracted into hexane (20 cm^3), filtered and the hexane removed from the filtrate *in vacuo* to yield (**28**) as slight yellow powder.

$^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ - 69 ppm; IR (Nujol) υ/cm^{-1}: 1530 cm^{-1}.

[1,3,5,7-{(Me$_3$Si)P=C(OSiMe$_3$)}$_4$(Ad)] (51)

To a solution of [LiP(SiMe$_3$)$_2$DME] (**23**) (0.36 g, 1.3 mmol) in cyclohexane (20 cm^3) was added a suspension of adamantane-1,3,5,7-tetracarbonyl dichloride (**50**) (0.50 g, 1.3 mmol) in cyclohexane (30 cm^3) at 5 °C. A colour change to yellow orange was observed. The suspension was warmed to ambient temperature. A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture was taken. No further characterisation of the mixture was attempted.

$^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 125.9 (s), 127.6 (s) ppm.

[1,3,5,7-(P≡C)$_4$(Ad)] (52)

To a solution of (**51**) in DME (10 cm^3) was added a catalytic amount of KOH (50 mg) and the resulting mixture stirred for 16 hours. Volatiles were removed from the mixture *in vacuo* to leave a grey powder containing (**52**).

$^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ - 33.5 (s) ppm.

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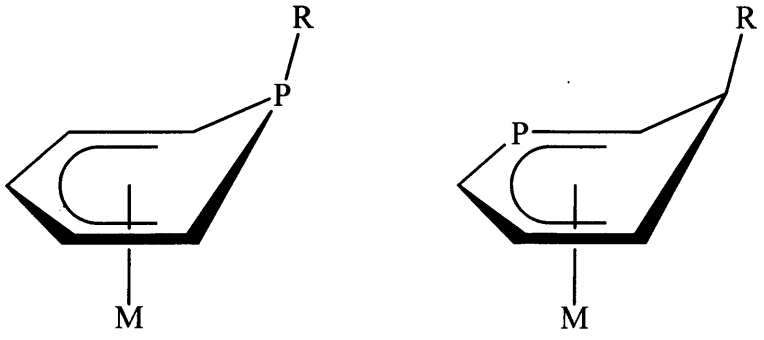
Chapter Four

4 Studies of the reactivity of a triphosphacyclohexadienyl anion

4.1 Introduction

4.1.1 Phosphorus substituted cyclohexadienyls

Two different types of η^5-co-ordination for a phosphacyclohexadienyl unit are possible (Figure 4.1). In type **A**, the metal is co-ordinated by an η^5-dienyl ligand in which the phosphorus atom has no specific role in the metal-ligand interaction. Some complexes of Fe, Mn and Cr featuring this co-ordination type have been reported in the literature.[1, 2] In type **B** co-ordination, the phosphorus is incorporated in the bonding part of the dienyl ligand which is interacting with the metal centre. The first example of such a type **B** compound, which also has been crystallographically characterised was [(η^5-2,4,6-triphenyl-2-*endo*-hydrophosphabenzene)(η^5-cyclopentadienyl)iron], and has been reported by *Nief* and *Fischer* in 1986.[3]

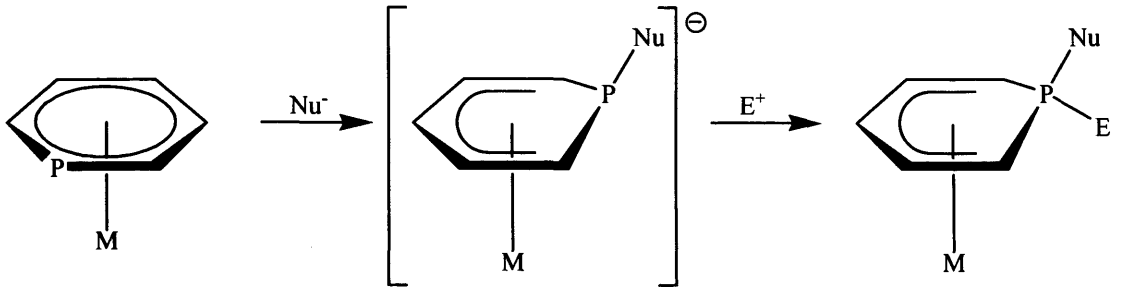


A **B**

Figure 4.1 η^5-co-ordination modes of a phosphacyclohexadienyl ligand

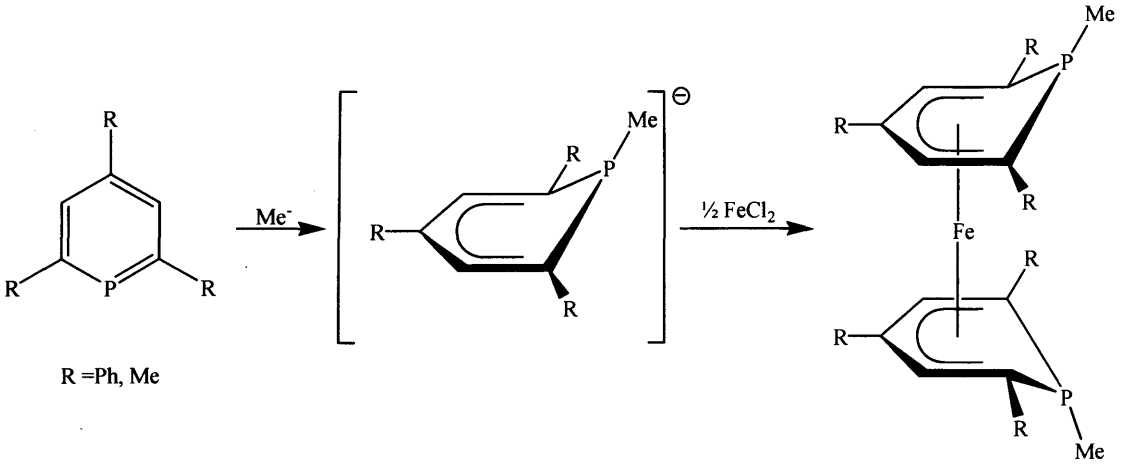
The synthesis of η^5-phosphacyclohexadienyl complexes usually involves nucleophilic attack at the electrophilic phosphorus centre of an η^6-phosphabenzene complex followed by a trapping reaction with an electrophile (Scheme 4.1).[4] Another approach to prepare η^5-phosphacyclohexadienyl complexes is the attack of a λ^3-

phosphinine with a nucleophile and subsequent reaction with a suitable metal precursor.[4]



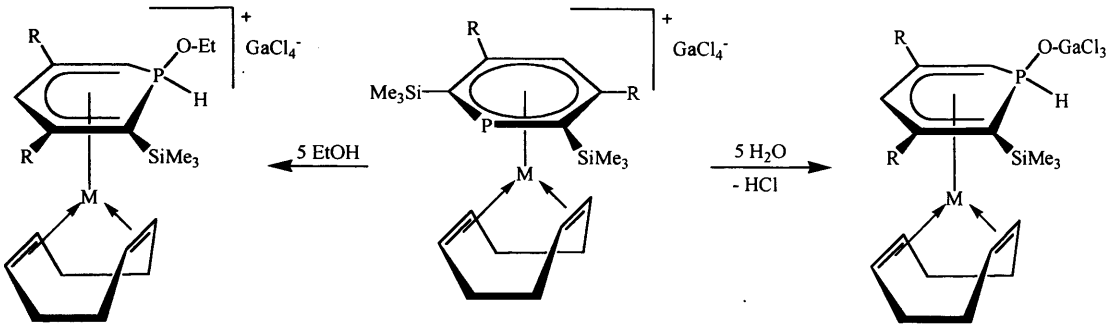
Scheme 4.1 General preparation of a phosphacyclohexadienyl complex

This approach was used in the synthesis of two bis(1-R-2,4,6-trisubstituted phosphinie)iron complexes by *Märkl et al.* in 1974 (Scheme 4.2).[5] Despite the fact that it was initially claimed by the authors the complexes would show η^6-co-ordination, it was later argued by *Dimroth et al.* that they were in fact bis-η^5-complexes.[6] This was then proven to be the case by *Massa* and *Baum* who obtained proof for η^5-co-ordination with an X-ray crystallographic study in the same year.[7]



Scheme 4.2 Synthesis of a bis-η^5-phosphacyclohexadienyl complex

Some η^5-phosphacyclohexadienyl complexes of iridium and rhodium have been reported recently.[8] *Le Floch et al.* published the synthesis and characterisation of the η^6-rhodium and -iridium complexes (**1**) and (**2**), which have been reacted with water and ethanol to give the corresponding η^5-phosphacyclohexadienyl complexes (**3** - **6**) (Scheme 4.3).



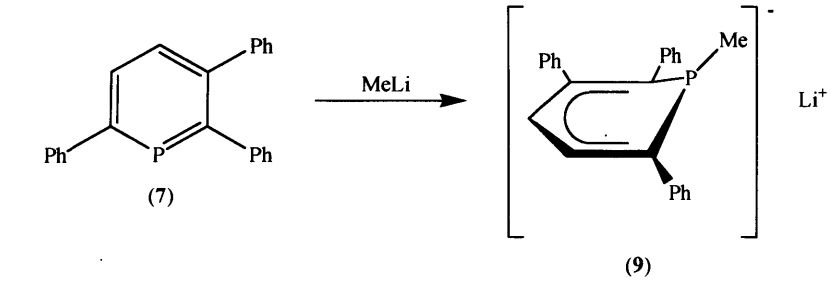
(5) M = Rh, R = Ph
(6) M = Ir, R = Me

(1) M = Rh, R = Ph
(2) M = Ir, R = Me

(3) M = Rh, R = Ph
(4) M = Ir, R = Me

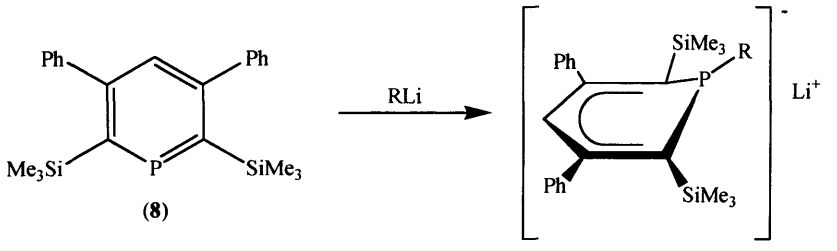
Scheme 4.3 Preparation of η^5-phosphacyclohexadienyl complexes of Ir and Rh

Very recently several anionic λ^4-phosphinines have been published by *Le Floch et al.*[4] These have been obtained by the reaction of the phosphinines (**7**) and (**8**) with alkyl lithium reagents in co-ordinating solvents such as diethyl ether and tetrahydrofuran (Scheme 4.4). Crystal structures of (**9 - 11**) were obtained and results from DFT calculations showed that the phosphacyclohexadienyl anions are more closely related to cyclopentadienyl anions than cyclohexadienyl anions.[4]



(7)

(9)

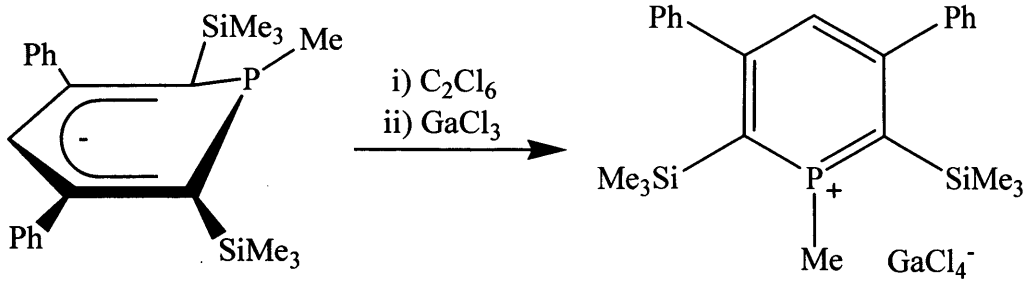


(8)

(10) R = Me
(11) R = Bu^t

Scheme 4.4 Preparation of some anionic λ^4-phosphinines

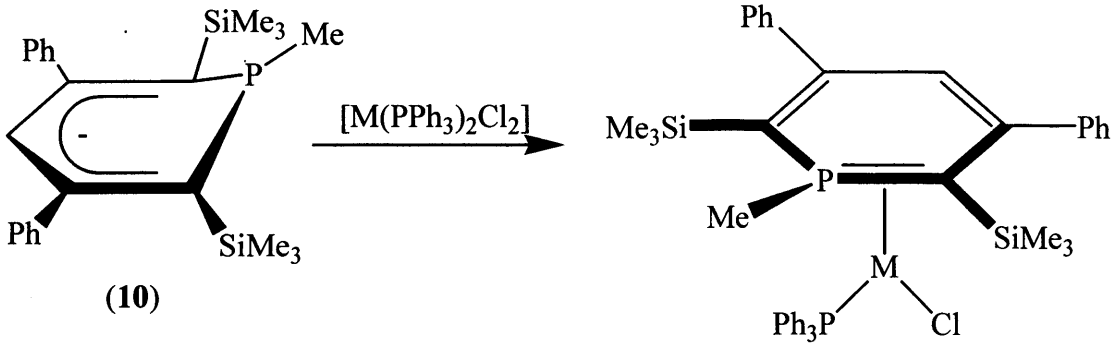
Compound (**10**) has been used in the synthesis of a 1-methyl-phosphininium compound. The reaction of (**10**) with C_2Cl_6 and subsequently $GaCl_3$ yielded the novel 1-methyl-phosphininium compound (**12**) (Scheme 4.5).[9]



(**10**) (**12**)

Scheme 4.5 Preparation of a 1-methyl-phosphininium compound

In a further reaction (**10**) was treated with $[M(PPh_3)_2Cl_2]$ (M = Pd, Pt) to give the η^2-palladium and platinum(II) complexes (**13**) and (**14**) (Scheme 4.6).[10]



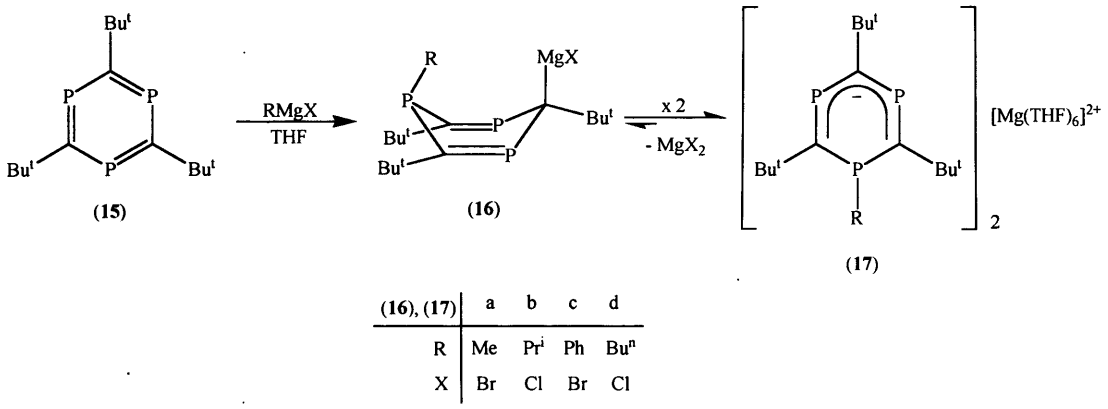
(**10**)

(**13**) M = Pd
(**14**) M = Pt

Scheme 4.6 Preparation of η^2-cyclohexadienyl palladium and platinum(II) complexes

4.1.2 Triphosphacyclohexadienyls

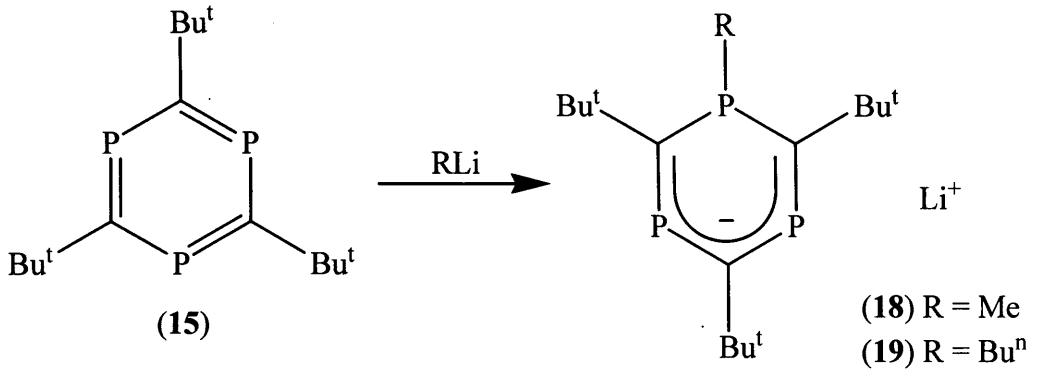
Similar to phosphacyclohexadienyls, triphosphacyclohexadienyls are obtainable from the reaction of a nucleophile with a triphosphabenzene. This has been shown by *Regitz et al.* in 2003 with the addition of Grignard reagents to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**15**), which yielded several triphosphacyclohexadienyl compounds (Scheme 4.7), one of which has been characterised by X-ray crystallography.[11]



(16), (17)	a	b	c	d
R	Me	Pr^i	Ph	Bu^n
X	Br	Cl	Br	Cl

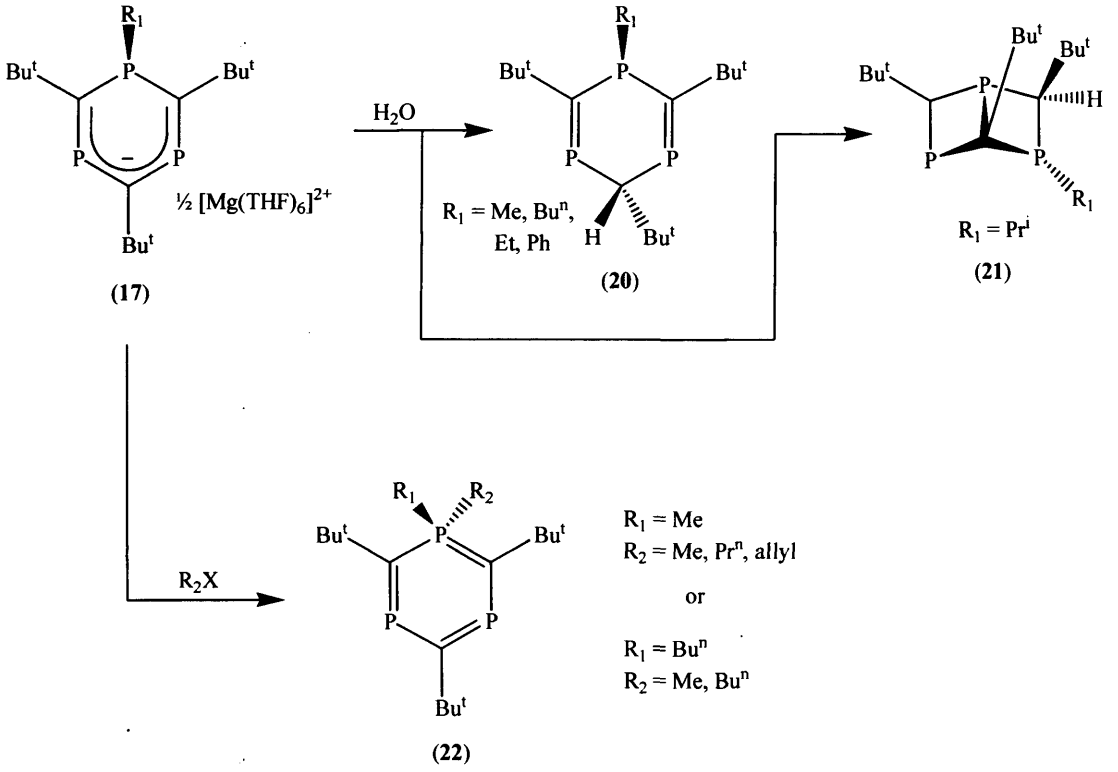
Scheme 4.7 Reaction of Grignard reagents with a triphosphabenzene

Similar reactions have been observed when Grignard reagents were replaced with organolithium compounds. The reaction of (**15**) with methyllithium or n-butyllithium yielded the corresponding lithium triphosphininuid salts (**18**) and (**19**) respectively.[12]



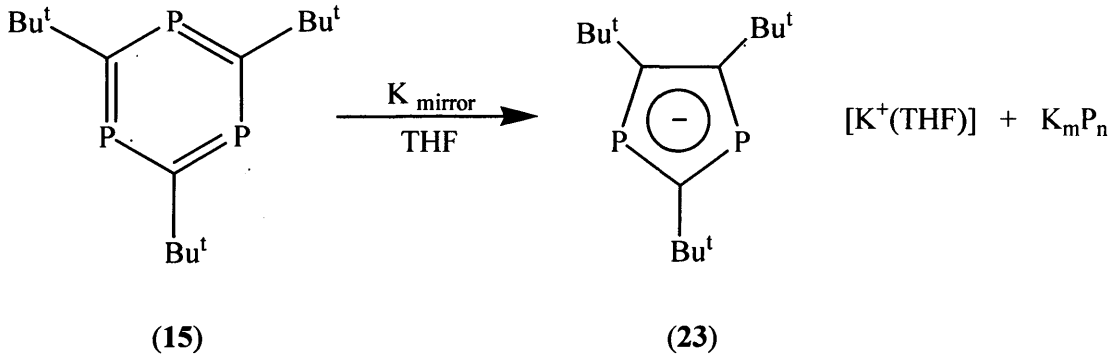
Scheme 4.8 Reaction of alkyl lithium reagents with a triphosphabenzene

Compounds (**17 a, c-d**) can be protonated to give the formal 1,4-addition products (**20**), while (**17 b**) reacts to give the 5,6-dihydro-1,3,5-triphospha-*Dewar*-benzene (**21**).[11] Several alkylation reactions of (**17**) have been carried out to give, in contrast to (**20**) obtained during protonation, the novel 1λ^5,3,5-triphosphinines (**22**) (Scheme 4.9).[12]



Scheme 4.9 Protonation and alkylation of a triphosphahexadienyl anion

It was also shown that (**18**) can react to give the 1,3-diphospholide ion (**23**) upon thermolysis.[13] Previously, a related reaction has been reported where 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**15**) reacts in an unprecedented fashion with potassium to give the diphospholyl ring anion (**23**) (Scheme 4.10).[14] It was assumed in that publication that the driving force for the reaction was the substantial aromatic character of the five-membered anionic ring in the product.

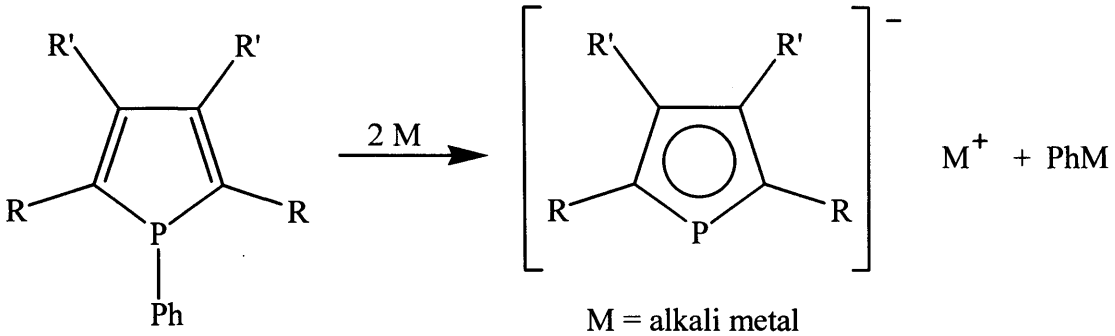


(**15**) (**23**)

Scheme 4.10 Alternative synthesis of a 1,3-diphospholyl anion

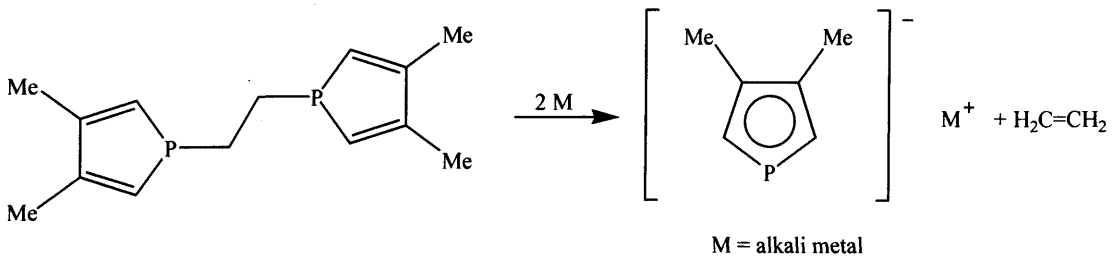
4.1.3 Phosphorus substituted cyclopentadienyls

The analogy between phospholyl anions and the ubiquitous cyclopentadienyl ligand[15-17] shows their importance and implies a huge potential for use as ligands in transition metal chemistry.[18] Phospholyl anions (also known as phosphacyclopentadienyl anions, phospholide anions or phosphacyclopentadienide anions) were first mentioned in a patent from *Braye* in 1967.[19] This work was later published in a paper which appeared in 1971.[20] The synthesis of phospholide anions involved the alkali metal cleavage of the phosphorus-phenyl bond of 1-phenyl substituted phospholes (Scheme 4.11).



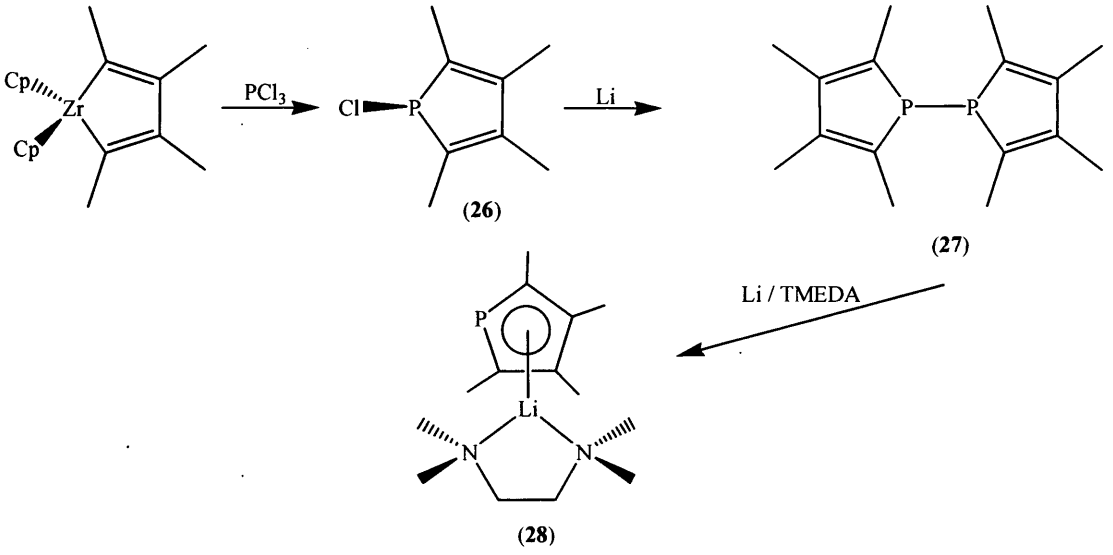
Scheme 4.11 Synthesis of phospholyl anions

One drawback of this method is the formation of phenylated by-products due to possible interference in subsequent reactions. The phenyl anion can be quenched with alkyl halides but this can also cause the phospholyl anion to become a functionalised phosphole, especially when the phosphorus centre is unhindered.[21] An improvement in the formation of phospholyl anions was made when bis-phospholylalkanes were used as precursors (Scheme 4.12).[22, 23]



Scheme 4.12 Alternative synthesis of a phospholyl anion

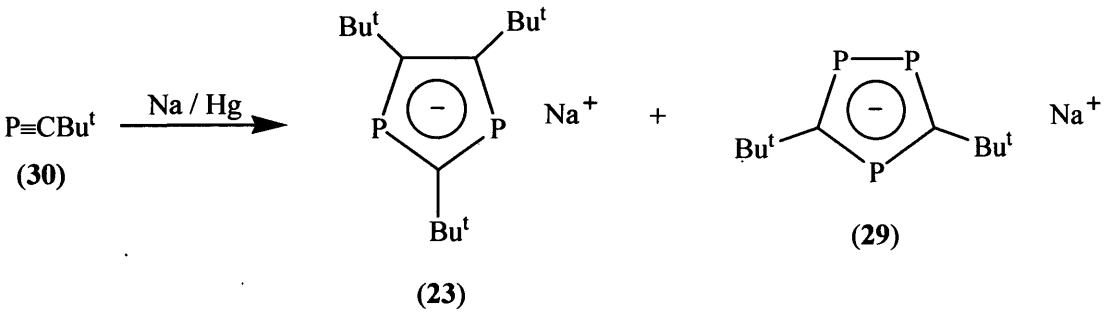
Higher yields were obtained when a chlorophosphole was reacted with excess lithium to yield the lithium salt of the phospholyl anion.[24] A convenient route for the preparation of the chlorophosphole involves the reaction of a zirconacyclopentadiene with PCl_3. Zirconacyclopentadienes are useful in the synthesis of symmetrical[25] and unsymmetrical phospholes.[26]



Scheme 4.13 Synthesis of phospholyl anions from chlorophospholes

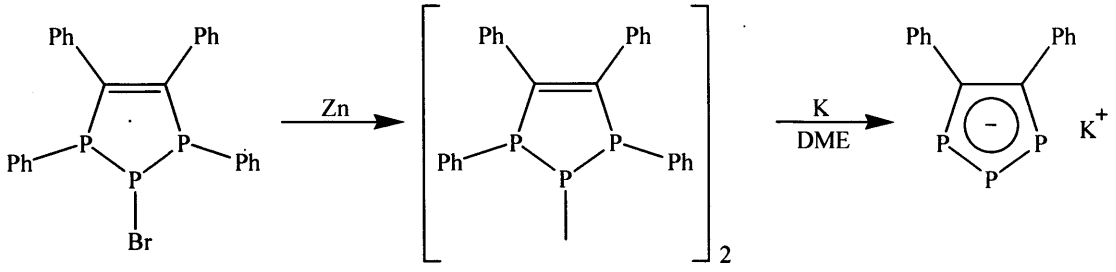
When (**26**) was reduced with one equivalent of lithium, the 1,1-octamethylbiphospholyl compound (**27**) was obtained which then reacts with excess lithium to yield the desired phospholyl anion salt (**28**) (Scheme 4.13). The X-ray structure of (**28**) revealed a monomeric molecule with η^5-co-ordination of the heterocycle to lithium and co-ordination of the alkali metal with TMEDA.[24]

Numerous methods for the preparation of a variety of polyphospholide anions have been reported in the literature.[18, 27] In 1985 *Becker* reported the preparation of the 2,5-bis-*tert*-butyl-1,3,4-triphospholide anion (**29**) by reacting $P{\equiv}CBu^t$ (**30**) with $[LiP(SiMe_3)_2]$.[28] Compound (**29**) was also prepared by an alternative method reported by *Nixon* and *Bartsch* in 1989. This involved the reaction of (**30**) with sodium amalgam to yield (**29**) as well the previously unknown 2,4,5-tris-*tert*-butyl-1,3-diphospholide anion (**23**) (Scheme 4.14).[29]



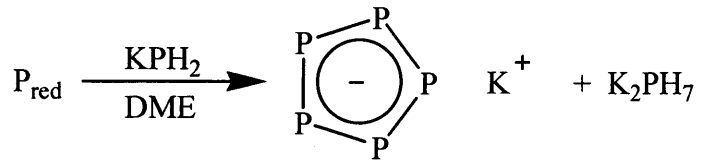
Scheme 4.14 Synthesis of di- and triphospholyl anions

The reaction occurs *via* a direct cleavage of the phosphaalkyne phosphorus-carbon bond by sodium followed by cyclisation with (**30**) to afford the desired products. This is contrary to earlier reports which suggested that a tantalum centre was required for the reaction to take place.[30] It is interesting to note that all nine possible phospholide ring anion isomers were obtained when a mixture of (**30**) and $Pr^iC{\equiv}P$ was reacted with sodium in monoglyme.[31] Almost one decade after the first synthesis of (**29**), in 1985, an example of a 1,2,3-triphospholide was reported (Scheme 4.15).[32]



Scheme 4.15 Synthesis of a 1,2,3-triphospholyl anion

The tetraphosphacyclopentadienide anion $[P_4CH]^-$ has received considerably less attention than its di- or triphospholyl counterparts. It can be obtained by nucleophilic cleavage of white phosphorus with sodium in diglyme.[33] This reaction also affords the pentaphosphacyclopentadienide anion (**31**). The synthesis of (**31**) was later improved and involved the reaction of red phosphorus and KPH_2. Potassium phosphide by-products precipitate out and can be removed to leave a solution of $[K][P_5]$.[34]



(31)

Scheme 4.16 Synthesis of the pentaphospholyl anion (31)

The common feature of phosphorus carbon heterocycles discussed so far is their extensive 6π electron delocalisation. This is evident from spectroscopic data and structural characterisations. A high degree of delocalisation is also supported by the observation that the phosphorus carbon bonds are significantly shorter than phosphorus carbon single bonds.[14] Spectroscopic evidence also supports the aromatic nature of phospholyl anions. Large $^{1}J_{PC}$ coupling constants (40 - 50 Hz) are a characteristic feature seen in their ^{13}C NMR spectra and result from high electronic delocalisation within the ring system. Furthermore, a downfield shift in the ^{31}P NMR resonances upon formation of phospholyl anions from phospholes was observed by *Quin* and *Orton*.[35] This area of organophosphorus chemistry has been recently reviewed.[18]

4.1.4 Co-ordination chemistry of phospholyl ring anions

4.1.4.1 Co-ordination of phospholyl ring anions to transition metals

The co-ordination of phospholyl anions to a metal centre can occur in five major ways, *viz.* A-E (Figure 4.2).

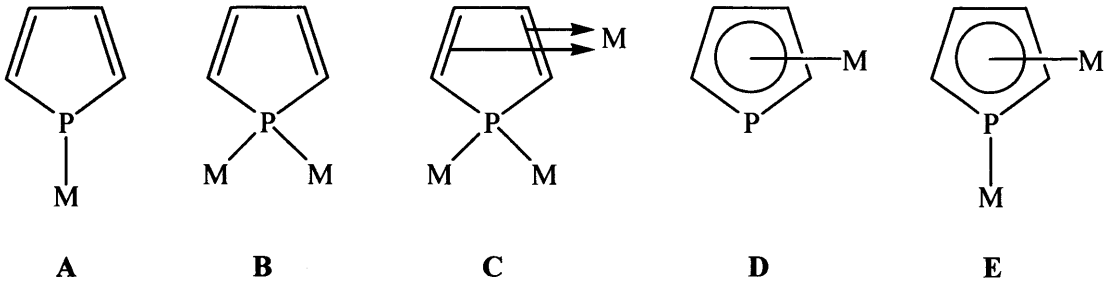
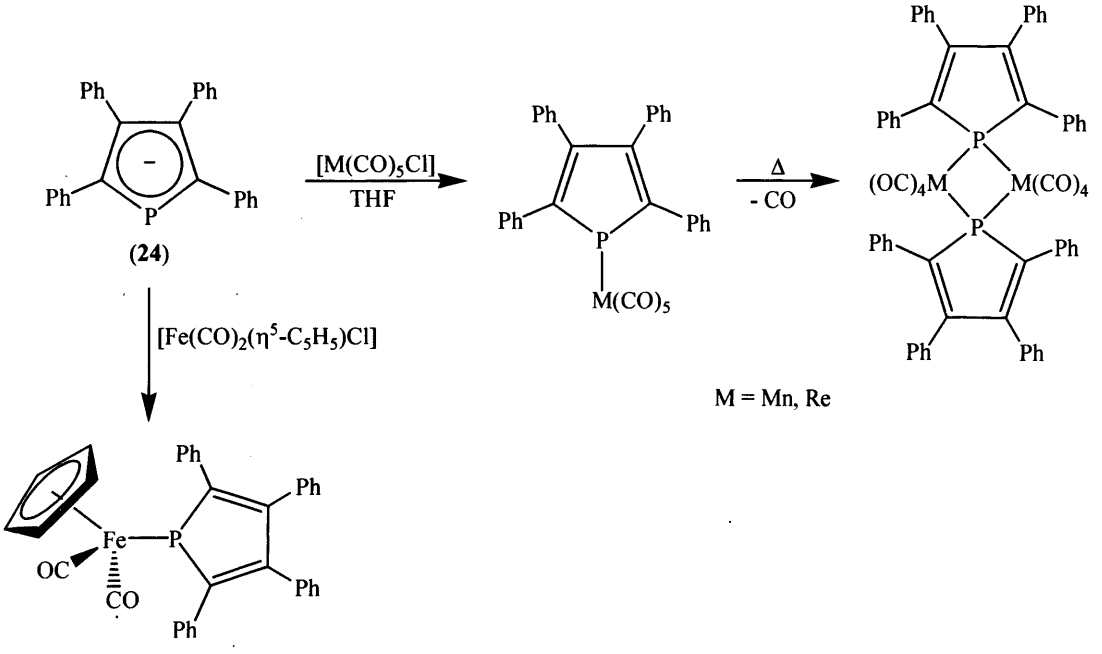


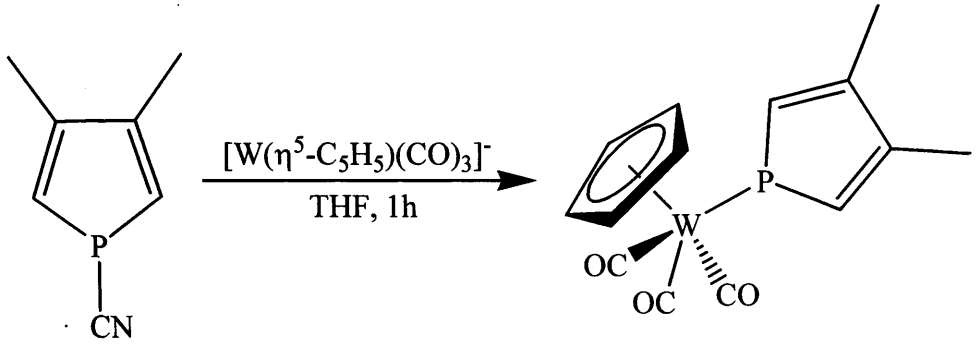
Figure 4.2 Co-ordination modes of phospholyl anions

In type **A** co-ordination, the phospholyl anion ligates in an η^1-fashion and it acts like a phosphide. In type **B** the phospholyl anion bridges two metal centres. *Abel* and *Towers* described complexes displaying type **A** co-ordination which result from the reaction of $[C_4Ph_4P]^-$ (**24**) and $[M(CO)_5Cl]$, (M = Mn, Re), or $[Fe(CO)_2(\eta^5\text{-}C_5H_5)Cl]$. When the product of the former reaction was heated, loss of CO and subsequent dimerisation to give a complex showing type **B** co-ordination was observed (Scheme 4.17).[36]



Scheme 4.17 Synthesis of two η^1-complexes derived from phospholyl anions

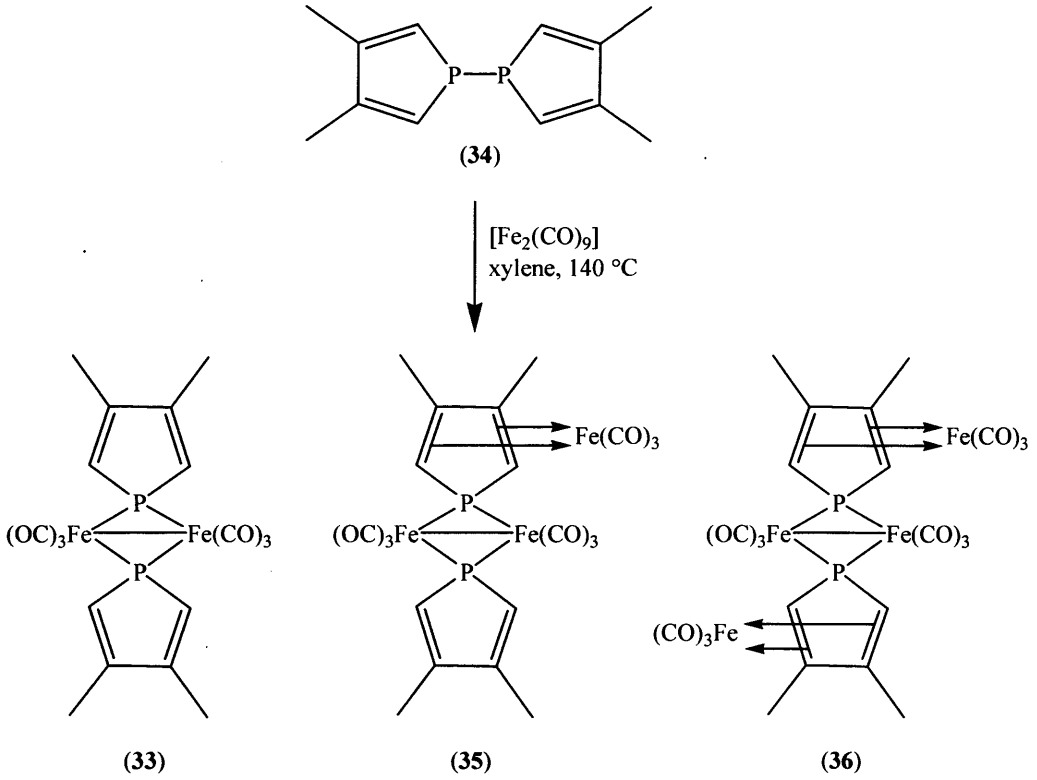
Mathey et al. described similar complexes containing tungsten. The X-ray structure of (**32**) shows that the phosphole ring is intermediate in planarity between 1-benzylphosphole, [C_4H_4P-CH_2Ph], and the tetramethylphospholyl anion, [C_4Me_4P]$^-$, remaining somewhat pyramidal about the phosphorus centre (Scheme 4.18).[37]



(**32**)

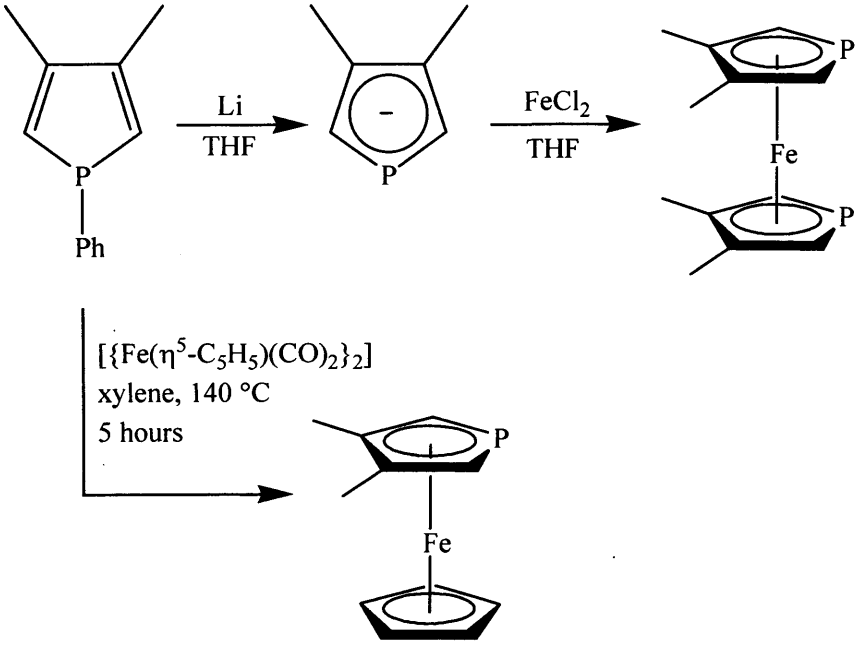
Scheme 4.18 Synthesis of an η^1-complex of a phospholyl anion

Type **B** co-ordination is shown in complex (**33**) which resulted from the reaction of bis-phosphole (**34**) and [$Fe_2(CO)_9$] in refluxing xylene. Complexes (**35**) and (**36**) were formed next to (**33**) in about the same yield. They both show type **B** and **C** co-ordination in the same molecule (Scheme 4.19).[38] Two diastereoisomers of (**36**) are possible. That shown in Scheme 4.19 is the isomer in which both $Fe(CO)_3$ fragments are *trans* with respect to the plane in which the phosphole rings lie. The $^{31}P\{^1H\}$ NMR spectrum of (**36**) shows only one resonance indicating the presence of only one isomer. The authors proposed the *trans*-structure shown since it seemed to be more sterically favourable.[38]



Scheme 4.19 Reaction of a bis-phosphole with $[Fe_2(CO)_9]$

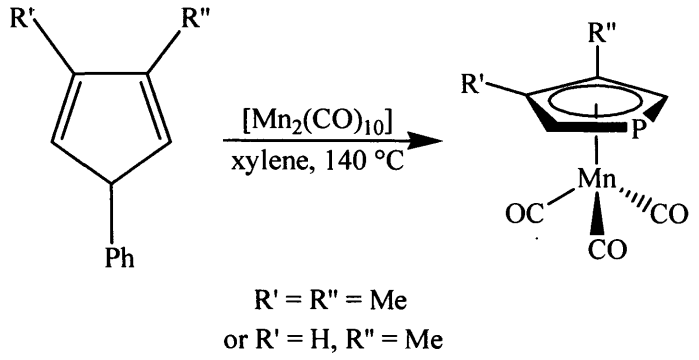
Complexes with type **D** co-ordination are frequently encountered. Examples include the simple phospha-ferrocene and 1,1'-disphospha-ferrocene complexes which have been prepared by *Mathey et al.* (Scheme 4.20).[21, 39]



Scheme 4.20 Synthesis of a phospha- and a 1,1'-diphospha-ferrocene

4.1 Introduction

Substantial attention has been paid to phospholyl manganese tricarbonyl complexes, known as phospha-cymantrenes. These compounds contain an η^5-phospholyl ligand and are not usually prepared from the phospholyl anion but from the reaction of the parent 1-phenylphosphole with $[Mn_2(CO)_{10}]$ (Scheme 4.21).[40, 41]

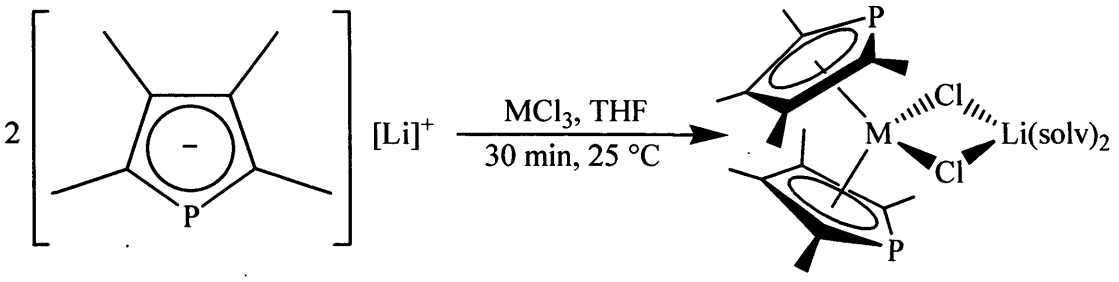


R' = R" = Me
or R' = H, R" = Me

Scheme 4.21 One route for the preparation of phospha-cymantrenes

Phospha-cymantrenes show CO stretches in their infrared spectra at higher wavenumbers compared with cymantrene, $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$. This implies that phospholyl rings are poorer π donors than Cp which leads to less electron density in the CO π^* orbitals.

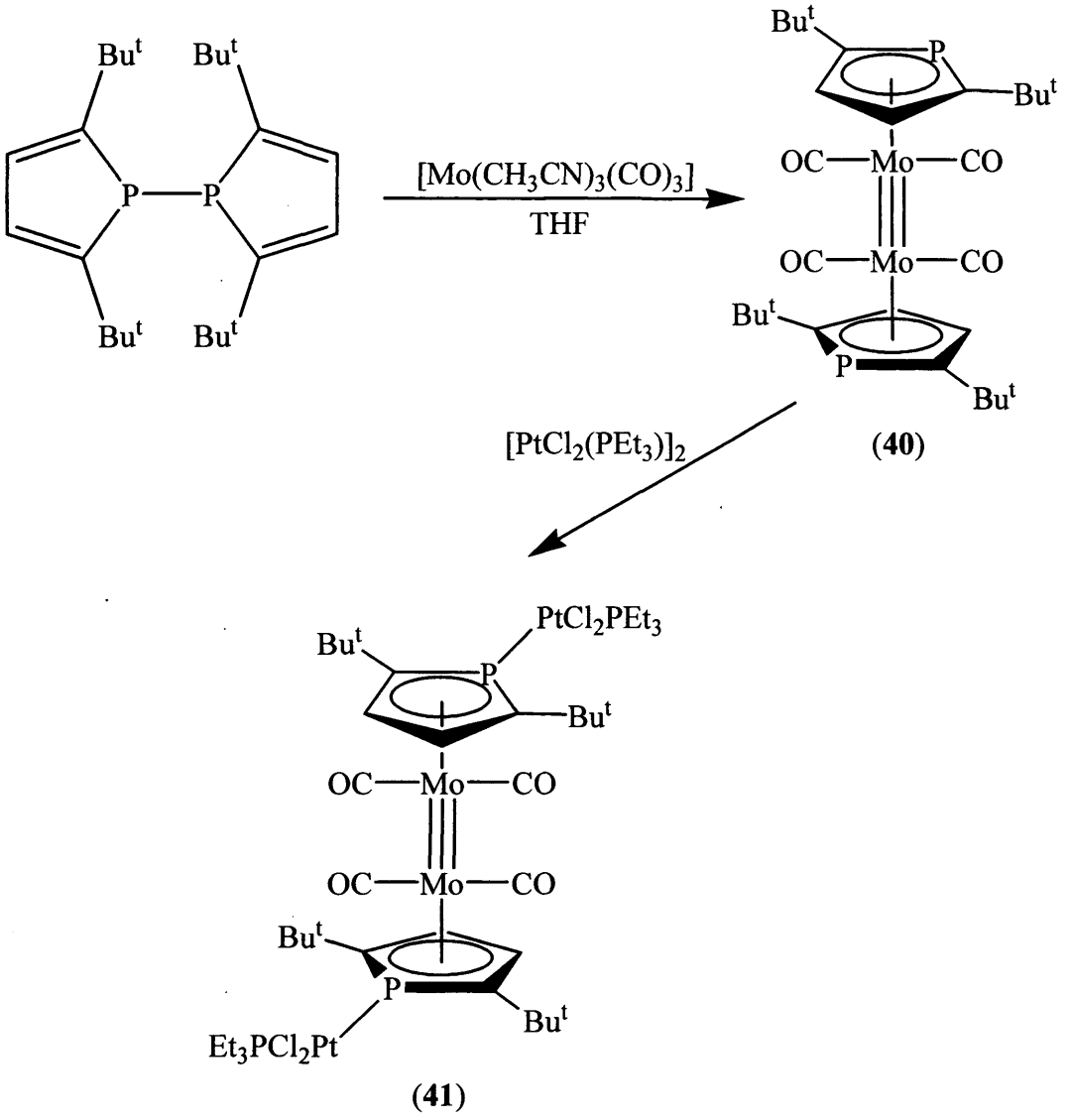
The synthesis of phospholyl complexes of the rare earth metals yttrium and lutetium was described by *Nief* and *Mathey* in 1989 (Scheme 4.22).[42] No π-hetero-cyclopentadienyl complexes of the rare earths had been previously been reported. Though none of the complexes were structurally characterised, the η^5-co-ordination of the phospholyl ligand was established from the large $^1J_{PC}$ coupling of around 45 Hz in (**37**) and (**38**). The magnitude of this coupling is similar to that of 49 Hz observed in the related zirconium complex, $[Zr(\eta^5\text{-}PC_4Me_4)_2Cl_2]$, which has been structurally characterised.[43]



(**37**) M = Y, solv = DME
(**38**) M = Lu, solv = Et_2O
solv = solvent used to recrystallise product

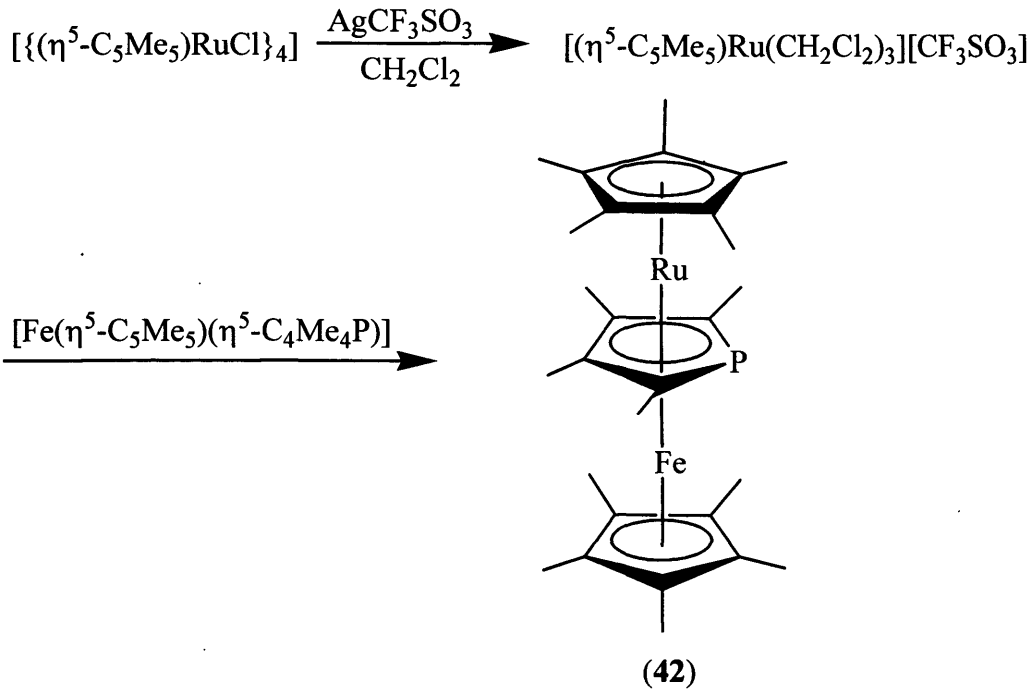
Scheme 4.22 Synthesis of two phospholyl complexes of the rare earths yttrium and lutetium

It was shown in theoretical studies that the negative charge of phospholyl anions is partially localised on the phosphorus centre.[44] This means that the initial interaction of a phospholyl anion with a transition metal electrophile involves attack at phosphorus and thus the "softer", heavier transition metals are more likely to form η^1- rather than η^5-complexes. *Mathey et al.* overcame this tendency by using the 2,5-di-*tert*-butylphospholyl anion (**39**) in which the phosphorus centre is sterically crowded.[45] The reaction of the bis-phosphole precursor of (**39**) with 1.3 equivalents of $[Mo(CH_3CN)_3(CO)_3]$ in THF led to the unusual complex (**40**) which contains a metal-metal triple bond. The reaction of (**40**) with $[\{PtCl_2(PEt_3)\}_2]$ led to the formation of complex (**41**) displaying type **E** ligation, despite the sterically crowded phosphorus lone pairs (Scheme 4.23).[46]



Scheme 4.23 Preparation of an η^5:η^1-phospholyl complex

Phospholyl anions can also act as bridging ligands in triple decker complexes. This was shown by *Herberich* and *Ganter* who obtained a cationic 30 valence electron triple decker complex (**42**) upon the reaction of [Ru(η^5-C_5Me_5)(solv)$_3$], (solv = DCM, acetone), with phospha-ferrocene (Scheme 4.24).[47]

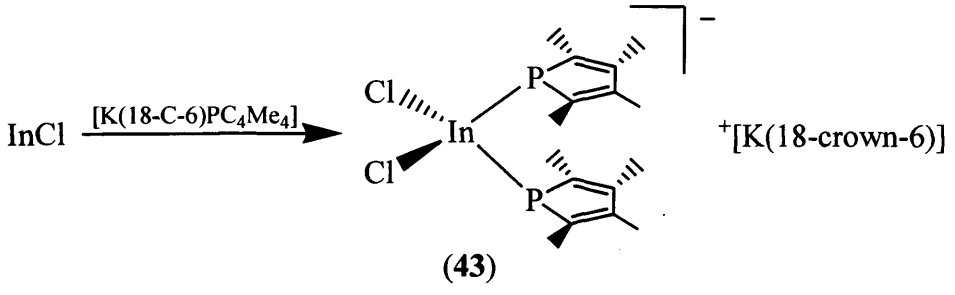


Scheme 4.24 Formation of the phospholyl triple decker complex (42)

4.1.4.2 Co-ordination of phospholyl ring anions to main group metals

Although many complexes of phospholyl anions involving transition metals have been reported, examples of p-block main group metal complexes are less common, as are alkali metal complexes.[24, 48]

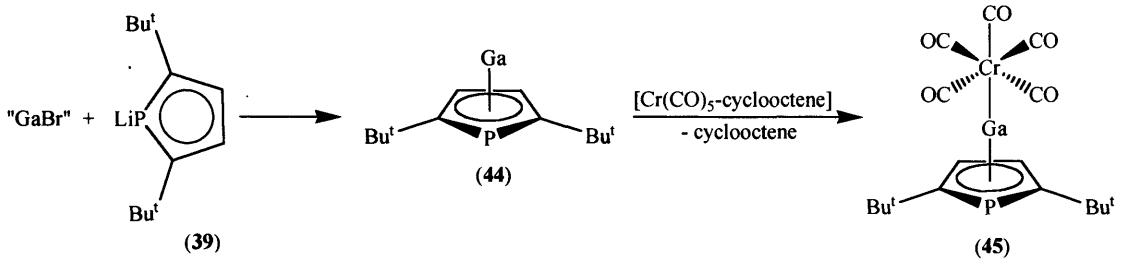
A phospholyl complex of indium has been reported in 1990.[49] The reaction of [K(18-crown-6)(PC_4Me_4)] with InCl led to the formation of [K(18-crown-6)][(Me_4C_4P)$InCl_2$] (**43**) (Scheme 4.25). It is believed that (**43**) was formed upon decomposition of the initially formed desired indium(I) derivative [(Me_4C_4P)In] by a disproportionation process.



Scheme 4.25 Preparation of an indium phospholyl complex

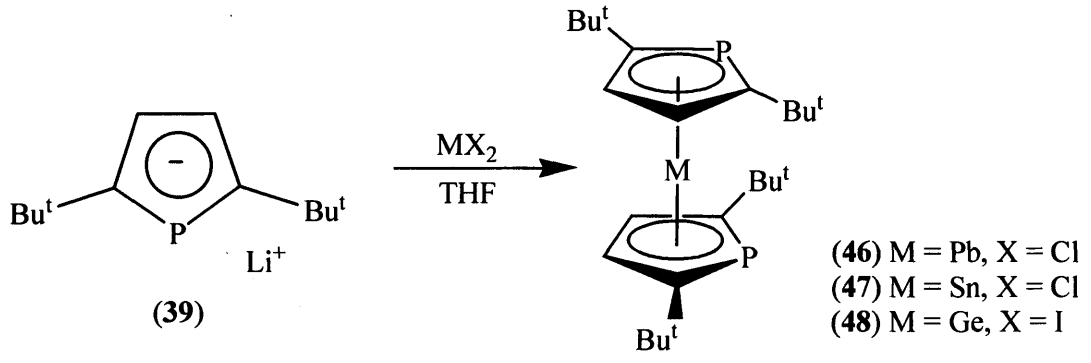
4.1 Introduction

The first monomeric polyhapto compound between a phospholyl anion and a main group metal was reported by *Mathey et al.* in 1999. The reaction of a metastable solution of GaBr with lithium 2,5-bis(*tert*-butyl)phospholide (**39**) yielded the η^5-phospholylgallium compound (**44**) (Scheme 4.26).[50] Compound (**44**) was characterised by NMR spectroscopy and mass spectrometry and later by an X-ray crystallographic study.[51] Its subsequent reaction with [$Cr(CO)_5$-cyclooctene] yielded the anticipated crystalline η^5-phospholylgallium(I) chromium pentacarbonyl compound (**45**).[50]



Scheme 4.26 Preparation of an η^5-phospholylgallium(I) chromium pentacarbonyl complex

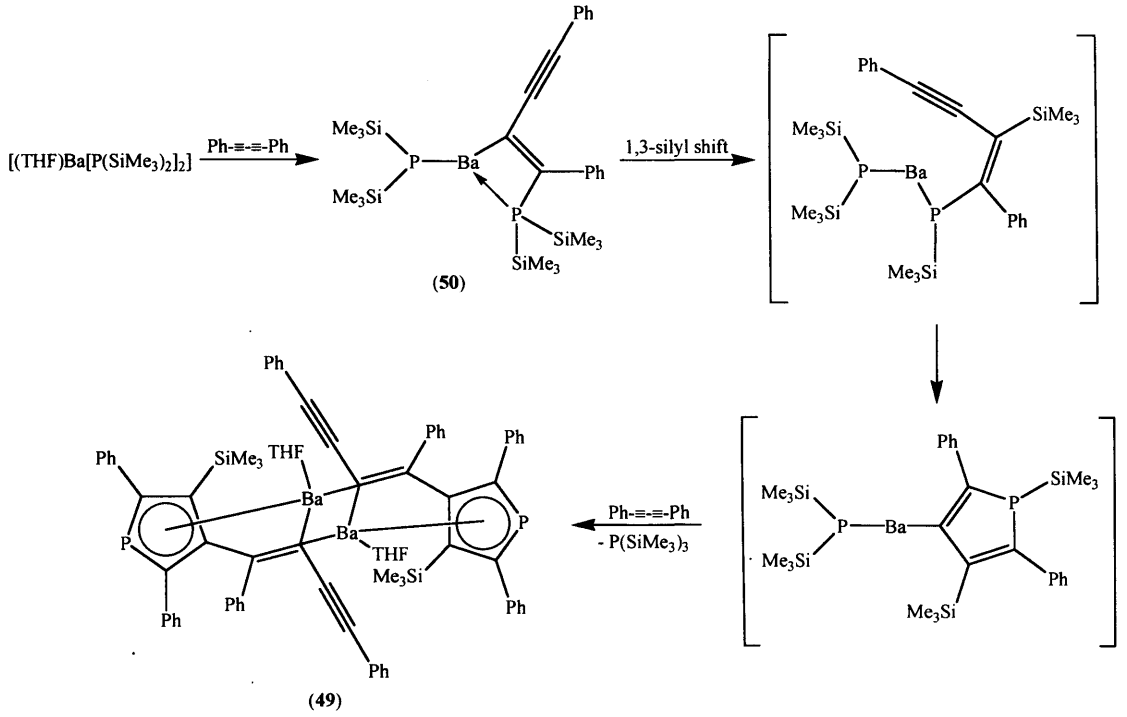
Several group 14 phospholyl sandwich complexes were reported by *Mathey et al.* in the same year.[52] Compounds (**46**) and (**47**) have been prepared by the reaction of (**39**) with the corresponding metal dichloride while (**48**) was prepared from GeI_2. X-ray crystallographic studies were carried out on (**46**) and (**47**) which showed extensive delocalisation within the heterocycle. This is supported by the observed large intracyclic $^1J_{PC}$ coupling constants ((**46**) = 51.4 Hz, (**47**) = 48.5 Hz and (**48**) = 47.0 Hz). The phospholyl rings were found to be planar and to bond *via* η^5-co-ordination to the metal/metalloid centre.[52]



Scheme 4.27 Preparation of some phospholyl sandwich complexes containing group 14 elements

4.1 Introduction

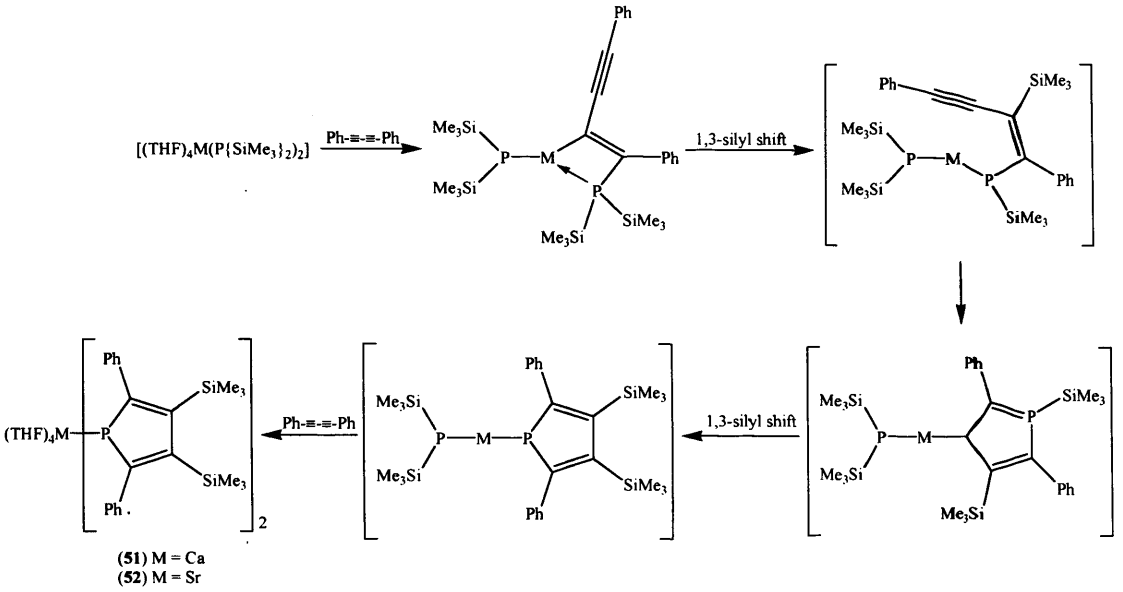
Westerhausen et al. reported the synthesis of a group 2 phospholyl compound.[53] The dimeric compound (**49**) was obtained from the reaction of $[(THF)Ba\{P(SiMe_3)_2\}_2]$ with diphenylbutadiyne in toluene. A reaction mechanism was proposed and is shown in Scheme 4.28.



Scheme 4.28 Proposed reaction mechanism for the formation of (49)

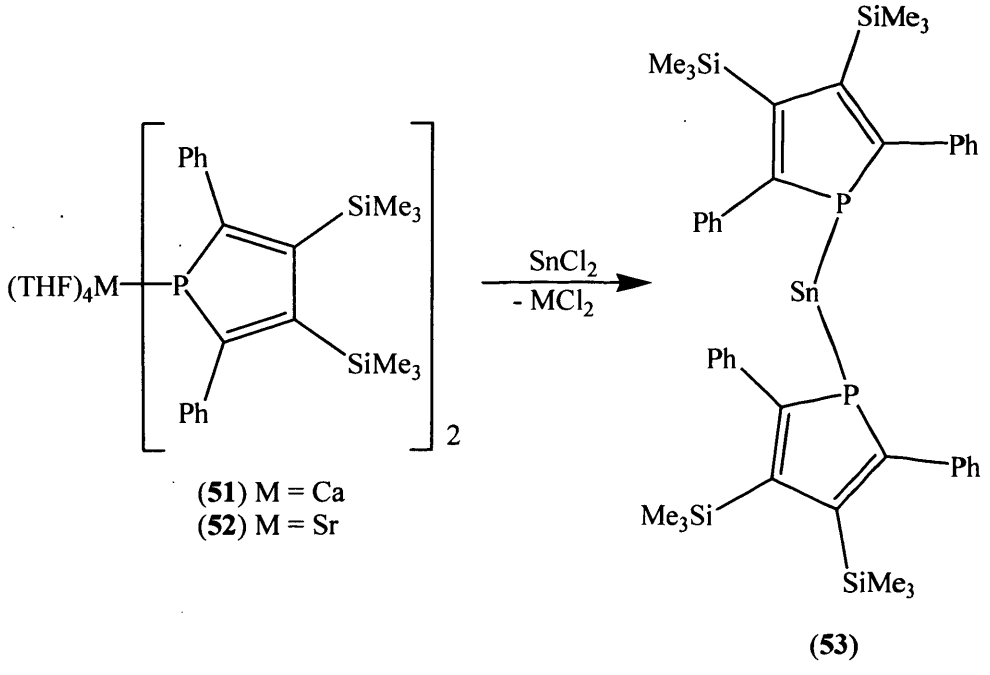
This mechanism was supported by the fact that the magnesium analogue of the intermediate, (**50**), could be isolated in the related reaction of $[Mg\{P(SiMe_3)_2\}_2]$. Compound (**49**) was found to be highly air- and moisture sensitive. Furthermore, its decomposition was observed when the neutral co-ligand THF was removed in vacuo to leave the barium centre in a low co-ordinate state.[53]

The same group reported further phospholyl compounds of other members of group 2, namely Ca and Sr.[54] In a similar approach to the preparation of (**49**), $[(THF)_4M\{P(SiMe_3)_2\}_2]$ (M = Ca, Sr) were reacted with diphenylbutadiyne. The proposed reaction mechanism is shown in Scheme 4.29.



Scheme 4.29 Proposed reaction mechanism for the formation of (51) and (52)

It was also shown that the η^1-bonded species (**51**) and (**52**) can be used as transfer reagents for the sterically shielded phosphacyclopentadienide ligand. The metathesis reaction of two equivalents of (**51**) or (**52**) with $SnCl_2$ in THF yielded the first structurally characterised 1,1'-diphosphastannocene (**53**) (Scheme 4.30). The molecular structure shows clearly that the phospholide heterocycles in (**53**) are not η^5-bonded to the tin(II) centre but η^1-ligated.[54]

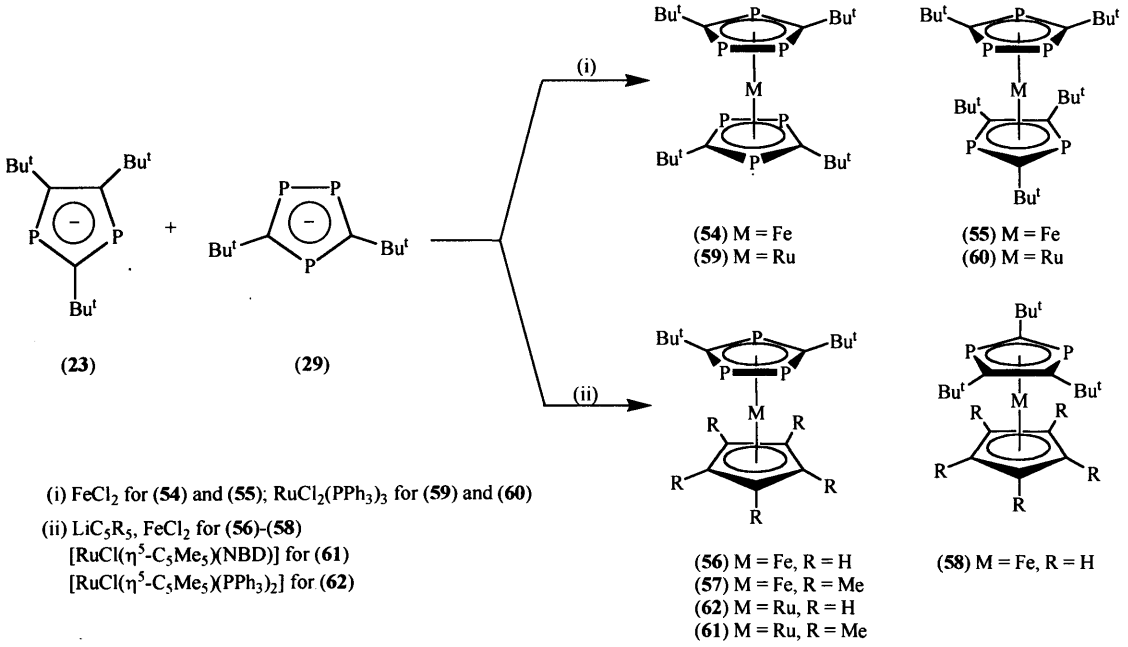


Scheme 4.30 Preparation of a 1,1'-diphosphastannocene (53)

4.1.5 Co-ordination chemistry of polyphospholyl anions

4.1.5.1 Co-ordination of polyphospholyl ring anions to transition metals

Polyphospholyl anions show, like their monosubstituted counterparts, several co-ordination modes. η^5 and η^5:η^1-complexes are common and η^1-complexes have also been reported. Of special interest are the 3,5-di-*tert*-butyl-1,2,4-triphospholyl (**29**) and 2,4,5-tri-*tert*-butyl-1,3-diphospholyl (**23**) anions. As shown in Scheme 4.14 and Scheme 4.10 compound (**23**) and (**29**) are readily available from P≡CBu^t (**30**) or 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**15**). Compounds (**23**) and (**29**) have been used in the preparation of a variety of compounds such as polyphospha-ferrocenes (**54**)-(**58**)[55-57] and -ruthenocenes (**59**)-(**62**)[58] (Scheme 4.31).



(i) $FeCl_2$ for (**54**) and (**55**); $RuCl_2(PPh_3)_3$ for (**59**) and (**60**)
(ii) LiC_5R_5, $FeCl_2$ for (**56**)-(**58**)
$[RuCl(\eta^5\text{-}C_5Me_5)(NBD)]$ for (**61**)
$[RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)_2]$ for (**62**)

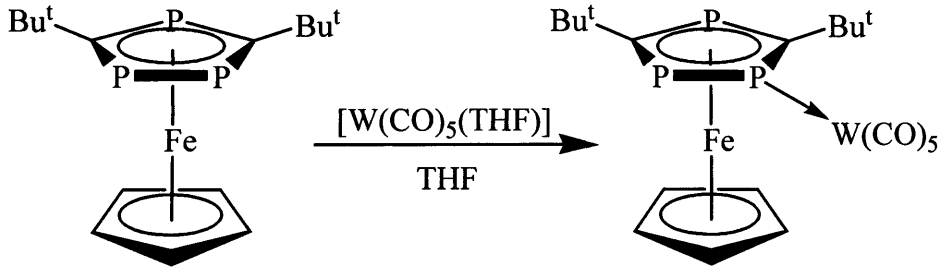
Scheme 4.31 Preparation of several polyphospha-ferrocenes and -ruthenocenes

A general observation which is made for phospholyl and polyphospholyl anions upon complexation is an upfield shift for the ^{31}P NMR resonances. The $^{31}P\{^1H\}$ NMR spectrum of (**56**) displays a triplet at 38.9 ppm and a doublet at 37.9 ppm whereas the free anion (**29**) shows a triplet at 247.7 ppm and a doublet at 243.5 ppm. Presumably this is the result of π electron density donation from the phospholyl anion to the metal upon co-ordination resulting in the reduction of the bond order of the bonds within the ring. This also is supported by the fact that, generally, an increase in the bond length within the ring is observed upon co-ordination. Similar

trends in P-C bond lengths and $^{31}P\{^{1}H\}$ NMR resonances are observed upon co-ordination of phosphaalkenes to transition metal fragments.[27]

The hexaphospha-ruthenocene (**59**) undergoes a fluxional process in solution which was analysed using variable temperature $^{31}P\{^{1}H\}$ NMR spectroscopy. At room temperature an $(AB_2)_2$ multiplet was observed which resolves into an AA'BB'CC' system at - 50 °C. This dynamic process corresponds to the rotation of the triphospholyl rings about the metal-ring centroid axis. A coupling of 37.5 Hz is observed at - 50 °C and is believed to originate from a "through space" inter-ring interaction between the two phosphorus centres which have become eclipsed upon cessation of the dynamic process.[58]

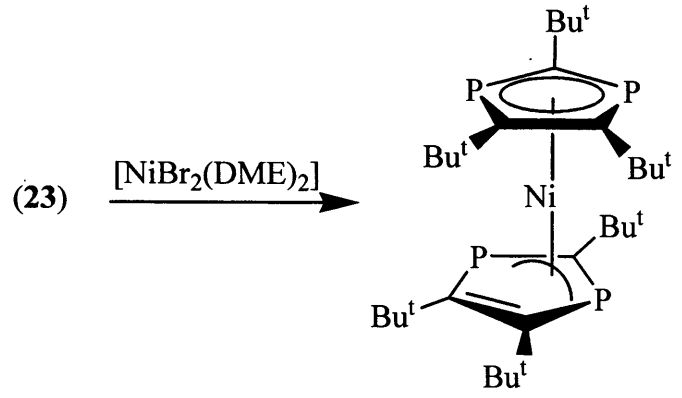
A complex featuring simultaneous η^5 and η^1-co-ordination was obtained when (**56**) was treated with a solution of $[W(CO)_5(THF)]$ (Scheme 4.32).[56] This complex highlights the ability of phosphametallocenes to form heterobimetallic complexes.



(**56**)

Scheme 4.32 Synthesis of an η^5:η^1-complex of the triphospha-ferrocene (56)

A different mode of co-ordination for (**23**) was seen when a solution of $[NiBr_2(DME)_2]$ was treated with a solution of the sodium salt of (**23**). This led not to the expected 20 electron tetraphospha-nickelocene, but to an 18 electron diamagnetic species, (**63**), containing one η^5- and one η^3-co-ordinated ring (Scheme 4.33).[59]

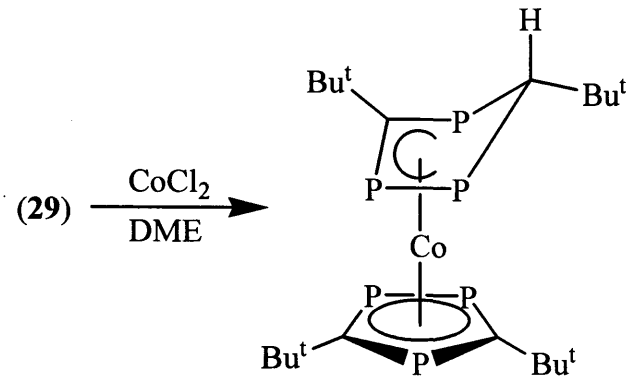


(63)

Scheme 4.33 Synthesis of an η^3:η^5-bis-diphospholyl complex of nickel

Compound (**63**) shows fluxional behaviour in solution as evidenced by its variable temperature $^{31}P\{^1H\}$ NMR spectra. This displays a sharp singlet at room temperature which resolves into four broad singlets at - 90 °C. Suggestions were made that a "ring-slippage" mechanism occurs *via* a 16 electron intermediate in which both rings are η^3-bond. The comparable complex $[Ni(\eta^5\text{-}P_3C_3Bu^t_2)(\eta^3\text{-}P_2C_3Bu^t_3)]$ also shows η^5:η^3-bonding but in contrast to (**63**) no fluxional behaviour was seen in solution. The inability of the triphospholyl ring (**29**) to η^3-bond was used to explain this difference.[60]

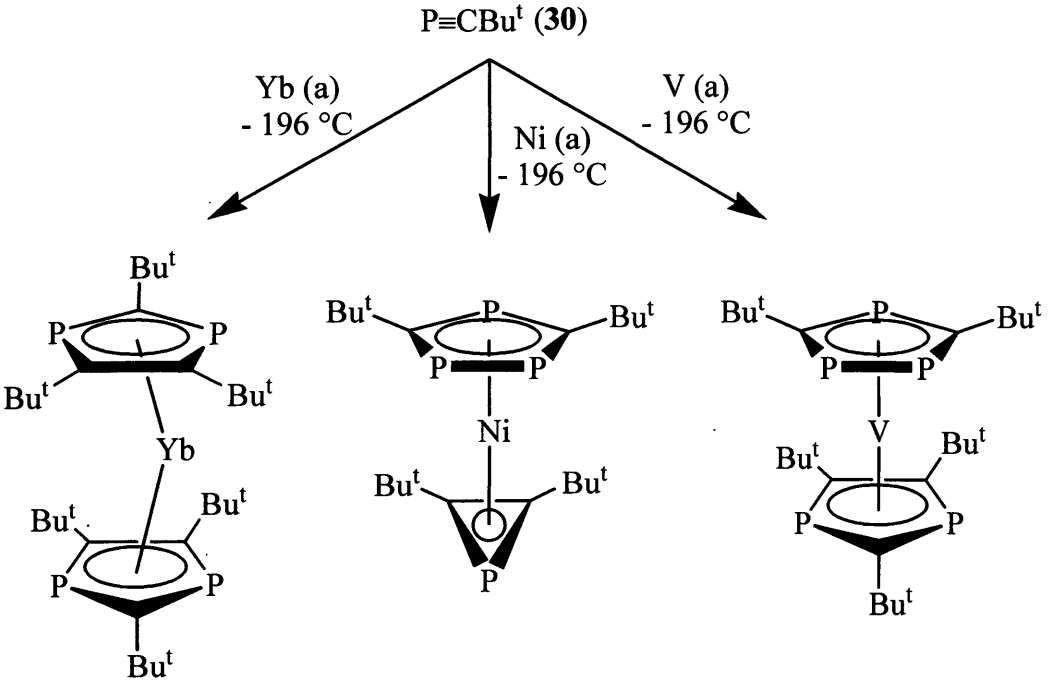
An unusual result was obtained when the lithium salt of (**29**) was reacted with $CoCl_2$. This led to the formation of (**64**), in which proton abstraction from the solvent was believed to have occurred. Compound (**64**) displays a planar η^5-bound ring and a non-planar η^4-ligated ring. The η^4-bound ring shows phosphorus-carbon and phosphorus-phosphorus bond lengths which are consistent with delocalisation over the four ligating atoms (Scheme 4.34).[61]



(64)

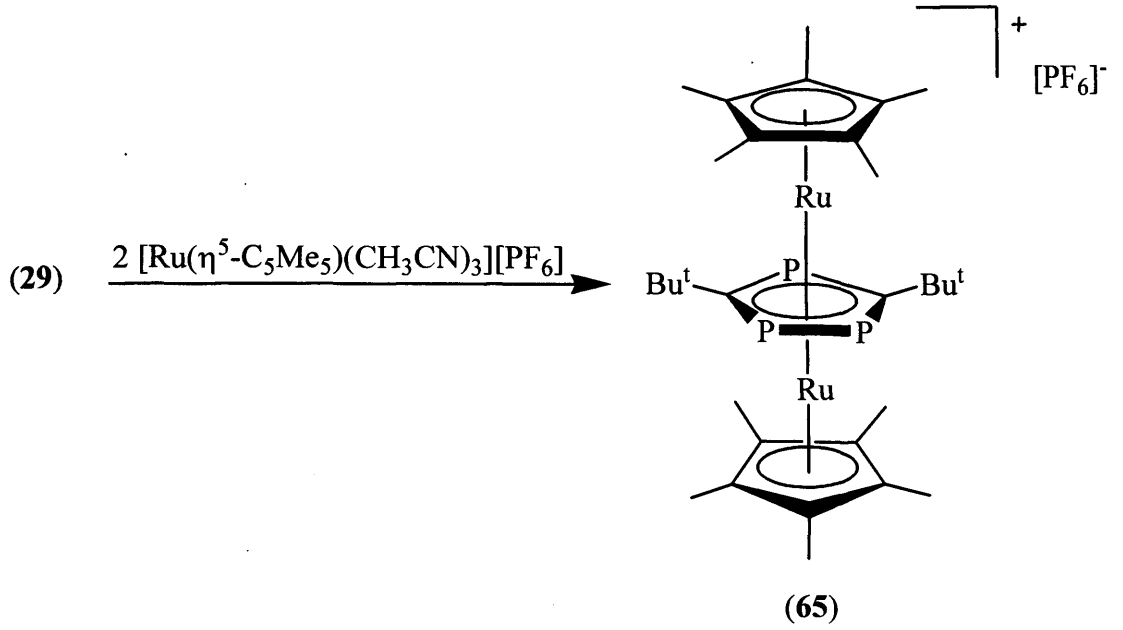
Scheme 4.34 Synthesis of an η^4:η^5-triphosphole, triphospholyl complex of cobalt

It is worthy of note that complexes of (**23**) and (**29**) have been prepared by the co-condensation of (**30**) with metal atoms, generated by metal vapour synthesis technique (MVS), at - 196 °C. Some examples are shown in Scheme 4.35.[62-64]



Scheme 4.35 Preparation of several transition metal-polyphospholyl complexes by MVS

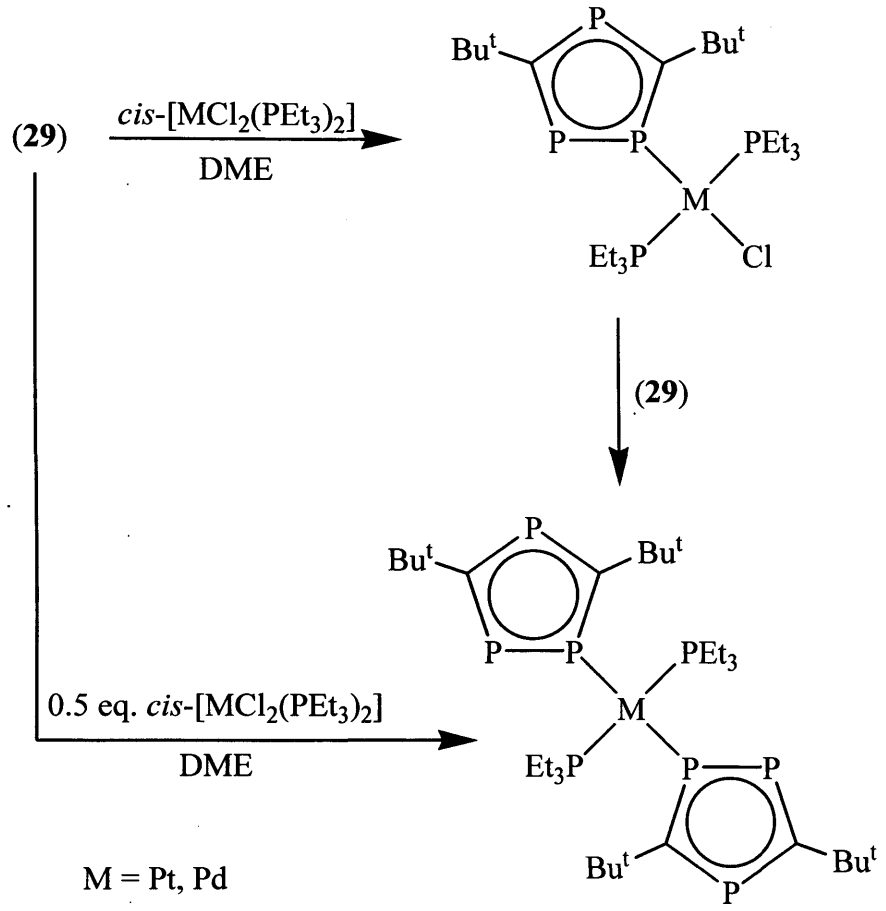
It was shown by *Nixon et al.* that the triphospholyl anion (**29**) can act as a bridging η^5-ligand in the formation of a triple decker complex. The reaction of (**29**) with two equivalents of $[Ru(\eta^5\text{-}C_5Me_5)(CH_3CN)_3][PF_6]$ in DME leads to the orange triple decker complex (**65**) (Scheme 4.36). Compound (**65**) was characterised spectroscopically as well as by an X-ray crystallographic study.[64]



(65)

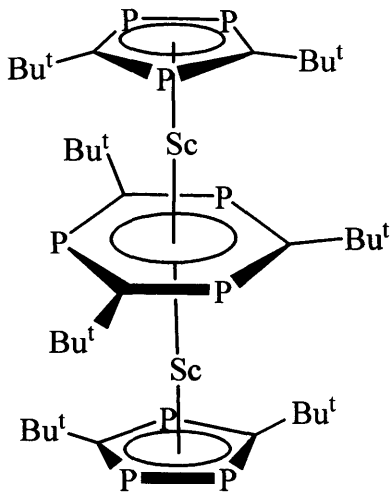
Scheme 4.36 Synthesis of a triple decker complex of the triphospholyl anion (29)

Solely η^1-co-ordination can occur in complexes of (**29**) as shown in the crystalline complexes *trans*-[MCl(η^1-$P_3C_2Bu^t_2$)(PEt_3)$_2$] and *trans*-[M(η^1-$P_3C_2Bu^t_2$)$_2$(PEt_3)$_2$] (M = Pt, Pd) which were obtained from the reaction of one or two equivalents of (**29**) with *cis*-[$MCl_2(PEt_3)_2$] respectively. The bis-triphospholyl complexes can also be prepared from the reaction of the mono-phospholyl complexes with (**29**) (Scheme 4.37).[65] All complexes seem to show a fluxional process in solution in which the metal undergoes a 1,2-intramolecular shift between the two adjacent phosphorus centres.



Scheme 4.37 η^1-co-ordination of the triphospholyl anion (29)

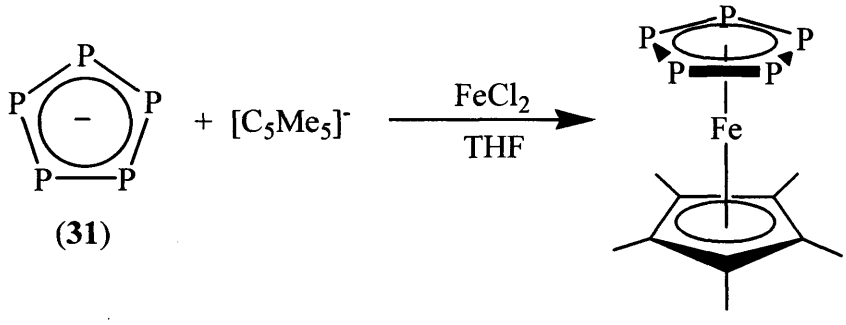
Anion (**29**) has also been used to stabilise compounds incorporating elements in unusual oxidation states. One example, in which the triphospholyl ring forms the outer layer of a 22-valence-electron triple decker Sc(I) complex was reported by *Nixon et al.* in 1996 and is shown in Figure 4.3.[66] Compound (**66**) was formed by co-condensation of scandium vapour with (**30**).



(66)

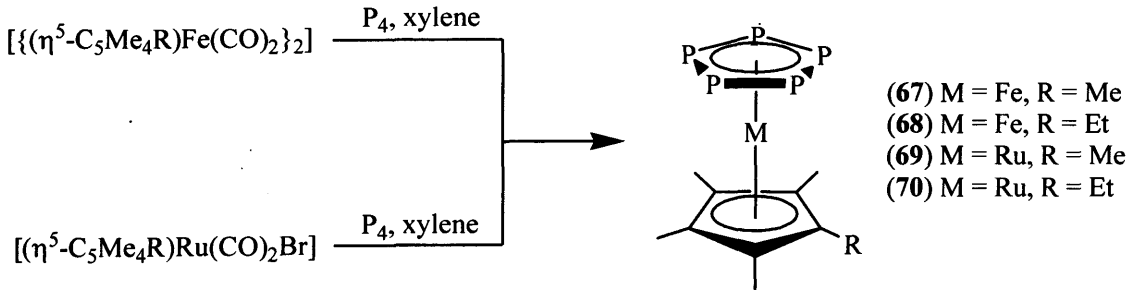
Figure 4.3 Unusual 22-valence-electron triple decker Sc(I) complex (66)

A lot of attention has been directed towards the pentaphospholyl anion (**31**). η^5-complexes of (**31**) have been prepared directly from the anion (Scheme 4.38)[67] as well as by an indirect route involving white phosphorus (Scheme 4.39).[68, 69]



(31) (67)

Scheme 4.38 Synthesis of a pentaphospha-ferrocene (67)

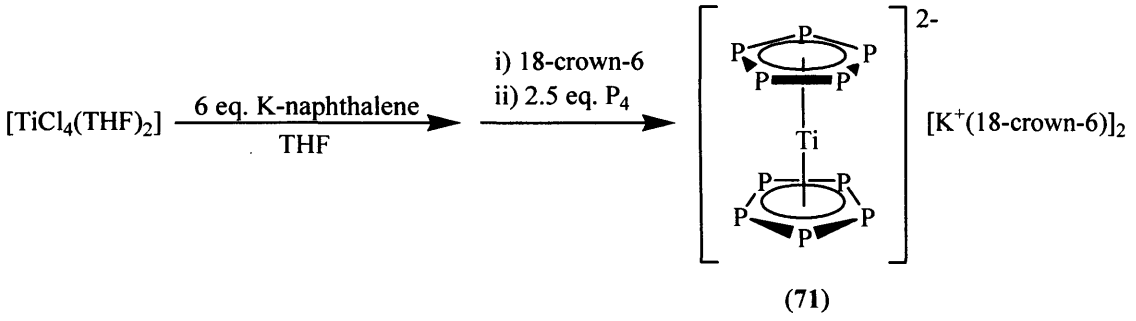


(67) M = Fe, R = Me
(68) M = Fe, R = Et
(69) M = Ru, R = Me
(70) M = Ru, R = Et

Scheme 4.39 Synthesis of several pentaphospha-ferrocenes and -ruthenocenes (67) - (70)

It is worthy to note that the decaphospha-ferrocene $[Fe(\eta^5\text{-}P_5)_2]$ has not been prepared and theoretical investigations suggest that this compound would not be stable due to a thermodynamic preference for the bis-η^1-isomer.[70] Recent theoretical investigations of ferrocene derivates with group 15 hetero-ligands, $[Fe(\eta^5\text{-}E_5)_2]$ and $[FeCp(\eta^5\text{-}E_5)]$ (E = N, P, As, Sb), concluded that the most stable species is the pentaphospha derivative.[71]

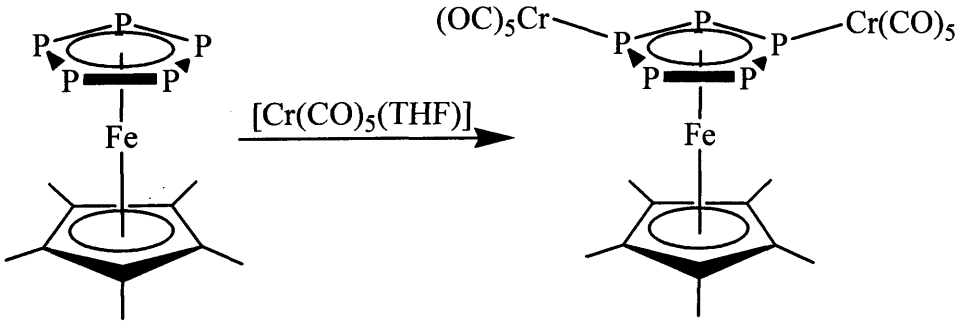
Very recently, a stable decaphospha-titanocene dianion, (**71**), was described.[72] Compound (**71**) is diamagnetic and has a sandwich structure with an angle of 1.5° between the planes. The existence of the $[Cp_2Ti]^{2-}$ ion is unknown, which demonstrates the great potential of phospholyl groups in the stabilisation of metal centres in low oxidation states.



(**71**)

Scheme 4.40 Preparation of a decaphospha-titanocene dianion (71)

It was demonstrated by *Scherer et al.* that (**31**) can act as a secondary donor *via* its phosphorus lone pairs after forming a sandwich complex with iron. Consequently, the reaction of (**67**) with a solution of $[Cr(CO)_5(THF)]$ leads to the formation of the η^5:η^1-complex (**72**) (Scheme 4.41).[73]

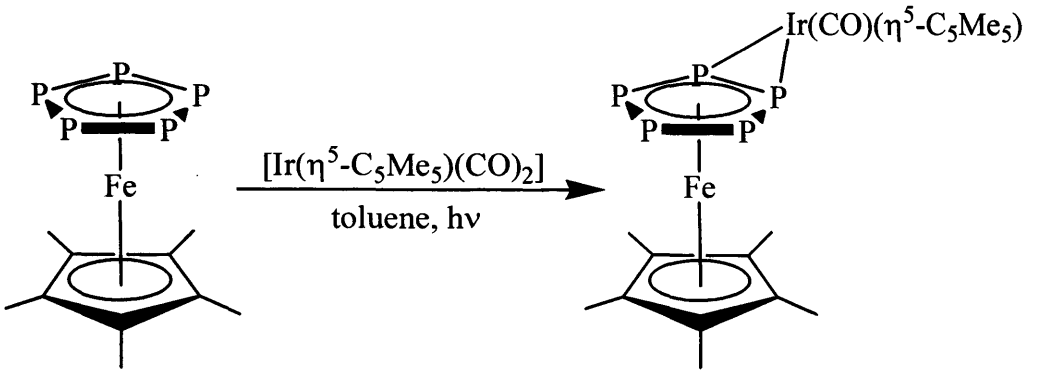


(**67**) (**72**)

Scheme 4.41 Synthesis of an η^1:η^5-complex of the pentaphospholyl anion (31)

4.1 Introduction

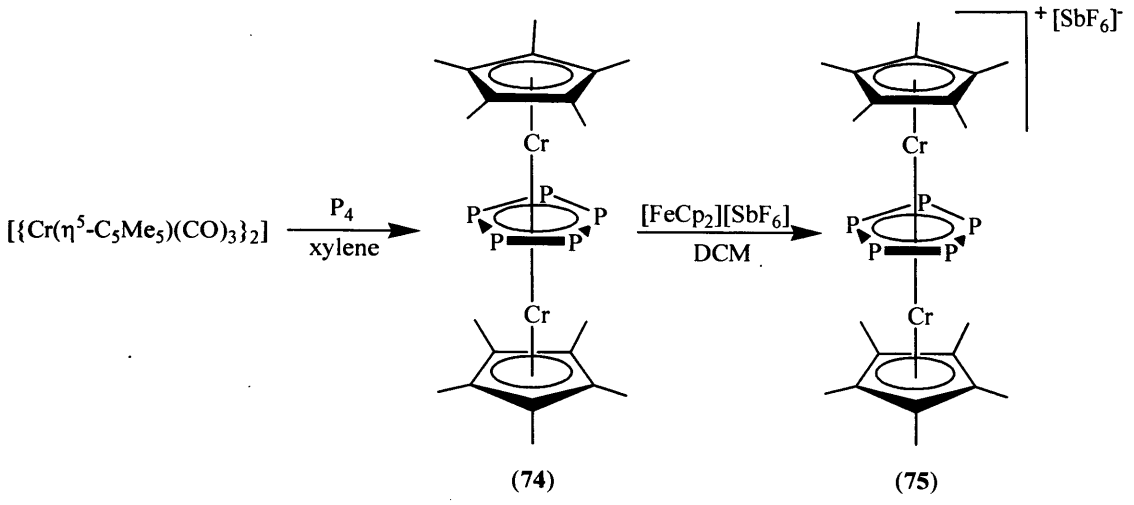
The reaction of (**67**) with $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ leads to complex (**73**) in which the unusual situation of simultaneous η^2:η^5-co-ordination is seen (Scheme 4.42).[74] No explanation was given for this unusual co-ordination mode which had never been previously observed in ferrocene chemistry.



(**67**) (**73**)

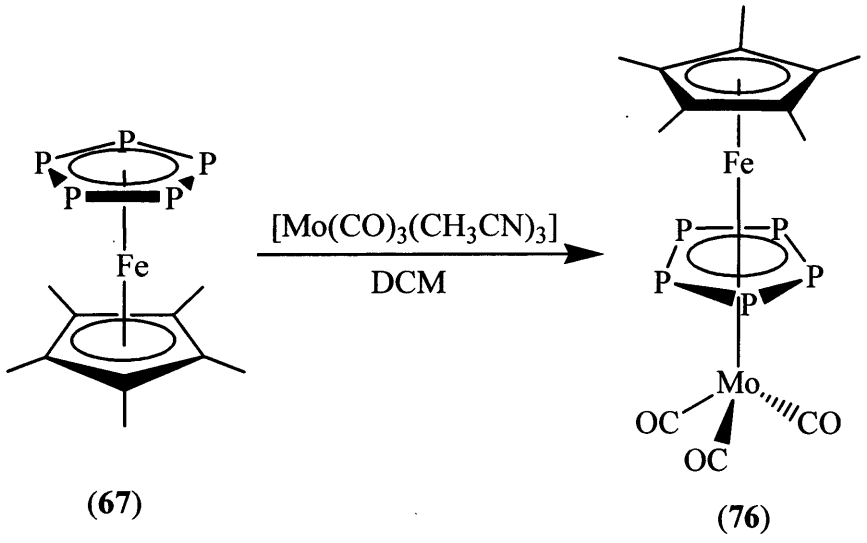
Scheme 4.42 Synthesis of an η^2:η^5-complex of the pentaphospholyl anion (31)

Different routes have been applied to prepare several neutral and ionic triple decker complexes of (**31**). *Scherer et al.* synthesised the neutral 27 valence electron triple decker complex (**74**), first from the reaction between $[\{Cr(\eta^5\text{-}C_5Me_5)(CO)_3\}_2]$ and white phosphorus in about 8 % yield.[75] The overall yield was later improved to about 60 % by *O'Hare et al.* by a modification of Scherer's procedure.[76] Additionally they were able to isolate the ionic triple decker complex (**75**), formed by a reversible one electron oxidation of (**74**), and structurally characterise it (Scheme 4.43). Significant lengthening of the Cr-Cr vector on going from (**74**) (2.729 Å) to (**75**) (3.185 Å) was observed. This was explained by the assumption that the oxidation of (**74**) occurs *via* removal of an electron from a Cr-Cr bonding orbital.



Scheme 4.43 Synthesis of a homobimetallic triple decker complex of (31)

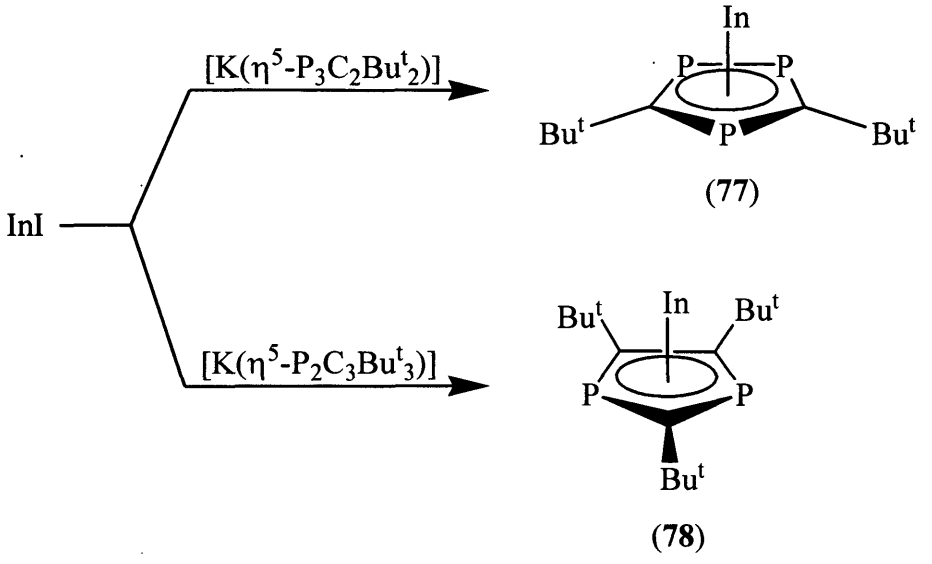
An alternative synthetic route to triple decker complexes employs stacking reactions of sandwich complexes of (**31**). An example of these reactions is that of (**67**) with $[Mo(CO)_3(CH_3CN)_3]$ in CH_2Cl_2. This leads to the mixed metal triple decker complex (**76**) in about 50 % yield (Scheme 4.44).



Scheme 4.44 Synthesis of a mixed metal triple decker complex of (31)

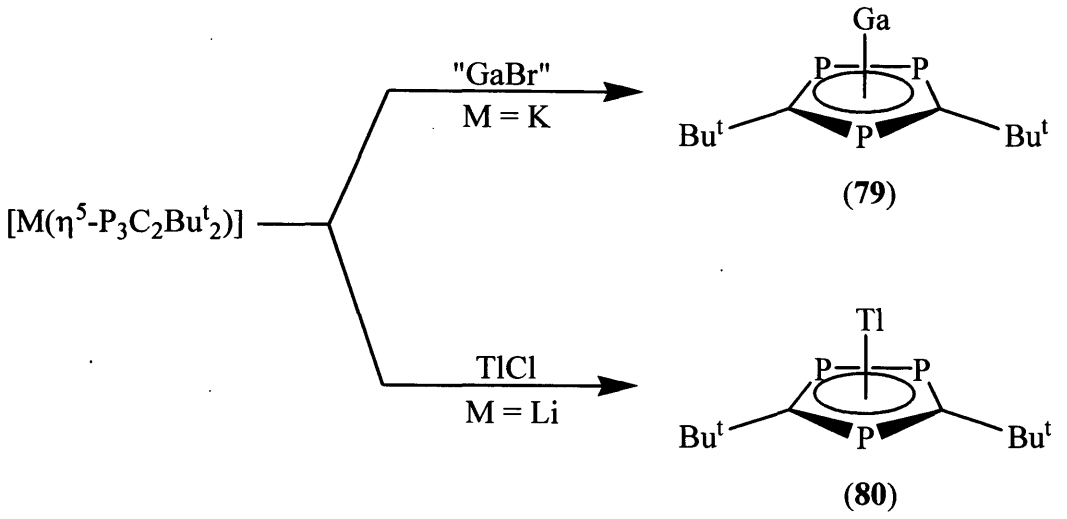
4.1.5.2 Co-ordination of polyphospholyl ring anions to main group metals

In recent years several examples of main group metal polyphospholyl compounds have been published. *Nixon et al.* reported the synthesis and X-ray crystal structure of $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$ (**77**).[77] Co-condensation of indium vapour and (**30**) at 77 K afforded a brown oil from which (**77**) could be isolated by sublimation and subsequent recrystallisation from toluene or petroleum ether. In addition, compound (**77**) could be synthesised in near quantitative yield by refluxing InI and the base free ligand salt $[K(P_3C_2Bu^t_2)]$ in toluene for 24 h. The same group reported the synthesis and structure of $[In(\eta^5\text{-}P_2C_3Bu^t_3)]$ (**78**) employing the same methodology.[78]



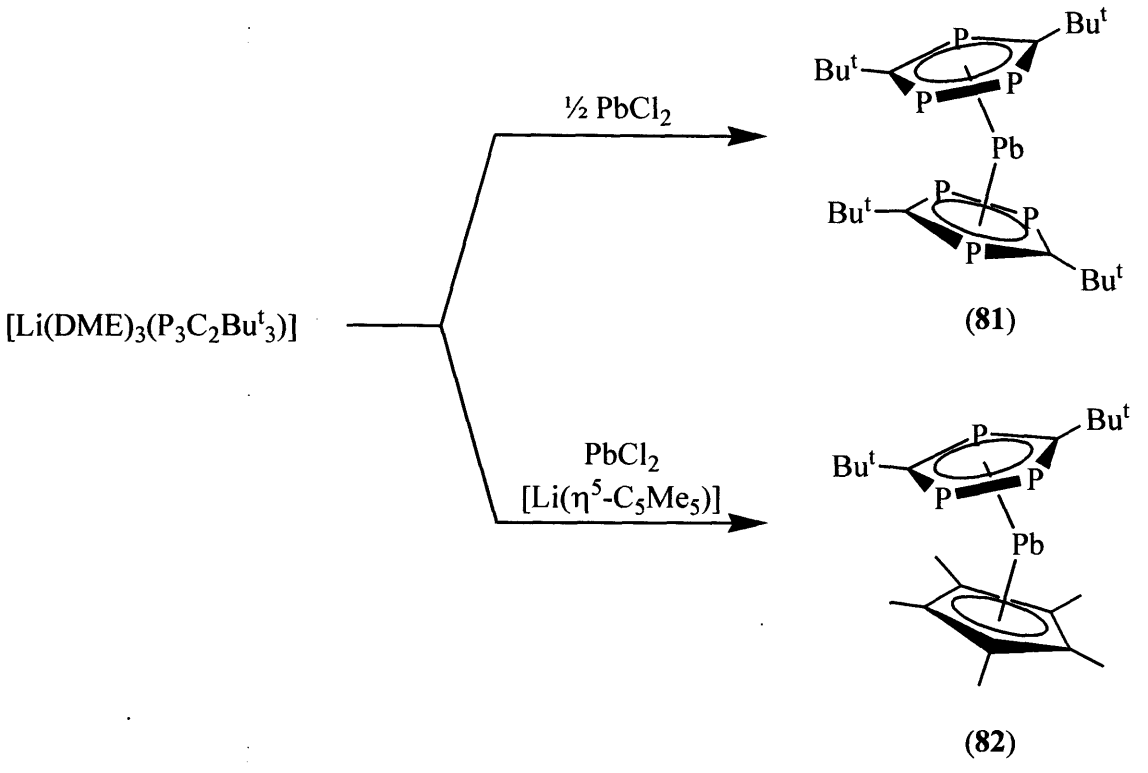
Scheme 4.45 Preparation of $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$ (77) and $[In(\eta^5\text{-}P_2C_3Bu^t_3)]$ (78)

This work was then extended to other members of group 13, *i.e.* Ga and Tl.[79] The reaction of $[K(P_3C_2Bu^t_2)]$ with a metastable solution of GaBr yielded $[Ga(\eta^5\text{-}P_3C_2Bu^t_2)]$ (**79**) quantitatively, while the related reactions with thallium halides only resulted in the precipitation of thallium metal and mixtures of neutral organo-phosphorus cage materials. To overcome this problem the lithium salt of the phospholyl anion was used. This resulted in the formation of $[Tl(\eta^5\text{-}P_3C_2Bu^t_2)]$ (**80**) (Scheme 4.46).



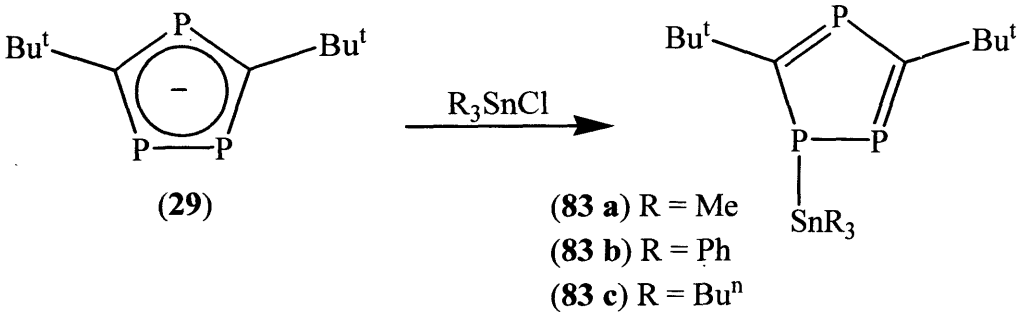
Scheme 4.46 Preparation of $[Ga(\eta^5\text{-}P_3C_2Bu^t_2)]$ (79) and $[Tl(\eta^5\text{-}P_3C_2Bu^t_2)]$ (80)

A novel triphospholyl lead(II) complex was described in 1999.[80] The reaction of anhydrous $PbCl_2$ with two equivalents of the lithium salt of the triphospholyl anion (**29**) yielded $[Pb(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (**81**) in a 48 % yield. Compound (**81**) was identified by NMR spectroscopy and mass spectrometry. The observation of an $[AB_2]_2$ pattern in the $^{31}P\{^1H\}$ NMR spectrum of the complex and the magnitude of the $^1J_{PbP}$ coupling favours an η^5-bonding mode for the heterocycles rather than η^1-co-ordination. A similar synthetic approach using an equimolar mixture of $[Li(DME)_3(P_3C_3Bu^t_2)]$ and $[Li(\eta^5\text{-}C_5Me_5)]$ with a slurry of $PbCl_2$ in THF yielded the heteroleptic complex $[Pb(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ (**82**). Compound (**82**) could be crystallised and an X-ray crystallographic study was carried out which showed (**82**) to be a bent monomeric sandwich complex. The centroid-lead-centroid angle was determined to be 142.2°.[80]



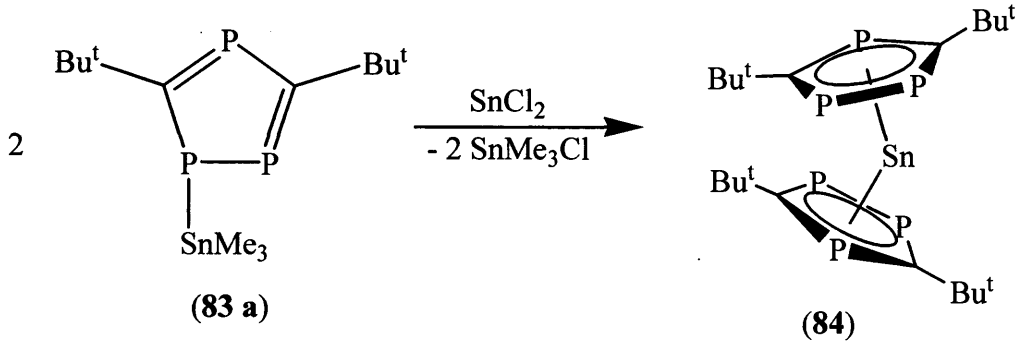
Scheme 4.47 Preparation of novel polyphospha plumbocenes

A 1-triorganylstannyl-1,2,4-triphosphole was reported by *Zenneck et al.* in 1999.[81] The reaction of $[Na(P_3C_2Bu^t_2)]$ with R_3SnCl (R = Me, Ph, Bu^n) yielded the 1-stannyl-3,5-di-*tert*-butyl-1,2,4-triphospholes (**83 a-c**) nearly quantitatively.



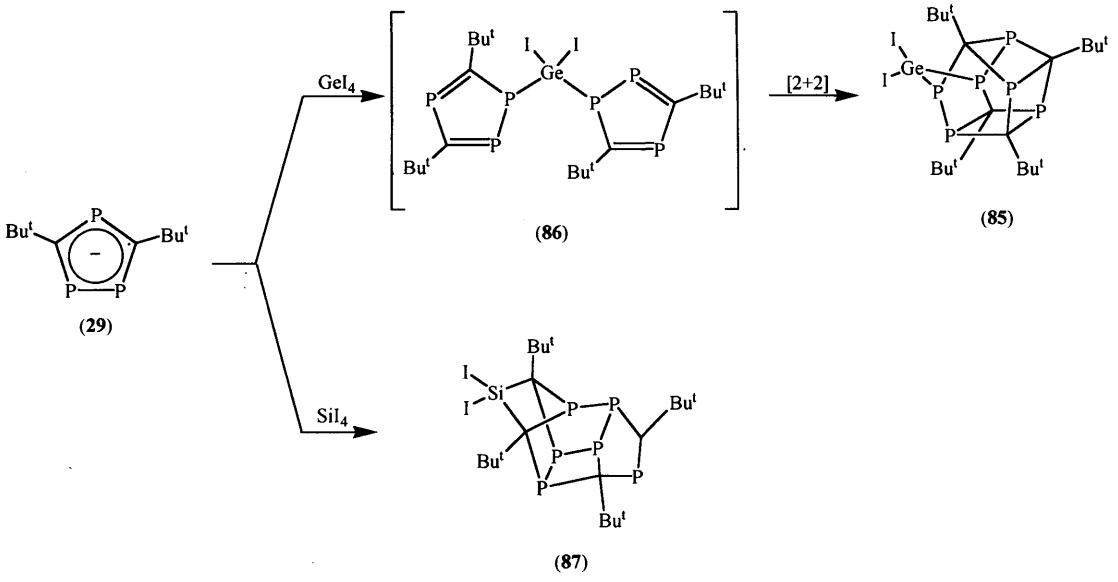
Scheme 4.48 Preparation of some 1-triorganylstannyl-1,2,4-triphospholes

Compound (**83 a**) was reacted with $SnCl_2$ to yield the sandwich compound (**84**) in 98 % yield. Due to the fact that no crystal structure was obtained, it could not be certain if this stannocene is bent or consists of parallel rings (Scheme 4.49).[81] The preparation and structural characterisation of the tin analogue of (**82**) has been mentioned in a review by *Nixon* but so far has not been published.[62]



Scheme 4.49 Preparation of a hexaphosphastannocene (84)

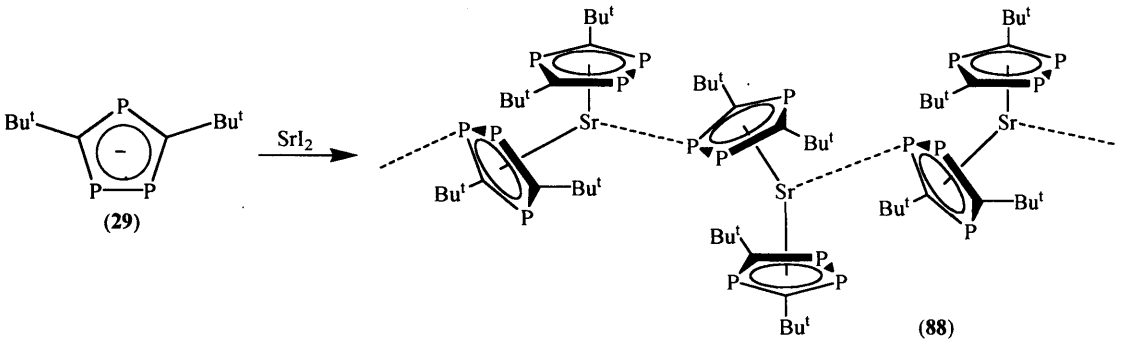
The reactions of the group 14 iodides SiI_4 and GeI_4 with $[K(P_3C_2Bu^t_2)]$ have been reported by *Nixon et al.*[82] The products were shown to be two novel cage compounds which have the general formula $P_6C_4Bu^t_4EI_2$ (E = Si, Ge). In these reactions, the cages arise from different intra-molecular coupling reactions of 1,2,4-triphospholyl rings (Scheme 4.50). Compound (**85**) results from the anticipated bis-$[(\eta^1\text{-}P_3C_2Bu^t_2)\text{-}GeI_2]$ intermediate (**86**) which then rapidly undergoes two further intramolecular [2+2] cycloaddition reactions.[82]



Scheme 4.50 Reactions of a triphospholyl anion with GeI_4 and SiI_4

Some group 2 complexes derived from the triphospholyl anion (**29**) have been reported. In 2000 *Nixon et al.* reported the synthesis and structural characterisation of the first hexaphosphastrontocene $[Sr(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (**88**).[83] Compound (**88**) was obtained when SrI_2 was reacted with the 3,5-di-*tert*-butyl-1,2,4-triphospholyl anion. A single X-ray crystallographic study revealed the polymeric character of (**88**) which

displays bent sandwich units linked in chains along a crystallographic c-glide plane. Each unit shows one solely η^5-bound triphospholyl ligand and a second η^5-ligand which also acts as a bridge linking the molecules into extended chains *via* a further η^1-interaction (Scheme 4.51). The pyrazine adduct of this hexaphosphastrontocene (**89**) has also been reported. Compound (**89**) was obtained quantitatively upon refluxing (**88**) in toluene, with excess pyrazine. The molecular structure shows (**89**) to be polymeric as well. The pyrazine units act as bridges linking the hexaphosphastrontocene molecules into zigzag chains.[83]



Scheme 4.51 Preparation of a hexaphosphastrontacene (88)

4.2 Research Proposal

Phospha- and polyphosphacyclopentadienide anions can be obtained as "decomposition" products which result from the reactions or thermal decomposition of phosphacyclohexadienyl anions. Phospha- and polyphosphacyclopentadienide anions are phosphorus-carbon heterocycles that show an extensive 6π-electronic delocalization. As such, they play a special role in phosphorus heterocyclic chemistry. Furthermore, their analogy with the ubiquitous cyclopentadienyl ligand implies a huge potential for their transition metal chemistry.[18] It was the object of the work described in this chapter to extend the work that has been conducted with these phosphorus-carbon heterocycles to the use of phosphacyclohexadienyl anions in the preparation of main group and transition metal polyphospholyl complexes.

4.3 Results and discussion

In an attempt to prepare a variety of complexes derived from the triphosphahexadienyl anion (**18**), several of its reactions with main group and transition metal halides were carried out. The reactions of (**18**) with $CoCl_2$ or $MnCl_2$ in diethyl ether or DME were followed by $^{31}P\{^1H\}$ NMR spectroscopy but only the previously reported 1,4-dihydro-1,3,5-triphosphine (**20**)[11] was identified in the $^{31}P\{^1H\}$ NMR spectra. Compound (**20**) was presumably formed by a metal mediated proton abstraction from the solvent used. To overcome this problem, reactions where carried out in hexane. It was believed that proton abstraction would be less likely in these cases. Despite the use of hexane, (**20**) was formed in the reaction of $CoCl_2$ with (**18**). The formation of (**20**) was also observed amongst many products from the reaction of (**18**) with $MnCl_2$ in hexane. Subsequent reactions of (**18**) with several main group and transition metals have been carried out.

When a solution of (**18**) in hexane was reacted with a suspension of BaI_2 in hexane and stirred overnight, an intensification of the orange colour was observed. In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture a strong singlet was observed at δ 190.6 ppm. Furthermore, two singlets in the ^1H NMR spectrum at δ 1.79 and 1.76 ppm were thought to correspond to two different *tert*-butyl groups. The ^{13}C NMR spectrum showed four clearly resolved triplets around δ 35.5 to 37.3 ppm for two inequivalent *tert*-butyl groups, while an unresolved multiplet was also seen at δ 166 ppm. These spectroscopic data indicate the formation of the formerly known phospholyl anion (**23**). This was confirmed by an X-ray crystallographic study. Crystals of (**23**) as the ether co-ordinated lithium salt (**90**) were obtained upon slow cooling of a hexane extract of the reaction mixture (Figure 4.4). The mechanism presumably involves the formation of cyclophosphane by-products, $[(PMe)_n]$, which were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture as unresolved multiplets around δ 17 ppm. These by-products were also observed upon thermolysis of (**18**). In addition, the phosphinidene, PMe, could be trapped in these thermolyses by excess (**15**) to yield a tricyclic tetraphospha-cage compound.[13, 84]

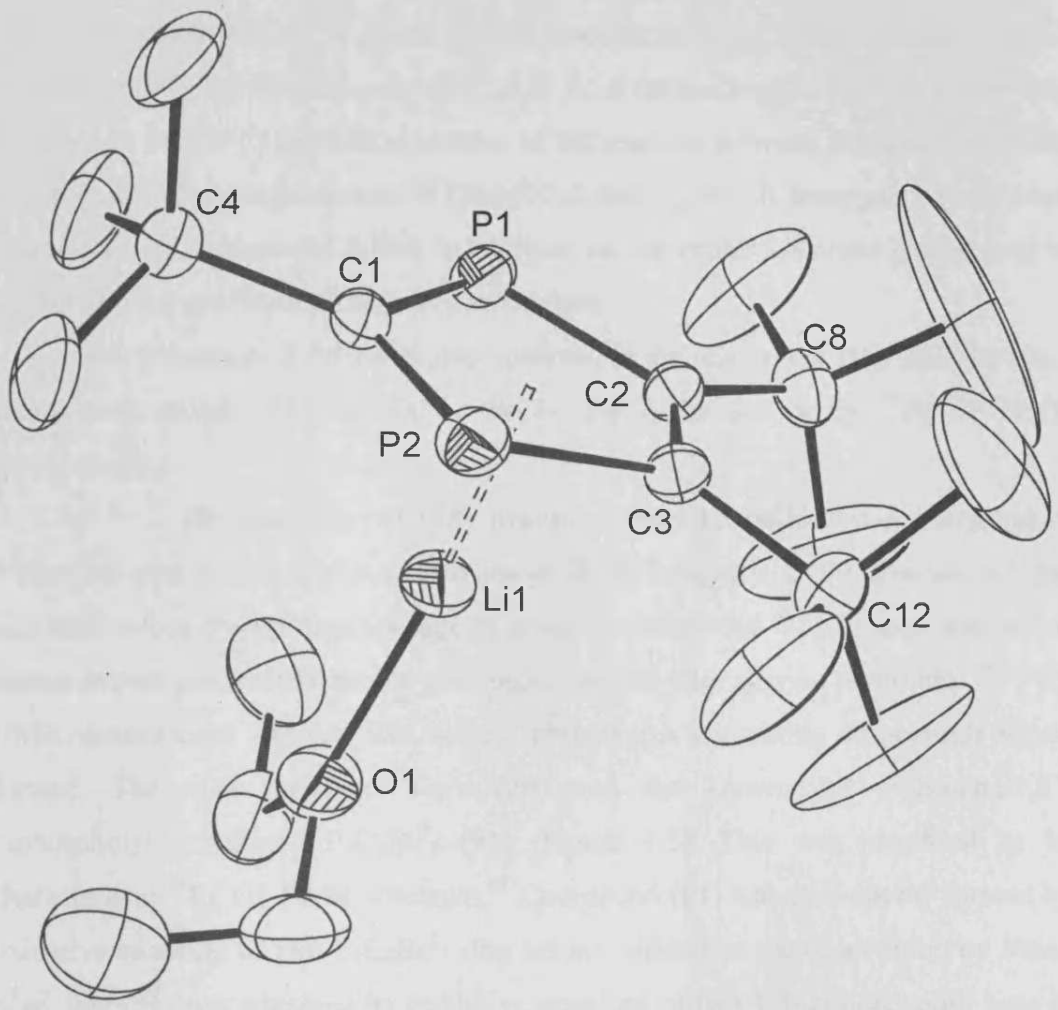


Figure 4.4 Molecular structure of $[(Et_2O)Li(\eta^5\text{-}P_2C_3Bu^t_3)]$ (90)

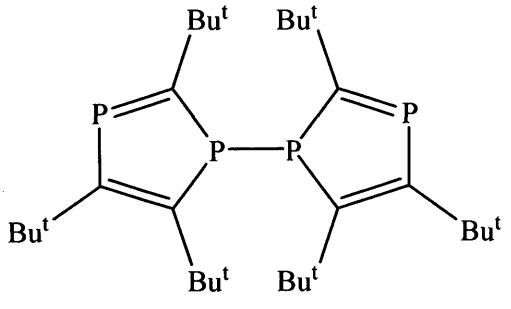
Selected bond length(Å) and angles(°): P(1)-C(1) 1.740(5), P(1)-C(2) 1.788(5), P(2)-C(3) 1.787(5), C(1)-P(2) 1.732(5), C(2)-C(3) 1.423(7), C(1)-P(1)-C(2) 96.8(2), C(1)-P(2)-C(3) 96.6(2), C(3)-C(2)-P(1) 114.7(3), P(2)-C(1)-P(1) 116.0(3), C(2)-C(3)-P(2) 115.6(3), P(1)-Li(1) 2.495(9), C(1)-Li(1) 2.341(9), Li(1)-C(3) 2.362(10), Li(1)-C(2) 2.375(10), Li(1)-P(2) 2.480(9), Li(1)-Ct(1) 1.936, O(1)-Li(1)-Ct(1) 165.63.

Two independent molecules were observed in the asymmetric unit of (**90**). The $P_2C_3Bu^t_3$ ring is planar and η^5-ligated to the lithium centre which is co-ordinated by one molecule of diethyl ether. The P-C bond distances in the ring (average 1.762 Å) and the C(2)-C(3) distance (1.423(7) Å) are comparable to those observed for $[K^+(THF)(P_2C_3Bu^t_3{}^-)]$ (P-C average 1.753(5) Å, C(2)-C(3) 1.416(6) Å) indicating

significant electron delocalisation in the phospholyl ring.[14] The lithium-centroid distance in (**90**) was determined to be 1.935 Å. A further singlet at δ 198.0 ppm was observed in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between (**18**) and BaI_2. This might result from the formation of $[Ba(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ but all attempts to isolate and characterise this compound failed. In addition, no molecular ion could be observed in the APCI mass spectrum of the reaction mixture.

The formation of (**90**) was also observed in the reaction of (**18**) with the other alkali earth metals, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, as shown by $^{31}P\{^{1}H\}$ NMR spectroscopy.

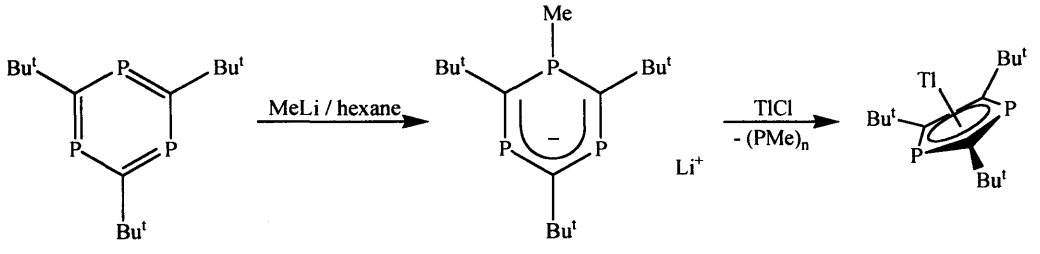
The reactivity of (**18**) towards group 15 halides was investigated. When (**18**) was reacted with a suspension of $BiCl_3$ in hexane, in the absence of light, an initial colour change from orange to green was observed. This colour changed to orange-brown and a black-brown precipitate formed after stirring overnight. $^{31}P\{^{1}H\}$ NMR spectroscopy showed that several phosphorus containing compounds where formed. The main products were (**20**) and the known 3,3'-diphospha-1,1'-biphospholyl compound $P_4C_6Bu^t_6$ (**91**) (Figure 4.5). This was identified by its characteristic $^{31}P\{^{1}H\}$ NMR spectrum.[85] Compound (**91**) was presumably formed by oxidative coupling of two $P_2C_3Bu^t_3$ ring anions, similar to the observation by *Nixon et al.* that (**91**) was obtained by oxidative coupling of two 1,3-diphospholide ions in the reaction of (**23**) with $[RuCl_2(COD)]_2$ in DME at - 30 °C.[85]



(**91**)

Figure 4.5 Structure of the 3,3'-diphospha-1,1'-biphospholyl compound (91)

This work was extended to an examination of the reactivity of (**18**) towards group 13 metal(I) halides. To this end, a solution of (**18**) was reacted with a suspension of TlCl in hexane. A colour change from orange to green was observed after stirring the suspension overnight. The reaction was followed by $^{31}P\{^{1}H\}$ NMR spectroscopy which showed a doublet to form at δ 190.8 ppm ($^{1}J_{PTl}$ = 159 Hz). In addition a complex multiplet around δ 17 ppm was observed which is thought to originate from the formation of the phosphinidene derived by-product, $[(PMe)_n]$. The ^{1}H NMR spectrum of the product exhibits two singlets for two inequivalent *tert*-butyl groups at δ 1.42 and 1.56 ppm. This spectroscopic evidence suggests the formulation of the product as $[Tl(\eta^5\text{-}P_2C_3But_3)]$ (**92**) (Scheme 4.52). The high solubility of this compound made it difficult to grow single crystals suitable for X-ray diffraction measurements from solution, but single crystals of (**92**) could be obtained by sublimation in a static high vacuum, as small yellow plates.



(**15**) (**18**) (**92**)

Scheme 4.52 Preparation of $[Tl(\eta^5\text{-}P_2C_3Bu^t_3)]$ (92)

The molecular structure of (**92**) is shown in Figure 4.6. The P-C bond distances in the ring (average 1.788 Å) and the C(2)-C(3) distance (1.517(9) Å) are in the same range as for (**90**). The thallium-centroid distance was determined to be 2.785 Å [*cf.* 2.71 Å for Cp*Tl,[86] 2.85 Å for (**80**)]. Compound (**92**) has a half sandwich structure with two independent molecules in the asymmetric unit. In one molecule the thallium is disordered over both sides of the phospholyl ring. The $P_2C_3Bu^t_3$ ring is essentially planar and η^5-co-ordinated to the thallium centre. As is the case for CpTl, Cp*Tl,[86] and (**80**), compound (**92**) shows a polymeric chain structure (Figure 4.7). The Ct-Tl-Ct angles were determined to be 162.82° and

171.32° for the two independent polymeric chains [*cf.* Ct-Tl-Ct 171° for (**80**)]. This is larger than the angles observed for CpTl (137°) and Cp*Tl (145°), presumably due to the greater steric demand caused by the bulky *tert*-butyl-groups in (**92**).

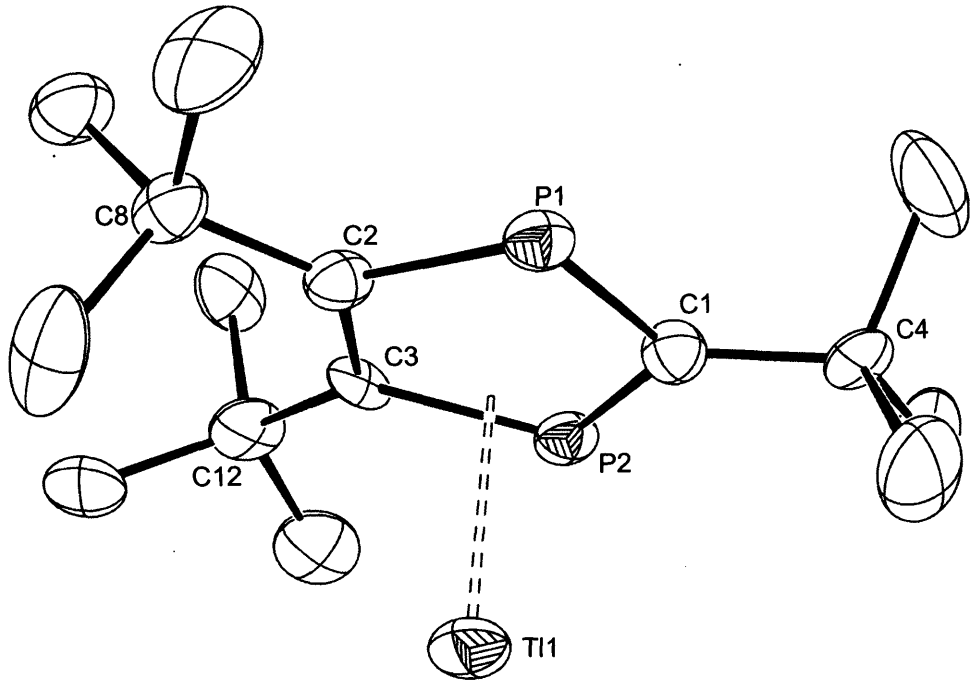


Figure 4.6 Molecular structure of [Tl(η^5-$P_2C_3Bu^t_3$)] (92)

Selected bond length (Å) and angles (°): Tl(1)-P(2) 3.185(4), Tl(1)-P(1) 3.197(5), P(1)-C(1) 1.758(16), P(1)-C(2) 1.800(16), P(2)-C(1) 1.762(17), P(2)-C(3) 1.833(16), C(2)-C(3) 1.517(9), P(2)-Tl(1)-P(1) 54.74(11), C(1)-P(1)-C(2) 99.9(8), C(1)-P(1)-Tl(1) 70.6(6), C(2)-P(1)-Tl(1) 74.4(5), C(1)-P(2)-C(3) 99.2(7), C(3)-P(2)-Tl(1) 72.8(5), P(1)-C(1)-P(2) 112.9(9), C(3)-C(2)-P(1) 114.6(11), C(2)-C(3)-P(2) 113.3(11), Ct(1)-Tl(1)-Ct(1) 162.81.

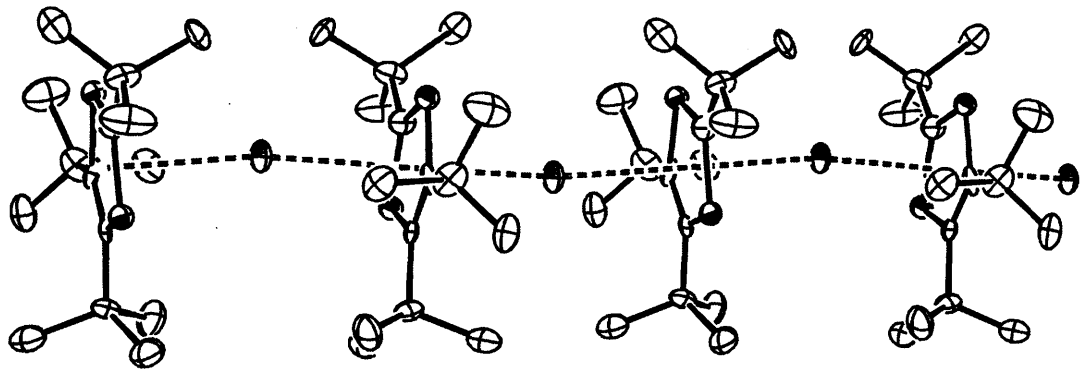
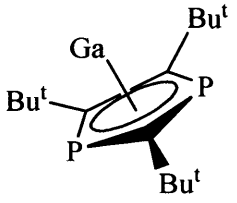


Figure 4.7 Polymeric chain structure of [Tl(η^5-$P_2C_3Bu^t_3$)] (92)

To investigate if [In(η^5-$P_2C_3Bu^t_3$)] (**78**),[78] which was originally prepared by the reaction of InI with [$KP_2C_3Bu^t_3$], could be prepared in the same fashion as (**92**), the reaction of (**18**) with InCl was carried out. When this reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy a singlet appeared at δ 182 ppm, which corresponds to the previously reported (**78**).[78]

In an extension of the series, the reaction of (**18**) with "GaI" was also attempted. When (**18**) was stirred with a suspension of "GaI" in hexane overnight the colour changed from orange to brown. A $^{31}P\{^1H\}$ NMR spectrum showed a singlet at δ 189.2 ppm, which was proposed to originate from the formation of [Ga(η^5-$P_2C_3Bu^t_3$)] (**93**). This was supported by the ^1H NMR spectrum of the product which showed the expected two singlets for the two inequivalent *tert*-butyl-groups at δ 1.76 and 1.79 ppm, in a 1:2 ratio. The very high solubility of the product made it difficult to obtain a crystalline material from solution. Despite numerous attempts to obtain single crystals, including by sublimation, none could be obtained. An EI mass spectrum of the obtained product showed a weak molecular ion which matched the calculated isotope profile for (**93**).

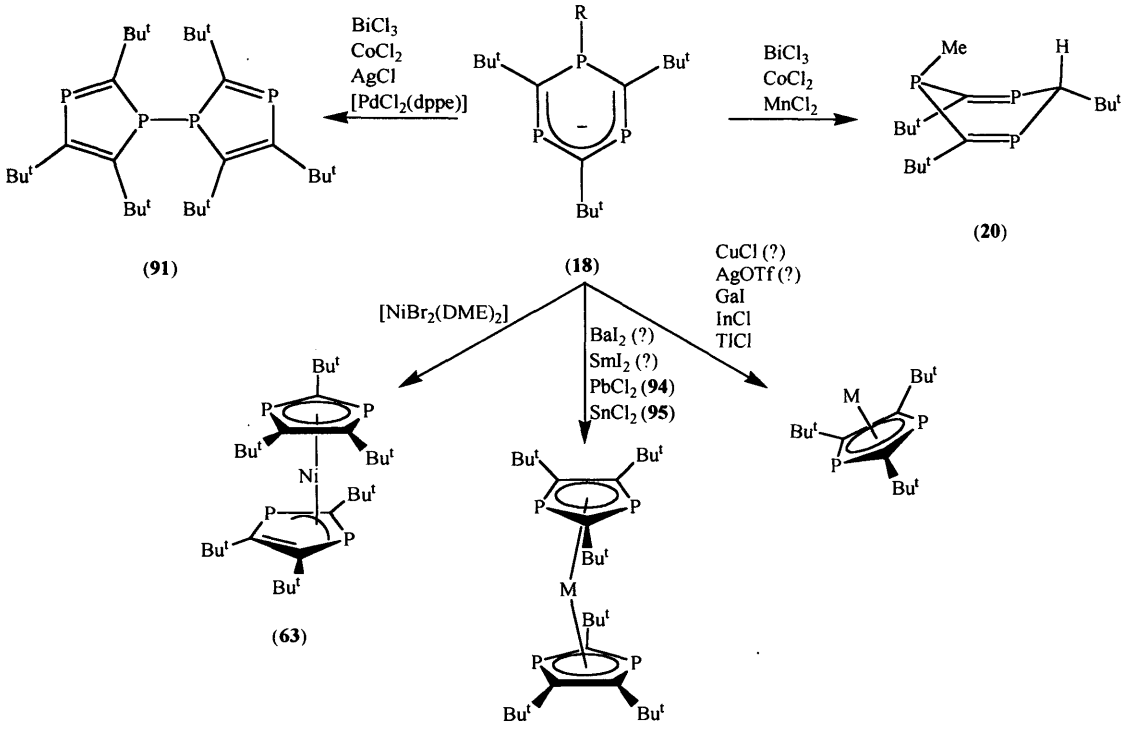


(**93**)

Figure 4.8 Proposed structure of [Ga(η^5-$P_2C_3Bu^t_3$)] (93)

In order to prepare the tetraphospha-analogues of the known lead and tin hexaphosphametallocenes, (**81**) and (**84**), the reactions of (**18**) with $PbCl_2$ and $SnCl_2$ were investigated. This work was conducted in co-operation with Dr. Matthew D. Francis. A suspension of $PbCl_2$ was reacted with a suspension of (**18**) for 16 hours, after which a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a singlet at δ 202.6 ppm with lead satellites ($^1J_{PPb}$ = 215 Hz). Furthermore, the ^1H NMR spectrum of the product displayed two singlets at δ 1.56 and 1.58 ppm corresponding to two inequivalent *tert*-butyl-groups. This led us to the assumption that the tetraphosphaplumbocene (**94**) had formed (Scheme 4.53). To confirm this, an X-ray

crystallographic study was carried out. Crystals suitable for X-ray crystallography were obtained upon slow cooling of a hexane extract of the reaction mixture. The molecular structure of (**94**) is shown in Figure 4.9.



Scheme 4.53 Different products formed in reactions of (18)

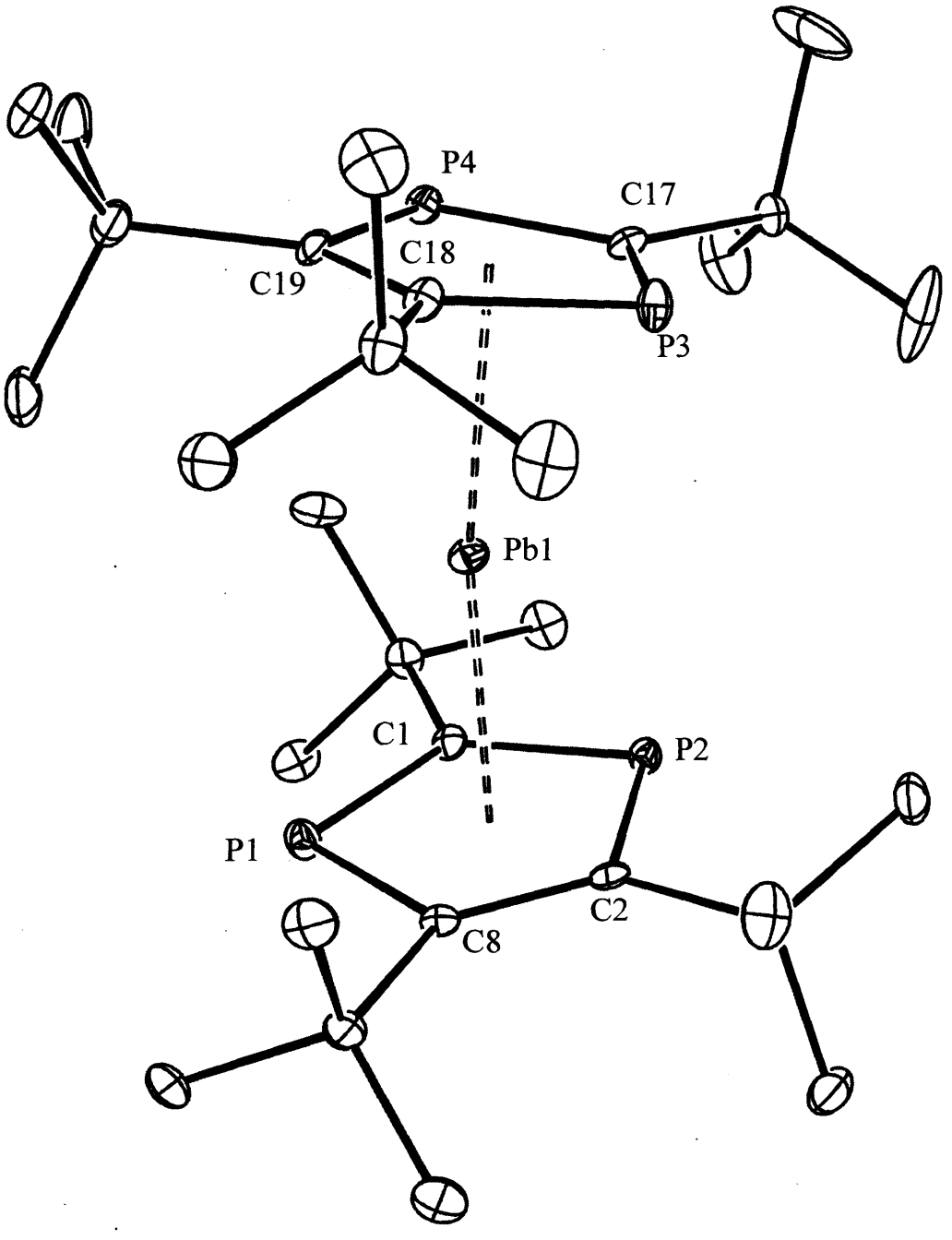
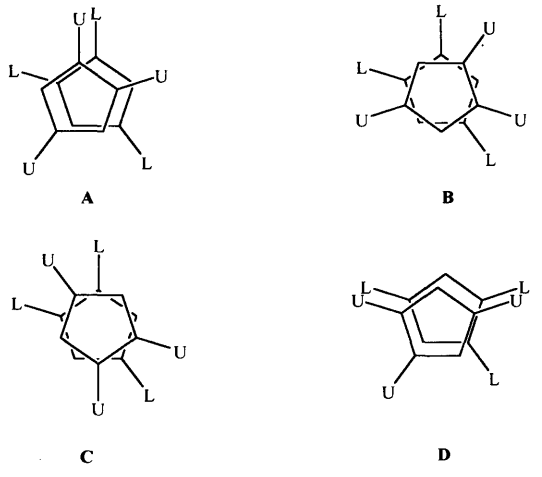


Figure 4.9 Molecular structure of $[Pb(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ (94)

Selected bond length (Å) and angles (°): P(1)-C(1) 1.737(5), P(1)-C(8) 1.790(5), P(2)-C(1) 1.743(5), P(2)-C(2) 1.812(5), P(3)-C(17) 1.738(5), P(3)-C(18) 1.815(5), P(4)-C(17) 1.738(5), P(4)-C(19) 1.797(6), C(1)-C(4) 1.538(7), C(2)-C(8) 1.412(7), C(2)-C(13) 1.563(7), Pb(1)-Ct(1) 2.551, Pb(1)-Ct(2) 2.568, P(2)-P(3) 5.124, (P2)-P(4) 5.137, P(1)-P(3) 6.045, P(1)-P(4) 5.449, Ct(1)-Pb(1)-Ct(2) 170.43, C(9)-C(8)-C(18)-C(24) 17.5.

Compound (**94**) has a bent sandwich structure similar to that in (**81**), Cp^*_2Pb[87] and 1,1',2,2',4,4'-hexa-*tert*-butyl-plumbocene.[88] The lead Cp-centroid distances in (**94**) were determined to be 2.560 Å (average) and the centroid-lead-centroid angle was measured at 170.43°. For comparison, the centroid lead centroid angle in Cp^*_2Pb is 151°. This difference might be explained by the greater steric demand of the *tert*-butyl groups in (**94**). The $P_2C_3Bu^t_3$ rings are planar and η^5-co-ordinated to the lead centre. The solid state structure of (**94**) shows the arrangement of the diphosphacyclopentadienyl rings in a near eclipsed conformation as shown in Figure 4.10 A. This geometry has also been found in other metallocenes, *e.g.* europocene[89] and the bismocenium[90] and stibocenium[91] cations. It has also been observed for hexa(trimethylsilyl)metallocenes of tin,[92] germanium,[93] magnesium[94] and iron.[95, 96] This arrangement is apparently energetically favoured in the solid state over the alternative, staggered arrangements (Figure 4.10 B and C).[97] The torsion angle of the near eclipsed *tert*-butyl groups, at C(8) and C(18), for (**94**) was determined to be 17.5°.



U represents a substituent on the upper ring; L represents a substituent on the lower ring

Figure 4.10 Schematic representation of eclipsed (A, D) and staggered (B, C) conformations of metallocenes in which the Cp rings each bear three substituents

Similar observations were made when another group 14 metal dihalide, $SnCl_2$, was reacted with a suspension of (**18**). A slightly broadened singlet at δ 196.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture was observed. The $^{119}Sn\{^1H\}$ NMR spectrum displays a singlet at δ - 493 ppm, while the ^1H NMR

spectrum shows two singlets at δ 1.35 and 1.37 ppm which correspond to the two inequivalent *tert*-butyl groups. To confirm the expected metallocene structure, X-ray crystallographic studies were carried out. Suitable crystals of (**95**) were obtained by slow cooling a hexane extract of the reaction mixture. The structure of (**95**) revealed it to have a sandwich structure, similar to that of (**94**) (Figure 4.11). Indeed, compound (**95**) is isostructural and isomorphous to (**94**). The tin Cp-centroid distance was measured to be 2.500 Å (average) and the centroid tin centroid angle is 171.28°. The centroid tin centroid angle in the comparable hexa(trimethylsilyl)stannocene was reported to be 162.2°,[92] while the same angle in Cp_2Sn[87] was found to be 145.8°. The conformation of the cyclopentadiene rings in (**95**) is very similar to that in (**94**), *i.e.* near eclipsed and the torsion angle of the near eclipsed *tert*-butyl groups at C(8) and C(18) was determined to be 18.5°.

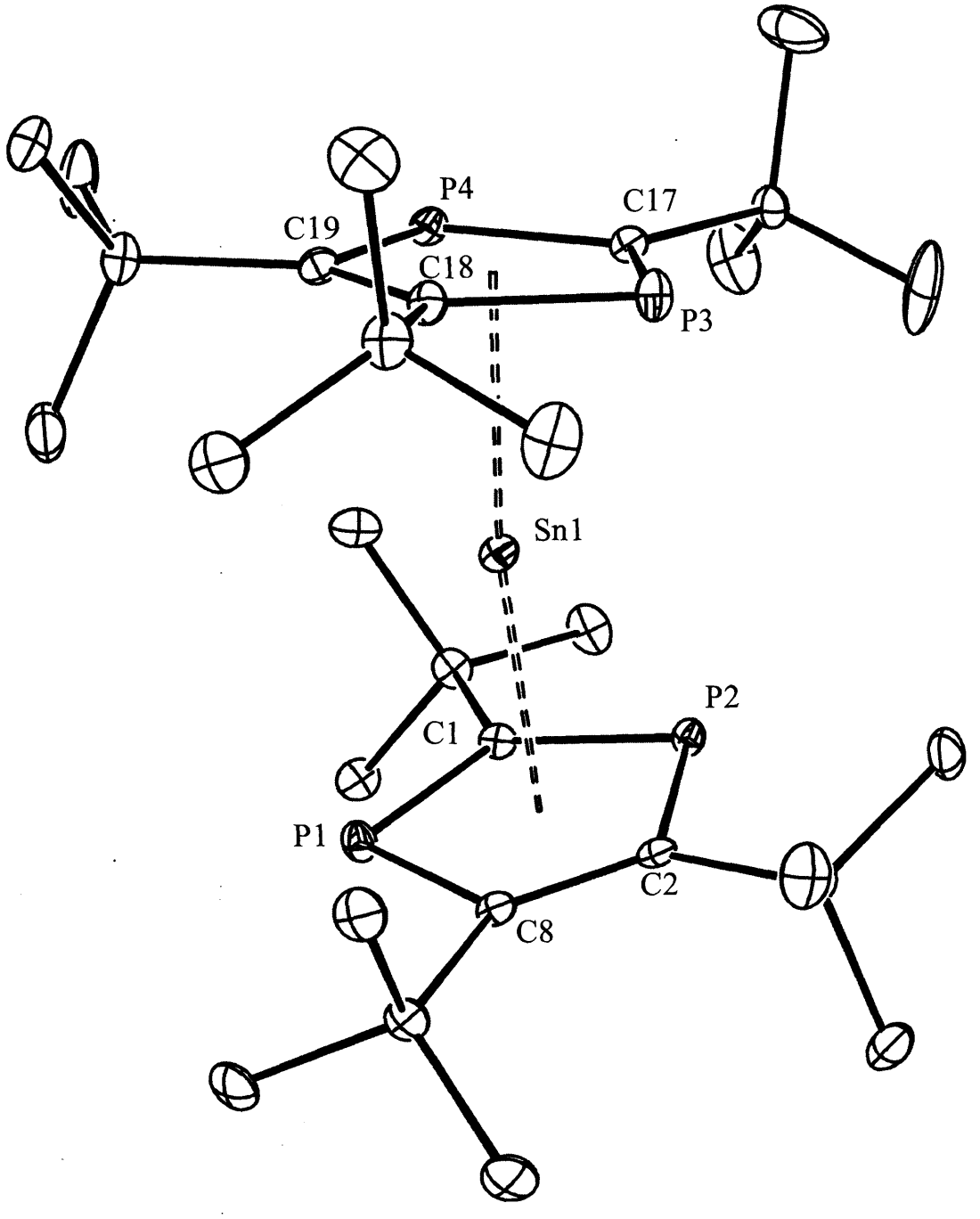


Figure 4.11 Molecular structure of $[Sn(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ (95)

Selected bond length (Å) and angles (°): P(1)-C(1) 1.734(3), P(1)-C(8) 1.798(3), P(2)-C(1) 1.745(3), P(2)-C(2) 1.808(3), P(3)-C(17) 1.733(3), P(3)-C(18) 1.805(3), P(4)-C(17) 1.740(3), P(4)-C(19) 1.800(3), C(2)-C(8) 1.394(4), C(4)-C(6) 1.545(4), C(18)-C(19) 1.406(4), P(1)-P(3) 5.888, P(1)-P(4) 5.309, P(2)-P(3) 5.000, P(2)-P(4) 4.995, Sn(1)-Ct(1) 2.491, Sn(1)-Ct(2) 2.509, Ct(1)-Sn(1)-Ct(1) 171.28, C(9)-C(8)-C(18)-C(24) 18.5.

Variable temperature NMR measurements were carried out on (**94**) and (**95**). Both compounds were found to be highly fluxional in solution as evidenced by their variable temperature $^{31}P\{^{1}H\}$ NMR spectra (Figure 4.13 and Figure 4.14). In that of (**94**), the diphospholyl ring resonances are seen at ambient temperature as a singlet at δ 202.6 ppm with lead satellites ($^{1}J_{PPb}$ = 215 Hz). This singlet is likely to be the result of a dynamic process involving rapid ring rotation. Similar ring rotations around the metal-ring centroid axis have been observed for $[Ru(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (**59**)[58] as well as in a series of other substituted ferrocenes and ruthenocenes.[98] At a temperature of -95 °C the variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of (**94**) showed partial resolution of the observed singlet at room temperature into two broad resonances (δ 217.5 and 184.1 ppm). Presumably, the ring rotation is slowed at low temperature, favouring a near eclipsed conformation, similar to that observed in the solid state molecular structure of (**94**). This leads to two inequivalent phosphorus chemical environments resulting in the two observed resonances. Figure 4.12 shows a schematic representation of the eclipsed conformation observed in (**94**) and (**95**) in which the chemically inequivalent phosphorus atoms are shown as P_A and P_B.

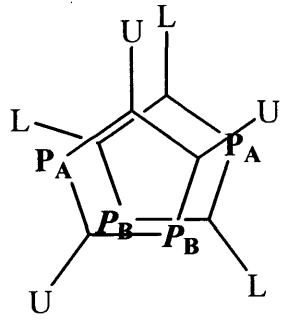


Figure 4.12 Schematic representation of the eclipsed conformation of (94) and (95)

The *Eyring* equation, $k = \left(\frac{k_B T_c}{h}\right) e^{\left(-\frac{\Delta G^{\ddagger}}{RT_c}\right)}$, was used to analyse the $^{31}P\{^{1}H\}$ NMR spectrum of (**94**), where $k = \frac{\pi \cdot \Delta \upsilon}{\sqrt{2}}$ near the coalescence temperature. Using $\Delta\upsilon$ = 4065 Hz and T_c = 193 K, the free energy of activation ($\Delta G^{\ddagger}$) for the ring rotation in (**94**) was found to be 31.96 kJ·mol^{-1}.

At ambient temperature, the diphospholyl rings resonances of compound (**95**) were observed as a singlet at δ 202.6 ppm in its $^{31}P\{^{1}H\}$ NMR spectrum. When the sample was cooled to - 80 °C this singlet resolved into two signals, which resolve further at - 95 °C to give two doublets at δ 220.1 and 171.1 ppm. The intra-ring coupling constant seen in these doublets is $^{2}J_{PAPB}$ = 34 Hz. Unfortunately tin satellites were not resolved on the signal at δ 171.1 ppm but the resonance at δ 220.1 ppm is beginning to show ^{117,119}Sn satellites, though the magnitude of the $^{1}J_{SnP}$ coupling could not be determined accurately. For sake of comparison, a $^{2}J_{PAPB}$ intra-ring coupling of 33 Hz was observed in the variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of the comparable compound $[Fe(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ (**96**).[99] *Nixon et al.* calculated a $\Delta G^{\ddagger}$ value of 59.55 kJ/mol for the ring rotation in (**96**),[99] while *Okuda* and *Herdtweck* reported that the silyl substituted ferrocene $[Fe\{\eta^5\text{-}1,1'\text{-}3,3'\text{-}5,5'\text{-}C_5H_2(SiMe_3)_3\}_2]$ (**97**) had a hindered ring rotation of $\Delta G^{\ddagger}$ = 46.05 kJ/mol.[95] The *Eyring* equation was applied to the results from the variable temperature $^{31}P\{^{1}H\}$ NMR spectroscopy of (**95**). Near the coalescence temperature, using $\Delta\upsilon$ = 6075 Hz and T_c = 213 K, a value for $\Delta G^{\ddagger}$ = 34.73 kJ·mol^{-1} was calculated for (**95**). The difference in calculated free Gibbs energy for (**94**) and (**95**) compared with (**96**) and (**97**) presumably results from the increased centroid metal distance, which in turn results in a reduced steric hinderance to the rotation of the $P_2C_3Bu^t_3$ rings.

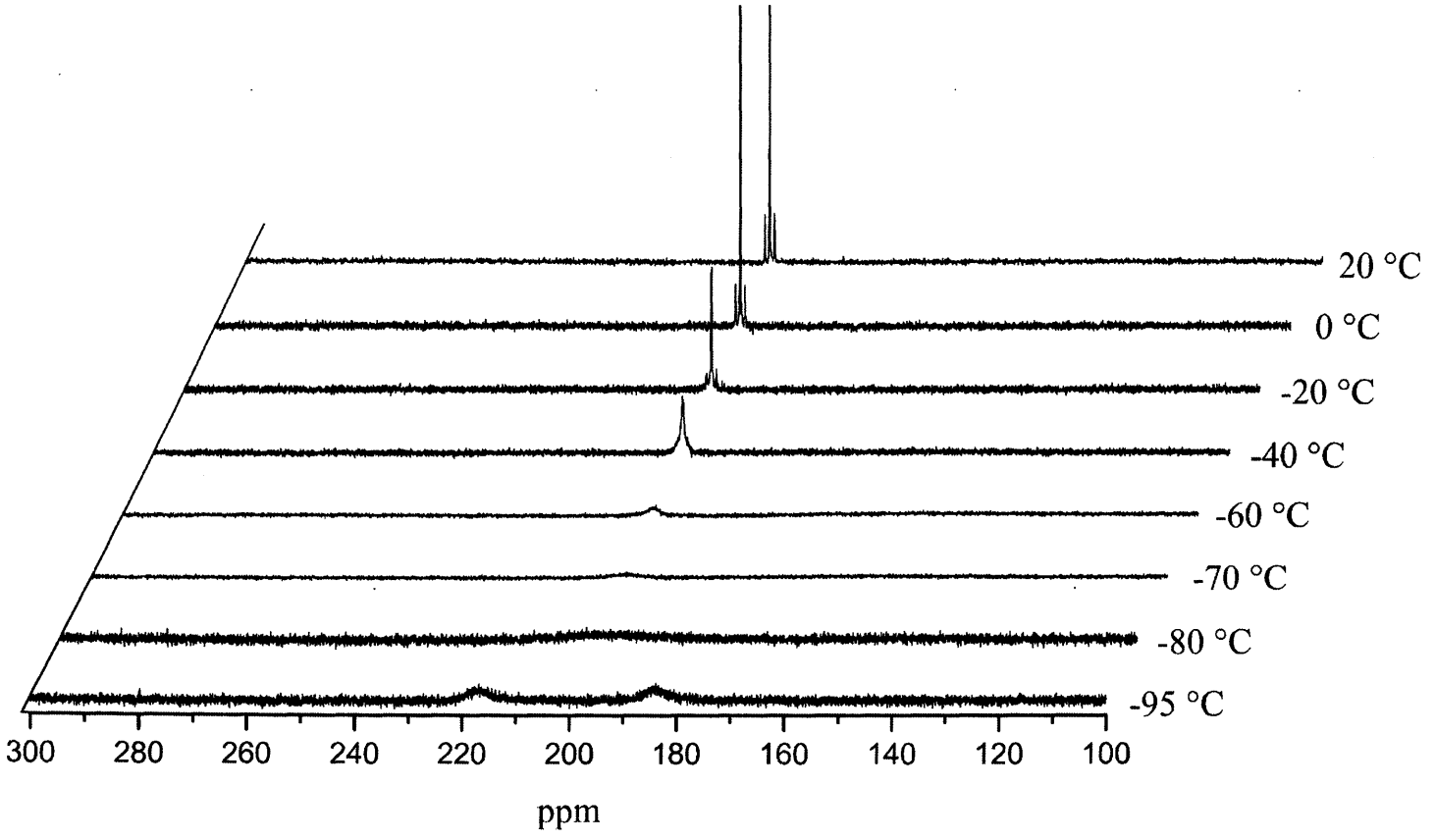


Figure 4.13 Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of $[Pb(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ in *d*8-toluene (94)

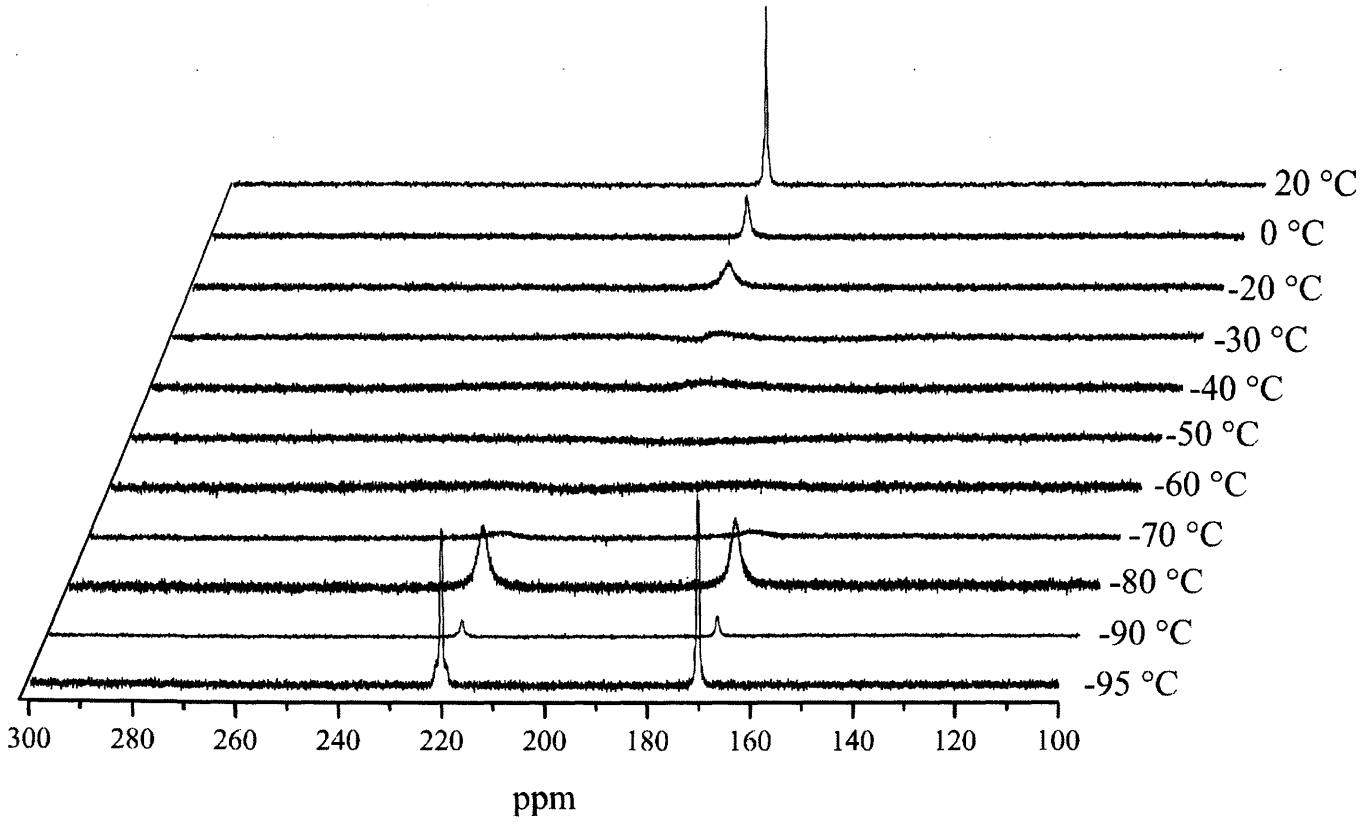


Figure 4.14 Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of $[Sn(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ in *d*8-toluene (95)

4.3 Results and discussion

In an attempt to extend the investigation into the reactivity of (**18**), several transition metal halides have been reacted with it. When the reaction of (**18**) with $[NiBr_2(DME)_2]$ was monitored by $^{31}P\{^1H\}$ spectroscopy, several phosphorus containing products were observed. A major product was found to be the previously reported complex $[Ni(\eta^5\text{-}P_2C_3Bu^t_3)(\eta^3\text{-}P_2C_3Bu^t_3)]$ (**63**),[59] identified by a singlet at δ 106.4 ppm in its $^{31}P\{^1H\}$ NMR spectrum. As mentioned earlier, reactions of (**18**) with $CoCl_2$ afforded a mixture of phosphorus containing compounds, mainly (**91**) and (**20**), recognized by their characteristic $^{31}P\{^1H\}$ NMR spectrum. Compound (**91**) was also formed when a solution of (**18**) was treated with a suspension of $[PdCl_2(dppe)]$ in hexane. This could be identified in the reaction mixture as the major product. When (**18**) was reacted with suspensions of $ZrCl_4$, Se_2Cl_2 or $SbCl_3$ only inseparable mixtures of phosphorus containing products resulted.

When a solution of (**18**) was reacted with a suspension of CuCl in hexane, a colour change from orange to green was observed after stirring overnight. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture displayed a singlet at δ 190.7 ppm which is very close the value observed for (**90**). It was not possible to determine whether this signal originated from the expected product, $[Cu(\eta^5\text{-}P_2C_3Bu^t_3)]$, or from (**90**). Mass spectrometric measurements have been carried out, but the expected isotope pattern for $[Cu(\eta^5\text{-}P_2C_3Bu^t_3)]$ was not observed. Despite numerous attempts, it proved impossible to obtain crystals suitable for X-ray crystallography.

The reaction of AgCl with (**18**) showed a large number of products in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, the major product being (**91**). However, when AgOTf was reacted with (**18**) the major product displayed a singlet at δ 190.1 ppm in its $^{31}P\{^1H\}$ NMR spectrum. Unfortunately, no crystals were obtained from this reaction and its mass spectrum did not show a molecular ion for $[Ag(\eta^5\text{-}P_2C_3Bu^t_3)]$.

A chemical shift of δ 197.1 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum of the mixture obtained when two equivalents of (**18**) were reacted with a suspension of SmI_2. Again, attempts to isolate and characterise the presumably formed product, $[Sm(\eta^5\text{-}P_2C_3Bu^t_3)_2]$, failed.

4.4 Conclusion

The reactions of the triphosphacyclohexadienyl anion, (**18**), with a variety of main group and transition metal halide complexes have been explored. In all, the "decomposition" of (**18**) to the diphosphacyclopentadienyl anion, (**23**), was observed. The reactions in which (**23**) was generated gave half sandwich complexes of the type $[M(P_2C_3Bu^t_3)]$, *e.g.* $[Tl(P_2C_3Bu^t_3)]$; or sandwich complexes, *e.g.* $[Pb(P_2C_3Bu^t_3)_2]$ and $[Sn(P_2C_3Bu^t_3)_2]$. Low temperature $^{31}P\{^1H\}$ NMR spectroscopic studies of the metallocenes revealed fluxional behaviour of the phospholyl rings. The reported compounds are volatile and have potential as precursors for chemical vapour deposition processes.

4.5 Experimental

For general experimental procedures refer to appendix I. $P_3C_3Bu^t_3$ (**15**)[100] and "GaI"[101] were prepared according to literature procedures. Other chemicals were commercially available and were purified according to published literature procedures.[102] ^{13}C NMR spectra of (**92 - 95**) were complicated by overlapping multiplets and could not be confidently assigned.

$[(Et_2O)Li(\eta^5\text{-}P_2C_3Bu^t_3)]$ (90)

To a solution of $P_3C_3Bu^t_3$ (**15**) (0.15 g, 0.5 mmol) in hexane (20 cm^3) was added a solution of MeLi (0.5 mmol in 2 cm^3 Et_2O) at - 78 °C. A colour change from yellow to orange was observed. The solution was slowly warmed to ambient temperature and stirred for 2 hours. The solvent was removed *in vacuo* and the residue suspended in hexane (10 cm^3). A suspension of BaI_2 (0.1 g, 0.25 mmol) in hexane (10 cm^3) was added and stirred for 16 hours. The solvent was removed *in vacuo* and the residue extracted in hexane. Slow cooling of this solution to - 30 °C resulted in orange crystals of (**90**).

(74 %, 0.13 g); ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 0.71 (t, 6H, Et_2O), 1.76 (s, 9H, $PC(Bu^t)P$), 1.79 (s, 18H, $P\{C(Bu^t)\}_2P$), 2.75 (q, 4H, Et_2O); $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6, 298 K): δ 13.4 (s, $(CH_3CH_2O)_2$), 35.6 (t, $PC\{C(CH_3)_3\}P$, $^3J_{PC}$ = 35 Hz), 35.8 (t, $P[C\{C(CH_3)_3\}]_2P$, $^3J_{PC}$ = 30 Hz), 36.8 (t, $PC\{C(CH_3)_3\}P$, $^2J_{PC}$ = 70 Hz), 37.3 (t, $P[C\{C(CH_3)_3\}]_2P$, $^2J_{PC}$ = 50 Hz), 64.9 (s, $(CH_3CH_2O)_2$), 166.2, 166.7 (m, ArC); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 189.2 (s, $PC(Bu^t)P$); $^7Li\{^1H\}$ NMR (116.8 MHz, C_6D_6, 298 K): δ - 4.4 (s, $Li(\eta^5\text{-}P_2C_3Bu^t_3)$);

$[Tl(\eta^5\text{-}P_2C_3Bu^t_3)]$ (92)

To a solution of $P_3C_3Bu^t_3$ (**15**) (0.15 g, 0.5 mmol) in hexane (20 cm^3) was added a solution of MeLi (0.5 mmol in 2 cm^3 Et_2O) at -78 °C. A colour change from yellow to orange was observed. The solution was slowly warmed to ambient temperature and stirred for 2 hours. The solvent was removed *in vacuo* and the residue dissolved in hexane (10 cm^3). A suspension of TlCl (0.12 g, 0.5 mmol) in hexane (10 cm^3) was added at - 80 °C. The solution was warmed to ambient temperature and stirred for 16

hours after which the colour changed from orange to green. The solvent was removed *in vacuo* and the residue extracted in hexane (5 cm^3). Slow cooling of this solution to - 30 °C resulted in a microcrystalline sample of (**92**). Crystals suitable for X-ray crystallography were obtained by sublimation under static vacuum.
(67 %, 0.17 g); mp. 198 - 200 °C, ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 1.42 (s, 9H, $PC(Bu^t)P$), 1.56 (s, 18H, $P(C\{Bu^t\})_2P$); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 190.8 (d, $PC(Bu^t)P$, $^1J_{PTl}$ = 159 Hz); MS EI: *m/z* (%) accurate mass calc. for $^{205}TlP_2C_{15}H_{27}$: 474.1327, found: 474.1327, IR (Nujol) υ/cm^{-1}: 2844 (s), 1633 (m), 1455 (s), 1380 (s), 1261 (s), 1095 (s), 1022 (s), 803 (s).

[Ga(η^5-$P_2C_3Bu^t_3$)] (93)

To a solution of $P_3C_3Bu^t_3$ (**15**) (0.15 g, 0.5 mmol) in hexane (20 cm^3) was added a solution of MeLi (0.5 mmol in 2 cm^3 Et_2O) at - 78 °C. A colour change from yellow to orange was observed. The solution was slowly warmed to ambient temperature and stirred for 2 hours. The solvent was removed *in vacuo* and the residue dissolved in hexane (10 cm^3). A suspension of "GaI" (0.13 g, 0.5 mmol) in hexane (10 cm^3) was added at - 80 °C. The solution was warmed to ambient temperature and stirred for 16 hours after which the colour changed from orange to brown. The solvent was removed *in vacuo* and the residue extracted in hexane (5 cm^3). Volatiles were removed *in vacuo* to yield (**93**) as a fine powder.
^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 1.76 (s, 9H, $PC(Bu^t)P$), 1.79 (s, 18H, $P\{C(Bu^t)\}_2P$); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 189.2 (s, $PC(Bu^t)P$); MS EI: *m/z* (%) 338.1 (M^+, 1 %); IR (Nujol) υ/cm^{-1}: 2852 (s), 1457 (s), 1378 (s), 1262 (s), 1201 (s), 1125 (s), 1019 (s), 831 (m), 801 (m), 719 (s).

[Pb(η^5-$P_2C_3Bu^t_3$)$_2$] (94)

A solution of $P_3C_3Bu^t_3$ (**15**) (0.15 g, 0.5 mmol) was dissolved in THF (10 cm^3) and TMEDA (1 cm^3). The solution was coooled to - 78 °C and MeLi (0.16 M, 3.44 cm^3, 0.55 mmol) was added dropwise. After 30 min the solution was warmed to room temperature and stirred for one hour. Volatiles were removed *in vacuo* and the residue dissolved in THF (10 cm^3). This was added dropwise to a suspension of $PbCl_2$ (0.08 g, 0.29 mmol) in THF (10 cm^3) at - 78 °C. Volatiles were removed and

the residue extracted with hexane and filtered. Slow cooling to - 55 °C gave (**94**) as a yellow crystalline solid.

(13 %, 24 mg); mp. 91 °C dec. ^{1}H NMR (300.5 MHz, C_7D_8, 298 K): δ 1.56 (s, 18H, PC(Bu^t)P), 1.58 (s, 36H, P{C(Bu^t)}$_2$P); ^{31}P{^{1}H} NMR (121.7 MHz, C_7D_8, 298 K): δ 202.6 (s, PC(Bu^t)P, $^{1}J_{PPb}$ = 215 Hz); MS EI: *m/z* (%) accurate mass calc. for $C_{30}H_{54}P_4{}^{208}Pb$: 746.2937, found 746.2942; IR (Nujol) υ/cm^{-1}: 2852 (s), 1644 (m), 1460 (s), 1377 (s), 1260 (s), 1096 (s), 1022 (s), 801 (s), 722 (s).

[Sn(η^5-P$_2$C$_3$Bu$^t_3$)$_2$] (95)

$P_3C_3Bu^t_3$ (0.15 g, 0.5 mmol) was dissolved in hexane (15 cm^3). The solution was cooled to - 78 °C and MeLi (0.16 M, 3.44 cm^3, 0.55 mmol) was added dropwise. An orange precipitate formed. The resultant mixture was warmed to ambient temperature and stirred for 1 hour. Volatiles were removed *in vacuo*. The resultant orange powder was suspended in hexane (10 cm^3) and was added as a slurry to $SnCl_2$ (50 mg, 0.26 mmol) suspended in hexane (30 cm^3) at ambient temperature. The resultant mixture was stirred for 4 days and volatiles were removed *in vacuo*. The residue was extracted with hexane (5 cm^3), filtered and concentrated. Cooling to - 30 °C gave (**95**) as a pale yellow crystalline solid.

(9 %, 16 mg). mp. 174 - 176 °C dec.; ^{1}H NMR (300.5 MHz, C_7D_8, 298 K): δ 1.35 (s, 18H, PC(Bu^t)P), 1.37 (s, 36H, P{C(Bu^t)}$_2$P); ^{31}P{^{1}H} NMR (121.7 MHz, C_7D_8, 298 K): δ 196.9 (s, PC(Bu^t)P); ^{119}Sn{^{1}H} NMR (112.1 MHz, C_6D_6, 298 K): δ - 493 (s); MS APCI: *m/z* (%) 389.1 ([M-P$_2$C$_3$Bu$^t_3$]$^+$, 100); IR (Nujol) υ/cm^{-1}: 2932 (s), 2730 (s), 1456 (s), 1363 (s), 1260 (s), 1218 (s), 1098 (s), 937 (w), 868 (m), 797 (s), 722 (m), 668 (m).

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Chapter Five

5 Preparation of alkyl and aryl group 15 chloride and hydride compounds

5.1 Introduction

5.1.1 Binary group 15 hydrides

Binary hydride complexes of the group 15 elements are important compounds which are frequently used as reducing agents or as precursors for electronic materials. Unfortunately in the case of hydrides of the heavier group 15 elements, the application of the compounds is limited by their low thermal stability.[1] All group 15 hydrides, EH_3 (E = N, P, As, Sb, Bi) are known. All of them are gases at room temperature, which, except NH_3, are extremely poisonous. The stability of the hydrides decreases upon descending the group. AsH_3 decomposes into the elements when heated to 250 - 300 °C, SbH_3 decomposes steadily at room temperature, while BiH_3 can only be kept at temperatures below - 45 °C.[2]

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
MP/ °C	- 77.8	- 133.5	- 116.6	- 88	-
BP/ °C	- 34.5	- 87.5	- 62.4	- 18.4	+ 16.8 (extrap)
Density/g·cm^{-3} (T °C)	0.643 (-34 °C)	0.746 (-90 °C)	1.640 (-64 °C)	2.204 (-18 °C)	-
$\Delta H_f°$ /kJ·mol^{-1}	- 46.1	- 9.6 (?)	66.4	145.1	277.8
Distance (M-H)/pm	101.7	141.9	151.9	170.7	-
Angle H-M-H	107.8°	93.6°	91.8°	91.3°	-

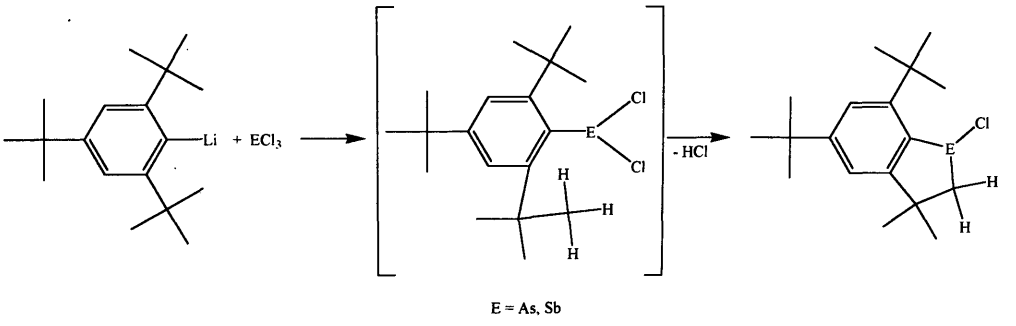
Table 5.1 Comparison of the physical properties of EH_3 (E = N, P, As, Sb, Bi)[2, 3]

Complexes of group 15 hydrides have been reported. Mostly they are unstable, of unpleasant odour and pyrophoric. The development of more "user-friendly" hydride compounds would make them more accessible for wider use in synthetic chemistry.[4] One potential way to achieve this is to employ bulky alkyl or aryl groups in the preparation of primary pnictanes.

5.1.2 Bulky alkyls and aryls in stabilizing group 15 halide and hydride complexes

The development of sterically bulky alkyl and aryl ligands has facilitated the renaissance of interest in main group chemistry that has occurred over the last 20 years. The interest in group 15 has largely revolved around the kinetic stabilisation of novel low co-ordination and/or low oxidation state complexes, *e.g.*, heteroalkynes, E≡CR;[5] heteroalkenes, RE=CR_2; dipnictenes, RE=ER[6] and pnictinidene complexes, L_nM=ER[7] (E = group 15 element). The most convenient precursors to such compounds are element dihalide and dihydride complexes, (REX_2, E = group 15 element, X = halide or hydride).

Often, supermesityl (Mes*, 1,3,5-tri-*tert*-butylphenyl) is used as a sterically bulky group and many examples of low co-ordinate group 15 species including it have been isolated, *e.g.* Mes*C≡As.[8] It has also been used in the synthesis of the first diphosphene, Mes*P=PMes* (**1**),[9] which was prepared by the reduction of Mes*PCl_2 with magnesium in THF. Attempts to synthesise Mes*ECl_2 (E = As, Sb) as potential precursors to diarsenes and distibenes by *Cowley et al.* failed, presumably due to an intramolecular dehydrochlorination of the corresponding dichloro compound (Scheme 5.1).[10, 11]



Scheme 5.1 Intramolecular dehydrochlorination of supermesityl dichloroarsine and -stibine

Subsequently *Weber et al.* succeeded in isolating Mes^*AsCl_2 at low temperature.[12] Despite its observed thermolability, it has been used to prepare the diarsene, $Mes^*As{=}AsMes^*$,[13] which is analogous to *Yoshifujis* diphosphene (**1**).[9] Mes^*AsH_2 has also been prepared by the reduction of Mes^*AsF_2 with lithium aluminium hydride.[10]

Power et al. reported the preparation of the homologous series of heavier element dichlorides [2,6-(C_6H_2-2,4,6-Me_3 or C_6H_2-2,4,6-Pr^i_3)$C_6H_3ECl_2$] (E = As, Sb, Bi).[14] They also reported the synthesis of the primary pnictanes ([2,6-(C_6H_2-2,4,6-Pr^i_3)$C_6H_3EH_2$], E = N, P, As, Sb)[15] (Figure 5.1).

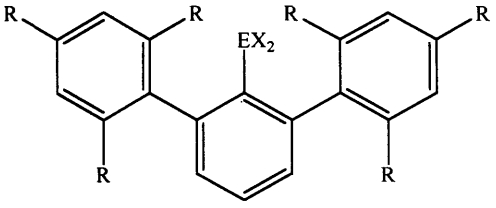


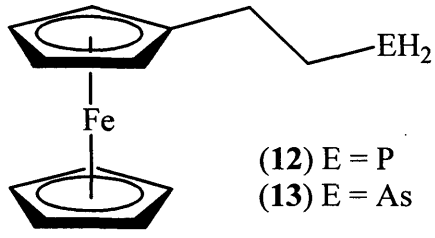
Figure 5.1 Terphenyl based group 15 complexes[14, 15]

	R	E	X	mp. / °C
(**2**)	Me	As	Cl	206 - 208
(**3**)	Me	Sb	Cl	263 - 265
(**4**)	Me	Bi	Cl	220 - 224
(**5**)	Pr^i	As	Cl	259 - 260
(**6**)	Pr^i	Sb	Cl	255 - 259
(**7**)	Pr^i	Bi	Cl	255 - 257
(**8**)	Pr^i	N	H	169 - 172
(**9**)	Pr^i	P	H	215 - 218
(**10**)	Pr^i	As	H	225 - 226
(**11**)	Pr^i	Sb	H	195 (dec.)

Compounds (**10**) and (**11**) were prepared by the reduction of (**5**) and (**6**) with $LiAlH_4$ in etheral solution. The attempted synthesis of a primary bismuthane by the reduction of (**7**) with $LiAlH_4$ resulted in the isolation of a previously reported dibismuthene, ArBi=BiAr, (Ar = 2,6-dimesitylphenyl), presumably *via* hydrogen elimination from [{2,6-(Mes)C_6H_3}BiH_2].[14] Nevertheless, the same group reported the structure of a secondary bismuth hydride, [{2,6-(Mes)C_6H_3}$_2$BiH], as recently as 2000.[16] So far no primary bismuth hydride has been structurally characterised. All

the primary pnictanes mentioned above show remarkable thermal stability which results from the kinetic protection afforded the group 15 centre.

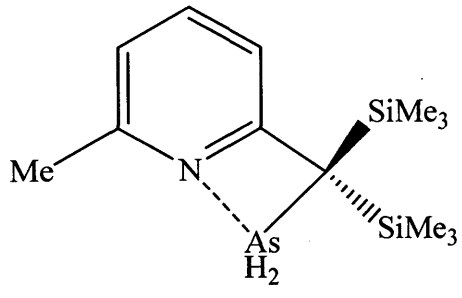
Apart from "classical" alkyl and aryl ligands, a number of organometallic or functionalized substituents have also been employed in the preparation of primary pnictanes. For example, *Henderson* and *Alley* utilised the ferrocenyl substituents for the preparation of a number of primary phosphines, *e.g.* (**12**), and a primary arsine (**13**)[17] which has a melting point of 44 - 46 °C (Figure 5.2).



(**12**) E = P
(**13**) E = As

Figure 5.2 Ferrocene based primary phosphine and arsine

Few examples of base stabilised primary pnictanes have been structurally characterised. Due to the thermal instability of arsenic hydride compounds this is not surprising. To overcome this problem *Raston et al.* prepared a primary arsine, [{C(SiMe$_3$)$_2$(6-Me-2-pyridyl)}AsH$_2$], which is stabilised by kinetic protection as well as by an intramolecular N-donation (**14**) (Figure 5.3).[18] The decomposition of this complex involves it darkening in colour from yellow to orange at around 120 °C and then at 160 °C it becomes dark red and gradually melts.

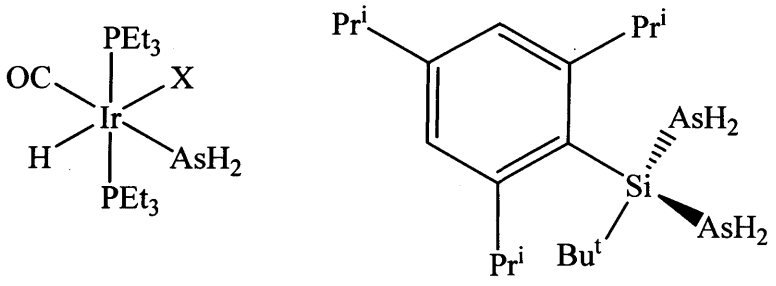


(**14**)

Figure 5.3 A primary arsine with an intramolecular donating nitrogen group

Some complexes of the AsH$_2$ fragment have also been synthesised and structurally characterised in the solid state which involves attachment to a transition

metal fragment such as in $[Ir(CO)ClH(PEt_3)_2(AsH_2)]$[19] (**15**) or to a silicon centre, *e.g.* $[\{2,4,6\text{-}(Pr^i)_3C_6H_2\}(Bu^t)Si(AsH_2)_2]$[20] (**16**) (Figure 5.4).



(**15**) X = Cl or Br (**16**)

Figure 5.4 Silicon and iridium based arsines

5.1.3 Phosphinidene chemistry

Phosphorus is only slightly more electropositive than carbon and thus, low valent organophosphorus compounds often have close analogies in their chemistry to their hydrocarbon counterparts.[21] For example, phosphinidenes (R-P̈ :) can be similar to carbenes (R_2C:) [7, 21] and can be stabilised by co-ordination to a transition metal fragment, *e.g.* ($RP=ML_n$).

The phosphinidene ligand (R-P̈ :) can use either two or four electrons when bonded to a transition-metal centre. In the 2-electron mode, it can give either η^1-bent or μ_2-pyramidal complexes. In the four-electron mode, it can give linear [R-P=M], μ_2-planar, μ_3-tetrahedral, or μ_4-bipyramidal complexes. Only the two-electron bent species are of major interest for a synthetic chemist.[22] It is well known that carbene complexes ($R_2C=ML_n$) can be either electrophilic (Fischer-type) or nucleophilic (Schrock-type). According to a recent DFT study, the nucleophilic type for phosphinidene complexes can be viewed as resulting from the combination of two triplets and the electrophilic type, a combination of two singlet states (Figure 5.5).[22-26] The electronics of phosphinidene complexes have been the topic of a number of reviews.[7, 22, 27]

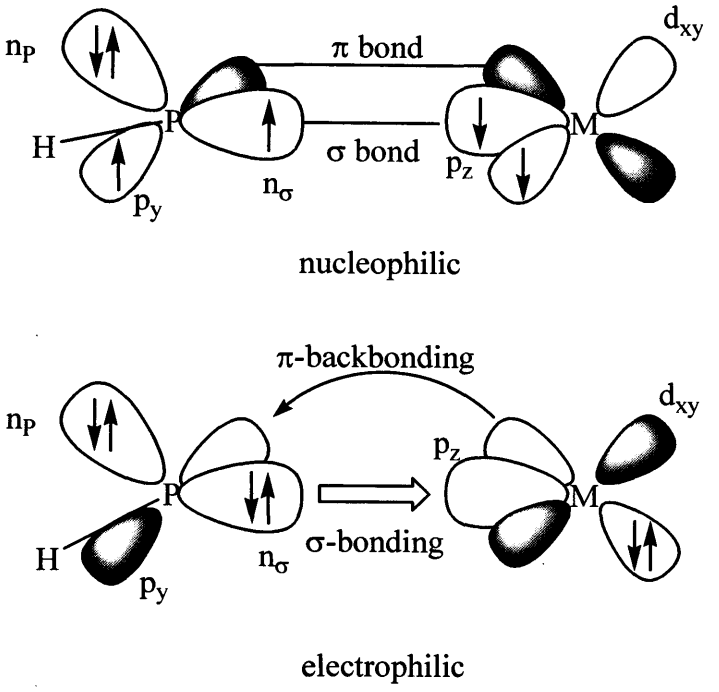
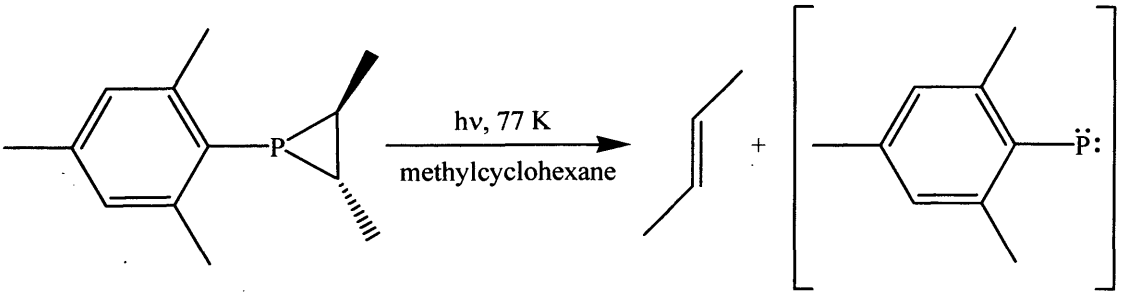


Figure 5.5 Electronic structures of terminal phosphinidene complexes

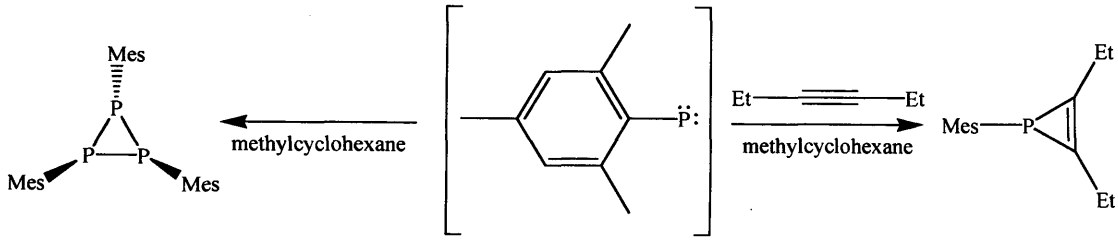
The preparation of free, stable phosphinidenes has been attempted by the reduction of dihalophosphanes[28] with alkali metals as well as by photolysis of diphosphenes.[29] In 1994 a free phosphinidene was detected by *Gaspar et al.* They identified mesitylphosphinidene (**17**) as a transient species after irradiation of a mesitylphosphirane at low temperatures (Scheme 5.2).[30]



(**17**)

Scheme 5.2 Preparation of a free phosphinidene

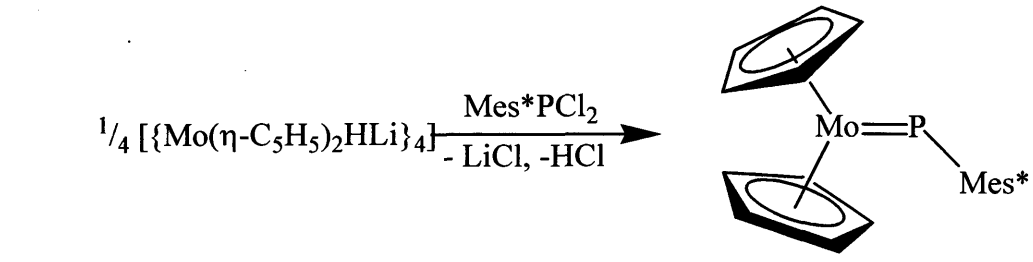
In the absence of a trapping agent, trimesitylcyclotriphosphine (**18**) was formed in yields of 30 % after warming to ambient temperature. With 3-hexyne present, 2,3-dimethyl-1-mesitylphosphirene (**19**) was formed in yields up of to 80 % (Scheme 5.3).



(18) (17) (19)

Scheme 5.3 Trapping reactions of a phosphinidene fragment

Many bridging phosphinidene complexes have been reported over the years[31, 32] but in 1987 the quest for terminal phosphinidene complexes was over when *Hitchcock et al.* published the first terminal phosphinidene metal complex.[23] This molybdenum complex (**20**), was formed by treatment of the tetramer $[Mo(\eta\text{-}C_5H_5)_2HLi]_4$ with Mes^*PCl_2 *via* salt metathesis and dehydrochlorination (Scheme 5.4). Since that time, many more terminal phosphinidene complexes have come forward involving many metals *e.g.* group 4 (Zr),[33] 5 (Ta),[34, 35] 6 (W),[36] 9 (Ir)[37] and even an actinide (U).[38] Transition metal phosphinidene complexes can be used as a source of free phosphinidene fragments, if mild techniques for decomplexation of the phosphinidene fragment can be developed.[27]

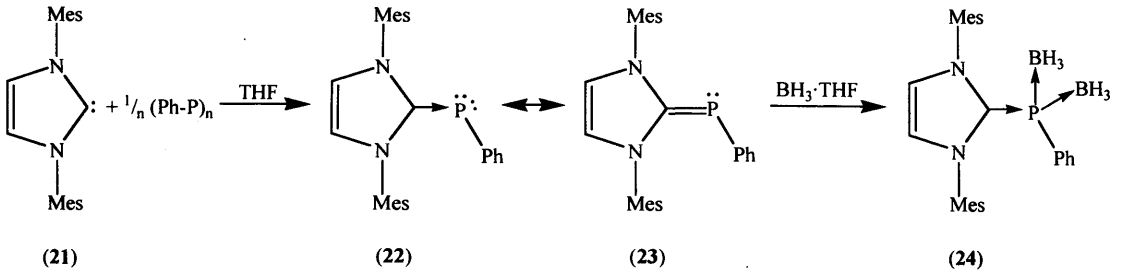


(**20**)

Scheme 5.4 Preparation of the first terminal phosphinidene

It is worth noting that phosphinidene fragments can also be stabilised with Lewis bases. In 1997 *Arduengo et al.* showed that the reaction of 1,3-dimesitylimidazol-2-ylidene (**21**) with cyclic oligomers of pnictinidenes yields carbene pnictinidene adducts.[39] Two different resonance forms are possible, (**22**) and (**23**). Compound (**22**) shows a donor-acceptor bond while (**23**) has a phosphaalkene

double bond. Addition of BH_3·THF to (**22**)/(**23**) resulted exclusively in the formation of the bis(borane) complex (**24**) which shows a simple dative C-P bond with little pπ-pπ overlap (Scheme 5.5).[40]



Scheme 5.5

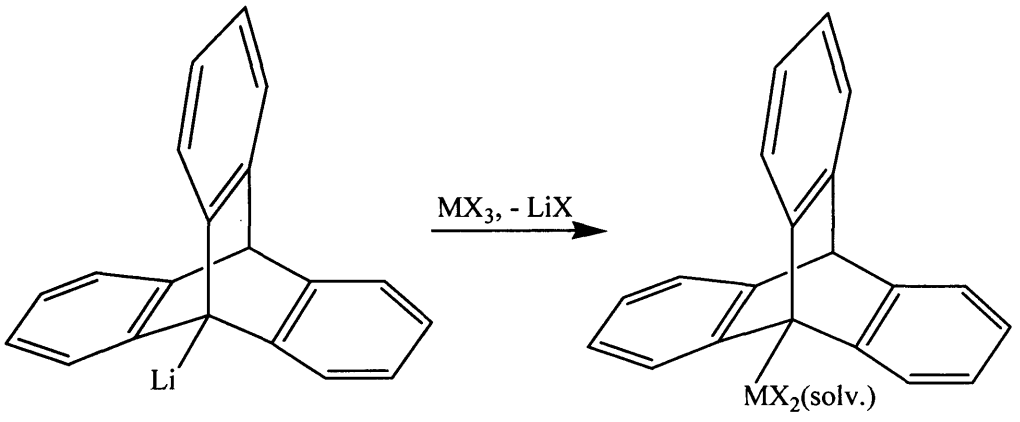
5.1.4 Triptycenyl as a sterically protecting ligand

Triptycene was synthesised by *Bartlett* in 1942.[41] Since then it has gained importance in material and polymer science and liquid crystal matrices.[4] The name, suggested by Professor Mason Hammond, was inspired by its shape; it suggested the triptych of antiquity, which is a book with three leaves hinged on a common axis.[41] Its unusual symmetry and rigid framework are of particular interest. Triptycene possesses all the characteristics likely to be required as a building block in the formation of molecular brakes or gears.[4]

A further interesting feature of triptycene is the special bridge head positions which lie on the three fold symmetry axis of triptycene. These are protected by the adjacent protons of three symmetrical phenylene rings. This situation ensures steric hindrance of a substituent attached to bridgehead positions and is the origin of the ligand's "cage protection" effect.[4]

In 1996 *Geoffroy et al.* prepared an interesting compound, 9-phosphinotriptycene (**25**).[42] Very recently the same group also reported the preparation of a rare example of an air-stable crystalline primary arsine namely [(tript)AsH_2] (**26**).[4] Independently we have also investigated the use of triptycene as ligand.[5]

Several group 14 complexes, *e.g.* [(tript)EH_3] (E = Si or Ge) and [(tript)$_3$GeCl],[4, 43] (tript = triptycenyl), have been reported to employ the triptycenyl ligand. The former are air stable, whilst the steric properties of the latter has led to its classification as molecular gear. A number of group 13 complexes have been recently published. *Jones et al.* managed to prepare and characterise a range of group 13 halide complexes by X-ray crystallography and spectroscopic techniques (Scheme 5.6).[5]



(**27**) M = Al, X = Cl, solv. = Et_2O
(**28**) M = Ga, X = Cl, solv. = THF
(**29**) M = In, X = Br, solv. = [LiBr(OEt_2)$_2$]

Scheme 5.6 Preparation of tripycenyl group 13 halide complexes

5.2 Research Proposal

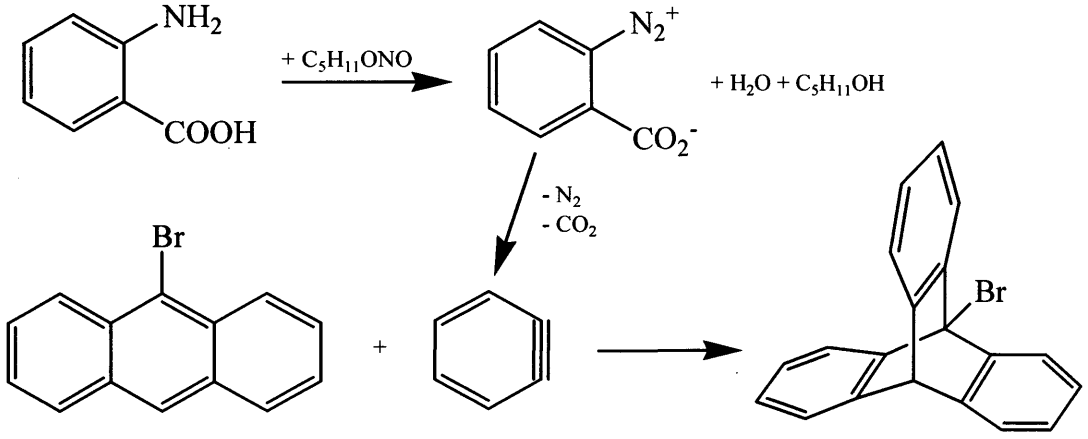
In group 15, the primary phosphane and arsane complexes, [(tript)EH_2], (E = P or As), have been recently reported as having high thermal stability due to the steric protection afforded by the triptycenyl ligand. It was the object of the work described in this chapter to extend this work to the preparation of the primary metal pnictanes, [(tript)EH_2], (E = Sb or Bi), and a full range of triptycenyl-group 15 dihalides, [(tript)ECl_2], (E = P, As, Sb or Bi). The latter were to be used as precursors to terminal pnictinidene-transition metal complexes.

5.3 Results and discussion

5.3.1 Improved synthesis of 9-lithiotriptycene

9-Bromotriptycene was prepared by *Bartlett et al.* in 1950 by a multiple step synthesis.[44] This synthesis seemed impractical, so the preparative method for triptycene by *Friedman* and *Logullo*[45] was adopted to synthesising 9-bromotriptycene. *Friedman* and *Logullo* found that anthranilic acid is readily diazotized by alkyl nitrites in aprotic media to give benzyne. This can then react in a Diels-Alder addition with 9-bromoanthracene to 9-bromotriptycene.

9-Bromoanthracene can be synthesised in high yield by the bromination of anthracene with NBS, which was published by *Weinshenker* in 1969.[46] 9-Bromoanthracene from this reaction can be used without further purification in the preparation of 9-bromotriptycene.

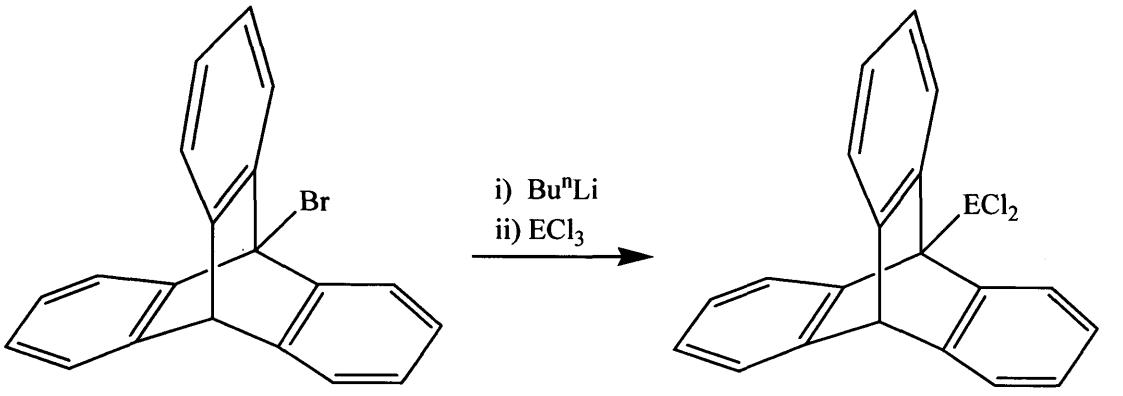


Scheme 5.7 Preparation of 9-bromotriptycene

9-Lithiotriptycene was prepared by *Wittig* and *Tochtermann* in 1962[47] and by *Kawada* and *Iwamura* in 1981 using an alternative route.[48] The later synthesis had a yield over 97 % but unfortunately involved benzene as solvent. It was shown during our investigations that the reaction of 9-bromotriptycene with Bu^nLi in refluxing THF gives 9-lithiotriptycene nearly quantitatively after ½ hour. This suspension could be used without further isolation or purification in further reactions.

5.3.2 Reactions of group 15 chlorides with 9-lithiotriptycene

The complexes [(tript)ECl_2], E = P (**30**), As (**31**) were previously prepared as *in situ* intermediates for the preparation of [(tript)EH_2] though no data were given in those reports[4, 42] and the complexes were not isolated. Therefore, the complexes [(tript)ECl_2], E = P (**30**), As (**31**), Sb (**32**) and Bi (**33**) have been synthesised by the reaction of lithiotriptycene with the corresponding group 15 trichloride (Scheme 5.8).



E = P (**30**), As (**31**), Sb (**32**), Bi (**33**)

Scheme 5.8 Preparation of [(tript)ECl_2], E = P, As, Sb, Bi

After addition of ECl_3 (E = P, As, Sb or Bi) to suspensions of 9-lithiotriptycene at low temperature, the mixtures were heated at reflux for 90 min (**30 - 32**) or stirred overnight at 25 °C (**33**), during which time orange coloured solutions were formed, indicating the completion of the reactions. The lithium chloride formed in the reactions was easily separated by removal of the volatiles *in vacuo* and extraction of (**30 - 33**) into toluene.

All complexes are thermally very robust and appear to be indefinitely stable in air in the solid state. The spectroscopic data for the complexes are consistent with their proposed structures, which in the cases of (**31 - 33**) were confirmed by X-ray crystallographic analyses.

Compound (**31**) was formed as a colourless crystalline product in 58 % yield. Its thermal stability (mp. 198 - 200 °C) is comparable with (**2**) which melts at 206 - 208 °C. Its crystal structure shows that the arsenic centre is significantly distorted from a pyramidal geometry. Compared with (**32**) and (**33**) the degree of pyramidalisation in (**31**) is, however, smaller. The Σ angles about arsenic is 296.65° (*cf.* Σ angles about Sb in (**32**) 292.32°, Σ angles about Bi in (**33**) 285.61°). This is in line with the expected increase in s-character of the lone pair of the group 15 centre in the series (**31** - **33**). The As-C bond length is similar to those recorded for related monomeric complexes employing sterically demanding ligands, *e.g.* (**2**).

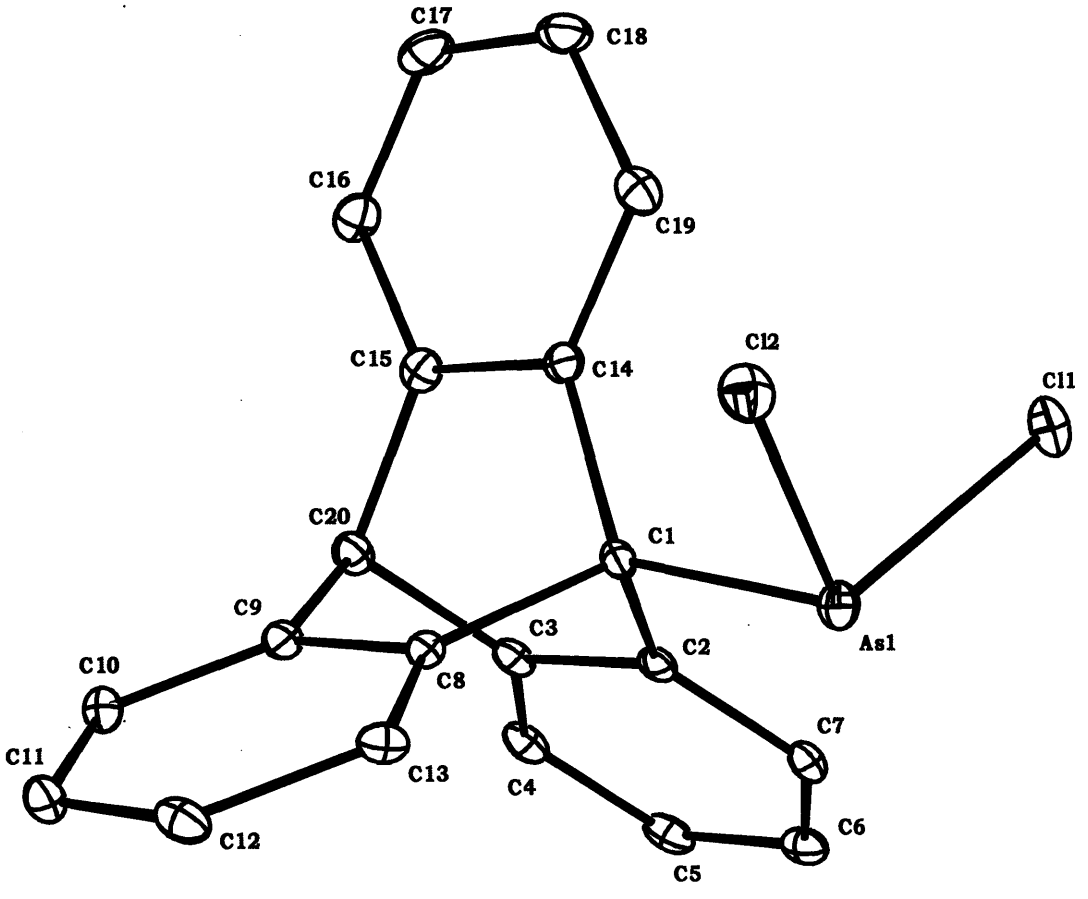


Figure 5.6 Molecular structure of [(tript)AsCl$_2$] (31)

Selected bond lengths (Å) and angles (°): As(1)-C(1) 1.980(3), As(1)-Cl(1) 2.1932(10), As(1)-Cl(2) 2.1945(9), C(1)-As(1)-Cl(1) 98.77(9), C(1)-As(1)-Cl(2) 98.04(9), Cl(1)-As(1)-Cl(2) 99.84(4).

Compound (**32**) was formed in a 52 % yield. Like (**31**) and (**33**), (**32**) crystallises in a monoclinic space group. Although all these complexes are isostructural, they are not isomorphous. The antimony carbon bond in (**32**) is of comparable length to that reported by *Power et al.* for (**6**) [2.187(5) Å]. As mentioned earlier, the s-character of the lone pair of antimony in increased in comparison with (**31**), seen by the Σ of angles about antimony at 292.32°. The melting point of (**32**) at 246 - 247 °C, highlights the thermal stability of this compound, which can be compared to (**3**) (263 - 265 °C) and (**6**) (255 - 259 °C).[14]

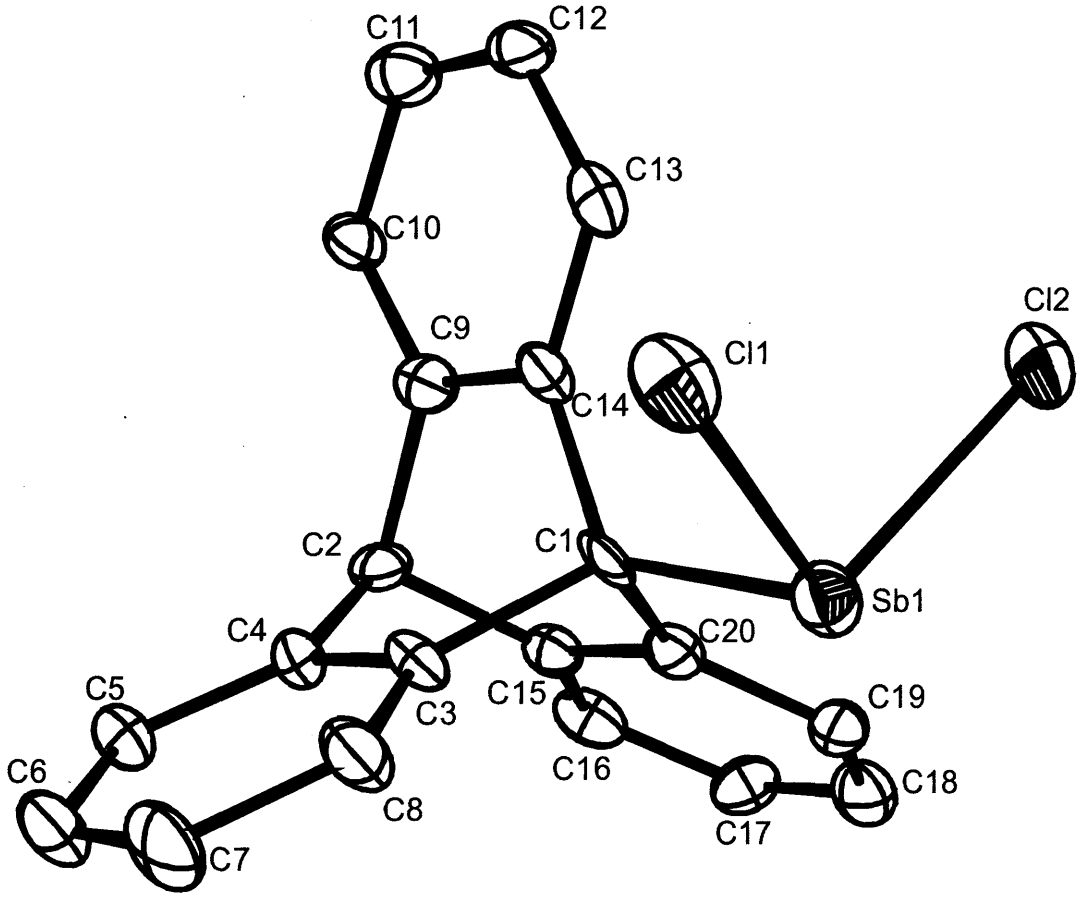


Figure 5.7 Molecular structure of [(tript)SbCl$_2$] (32)

Selected bond lengths (Å) and angles (°): Sb(1)-C(1) 2.216(8), Sb(1)-Cl(1) 2.380(2), Sb(1)-Cl(2) 2.370(2), C(1)-Sb(1)-Cl(1) 97.2(2), C(1)-Sb(1)-Cl(2) 97.27(19), Cl(1)-Sb(1)-Cl(2) 95.37(8), Sb(2)-C(21) 2.224(8), Sb(2)-Cl(3) 2.362(2), Sb(2)-Cl(4)

2.369(2), C(21)-Sb(2)-Cl(3) 97.1(2), C(21)-Sb(2)-Cl(4) 99.2 (2), Cl(3)-Sb(2)-Cl(4) 96.13(8).

In contrast to (**31**) and (**32**) the yield of colourless, crystalline (**33**) was only 11 %. Milder reaction conditions than those used in the preparation of (**31**) and (**32**) where necessary to obtain (**33**). The best yields were obtained when the reaction mixture was stirred overnight in the absence of light. The melting point of (**33**) (155 °C) reveals its thermal stability, which can be compared to that of (**4**) (220 - 224 °C).[14] The crystal structure of (**33**) shows that the Σ of angles around bismuth is 285.61°, thus showing the highest s-character of the lone pair in this series. The bismuth carbon bond length can be compared with that in the only other structurally characterised example of a monomeric, alkyl or aryl bismuth dihalide complex (**4**) with [2.267(5) Å].

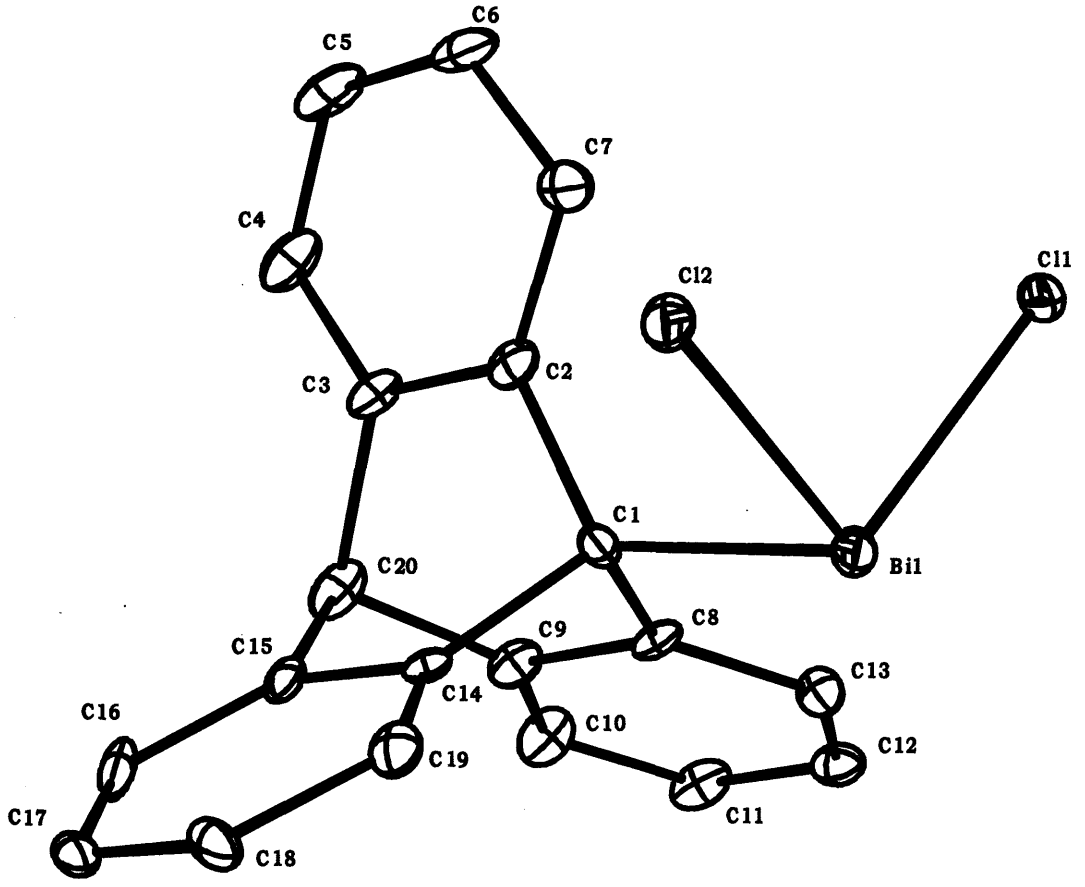


Figure 5.8 Molecular structure of [(tript)$BiCl_2$] (33)

Selected bond lengths (Å) and angles (°): Bi(1)-C(1) 2.299(11), Bi(1)-Cl(1) 2.523(3), Bi(1)-Cl(2) 2.468(3), C(1)-Bi(1)-Cl(1) 96.6(3), C(1)-Bi(1)-Cl(2) 91.0(3), Cl(1)-Bi(1)-Cl(2) 98.01(10).

5.3.3 Triptycenyl group 15 hydride complexes

The primary pnictanes, [(tript)EH_2], E = P (**25**) or As (**26**), have previously been synthesised using a one-pot procedure involving the reaction of 9-lithiotriptycene with either PCl_3 or $AsCl_3$ followed by *in-situ* reduction with $LiAlH_4$.[4, 42] In the case of the arsine, the compound could only be isolated in an 11 % yield, whilst the synthesis of the primary stibane, [(tript)SbH_2] (**34**), failed. Independently, we have examined the reactions of the isolated and recrystallised halide complexes, (**31**) and (**32**), with $LiAlH_4$ in diethyl ether which lead smoothly to the primary pnictanes, (**26**) and (**34**), in good yields (67 % and 65 % respectively). Unfortunately, the related reaction of (**33**) with $LiAlH_4$ did not lead to the bismuthane, [(tript)BiH_2], but to decomposition and the deposition of elemental bismuth. This is not surprising as to date there are no known primary bismuthanes and only one structurally characterised secondary bismuthane, [{2,6-$(Mes)_2C_6H_3$}$_2$BiH] (**35**) has been reported.[15]

The spectroscopic data and X-ray structure for air stable (**26**) are identical to those reported by *Geoffroy et al.*[4], but the crystal structure, obtained in our independent investigation has been included here (Figure 5.9).

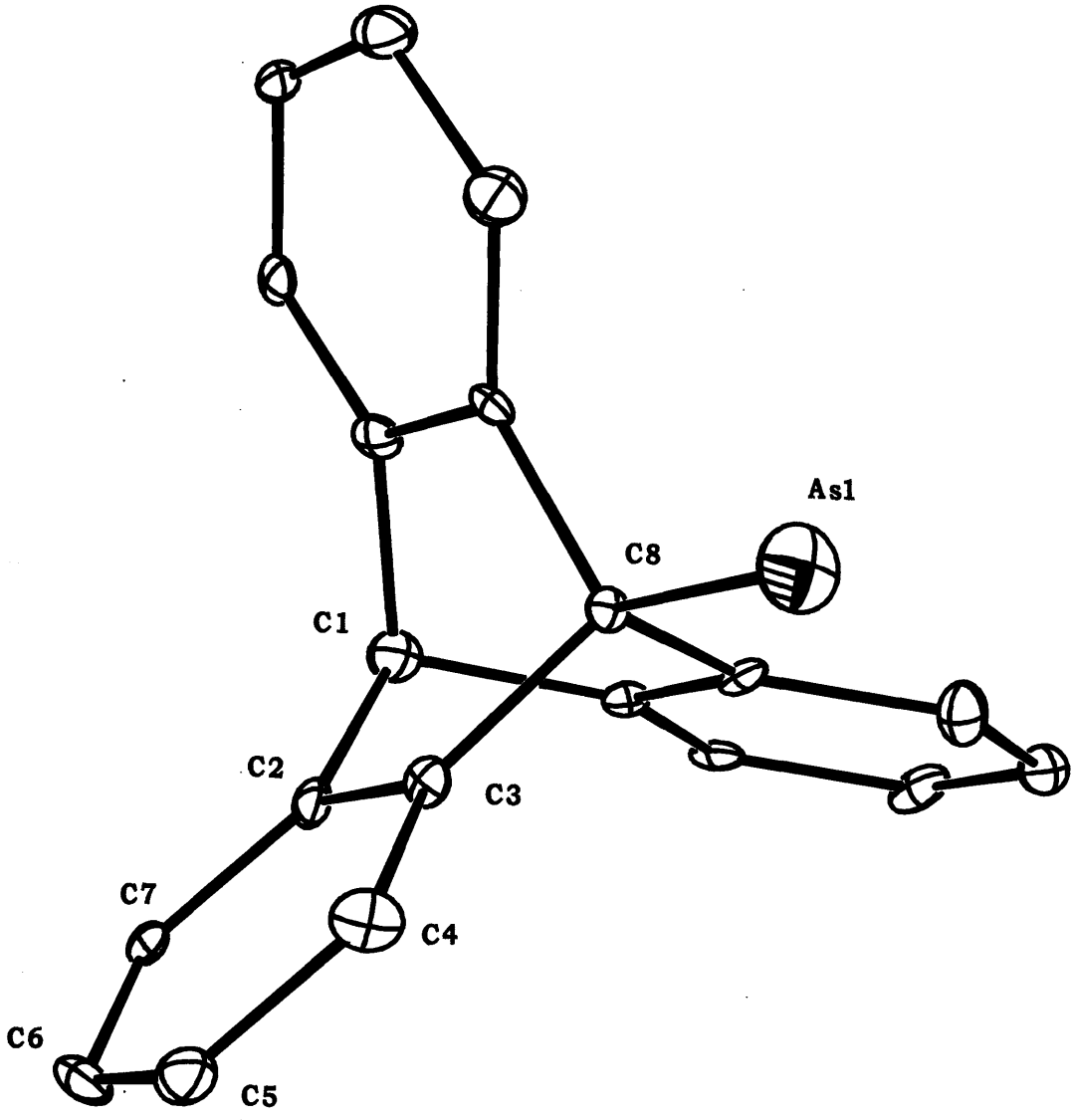


Figure 5.9 Molecular structure of [(tript)AsH$_2$] (26)

Selected bond length (Å) and angles (°) for (**26**): As(1)-C(8) 2.030(13), C(3)-C(8)-As(1) 112.9(7), Symmetry operation: - x + 1, y, - z + ½.

Crystals of (**34**) suitable for X-ray diffraction were obtained from diethyl ether. Its molecular structure (Figure 5.10) shows it to be monomeric, as is the case for the only other structurally characterised uncoordinated primary stibane, (**11**).[15] Unfortunately, its hydride ligands could not be located but the Sb-C bond length of 2.206(6) Å is not significantly different (within 3 e.s.d's) to those in both (**32**) and (**11**) (2.17 Å avg.).

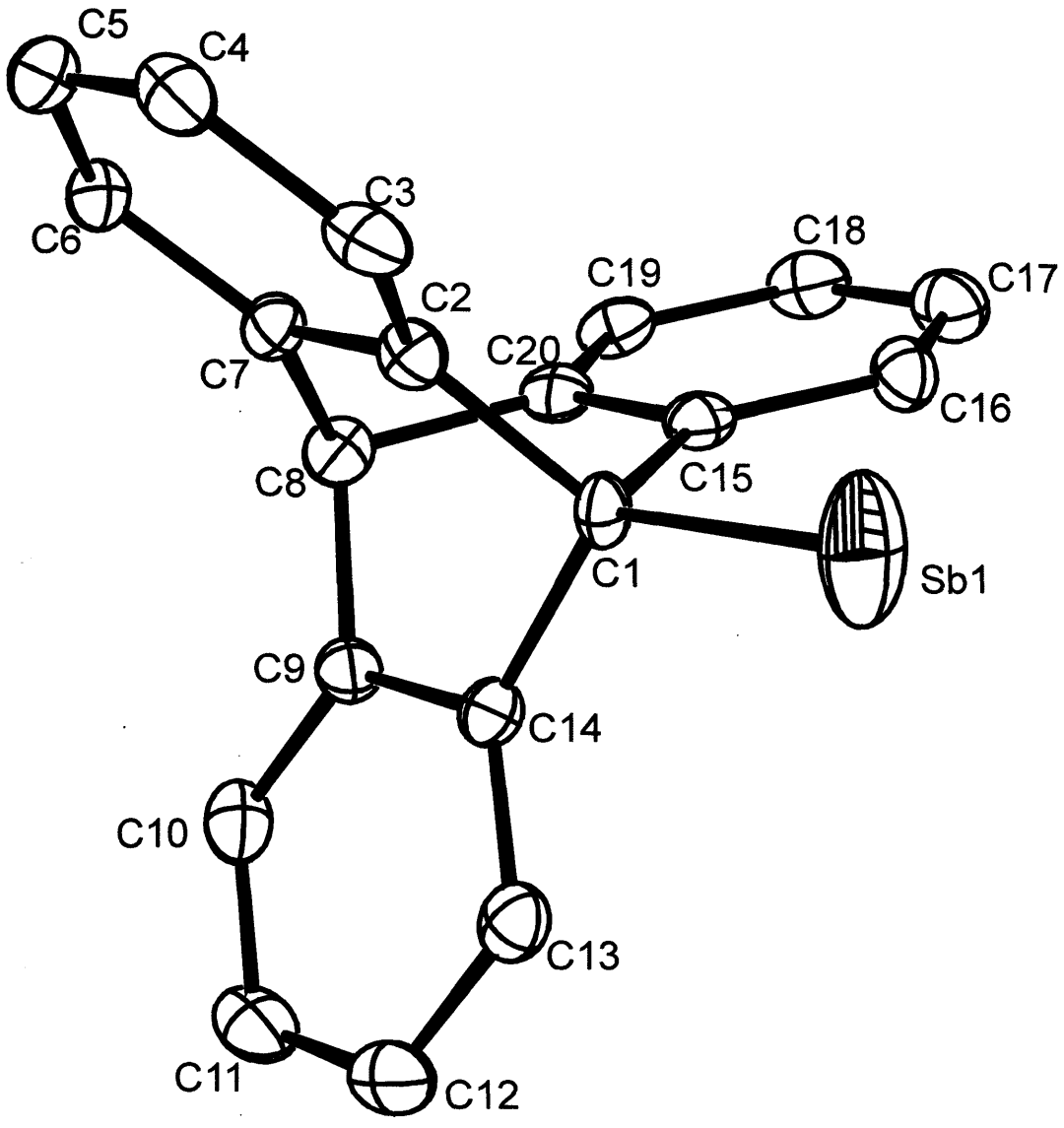


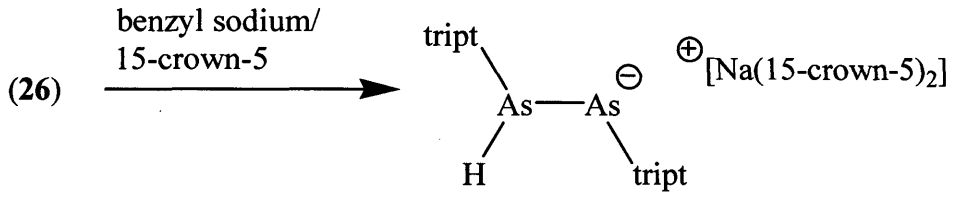
Figure 5.10 Molecular structure of [(tript)SbH_2] (34)

Selected bond length (Å) and angles (°) for (**34**): Sb(1)-C(1) 2.206(6), Sb(1)-C(1)-C(14) 111.9(4), Sb(1)-C(1)-C(8) 116.2(4), Sb(1)-C(1)-C(2) 112.8(4).

The infrared spectrum of (**34**) exhibits a broad Sb-H stretching absorption at 1865 cm^{-1} (*cf.* As-H stretch in (**26**), 2102 cm^{-1}), whilst its ^1H NMR spectrum displays a resonance at δ 3.16 ppm which was assigned to the hydride ligands (*cf.* δ 3.13 ppm for the AsH resonance for (**26**)). These data are consistent with those for related primary stibanes, *e.g.* [{$(Me_3Si)_2HC$}SbH_2][1] and (**11**)[15] which show Sb-H stretches at 1860 and 1875 cm^{-1} in their infrared spectra and hydride resonances at δ 2.12 and

2.66 ppm in their ^{1}H NMR spectra. A comment should be made about the high thermal stability of (**34**) (dec. 170 °C) which presumably arises from the kinetic protection afforded by the 9-triptycenyl ligand and is comparable to the stability of the bulky terphenyl substituted stibane [{2,6-(Ar')$_2$C$_6$H$_3$}SbH$_2$] (Ar' = C$_6$H$_2$-2,4,6-Pr$^i_3$) (**11**) (dec. 195 °C).

In an attempt to functionalise the primary arsine, (**26**), it was reacted with benzyl sodium in the presence of 15-crown-5. This did not led to the expected formation of [(tript)As(H)Na] but instead to the formation of (**35**) (Scheme 5.9). Compound (**35**) was presumably formed by a further reduction of the initially formed intended product, [(tript)As(H)Na].



(**35**)

Scheme 5.9 Preparation of [(tript)-As-As(H)-(tript)][Na(15-crown-5)$_2$] (35)

Unfortunately, due to the small yield of the compound (< 1 %), no data other than the X-ray crystal structure of this compound was obtained (Figure 5.11). Compound (**35**) crystallises in the monoclinic space group P2(1)/n with a heavily disordered [Na-(15-crown-5)] cation in the asymmetric unit. The arsenic-arsenic bond length in (**35**) was determined with 2.3970(16) Å. Compound (**35**) can be compared to [Li(THF){As(Bu^t)As(Bu^t)$_2$}]$_2$ which was reported by *Jones et al.* in 1986 and shows a As-As bond length of 2.403(2) Å.[49] The hydrogen atom of As was placed in a calculated position and is disordered over two sites. The arsenic carbon bond was determined to be 2.018(8) Å.

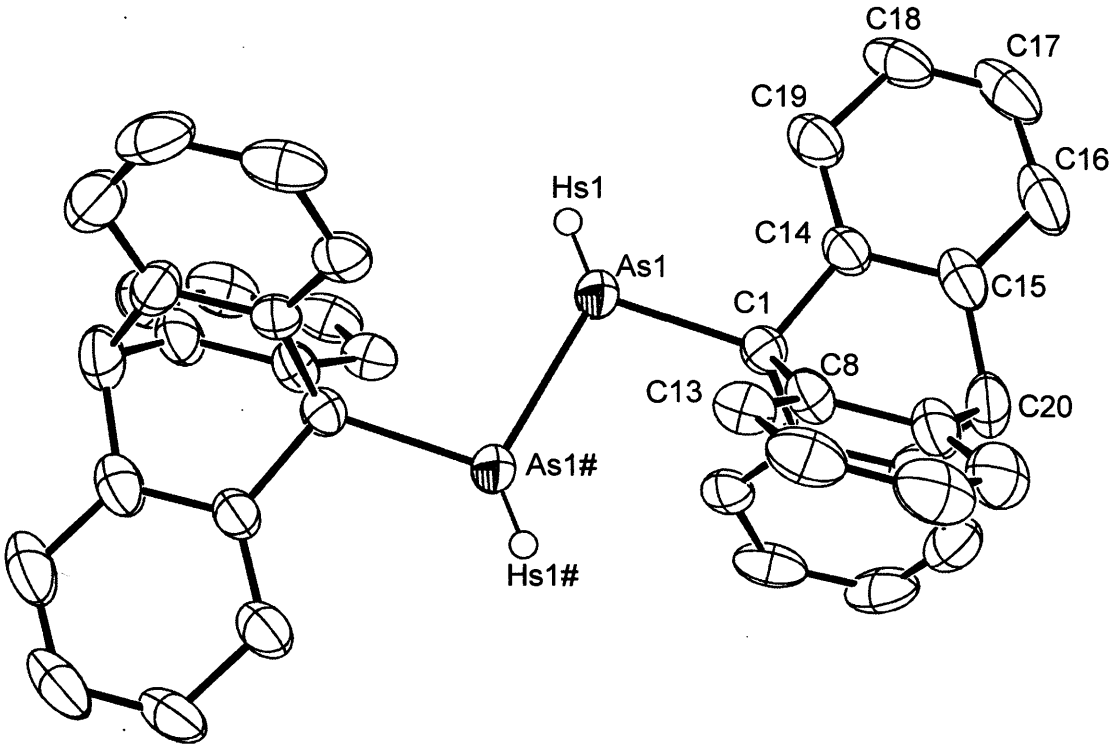
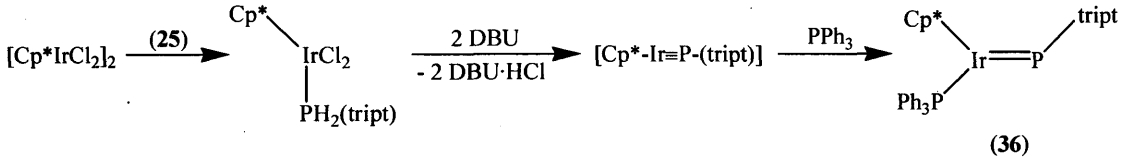


Figure 5.11 Anionic component of [(tript)-As-As(H)-(tript)][Na(15-crown-5)$_2$] (35)

Selected Bond length (Å) and angles (°): As(1)-C(1) 2.018(8), As(1)-As(1)# 2.3970(16), C(1)-As(1)-As(1)# 99.9(2), Symmetry operation # -x,-y,-z+1

5.3.4 Attempted synthesis of triptycenyl pnictinidene complexes

As recently as 2002, *Lammertsma et al.* reported the synthesis of several novel terminal iridium phosphinidene complexes, [Cp*(L)Ir=PMes*] (L = CO, PPh_3).[37] In an analogous fashion to those reported complexes, we attempted the reaction of one equivalent of $[Cp^*IrCl_2]_2$ with two equivalents of (**25**), followed by subsequent addition of two equivalents of DBU. A $^{31}P\{^1H\}$ NMR spectrum of this reaction mixture showed many phosphorus containing products of which none could be isolated or characterised. However, when the reaction of $[Cp^*IrCl_2]_2$ and (**25**) was carried out and subsequently was reacted with DBU in the presence of triphenylphosphine, the $^{31}P\{^1H\}$ NMR spectrum of an etheral extract of the reaction mixture displayed a doublet at δ 685.8 ppm ($^2J_{PP}$ = 122 Hz) which is believed to originate from the formation of [Cp*(PPh_3)Ir=P(tript)] (**36**). Unfortunately compound (**36**) proved not to be thermally stable and decomposed in solution. Because of this it was not possible to isolate or characterise it further. Due to the thermally unstable nature of the presumably formed phosphinidene compound (**36**), no attempts were undertaken to prepare arsinidene or stibinidene compounds from (**26**) or (**34**). This work has been conducted in cooperation with Dr. Mark Waugh.



Scheme 5.10 Preparation of a terminal phosphinidene complex

5.4 Conclusion

The preparation of several crystalline and air stable triptycene group 15 chlorides, $[HC(C_6H_4)_3CECl_2]$ (E = P, As, Sb, Bi), and hydride compounds, $[HC(C_6H_4)_3CEH_2]$ (E = As, Sb) has been described. In addition, the use of $[HC(C_6H_4)_3CPH_2]$ (**25**) as precursor to a transition metal terminal pnictinidene complex has been investigated, which showed the presumably formed phosphinidene compound to be thermally unstable.

5.5 Experimental

For general experimental procedures refer to appendix I. 9-Bromotriptycene[50] and 9-lithiotriptycene[42] were prepared by slight modifications of literature procedures. Other chemicals were commercially available and were when necessary purified according to literature procedures.[51]

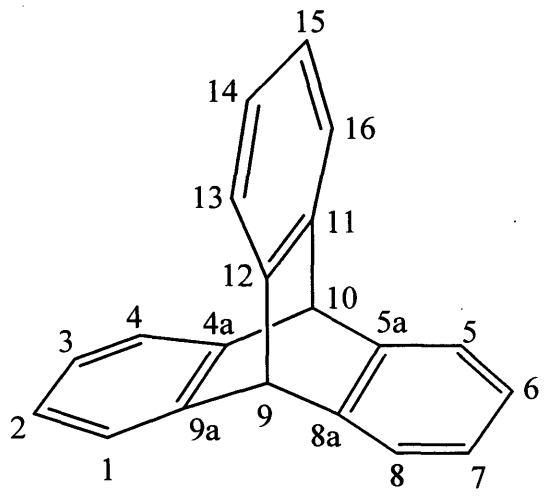


Figure 5.12 Numbering scheme for NMR assignment

[(tript)PCl_2] (30)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to - 78 °C and Bu^nLi (2.00 cm^3 of a 1.6M solution in hexane, 3.00 mmol) added. The resultant suspension was warmed to room temperature and refluxed for ½ h. The suspension was then cooled to - 78 °C and PCl_3 (0.40 cm^3, 4.5 mmol) added dropwise. Warming to room temperature gave an orange solution, which was heated to reflux for 90 minutes. The solvent was removed *in vacuo* and the residue extracted into toluene (30 cm^3). This was filtered and the solvent removed under vacuum to give (**30**) as an off-white powder.

(0.67 g, 63 %); mp. 222 - 227 °C; ^1H NMR (300 MHz, C_6D_6, 298 K) δ 5.02 (s, 1H, C10H), 6.67 - 7.60 (m, 12H, Ar-CH); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 54.6 (C10), 59.3 (d, $^1J_{PC}$ = 63.4 Hz, C9), 124.8 (d, $^4J_{PC}$ = 2.3 Hz, C2, C7, C14), 123.9 (C4, C5, C16), 125.7 (C3, C6, C15), 126.1 (d, $^3J_{PC}$ = 4.6 Hz, C1, C8, C13), 142.9 (d, $^2J_{PC}$ = 17.3 Hz, C9a, C8a, C12), 147.7 (d, $^3J_{PC}$ = 5.8 Hz, C4a, C5a, C11); $^{31}P\{^1H\}$ NMR

(121.7 MHz, C_6D_6, 298 K) δ 182.1 (s); MS EI: m/z (%) 355 (M^+, 35), 253 (tript, 100); IR (Nujol) ν/cm^{-1} 1287(w), 1257 (w), 1197 (m), 1132 (m), 1036 (m), 936 (sh), 896 (w), 845 (w), 820 (sh), 730 (s), 690 (w), 486 (m), 480 (m); Accurate mass MS (EI) calc. $C_{20}H_{13}PCl_2$: 354.0126, observed: 354.0128.

[(tript)$AsCl_2$] (31)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to -78 °C and Bu^nLi (2.00 cm^3 of a 1.6 M solution in hexane, 3.00 mmol) added. The resultant suspension was warmed to room temperature and refluxed for ½ h. The suspension was then cooled to - 78 °C and $AsCl_3$ (0.40 cm^3, 4.5 mmol) added dropwise. Warming to room temperature gave an orange solution, which was heated to reflux for 90 minutes. The solvent was removed *in vacuo* and extracted into toluene (30 cm^3). Concentration and placement at - 30 °C overnight gave colorless crystals of (**31**).

(0.70 g, 58 %), mp. 198 - 200 °C, ^1H NMR (400 MHz, CD_2Cl_2, 300 K): δ 5.40 (s, 1H, C10H), 6.99 - 7.39 (m, 12H, Ar-H); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 54.1 (C10), 54.4 (C9), 124.3 (C2, C7, C14), 125.2 (C4, C5, C16), 125.7 (C3, C6, C15), 126.0 (C1, C8, C13), 145.3 (C9a, C8a, C12), 147.3 (C4a, C5a, C11); MS APCI m/z (%): 309 (M^+, 100); IR (Nujol) ν/cm^{-1}: 479 (m, As-Cl).

[(tript)$SbCl_2$] (32)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to -78 °C and Bu^nLi (2.00 cm^3 of a 1.6 M solution in hexane, 3.00 mmol) added. The resultant suspension was warmed to room temperature and refluxed for ½ h. The suspension was then cooled to - 78 °C and a solution of $SbCl_3$ (1.03 g, 4.5 mmol) in THF (10 cm^3) added dropwise. Warming to room temperature gave an orange solution, which was heated to reflux for 90 minutes. The solvent was removed *in vacuo* and the residue extracted into toluene (30 cm^3). Hexane was added until precipitation commenced and the solution was filtered and placed at - 30 °C overnight to gave colourless crystals of (**32**).

(0.70 g, 52 %), mp. 246 - 247 °C, ^1H NMR (300.5 MHz, C_6D_6, 298 K) δ 5.41 (s, 1H, C10H), 7.03 - 7.54 (m, 12H, Ar-H), $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2, 298 K) δ

54.3 (C10), 54.4 (C9), 122.5 (C2, C7, C14), 124.9 (C4, C5, C16), 126.1 (C3, C6, C15), 126.4 (C1, C8, C13), 145.4 (C9a, C8a, C12), 147.9 (C4a, C5a, C11); MS APCI m/z (%): 444 (M^+, 100); IR (Nujol) ν cm^{-1}: 545 (m), 465 (m) Sb-Cl; Accurate mass MS (CI) calc. mass for $C_{20}H_{13}{}^{121}SbCl_2$: 444.9505, measured mass: 444.9518.

[(tript)$BiCl_2$] (33)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to - 78 °C and Bu^nLi (2.00 cm^3 of a 1.6 M solution in hexane, 3.00 mmol) added. The resultant suspension was warmed to room temperature and refluxed for ½ h. The suspension was then cooled to - 78 °C and a solution of $BiCl_3$ (1.42 g, 4.5 mmol) in THF (10 cm^3) added dropwise. The suspension was warmed to room temperature and stirred for 16 hours in the absence of light. The solvent was removed *in vacuo* and the residue extracted into toluene (30 cm^3). Hexane was added until precipitation commenced and the solution was filtered and placed at - 30 °C overnight which gave colourless crystals of (**33**) (0.20 g, 13 %). mp. 155 °C, ^1H NMR (300.5 MHz, C_6D_6, 298 K) δ 5.10 (s, 1H, C*H*), 6.60 - 7.30 (m, 12H, Ar-H), $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6, 298 K) δ 53.3 (C10), 53.2 (C9), 122.5 (C2, C7, C14), 124.0 (C4, C5, C16), 124.9 (C3, C6, C15), 127.9 (C1, C8, C13), 144.4 (C9a, C8a, C12), 146.9 (C4a, C5a, C11); MS CI m/z (%): 533 (M^+, 15), 253 (tript, 100]; IR (Nujol) ν/cm^{-1}: 475 (m, Bi-Cl); Accurate mass MS (CI) calc. mass for $C_{20}H_{13}Bi^{35}Cl_2$: 532.0193, measured mass: 532.0188.

[(tript)AsH_2] (26)

A suspension of [(trip)$AsCl_2$] (0.65 g, 1.6 mmol) in diethyl ether (20 cm^3) was added to a solution of $LiAlH_4$ (0.08 g, 2.00 mmol) in diethyl ether (20 cm^3) at - 78°C. The resultant suspension was warmed to room temperature and stirred in the absence of light for 60 hours. The solution was filtered, concentrated to *ca.* 20 cm^3 at placed at - 30 °C overnight to give colourless crystals of (**26**).

(0.36 g, 67 %); mp. 235 - 240 °C dec. ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 3.13 (s, 2H, AsH), 5.16 (s, 1H, C_3CH), 6.76 - 7.47 (m, 12H, ArH); IR (Nujol) υ/cm^{-1}: (m, $\nu_{As\text{-}H}$ 2102); Accurate mass MS (CI) calc. mass for $C_{20}H_{15}As$: 330.0384, measured mass: 330.0384.

[(tript)SbH_2] (34)

A suspension of [(tript)$SbCl_2$] (0.50 g, 1.1 mmol) in diethyl ether (20 cm^3) was added to a solution of $LiAlH_4$ (0.08 g, 2.00 mmol) in diethyl ether (20 cm^3) at - 78 °C. The resultant suspension was warmed to room temperature and stirred in the absence of light for 60 hours. The solution was then filtered, concentrated to *ca.* 20 cm^3, and placed at - 30 °C overnight to give colourless crystals of (**34**)
(0.36 g, 67 %), mp. 170 - 172 °C dec., ^1H NMR (300.5 MHz, C_6D_6, 298 K) δ 3.16 (s, 2H, SbH_2), 5.16 (s, 1H, C10-H), 6.82 - 6.75 (m, 6H, ArH), 7.20 - 7.49 (m, 6H, ArH); $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6, 298 K) δ 54.9 (C10), 55.1 (C9), 123.5 (C2, C7, C14), 124.9 (C4, C5, C16), 125.1 (C3, C6, C15), 126.1 (C1, C8, C13), 146.6 (C9a, C8a, C12), 148.7 (C4a, C5a, C11); MS CI m/z (%): 377 (M^+, 20), 253 ($tript^+$, 100); IR (Nujol) ν/cm^{-1}: 1865 (m, Sb-H); Accurate mass MS (CI) calc. mass for $C_{20}H_{15}{}^{121}Sb$: 376.0106, measured mass: 376.0200.

[(tript)-As-As(H)-(tript)][Na(15-crown-5)$_2$] (35)

A solution of (**26**) (0.325 g, 1.0 mmol) in toluene (10 cm^3) was added to a solution of benzyl sodium (0.120 g, 1.0 mmol) in toluene (20 cm^3) at - 78 °C. 15-Crown-5 (350 μl) was added and the mixture slowly warmed to ambient temperature. A yellow precipitate was formed. Volatiles were removed *in vacuo* and the residue extracted in THF and hexane was added to the point of first crystallisation. Cooling to - 30 °C resulted in colourless crystals of (**35**). Yield < 1 %.

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Chapter Six

6 Miscellaneous results

6.1 Introduction

The miscellaneous results in this chapter were achieved during the investigations described in other chapters. The results in formamidinate and phenolate chemistry came about during a six month visit to the laboratory of Dr. Peter Junk, Monash University in Melbourne, Australia.

6.2 Results and discussion

6.2.1 Further investigations into iridium (I) chemistry

Due to the success we had in the preparation of the iridaphosphirene $[Ir(CO)(PPh_3)_2\{\eta^2=C(Bu^t)P(Cy)\}]$, from Vaska's compound $[IrCl(CO)(PPh_3)_2]$ and $[CyP=C(Bu^t)MgCl]$ (**1**) described in chapter two, it was sought to examine the reactivity of (**1**) towards $[IrCl(PR_3)_3]$, R = Et or Ph to extend this work. As part of this study a number of unexpected results were obtained in the preparation of the iridium precursors and in their subsequent reactions with (**1**). These included the isolation and structural characterisation of the known orthometallated isomer of Vaska's compound, $[IrHCl(CO)(PPh_3)\{\eta^2\text{-}PPh_2(C_6H_4)\}]$, and the Ir(I) complexes, $[IrCl(COD)(PEt_3)_n]$, n = 1 or 2.

In an attempt to synthesise $[IrCl(PEt_3)_3]$ by the reaction of three equivalents of PEt_3 with $[\{Ir(COD)Cl\}_2]$ in diethyl ether, by the published route,[1] two crystalline products were formed. After manual separation both compounds were found to contain the cyclooctadiene ligand by NMR spectroscopy. Integration of the ^1H NMR spectrum of the minor orange product suggested its formulation as $[IrCl(COD)(PEt_3)]$, (**2**), whilst the major yellow product analysed spectroscopically as $[IrCl(COD)(PEt_3)_2]$, (**3**).

$$[Ir(COD)Cl]_2 \xrightarrow{n\ PEt_3\ /\ Et_2O} [IrCl(COD)(PEt_3)_n]$$

(**2**) n = 1
(**3**) n = 2

Scheme 6.1 Preparation of some iridium triethylphosphine compounds

X-ray crystallography subsequently proved these deductions (*vide infra*) and, subsequently, both compounds were intentionally prepared in good yields by the reactions of 1 or 2 equivalents of PEt_3 with $[\{Ir(COD)Cl\}_2]$. In retrospect, the fact that $[IrCl(PEt_3)_3]$ was not formed in the initial reaction is not surprising as it has been previously shown that only strongly π-acidic phosphines will displace the COD ligand from $[\{Ir(COD)Cl\}_2]$.[2] Synthesis of the mono-phosphine complex, (**2**), has been reported before[2, 3] but very little characteristic data were included in these accounts. The olefinic proton and carbon centres of the co-ordinated COD ligand that are *trans-* to the phosphine ligand resonate at significantly lower field than those *trans-* to the chloride, as expected. In addition, a $^2J_{PC}$ coupling is only seen between the phosphorus centre and the olefinic carbons *trans-* to it. Compound (**3**) was unknown prior to this report. As already mentioned, the integration of its ^1H NMR spectrum suggested its empirical formula but little information about its co-ordination geometry could be gained from its ^1H- or $^{31}P\{^1H\}$ NMR spectra. These display broad peaks which are indicative of a fluxional process occurring in solution. This also meant that no meaningful data could be obtained from the ^{13}C NMR spectrum of (**3**). Efforts were made to examine the fluxional nature of the compound in solution using variable temperature NMR experiments but no resolution of the spectra was observed. The fluxional process is most likely due to an exchange between compounds (**3**) and (**2**) brought about by a rapid decomplexation / complexation of one PEt_3 ligand. Closely related exchange processes have been reported for complexes of the type $[IrCl(COD)(PR_3)_n]$.[2]

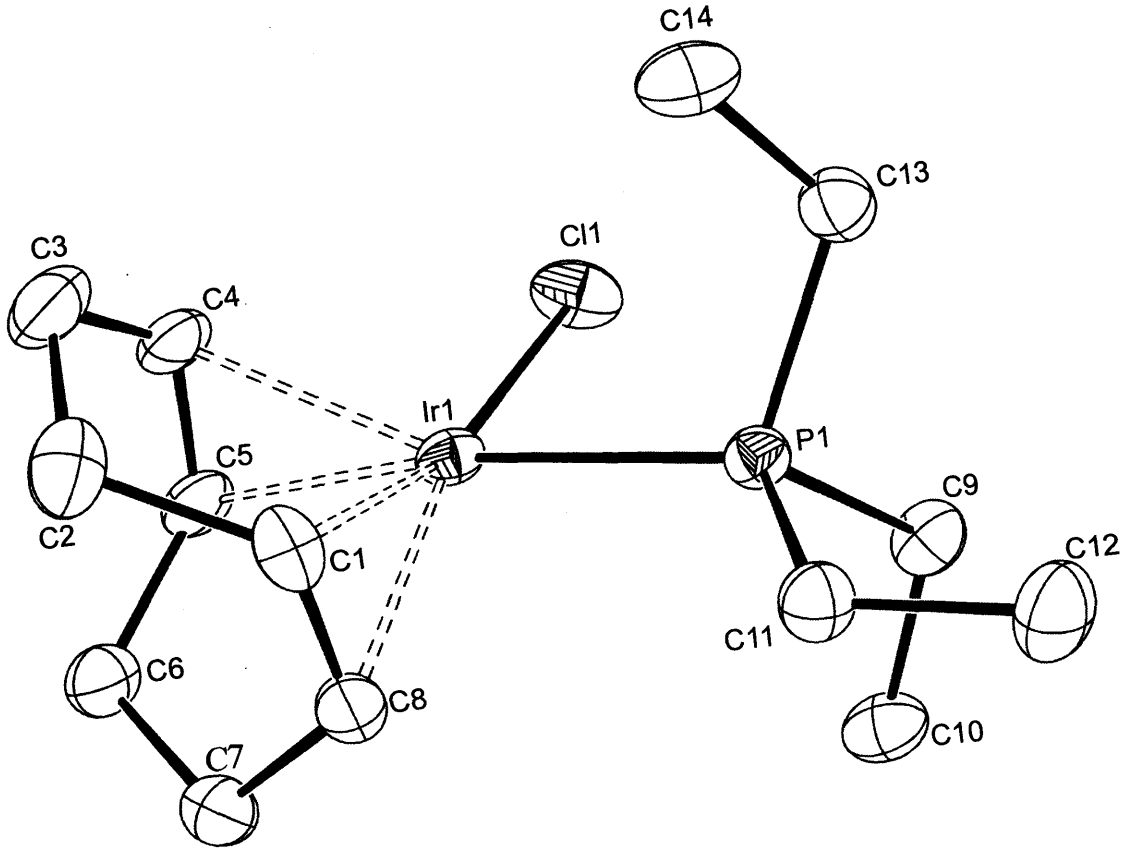


Figure 6.1 Molecular structure of [IrCl(COD)(PEt_3)] (2)

Selected bond lengths (Å) and angles (°): Ir(1)-C(8) 2.104(4), Ir(1)-C(1) 2.133(5), Ir(1)-C(4) 2.188(5), Ir(1)-C(5) 2.206(5), Ir(1)-P(1) 2.3076(14), Ir(1)-Cl(1) 2.3622(13), C(1)-C(8) 1.424(7), C(4)-C(5) 1.385(7), P(1)-Ir(1)-Cl(1) 87.33(5).

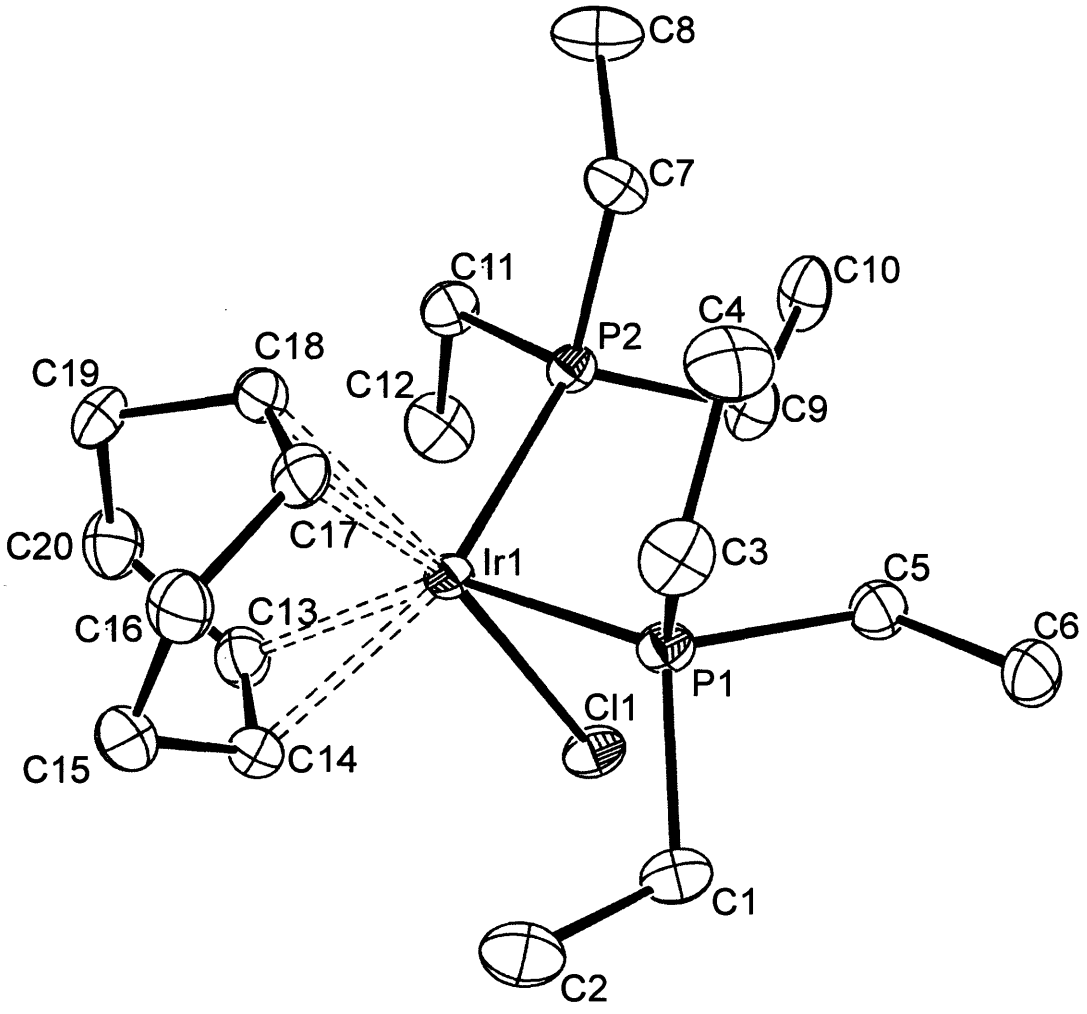


Figure 6.2 Molecular structure of [IrCl(COD)(PEt_3)$_2$] (3)

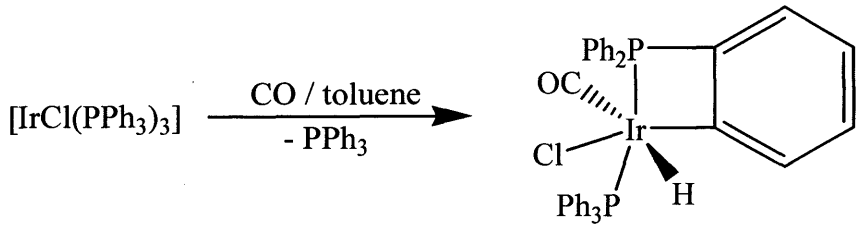
Selected bond lengths (Å) and angles (°): Ir(1)-C(13) 2.143(4), Ir(1)-C(14) 2.144(4), Ir(1)-C(17) 2.160(4), Ir(1)-C(18) 2.164(4), Ir(1)-P(2) 2.3662(10), Ir(1)-P(1) 2.3997(11), Ir(1)-Cl(1) 2.4243(11), P(2)-Ir(1)-P(1) 100.42(4), P(2)-Ir(1)-Cl(1) 89.57(4), P(1)-Ir(1)-Cl(1) 82.70(4).

The molecular structures of (**2**) and (**3**) are shown in Figure 6.1 and Figure 6.2 respectively. The iridium centre of (**2**) possesses a distorted square planar geometry with the chloride ligand *cis*- to the phosphine. A similar arrangement has recently been observed in the phosphole-iridium complex, [IrCl(COD){P(Ph)C_2Me_2-C_2H_2}].[4] It is noteworthy that the olefinic carbon centres *trans*- to the phosphine ligand in (**2**) are significantly more distant than those *cis*- (2.197 Å avge, *versus* 2.118 Å avge.) and concomitantly the C(4)-C(5) bond length [1.385(7) Å] is shorter

than the C(1)-C(8) distance [1.424(7) Å]. Both facts are compatible with the observed downfield NMR shifts of the olefinic fragment *trans-* to the phosphine relative to those *cis-*. Finally the Ir-Cl and Ir-P bond lengths fall within the normal range for such complexes.[5]

The structural characterisation of (**3**) represents the first of any compound of the type $[IrCl(COD)(PR_3)_2]$. The co-ordination geometry about the iridium centre can be considered as distorted trigonal bipyramidal with both phosphines in equatorial positions and the COD ligand taking up axial and equatorial sites. As would be expected with this arrangement, the axial olefinic fragment is significantly more distant from the iridium centre than the equatorial fragment. In addition, both Ir-P bond lengths (2.383 Å avge.) are longer than that in (**2**), presumably for both steric and electronic reasons.

When the reactions of either (**2**) or (**3**) with the phosphavinyl Grignard reagent, (**1**), were examined, only intractable mixtures of products resulted. Similarly, a number of inseparable products were formed in the reaction of $[IrCl(PPh_3)_3]$ with (**1**) in toluene. In an attempt to generate more separable derivatives of these products, carbon monoxide was bubbled through the mixture for 30 min and the solution was left under a CO atmosphere for several days after which time a small amount of colourless crystals deposited.



(**4**)

Scheme 6.2 Preparation of $[IrHCl(CO)(PPh_3)\{\eta^2\text{-}PPh_2(C_6H_4)\}]$ (4)

The spectroscopic data for these suggested the presence of a hydride ligand on the iridium centre. On closer inspection the data were found to be identical to those reported for the orthometallated isomer of Vaska's compound,

[IrHCl(CO)(PPh_3){η^2-$PPh_2(C_6H_4)$}], (**4**).[6] This compound presumably formed in the present reaction due to the presence of unreacted [$IrCl(PPh_3)_3$] which gave Vaska's compound upon treatment with CO. This subsequently isomerised in solution at room temperature over several days. Despite several previous reports[6, 7] detailing the synthesis and reactivity of (**4**) it has not been crystallographically characterised. Perhaps this is due to the original account of this compound which suggested that it is thermally unstable in the solid state and solution at 25 °C. Obviously, this work has shown this not to be the case. It has been proposed that (**4**) exists as 2 isomers,[6] the predominant one having the hydride ligand *trans-* to the CO ligand. Our spectroscopic data matched that originally assigned to this isomer so an X-ray crystal structure analysis on (**4**) was carried out. This confirmed the original proposal (Figure 6.3).

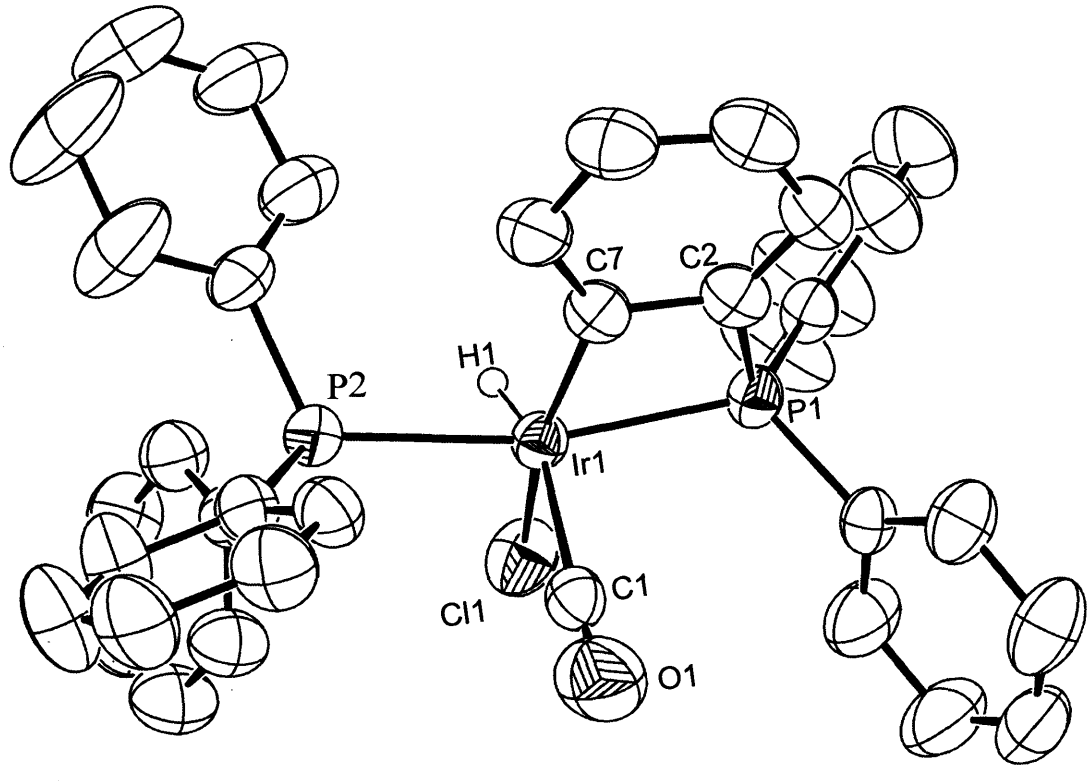


Figure 6.3 Molecular structure of [IrHCl(CO)(PPh_3)$_2${η^2-$PPh_2(C_6H_4)$}] (4)

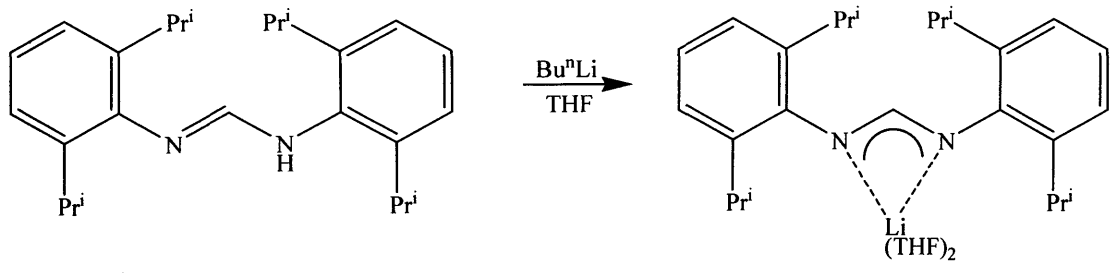
Selected bond lengths (Å) and angles (°): Ir(1)-C(1) 2.028(6), Ir(1)-C(7) 2.053(5), Ir(1)-P(1) 2.3210(14), Ir(1)-P(2) 2.3405(13), Ir(1)-Cl(1) 2.4321(14), Ir(1)-H(1) 1.55(2), C(1)-Ir(1)-C(7) 94.68(18), C(1)-Ir(1)-P(1) 90.98(13), C(7)-Ir(1)-P(1) 68.19(13), C(1)-Ir(1)-P(2) 95.68(13), C(7)-Ir(1)-P(2) 97.88(13), P(1)-Ir(1)-P(2)

165.07(4), C(1)-Ir(1)-Cl(1) 92.17(14), C(7)-Ir(1)-Cl(1) 165.09(12), P(1)-Ir(1)-Cl(1) 98.50(5), P(2)-Ir(1)-Cl(1) 94.60(5), C(1)-Ir(1)-H(1) 175(2), C(7)-Ir(1)-H(1) 81(2), P(1)-Ir(1)-H(1) 85(2), P(2)-Ir(1)-H(1) 88(2), Cl(1)-Ir(1)-H(1) 92(2).

Compound (**4**) is monomeric and the iridium centre possesses a distorted octahedral geometry with the two phosphorus centres *trans-* to each other. The X-ray data were of sufficient quality for the location and isotropic refinement of the hydride ligand to be carried out. This was found to be *trans-* to the carbonyl ligand. The Ir-P, Ir-H and Ir-Cl bond lengths are all in the normal ranges and the distance from the iridium centre to the metallated carbon atom, [Ir(1)-C(7) 2.053(5) Å] is close to that in the related complex $[IrH(PPh_3)_2\{PPh_2(C_6H_4)\}]$ (2.062 Å).[8]

6.2.2 Main group formamidinate chemistry

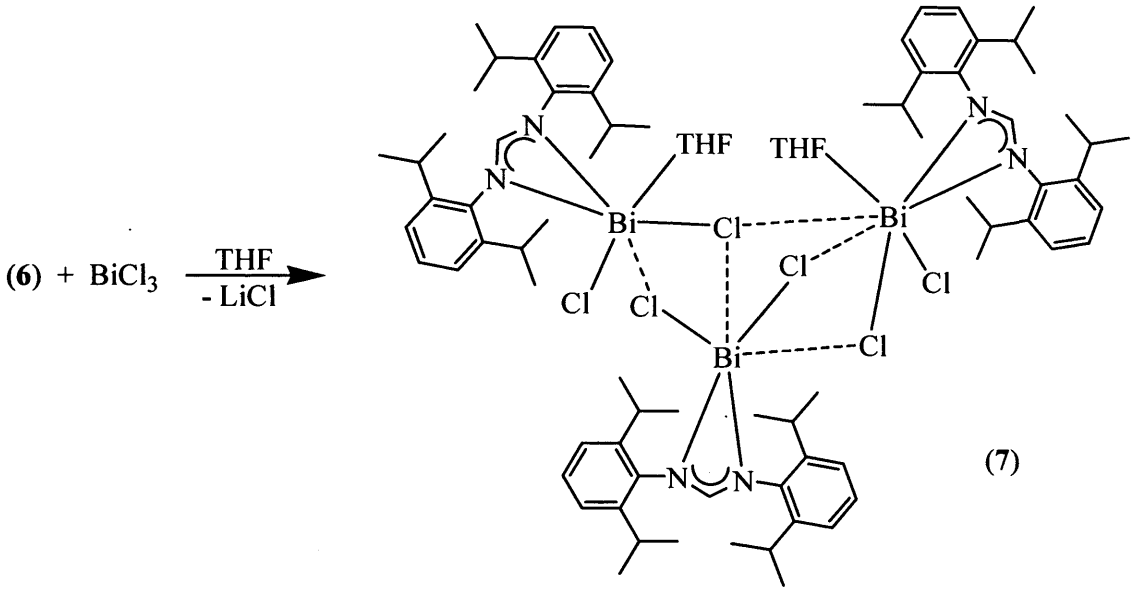
There is significant academic interest in the use of sterically encumbered aromatic substituents to isolate kinetically stable low valent species, *e.g.* main group compounds.[9-12] One example of a ligand class containing such substituents are the N-N'-di(aryl)formamidinates. Several lithium and sodium complexes of N-N'-di(2,6-dialkylphenyl)formamidinates have been reported recently.[13] One of those, N-N'-di(2,6-diisopropylphenyl)formamidinate (Fiso) (**6**), was used in an attempt to prepare some group 15 complexes. Compound (**6**) is readily lithiated when HFiso (**5**) is treated with Bu^nLi in THF or DME (Scheme 6.3).[13]



(**5**) (**6**)

Scheme 6.3 Preparation of [Li{η^2-N-N'-di(2,6-isopropylphenyl)formamidinate}$(THF)_2$] (6)

When a solution of (**6**) was reacted with a solution of $BiCl_3$ in THF and stirred in the absence of light overnight, a colour change from yellow to brown was observed. Slow cooling of a toluene extract resulted in colourless crystals of (**7**).



(7)

Scheme 6.4 Reaction of (6) with $BiCl_3$

The molecular structure showed (**7**) to crystallise in a monoclinic space group with two molecules of toluene in the asymmetric unit. There are three independent bismuth centres, two co-ordinated by a molecule of THF and one not. All bismuth centres have distorted octahedral geometries and the formamidinate ligand NCN backbones appear to be largely delocalised. The μ^2-bridging bismuth chloride bonds are in the expected range while the μ^3-bridging chloride showed longer bond distances to Bi(1) and Bi(2).

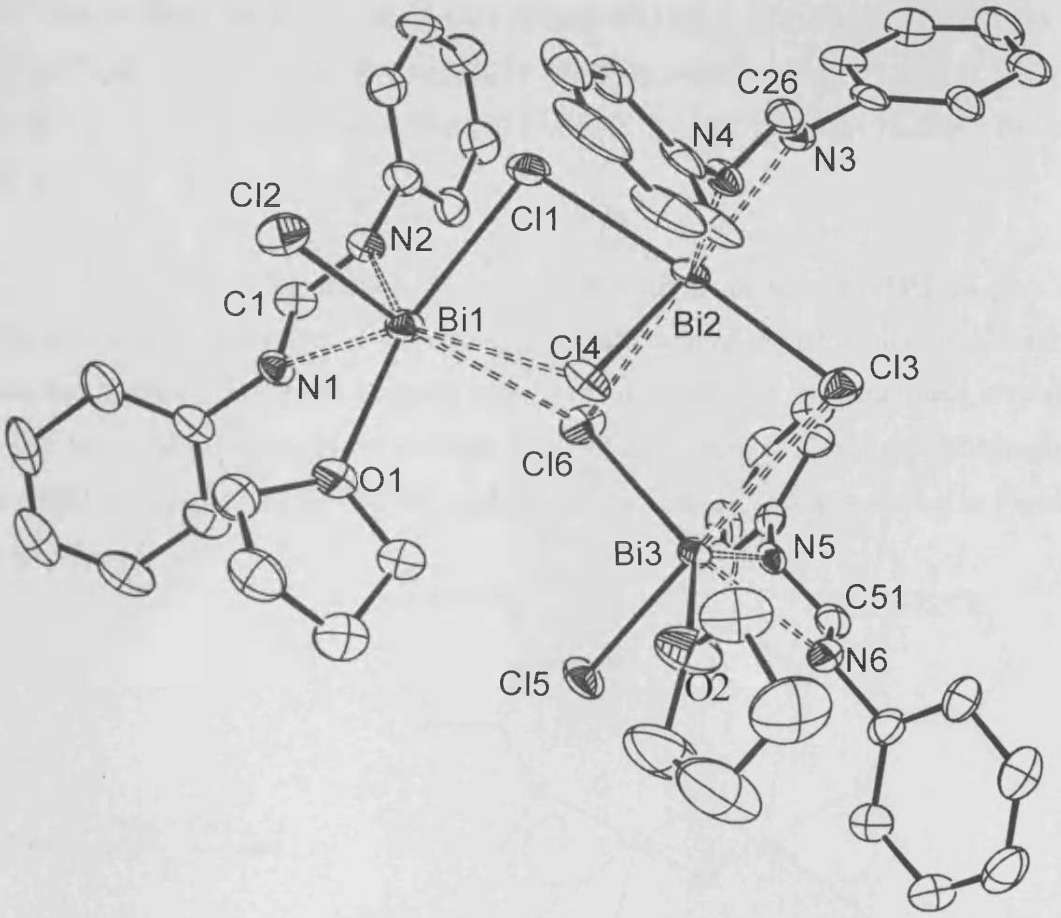
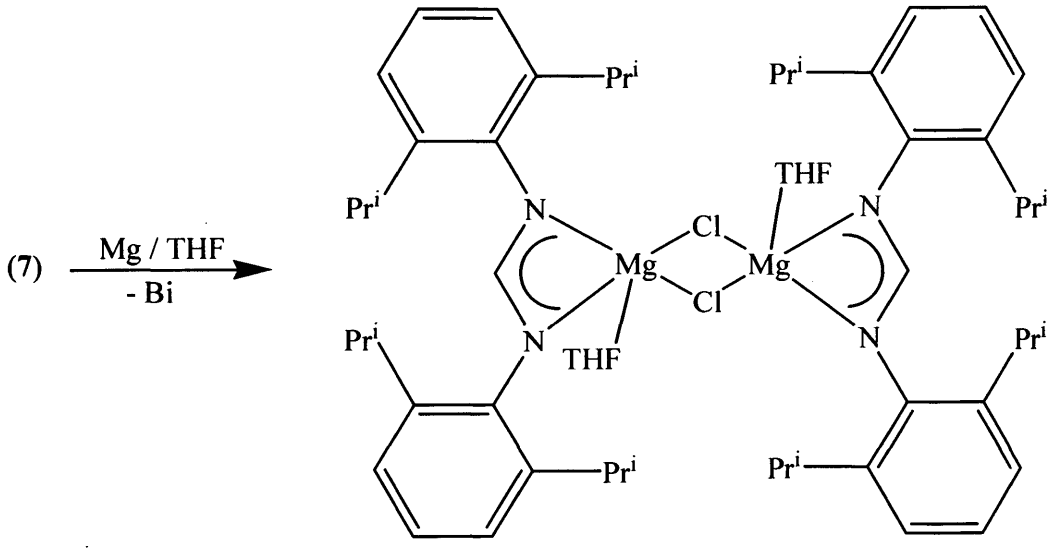


Figure 6.4 Molecular structure of (7) (isopropyl groups obmitted for clarity)

Selected bond length (Å) and angles (°): Bi(1)-N(2) 2.333(5), Bi(1)-N(1) 2.360(5), Bi(1)-Cl(2) 2.4893(19), Bi(1)-Cl(1) 2.7965(18), Bi(1)-Cl(4) 3.415, Bi(1)-Cl(6) 3.1874(19), Cl(1)-Bi(2) 2.7441(17), N(1)-C(1) 1.320(8), C(1)-N(2) 1.313(8), Bi(2)-N(4) 2.253(5), Bi(2)-N(3) 2.438(5), Bi(2)-Cl(4) 2.5878(17), Bi(2)-Cl(3) 2.6230(17), Bi(2)-Cl(6) 3.3753(18), C(2)-C(3) 1.408(9), Bi(3)-N(5) 2.292(5), Bi(3)-N(6) 2.387(5), Bi(3)-Cl(5) 2.4727(17), Bi(3)-Cl(6) 2.7512(17), Bi(3)-Cl(3) 3.3137(18), N(3)-C(26) 1.309(8), N(4)-C(26) 1.338(8), N(5)-C(51) 1.325(7), N(6)-C(51) 1.318(8), N(2)-Bi(1)-N(1) 56.86(18), N(2)-Bi(1)-Cl(2) 94.44(14), N(1)-Bi(1)-Cl(2) 89.85(13), N(2)-Bi(1)-O(1) 136.19(17), N(1)-Bi(1)-O(1) 79.34(16), Cl(2)-Bi(1)-O(1) 84.16(11), N(2)-Bi(1)-Cl(1) 77.23(14), N(1)-Bi(1)-Cl(1) 133.74(13), Cl(2)-Bi(1)-Cl(1) 88.15(6), O(1)-Bi(1)-Cl(1) 146.09(11), N(2)-Bi(1)-Cl(6) 93.35(14), N(1)-Bi(1)-Cl(6) 102.51(13), Cl(2)-Bi(1)-Cl(6) 167.58(5), O(1)-Bi(1)-Cl(6) 96.84(11),

Cl(1)-Bi(1)-Cl(6) 84.15(5), Bi(2)-Cl(1)-Bi(1) 94.14(5), C(1)-N(1)-C(2) 123.3(5), C(1)-N(1)-Bi(1) 92.8(4), C(2)-N(1)-Bi(1) 142.9(4), N(2)-C(1)-N(1) 116.2(6), Bi(3)-Cl(6)-Bi(1) 119.62(6), Bi(3)-Cl(6)-Bi(2) 81.61(4), Bi(1)-Cl(6)-Bi(2) 76.31(4), Bi(2)-Cl(3)-Bi(3) 84.69(5).

In an attempt to reduce (**7**) with elemental magnesium in THF to give a dibismuthene compound, a colour change to black was observed, which presumably was the result of elemental bismuth been formed (Scheme 6.5). Colourless crystals could be obtained upon slow cooling of a toluene extract. X-ray crystallography revealed the product to be (**8**), the molecular structure of which is shown in Figure 6.5.



(**8**)

Scheme 6.5 Preparation of [{FisoMg(THF)}$_2$(μ-Cl)$_2$] (8)

Compound (**8**) crystallises in a tetragonal space group with two independent molecules in the asymmetric unit. The two magnesium atoms are bridged by two chlorides with an average magnesium chlorine distance of 2.424 Å. The bond length between C(1) and N(1) was determined to be 1.314(6) Å whilst that between C(1) and N(2), 1.312(6) Å, both indicating the delocalisation of the backbone.

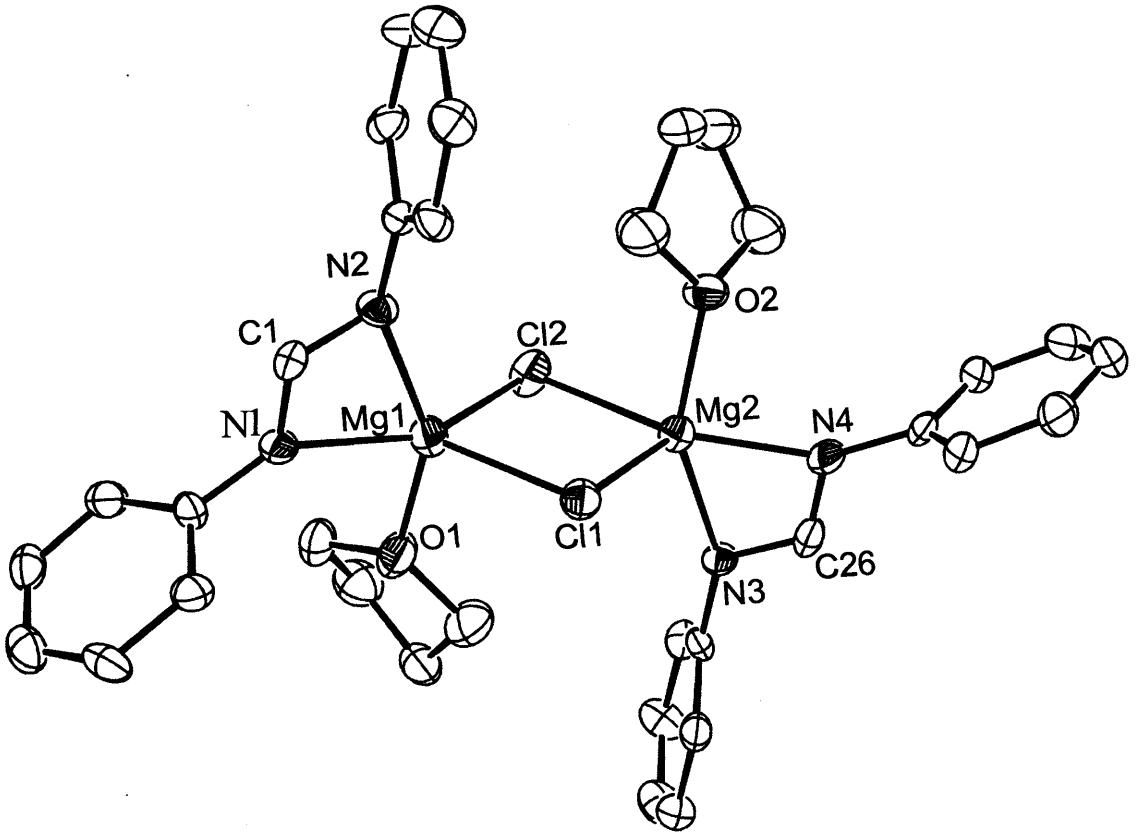


Figure 6.5 Molecular structure of [{FisoMg(THF)}$_2$(μ-Cl)$_2$] (8) (Pr^i groups omitted for clarity)

Selected bond length (Å) and angles (°): Cl(1)-Mg(1) 2.406(2), Cl(1)-Mg(2) 2.410(2), Mg(1)-N(1) 2.076(5), Mg(1)-N(2) 2.188(4), Mg(1)-Cl(2) 2.449(2), N(1)-C(1) 1.314(6), N(1)-C(2) 1.425(6), C(1)-N(2) 1.312(6), Cl(2)-Mg(2) 2.434(2), Mg(2)-N(4) 2.080(5), Mg(2)-N(3) 2.193(4), N(2)-C(14) 1.430(6), C(2)-C(7) 1.408(7), C(2)-C(3) 1.419(7), Mg(1)-Cl(1)-Mg(2) 88.55(7), N(1)-Mg(1)-N(2) 63.83(17), N(1)-Mg(1)-Cl(1) 121.58(13), N(2)-Mg(1)-Cl(1) 103.35(13), O(1)-Mg(1)-Cl(2) 88.98(12), N(1)-Mg(1)-Cl(2) 146.13(14), N(2)-Mg(1)-Cl(2) 107.61(13), Cl(1)-Mg(1)-Cl(2) 92.07(7), C(1)-N(1)-C(2) 122.6(5), C(1)-N(1)-Mg(1) 91.0(4), C(2)-N(1)-Mg(1) 145.3(3), N(2)-C(1)-N(1) 118.4(5), Mg(2)-Cl(2)-Mg(1) 87.04(7).

A further compound was isolated after the reduction with magnesium was attempted which proved to be a magnesium bromide THF adduct. The molecular structure is depicted in Figure 6.6.

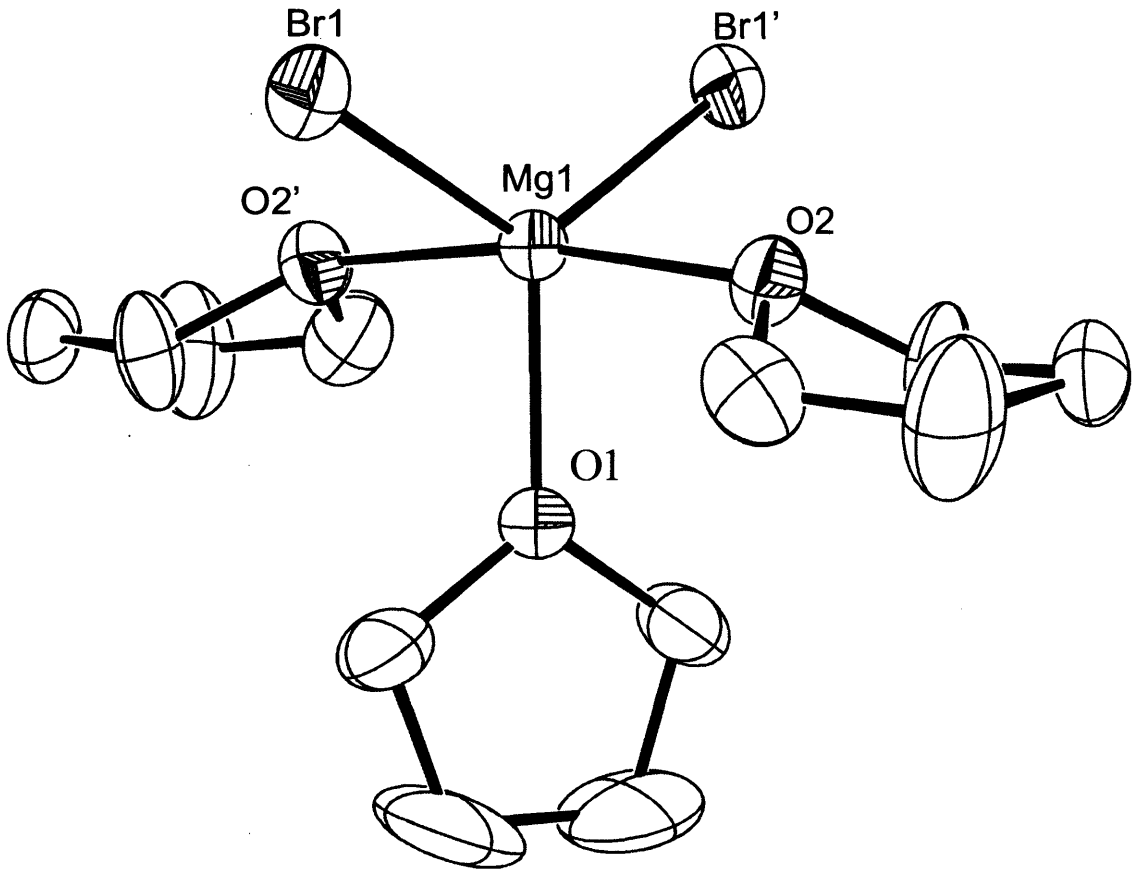
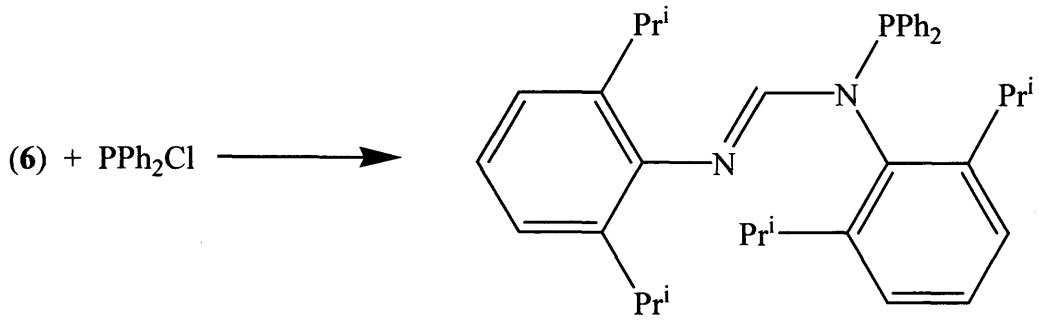


Figure 6.6 Molecular structure of $[MgBr_2(THF)_3]$ (9)

Selected bond length (Å) and angles (°): Br(1)-Mg(1) 2.502(2), Mg(1)-O(1) 2.041(10), Mg(1)-O(2) 2.131(7), O(1)-Mg(1)-O(2) 84.8(2), O(1)-Mg(1)-Br(1) 116.94(9), O(2)-Mg(1)-Br(1) 92.29(19), O(2)'-Mg(1)-O(2) 169.6(4), Symmetry operation ': -x + 1, y, -z + ½.

Compound (**9**) has been reported previously,[14-16] but no crystallographic information were given in the original reports.[14] The magnesium centre in (**9**) shows trigonal bipyramidal geometry with both bromines and one THF on the equatorial and the other two THF molecules on the axial sites. The O(2)'-Mg(1)-O(2) angle is 167.6(4)°, slightly bent from the ideal angle of 180°, whilst the O(1)-Mg(1)-Br(1) angle was measured at 116.94(9)° slightly distorted from the ideal 120°. Compound (**9**) is isostructural to the recently reported $[MgI_2(THF)_3]$[17] which shows the angle between the two axial THF groups and the magnesium centre to be 167.6° while the angles in the equatorial plane average 119.34°.

When the reaction of (**6**) with ECl_3 (E = P, Sb) was carried out, it led only to the formation of inseparable product mixtures. When (**6**) was reacted with PPh_2Cl in THF no colour change was observed, but the expected product (**10**) was formed and could be isolated as colourless crystals.



(**10**)

Scheme 6.6 Reaction of (6) with PPh_2Cl

Compound (**10**) crystallises in the monoclinic space group P2(1)/c with two independent molecules in the asymmetric unit (Figure 6.7). The PPh_2 group is bonded by a covalent interaction to a nitrogen atom. The P(1)-N(1) bond length is 1.7314(15) Å and the C(1)-N(1) bond length is 1.379(2) Å, while the C(1)-N(2) bond length is 1.270(2) Å. This indicates localisation of the double bond between C(1) and N(2). Comparable values for nitrogen carbon single bonds and nitrogen carbon double bonds were found to be 1.346 Å and 1.277 Å respectively.[18] The angles around phosphorus were determined in the range 100 - 104°, while the angles around N were found to be from 117 - 123°. The ^1H NMR of (**10**) spectrum shows only two septets for the $CH(CH_3)_2$ protons and a doublet and multiplet for the methyl groups which indicates the existence of only one isomer in solution.

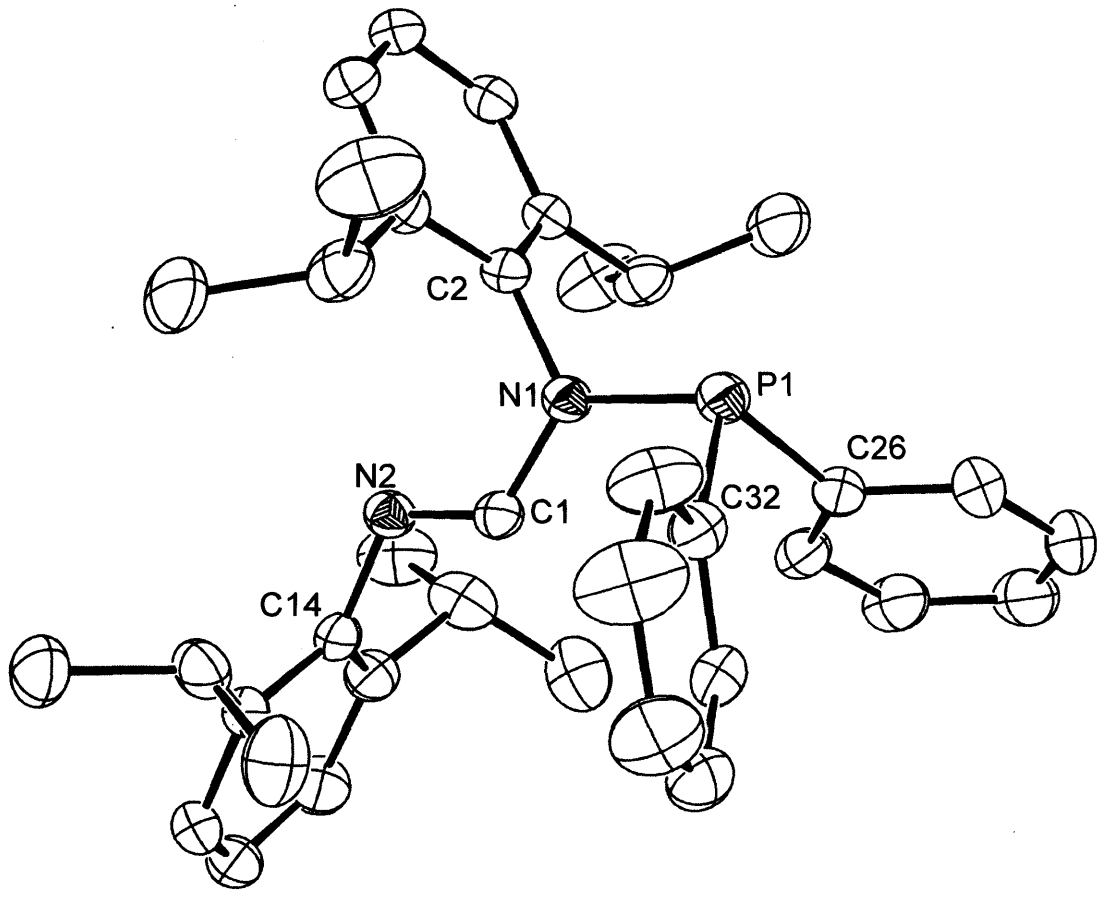


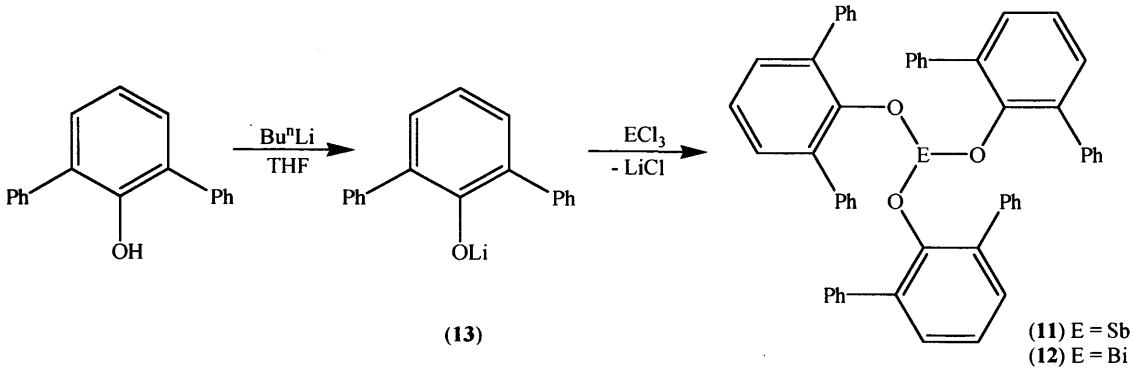
Figure 6.7 Molecular structure of [(Fiso)PPh_2] (10)

Selected bond length (Å) and angles (°): P(1)-N(1) 1.7314(15), N(1)-C(1) 1.379(2), C(1)-N(2) 1.270(2), N(1)-P(1)-C(26) 104.74(9), N(1)-P(1)-C(32) 103.52(8), C(26)-P(1)-C(32) 100.60(8), C(1)-N(1)-C(2) 119.08(14), C(1)-N(1)-P(1) 123.02(11), C(2)-N(1)-P(1) 117.87(12), N(2)-C(1)-N(1), 123.48(15), C(1)-N(2)-C(14) 117.32(14).

6.2.3 Group 15 phenoxide chemistry

The preparation of sterically encumbered group 15 compounds using phenols was attempted. Several antimony phenoxydichlorides have been published previously.[19] These compounds were prepared by hydrogen chloride elimination from a mixture of antimony trichloride and phenols. Another preparative route is the lithiation of phenols with lithium alkyl reagents such as butyl lithium and subsequent reaction with a group 15 halide. In an attempt to prepare a bulky phenoxy antimonydichloride, a solution of 2,6-(diphenyl)phenol was reacted with Bu^nLi and

the mixture subsequently reacted in 1:1 stoichiometry with a solution of $SbCl_3$ in THF. The expected antimony phenoxy dichloride was not formed but instead tris(2,6-diphenylphenoxo)antimony (**11**) was isolated in a low yield (Scheme 6.7).



Scheme 6.7 Preparation of tris(2,6-diphenylphenoxo)antimony and -bismuth

Colourless crystals of (**11**) were obtained upon slow cooling of a toluene extract. It is a monomer with a pyramidal antimony centre. The O-Sb-O angles average at 86.87°, which suggest the lone pair at antimony has predominately s-character and thus is not stereochemically active. The molecular structure of (**11**) is depicted in Figure 6.8.

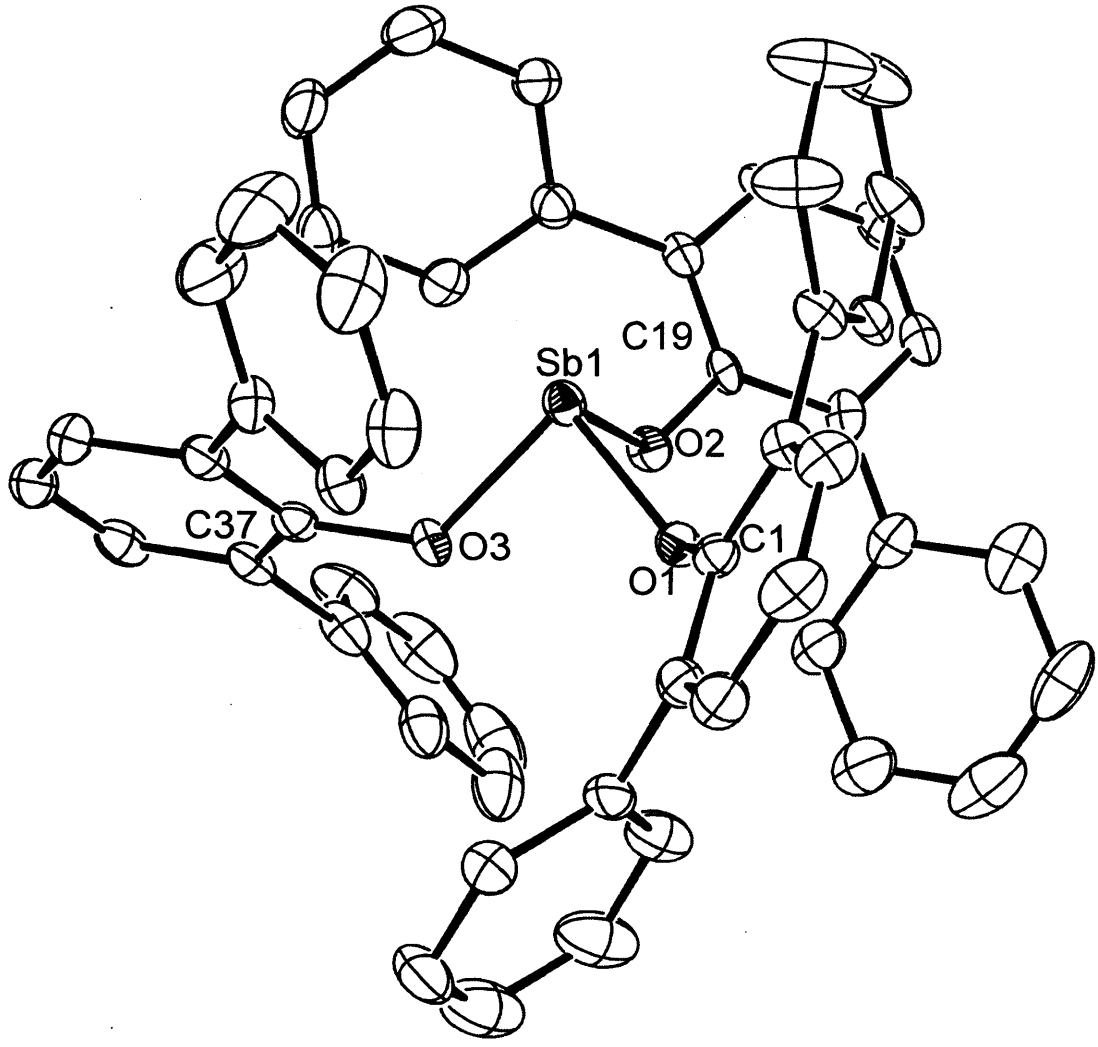


Figure 6.8 Molecular structure of tris(2,6-diphenylphenoxo)antimony (11)

Selected bond length (Å) and angles (°): Sb(1)-(O1) 1.973, Sb(1)-O(2) 1.978, Sb(1)-O(3) 1.976, C(1)-O(1) 1.372, C(19)- O(2) 1.361, C(37)-O(3) 1.366, O(1)-Sb(1)-(O2) 86.91, O(2)-Sb(1)-O(3) 86.78, O(1)-Sb(1)-O(3) 86.92.

A similar reaction was observed when $BiCl_3$ was reacted with (**13**) in THF in a 1:1 stoichiometry. When a toluene extract of the reaction mixture was slowly cooled to -30 °C colourless crystals of (**12**) were obtained. Compound (**12**) crystallises in a monoclinic space group as monomer (Figure 6.9). The O-Bi-O angles are similar to those in (**11**) and average 86.29°. The Bi-O-C angles average 124.2°, comparable with those in related compounds.[20]

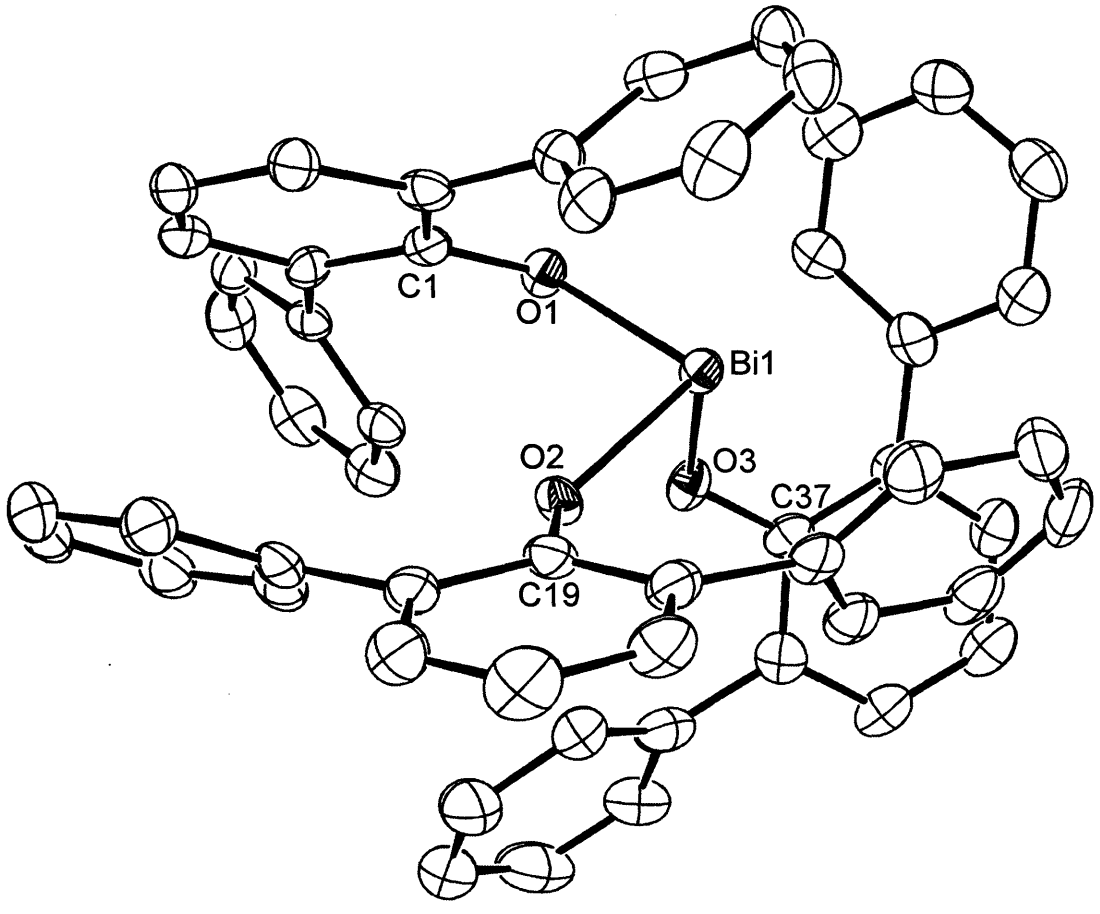
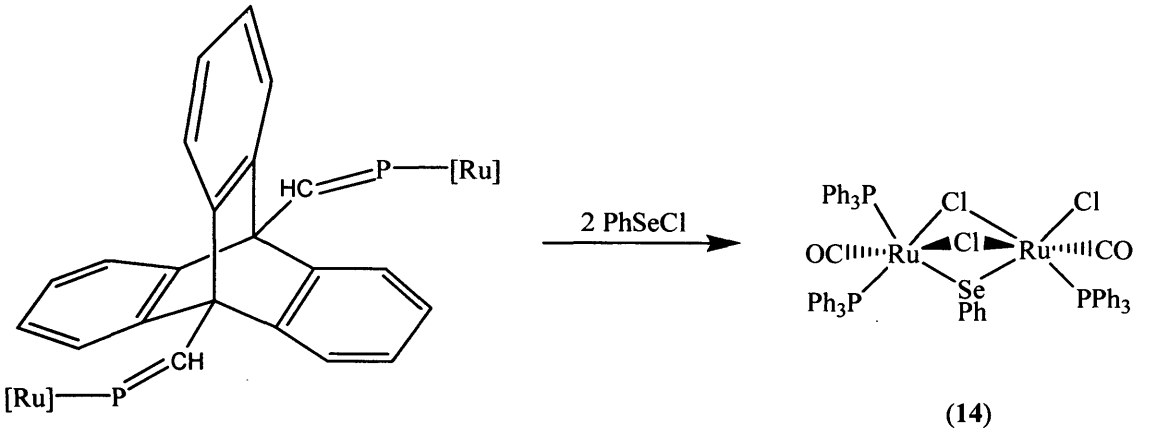


Figure 6.9 Molecular structure of tris(2,6-diphenylphenoxo)bismuth (12)

Selected bond length (Å) and angles (°): Bi(1)-O(1) 2.108(3), Bi(1)-O(2) 2.119(3), Bi(1)-O(3) 2.134(4), O(1)-C(1) 1.371(6), O(2)-C(19) 1.335(6), O(3)-C(37) 1.340(6), O(1)-Bi(1)-O(2) 87.69(13), O(1)-Bi(1)-O(3) 84.42(13), O(2)-Bi(1)-O(3) 86.76(14), O(1)-C(1)-C(6) 118.7(5), O(1)-C(1)-C(2) 120.7(5), C(6)-C(1)-C(2) 120.6(5), C(1)-O(1)-Bi(1) 121.3(3), C(19)-O(2)-Bi(1) 129.6(3),C(37)-O(3)-Bi(1) 121.7(3).

6.2.4 Ruthenium phosphaalkenyl chemistry

When an attempt was made to react the bis-ruthenium phosphaalkenyl complex, $[\{(PPh_3)_2(CO)ClRu\}_2\{\mu\text{-}P{=}C(H)\text{-}C(C_6H_4)_3CC(H){=}P\}]$ with PhSeCl, the only isolatable product was found to be (**14**). The mechanism is unknown at present.



(**14**)

[Ru] = $[RuCl(CO)(PPh_3)_2]$

Scheme 6.8 Preparation of $[Ru(CO)(PPh_3)_2\text{-}(\mu\text{-}Cl)_2\text{-}(\mu\text{-}SePh)\text{-}Ru(PPh_3)(CO)Cl]$ (14)

Compound (**14**) crystallises in a monoclinic space group with two dichloromethane molecules in the asymmetric unit. Both ruthenium centres show octahedral geometry and are bridged by two chlorides and one phenylselenide fragment. The $^{31}P\{^1H\}$ NMR spectrum of the complex shows a doublet at δ 56.7 ppm ($^2J_{PP}$ = 5 Hz) for the $P(1)Ph_3$, a doublets at δ 49.5 ppm ($^2J_{PP}$ = 18 Hz) for $P(2)Ph_3$ and a doublet of doublets at δ 25.8 ppm ($^2J_{PP}$ = 18 Hz, $^4J_{PP}$ = 5 Hz) for $P(3)Ph_3$. The IR spectrum of (**14**) displays two strong CO stretching absorptions at 1944 and 1955 cm^{-1} and its FAB mass spectrum displays a molecular ion that exhibits the characteristic isotope pattern expected for (**14**).

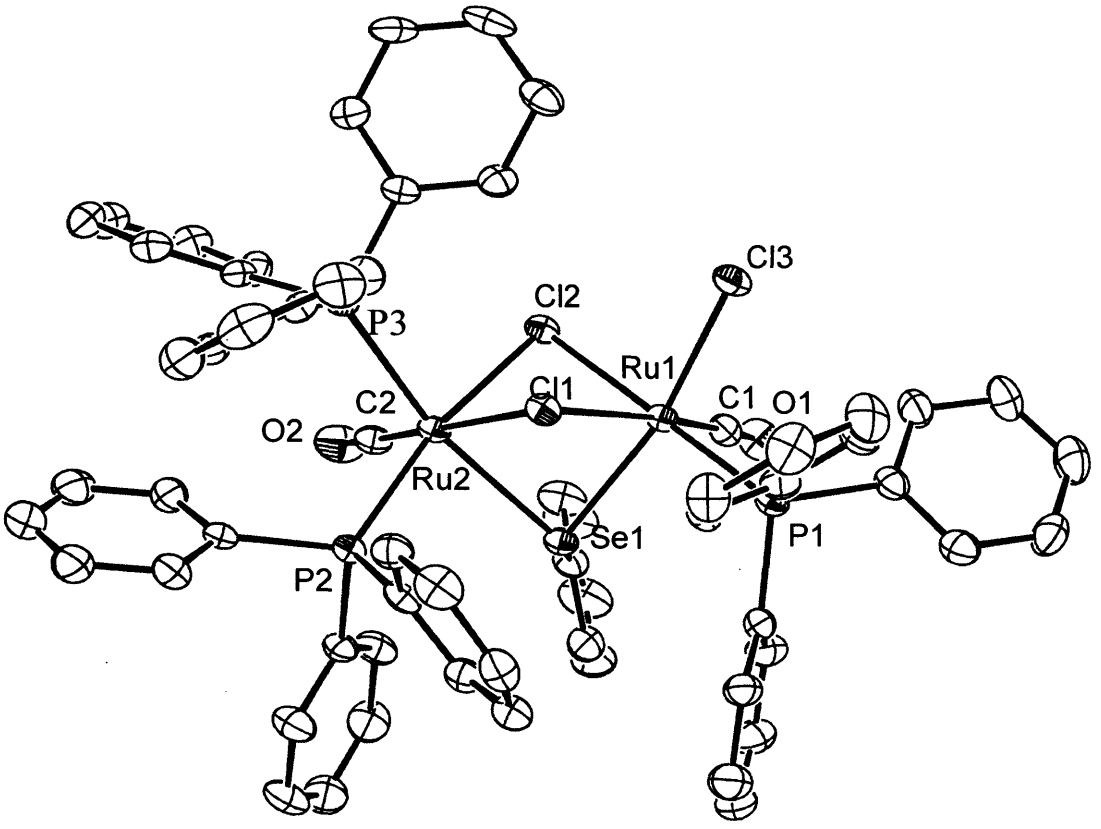


Figure 6.10 Molecular structure of [Ru(CO)(PPh$_3$)$_2$-(μ-Cl)$_2$-{μ-Se(Ph)}-Ru(PPh$_3$)(CO)Cl] (14)

Selected bond length (°) and angles (Å): Ru(1)-C(1) 1.822(5), Ru(1)-P(1) 2.2840(15), Ru(1)-Cl(3) 2.4085(13), Ru(1)-Se(1) 2.4652(6), Ru(1)-Cl(2) 2.5165(13), Ru(1)-Cl(1) 2.5241(12), Ru(2)-C(2) 1.832(6), Ru(2)-P(2) 2.3180(13), Ru(2)-P(3) 2.4297(13), Ru(2)-Cl(2) 2.4706(12), Ru(2)-Cl(1) 2.4720(13), Ru(2)-Se(1) 2.5535(7), C(1)-Ru(1)-P(1) 89.45(17), C(1)-Ru(1)-Cl(3) 98.11(16), P(1)-Ru(1)-Cl(3) 89.87(5), C(1)-Ru(1)-Se(1) 93.84(16), P(1)-Ru(1)-Se(1) 96.41(4), Cl(3)-Ru(1)-Se(1) 166.56(4), C(1)-Ru(1)-Cl(2) 92.66(17), P(1)-Ru(1)-Cl(2) 177.89(4), Cl(3)-Ru(1)-Cl(2) 89.83(4), Se(1)-Ru(1)-Cl(2) 83.45(3), C(1)-Ru(1)-Cl(1) 169.69(17), P(1)-Ru(1)-Cl(1) 97.08(4), Cl(3)-Ru(1)-Cl(1) 89.91(4), Se(1)-Ru(1)-Cl(1) 77.56(3), Cl(2)-Ru(1)-Cl(1) 80.83(4), C(2)-Ru(2)-P(2) 90.44(16), C(2)-Ru(2)-P(3) 95.90(17), P(2)-Ru(2)-P(3) 100.49(4), C(2)-Ru(2)-Cl(2) 89.60(16), P(2)-Ru(2)-Cl(2) 168.49(5), P(3)-Ru(2)-Cl(2) 90.96(4), C(2)-Ru(2)-Cl(1) 171.31(16), P(2)-Ru(2)-Cl(1) 96.20(5), P(3)-Ru(2)-Cl(1) 88.41(4), Cl(2)-Ru(2)-Cl(1) 82.77(4), C(2)-Ru(2)-Se(1) 98.07(16), P(2)-Ru(2)-Se(1) 86.01(4), P(3)-Ru(2)-Se(1) 164.54(4), Cl(2)-Ru(2)-Se(1) 82.58(3), Cl(1)-Ru(2)-Se(1) 76.88(3), C(3)-Se(1)-Ru(1) 108.84(15), C(3)-Se(1)-Ru(2)

112.32(17), Ru(1)-Se(1)-Ru(2) 82.788(19), Ru(2)-Cl(1)-Ru(1) 83.26(4), Ru(2)-Cl(2)-Ru(1) 83.45(4).

6.3 Experimental

For general experimental procedures refer to appendix I. Compound (**6**),[13] [{Ir(COD)Cl}$_2$][21] and (**13**)[22] were prepared according to published literature procedures. Other chemicals are commercially available and were purified according to published literature procedures.[23] ^{13}C NMR spectra of (**7**), (**8**), (**10-12**) and (**14**) were complicated by overlapping multiplets in the aromatic region and these signals could not be confidently assigned.

[IrCl(COD)(PEt$_3$)] (2)

To a cold (- 78 °C) suspension of [{Ir(COD)Cl}$_2$] (0.2 g, 0.3 mmol) in diethyl ether (20 cm^3) was added PEt$_3$ (100 µl, 0.70 mmol) by syringe. The resulting solution was allowed to warm to room temperature, during which time it changed from orange to yellow. Stirring was maintained for 30 min. after which the solution was filtered and concentrated to ca. 5 cm^3. Cooling to -35 °C resulted in orange crystals of (**2**). (yield: 185 mg; 69 %); mp. 83 - 85 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.81 - 0.92 (m, 9H, CH_3), 1.42 - 1.75 (m, 6H, PCH_2), 1.91 - 2.13 (m, 8H, COD-CH_2), 2.96 (m, 2H, COD-CH, *trans*-Cl), 5.27 (m, 2H, COD-CH, *cis*-Cl); ^{13}C NMR (101.6 MHz, C_6D_6, 298 K): δ 7.8 (d, PCH_2-CH_3, $^2J_{PC}$ = 1.1 Hz), 12.9 (d, PCH_2-CH_3, $^1J_{PC}$ = 30.3 Hz), 29.1 (COD-CH_2), 34.1 (COD-CH_2), 49.5 (COD-CH, *trans*-Cl), 91.8 (COD-CH, *cis*-Cl, $^2J_{PC}$ = 14.4 Hz); ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 10.9 (s); MS FAB (Noba matrix): m/z (%) 109.0 ($CODH^+$, 85 %), 453.9 (M^+, 25 %); IR (Nujol) ν/cm^{-1}: 1454 (s), 1377 (m), 1032 (s), 900 (m), 811 (m), 765 (s).

[IrCl(COD)(PEt$_3$)$_2$] (3)

To a cold (- 78 °C) solution of (**2**) (0.09 g, 0.2 mmol) in 50:50 Et_2O/hexane (20 cm^3) was added PEt$_3$ (30 µl, 0.2 mmol) over 5 min. The resulting yellow solution was allowed to warm to room temperature and stirring was maintained for 30 min. The solution was concentrated to ca. 5 cm^3 and cooled to - 35 °C to yield yellow crystals of (**3**). (yield: 110 mg; 100 %); mp. 91 - 92 °C, colour change from yellow to orange-red at 85 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.88 - 1.10 (br. m, 18H, CH_3),

1.70 - 1.80 (br. m, 12H, PCH_2), 2.16 - 2.27 (br. m, 8H, COD-CH_2), 3.4 (br., 4H, COD-CH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ - 24 (br.); MS FAB Noba matrix: m/z (%) 537.24 ($[M-Cl]^+$, 17 %); IR (Nujol) ν/cm^{-1}: 1460 (s), 1377 (s), 1037 (m), 723 (m).

[IrHCl(CO)(PPh_3)$_2${η^2-$PPh_2(C_6H_4)$}] (4)

To a cold (- 78 °C) solution of [IrCl(PPh_3)$_3$] (0.5 g, 0.05 mmol) in toluene (10 cm^3) was added a solution of [CyP=C(Bu^t)MgCl] (**1**) (16 mg, 0.05 mmol) in toluene (5 cm^3). The solution was allowed to warm to ambient temperature and CO gas was bubbled through the mixture for 30 min. The solution was stored under CO atmosphere for several days after which time a small amount of colourless crystals was deposited. Yield (< 1 %)

[(Fiso)$_3Bi_3Cl_6(THF)_2$] (7)

To a solution of LiFiso (1.38 mmol) in THF (20 cm^3) was added a solution of $BiCl_3$ (0.44 g, 1.38 mmol) in THF (10 cm^3) at -78 °C. An immediate colour change to yellow brown was observed. The solution was allowed to warm to ambient temperature and stirring was maintained for 16 hours. All volatiles were removed *in vacuo* and the residue was extracted in toluene (20 cm^3). Concentration and cooling to - 30 °C resulted in yellow crystals of (**7**). (0.35 g, 39 %); mp. 97 - 99 °C dec.; ^1H NMR (300 MHz, C_6D_6, 298 K) δ 1.30 (d, 24 H, CH_3, $^3J_{HH}$ = 6.7 Hz), 1.49 (s, 8H, CH_2), 3.53 (s, 8H, CH_2O), 3.57 (m, 4H, $CH(CH_3)_2$), 7.02 - 7.48 (m, 7H, ArH and NC(H)N); IR ν/cm^{-1}(Nujol): 2910 (s, br), 1661 (s), 1540 (s), 1455 (s), 1372 (s), 1317 (m), 1256 (s), 1189 (m), 1100 (m), 1028 (m), 800 (s), 755 (s), 722 (s), 503 (w), 463 (w), 436 (w); MS(APCI) m/z (%): 366 [$HFisoH^+$, 100].

[{FisoMg(THF)}$_2$(μ-Cl)$_2$] (8)

To a solution of (**7**) (1.0 mmol) in THF (20 cm^3) was added elemental magnesium powder. This suspension was stirred for 16 hours. Volatiles were removed *in vacuo* and the residue extracted in toluene. Slow cooling of which led to the formation of colourless crystals of (**8**). mp. 210 - 212 °C; ^1H NMR (300 MHz, C_6D_6, 298 K) δ

1.37 (br, 48H, CH_3), 1.59 (s, 8H, CH_2), 3.55 (br, 8H, CH_2O), 3.75 (br, 8H, $CH(CH_3)_2$), 7.23 (br, 14H, ArH and NC(H)N); IR ν/cm^{-1} (Nujol): 2902 (br, s), 1936 (w), 1665 (m), 1592 (m), 1538 (s), 1463 (s), 1378 (s), 1360 (s), 1319 (s), 1266 (s), 1195 (s), 1098 (s), 1025 (s), 952 (w), 921 (w), 875 (s), 804 (s), 761 (s).

[(Fiso)PPh_2] (10)

To a solution of LiFiso (1.38 mmol) in diethyl ether (20 cm^3) was added PPh_2Cl (0.25 cm^3, 1.38 mmol) at - 78 °C. The solution was allowed to warm to ambient temperature and stirring was maintained for 16 hours. All volatiles were removed *in vacuo* and the residue was extracted in diethyl ether (10 cm^3). Concentration and cooling to - 30 °C of this solution resulted in colourless crystals of (**10**). (0.31 g, 41 %); mp. 172 - 175 °C; ^1H NMR (300 MHz, C_6D_6, 298 K) δ 1.25 (m, 12H, CH_3) 1.39 (d, 12H, CH_3, $^3J_{HH}$ = 6.8 Hz), 3.35 (sep, 2H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 3.60 (sep, 2H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 7.05 - 7.35 (m, ArH), 7.79 (t, 1H, NC(H)N, $^3J_{PH}$ = 7.6 Hz); ^{31}P NMR (121.7 MHz. C_6D_6, 298 K) δ 51.9 (s); IR ν/cm^{-1}(Nujol): 2922 (br, s), 1622 (s), 1578 (s), 1456 (s), 1378 (s), 1316 (s), 1272 (s), 1227 (s), 1183 (s), 1133 (s), 1083 (s), 1039 (s), 988 (s), 927 (w), 806 (s), 744 (s), 694 (s).

[Tris(2,6-diphenylphenoxo)antimony] (11)

To a solution of $SbCl_3$ (0.46 g, 2.0 mmol) in THF (10 cm^3) was added a solution of (**13**) (2.0 mmol (0.5 g 2,6-{diphenyl}-phenol) in THF (20 cm^3) at - 78 °C. The solution was allowed to warm to ambient temperature and stirring was maintained for 16 hours. All volatiles were removed *in vacuo* and the residue was extracted in toluene (20 cm^3). Concentration, addition of hexane and cooling to - 30 °C resulted in colourless crystals of (**11**). (0.23 g, 13 % based on $SbCl_3$); mp: 206 - 208 °C dec.; ^1H NMR (300 MHz, C_6D_6, 298 K) δ 7.02 - 7.60 (m, 39H, ArH); IR ν/cm^{-1}(Nujol): 2920 (s, br), 1580 (w) 1455 (s), 1408 (m), 1378 (s), 1071 (w), 848 (s), 762 (s), 697 (s).

[Tris(2,6-diphenylphenoxo)bismuth] (12)

To a solution of $BiCl_3$ (0.63 g, 2.0 mmol) in THF (10 cm^3) was added a solution of (**13**) (2.0 mmol (0.5 g 2,6-{diphenyl}-phenol) in THF (20 cm^3) at - 78 °C. The solution was allowed to warm to ambient temperature and stirring was maintained for 16 hours. All volatiles were removed *in vacuo* and the residue was extracted in toluene (20 cm^3). Concentration, addition of hexane and cooling to - 30 °C resulted in colourless crystals of (**12**). (0.28 g, 15 % based on $BiCl_3$); mp: 239 - 241 °C dec.; ^1H NMR (300 MHz, C_6D_6, 298 K) δ 7.03 - 7.60 (m, 39H, ArH); IR ν/cm^{-1} (Nujol): 2920 (s, br), 1582 (w), 1460 (s), 1378 (s), 1262 (w), 1221 (m), 1048 (w), 1026 (w) 840 (s), 756 (s), 698 (s).

[Ru(CO)(PPh_3)$_2$-(μ-Cl)$_2$-{μ-Se(Ph)}-Ru(PPh_3)(CO)Cl] (14)

To a solution of [{(PPh_3)$_2$(CO)ClRu}$_2${μ-P=C(H)-C(C_6H_4)$_3$CC(H)=P}] (prepared *in situ* from [P≡CC(C_6H_4)$_3$CC≡P] (34 mg, 0.1 mmol) and [RuHCl(CO)(PPh_3)$_2$] (200 mg, 0.2 mmol)) in dichloromethane was added a solution of PhSeCl (40 mg, 0.2 mmol) in dichloromethane at - 78 °C. An immediate colour change from orange to yellow was observed. The solution was allowed to warm to ambient temperature and stirring was maintained for 16 hours. All volatiles were removed *in vacuo* and the residue was extracted in dichloromethane (3 cm^3) and layered with hexane which resulted in orange crystals of (**14**). mp. 197 - 202 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.77 - 7.95 (m, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 25.8 (dd, PPh_3, $^2J_{PP}$ = 18 Hz, $^4J_{PP}$ = 5 Hz), 49.5 (d, PPh_3, $^2J_{PP}$ = 18 Hz), 56.7 (d, PPh_3, $^2J_{PP}$ = 5 Hz); MS FAB: *m/z* (%) 1308.0 (M^+, 100); IR (Nujol) υ/cm^{-1}: 2925 (s), 2726 (m), 1955 (s), 1944 (s), 1456 (s), 1377 (s), 1261 (s), 1156 (m), 1091 (s), 1020 (s), 801 (s), 721 (s).

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APPENDIX I

General experimental details

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon.[1, 2] All glassware was flame dried *in vacuo* prior to use. The solvents hexane, diethyl ether, tetrahydrofuran, dimethoxyethane and toluene were predried over sodium wire, refluxed for several hours over either potassium or Na/K alloy, distilled and then freeze/thaw degassed prior to use. Dichloromethane and acetonitrile were refluxed over calcium hydride for several hours, distilled and then freeze/thaw degassed prior to use. All deuterated solvents were purified and dried in a similar manner. Commercially available chemicals were purified, when necessary, according to literature procedures.[3] ^{1}H and ^{13}C spectra were recorded on Bruker DXP400, Bruker DXP500 or Jeol Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^{1}H resonances of the solvent used. ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 spectrometer, operating at 121.4 MHz and were referenced to 85 % H_3PO_4 in D_2O as an external standard. ^{7}Li NMR spectra were recorded on a Jeol Eclipse 300 spectrometer, operating at 116.8 MHz and were referenced to LiCl in D_2O (1 M) as an external standard. ^{19}F NMR spectra were recorded on a Jeol Eclipse 300 spectrometer, operating at 282.8 MHz and were referenced to $CFCl_3$ as an external standard. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 Fourier transform spectrometer. Mass spectra were recorded using a VG Fisons Platform II instrument under EI or APCI conditions or were recorded at the EPSRC mass spectrometry service at the University of Wales, Swansea. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses were recorded at the University of Warwick or at Medac Ltd. Crystals for X-ray structural determination were mounted in silicone oil. Measurements have been conducted either by Prof. Cameron Jones or myself. Crystallographic measurements were made using a Nonius Kappa-CCD diffractometer. The structures were solved by direct methods and refined on F^2 by fullmatrix least-squares (SHELX 97)[4] using all unique data.

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APPENDIX II

Publications in support of this thesis

- Brym M., Jones C. and Wilton-Ely J. D. E. T., Auration, argentation and mercuration reactions of an iridaphosphirene, *Inorg. Chem.*, submitted for publication

- Baker R. J., Brym M., Jones C., Waugh M., 9-Triptycenyl complexes of group 13 and 15 halides and hydrides, *J. Organomet. Chem.*, 2004, **689**, 781-790

- Brym M., Jones C., Waugh M., Hey-Hawkins E., Majoumo F., Reactions of phosphavinyl Grignard reagents with aldehydes: synthesis, characterisation and further reactivity of beta-phosphaallylic alcohols, *New J. Chem.*, 2003, **27**, 1614-1621

- Brym M., Jones C., Synthesis, characterisation and reactivity of the first diphosphaalkyne, *J. Chem. Soc., Dalton Trans.*, 2003, 3665-3667
  Highlighted as Hot Paper in Dalton Transactions

- Brym M., Jones C., The synthesis and structural characterisation of $[IrCl(COD)(PEt_3)_n]$, n = 1 or 2, and orthometallated Vaska's compound, $[IrHCl(CO)(PPh_3)\{\eta^2\text{-}PPh_2(C_6H_4)\}]$, *Transit. Met. Chem.*, 2003, **28**, 595-599

- Brym M., Jones C., Waugh M., The reactivity of an iridaphosphirene complex, $[Ir\{=C(Bu^t)P(Cy)\}(CO)(PPh_3)_2]$, Cy = cyclohexyl, toward electrophiles, *J. Chem. Soc., Dalton Trans.*, 2003, 2889-2893
  Highlighted as Hot Paper in Dalton Transactions

- Brym M., Jones C., Richards A. F., Synthesis, characterisation and reactivity of a novel iridaphosphirene complex, $[Ir\{=C(Bu^t)P(Cy)\}(CO)(PPh_3)_2]$, Cy = cyclohexyl, *J. Chem. Soc., Dalton Trans.*, 2002, 2800-2801

Conference Papers

04/02 *"Investigating the reactivity of phosphavinyl Grignard reagents with main group and transition metal halide complexes"*, South West Region, Dalton Meeting at the University of Bath, **1st prize**

06/03 *"StarWars© Meets Chemistry -Triptycene As A Steric Protecting Group In Group 15 Chemistry"*, Dalton Group 13-15 Discussion Group Meeting at Kings College London

07/04 *"Diphosphaalkyne and Triphosphabenzene Chemistry"*, Dalton Group 13-15 Discussion Group Meeting at University College London, **2nd prize**