Novel Functionalised Phosphines Relevant to The Methoxycarbonylation of Ethylene

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Abstract

Several novel *o*-xylene bridged diphosphine ligands have been synthesised, and their activity tested in the palladium catalysed methoxycarbonylation of ethylene. Particular interest has been paid to the synthesis of phosphine ligands with *tertiary*-alkyl groups pendant to the phosphorus atoms.

Results obtained from catalysis compare favourably with ligand systems described in the chemical literature, with 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene and 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene providing highly active catalyst systems, with selectivity towards methylpropionate.

Alternative synthetic strategies are described, which have provided novel routes to the phosphines of interest. These methodologies having increased the scope of phosphine ligand synthesis with di-*tertiary*-alkyl substituted species.

Several complexes of the new ligands have been prepared and characterised, giving insight into the properties of the novel ligands.

List of abbreviations

Abbreviation	Meaning
Ad	Adamantyl
BM	Bohr Magnetons
Br	Broad (NMR)
Cm	Centimetres
Cp	Cyclopentadienyl
d	Doublet (NMR)
DBA	*trans, trans* dibenzylideneacetone
DCM	Dichloromethane
dppe	1,2-*bis*(diphenylphosphino)ethane
dppp	1,3-*bis*(diphenylphosphino)propane
Et	Ethyl
g	Grams
GC	Gas Chromatography
Hz	Hertz
IR	Infrared
L	Litres
m	Multiplet (NMR)
M	Molar
Me	Methyl
MEP	Methylpropionate
MHz	Megahertz
ml	Millilitres
mmol	Millimoles

mol	Moles
MS (APCI)	Atmospheric Pressure Chemical Ionisation Mass Spectrometry
MS (FAB)	Fast Atom Bombardment Mass Spectrometry
NMR	Nuclear Magnetic Resonance
OAc	Acetate
ppm	Parts Per Million
R	Any Alkyl Group
s	Singlet
t	Triplet
t	Tertiary
t-bu	Tertiary Butyl
THF	Tetrahydrofuran
XRD	X-Ray Diffraction

Chapter One

Introduction

1.1.1 The phosphine; electronic and steric properties

Many properties of phosphine ligands make them desirable species to use and study in complexation chemistry and homogeneous catalysis. The synergic nature of a phosphine-metal bond means that a phosphine ligand can act as a σ-base, whilst also having π-acid characteristics. These property allows phosphine ligands to assist in the stabilisation of metal complexes in low oxidation states.

The σ-basic character of a phosphine-metal bond is derived from σ donation of the phosphorus loan pair of electrons. The π-acidic character being due to back donation of electron density from the metal to the phosphine. The back donation is thought to be into either σ* antibonding molecular orbitals on the phosphine or empty d-orbitals on the phosphorus atom (Figure 1).[1,2,3,4]

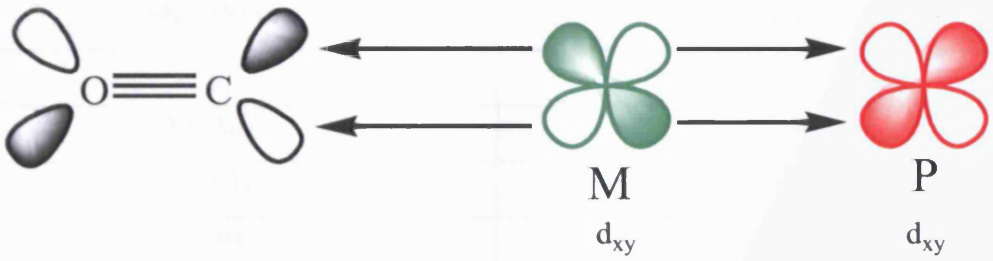


Figure 1.

A second desirable feature of phosphine ligands is that they may be "tuned" for a particular purpose. Groups pendant on the phosphorus atom giving differing electronic as well as steric properties to the phosphine.

The steric properties of a coordinated monodentate phosphine are often defined by the cone angle, a parameter first described by Tolman.[5] The cone angle is measured by drawing a cone such that the lines touch the outer most part of the groups bonded to the phosphorus atom, and the lines intersect at the centre of the metal atom (Figure 2).

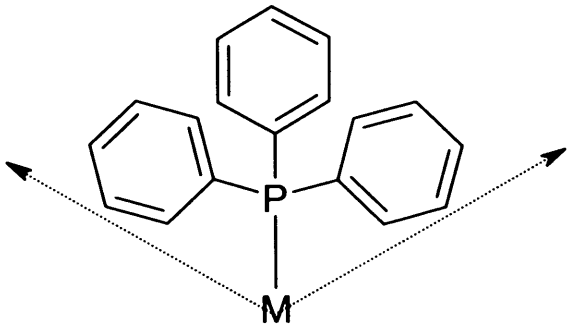


Figure 2. Tolman cone angle

A simple measure of the σ-basicity of a phosphine is to take the pKa of the conjugate acid (i.e. the phosphonium salt), a high pKa indicating a more basic phosphine (Table 1). This method is not a true reflection of just σ-basicity, but rather a measure of the overall characteristics of the phosphine.

Phosphine	pKa
$P(t\text{-Bu})_3$	11.40
$P(Et)_3$	8.69
$P(Ph)_3$	2.73

Table 1. Relative pKa of selected phosphines.

Tolman[6] also devised a now widely accepted methodology to measure the relative π-acidity of a particular phosphine ligand. The π-acidity of a phosphine ligand has an effect upon other π-acidic co-ligands coordinated to a metal atom. Because a phosphine with high π-acidity will accept more of the electron density from the metal, this lessens the available electron density shared between the other coordinated ligands bound to the same d orbital. Synthesis of a number of phosphine metal-carbonyl species allowed Tolman[6] to compare the relative π-acidity of the phosphine ligands by comparison of their IR spectra. As the electron density is removed from the metal by the phosphine ligand, the carbonyl ligands receive less back bonding from the metal. This has the effect of strengthening the C-O bond (the acceptor orbitals of

CO are antibonding) shifting the A_1 band in the IR to a lower wave number in the IR spectrum. By comparison of the wavelength at which the A_1 band is observed, comparison of the relative π-acidity of different phosphine ligands can be made.

1.2 Phosphines in homogeneous catalysis

Because of the properties described in section 1.1, phosphine ligands have become widely associated with homogeneous catalytic reactions. Phosphines can be used to stabilise reactive, coordinatively unsaturated intermediates, impart chirality on a reaction or stabilise a particular oxidation state of the metal complex.

1.2.1 Bidentate phosphine ligands

Bidentate phosphine ligands have become increasingly important in homogeneous catalysis. This is particularly apparent in reactions where the catalyst is a four coordinate species. In these cases the tethering of the two phosphine donors often restricts the phosphine to coordinate with the two donor phosphorus atoms mutually *cis* to one another. This arrangement leaves the two other possible coordination sites *trans* to the phosphine available for coordination of the reacting substrates. This arrangement of ligands being the most favourable for reaction between coordinated substrates.

Bidentate ligands may also be used to help stabilise the metal in a particular oxidation state, through careful control of ligand bite angle.[7, 8, 9] A pertinent example being the nickel catalysed hydrocyanation of styrene (Figure 3) described by van Leeuwen.[10]

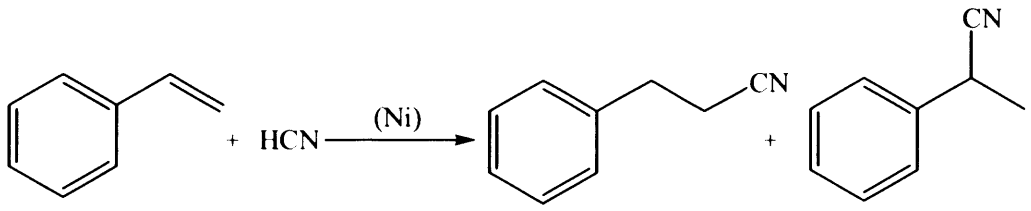


Figure 3. Hydrocyanation of styrene

The rate limiting step in the reaction is known to be the reductive elimination of the product from a Ni(II) phosphine species. A significant influence upon the yield of the

reaction is observed as the bite angle of the bidentate phosphine (Figure 4) ligand employed is altered (Table 2). The bite angle of the phosphine ligand also influences a side reaction where excess HCN can poison the catalyst by displacing the coordinated styrene substrate, to give a catalytically inactive Ni(II) species.

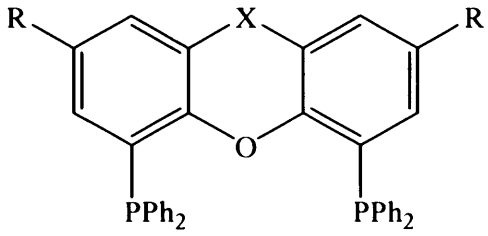


Figure 4. Structure of bidentate phosphine ligands used in the hydrocyanation reactions.[10]

The largest yields are observed with ligands that give a bite angle of 105-106°. The effect can be attributed to the stabilisation of the tetrahedral Ni(0) species by the phosphine ligand aiding the reductive elimination of the product. The bite angle of the phosphine can also disfavour the formation of the catalytically inactive square planar Ni(II) species and retards catalyst poisoning.

X	R	Natural bite angle	Yield (%)
H,H	H	101°	35-41
$SiMe_2$	H	105°	94-95
S	Me	106°	69-92
CMe_2	H	109°	27-75
Direct bond	H	131°	0.7
PPh_3		-	0
$Ph_2P(CH)_2PPh_2$		78°	51
$Ph_2P(CH)_3PPh_2$		87°	4-11
$Ph_2P(CH)_4PPh_2$		98°	3-8
BINAP		85°	4

Table 2.

1.2.2 Methoxycarbonylation of ethylene

Much of the work carried out in this area has concentrated upon the efficient synthesis of polyketones (Figure 5). The polymer being highly valued for its thermoplastic

properties and the ease with which they may be derivatised to form further functionalised polymers.

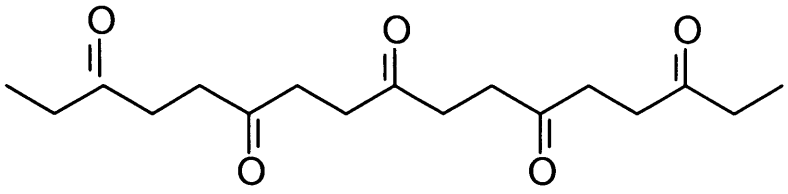


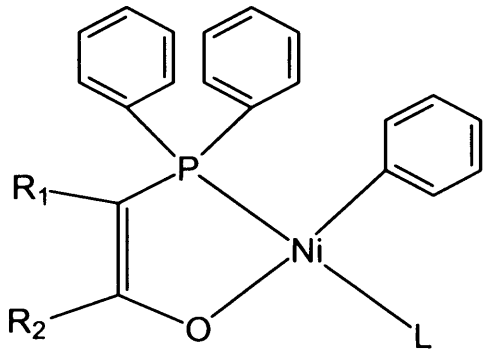
Figure 5. Structure of polyketones.

Polyketones were first synthesised (non catalytically) by Brubaker at Du pont during the 1950's.[11] Using free radical initiation and extreme pressure (500 - 1500 bar) it was possible to produce polyketone. However, the molecular weight of the product was low, and the incorporation of carbon monoxide into the polymer chain was irregular.

During subsequent years many attempts have been made to synthesis polyketones catalytically, to control both CO incorporation and to increase the molecular weight of the polymer produced, these attempts have been based around several different transition metal catalyst systems.

The first was reported by Reppe and Magin in 1951.[12] The system was based on the nickel complex $K_2Ni(CN)_4$. The catalyst gave low molecular weight polyketone along with substantial proportions of diethylketone and propionic acid.

Further work with Nickel based systems has more recently been undertaken by Klabunde et al (Figure 6).[13] The complexes employed contained bidentate phosphorus - oxygen ligands similar to those found in Shells SHOP process used for the oligomerisation of alkenes. However, the yield of polymer per gram of catalyst remained low.



Where, R_1 : Ph / H
R_2 :Ph / OMe
L : PEt_3 / PPh_3

Figure 6. Complexes studied by Klabunde

Rhodium carbonyls have also been reported as catalysts for ethylene carbonylation.[14] However, yields of high molecular weight polymer were generally low and only formed along with significant amounts of di/triketones.

The first palladium-based catalysts (*bis*(phosphine)palladiumdichloride) were reported by Gough at ICI in 1957.[15] The synthesis of polyketone proceeded at reasonable rates (300 g g^{-1}(Pd) h^{-1}) but required harsh reaction conditions (250°c, 2000 bar) for this rate to be achieved. Also, yields of polymer (gram polymer / grams Pd cat) were low.

Not until the early 1980's was it reported that related palladium complexes (e.g. cationic [*bis*(triphenylphosphine)palladium(II)tetraflouroborate] in aprotic solvents could be used to give polyketone under mild reaction conditions. However the above catalytic system, employed by Sen and co workers still suffered from low reaction rates and only produced low molecular weight polymer.[16]

Around the same period, related cationic palladium phosphine complexes with weakly/non co-ordinating anions were being used for the alkoxycarbonylation of ethene to give methylpropionate by Shell in Amsterdam with 98% selectivity.[17]

Upon replacement of the monodentate triphenylphosphine ligands used in methyl propionate synthesis, with a bidentate tertiary phosphine ligand (e.g. 1,3-

bis(diphenylphosphino)propane) a change in catalyst selectivity (from methyl propionate to polyketone) was observed. Under identical conditions to those used for the synthesis of methyl propionate (85°c, 45 bar), the bidentate ligands gave high molecular weight polyketones at very high rates (6000 g g^{-1}(Pd) h^{-1}), turnovers of around 10^6 could be achieved.[17]

The polymerisation catalysts developed by Drent[17] at Shell are believed to operate according to the following catalytic mechanism, where two catalytic cycles operate in tandem (Figure 7).

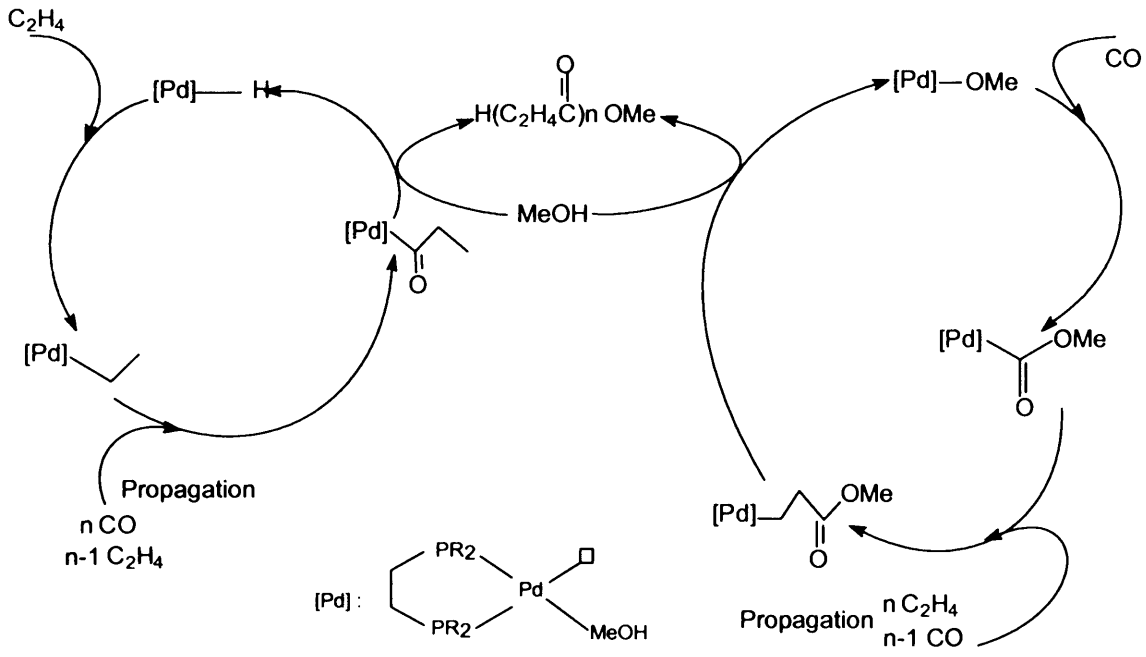


Figure 7. Catalytic cycle for methoxycarbonylation of ethylene

It is thought that the selectivity of the catalyst can be determined by how the two phosphorus donors are arranged around the metal atom.[17, 18] The bidentate ligands being constrained so that the two phosphine donors are mutually *cis* to one another, this being the most favourable arrangement for propagation of the growing polymer chain. Two monodentate ligands are able to isomerise from *cis* to *trans* (and *trans* to *cis*). This process is believed to be responsible for preventing chain growth, with the phosphine ligands blocking the sites required for coordination of further substrate molecules by isomerisation.

From this hypothesis Drent made the generalisation that all monodentate phosphine ligands gave cationic palladium catalysts with selectivity towards methyl propionate and bidentate ligands change the selectivity of this system to polyketones.[18] This observation has subsequently been proved to be untrue.

Simply by changing the substituents on the phosphorus atoms in the bidentate phosphine ligand to bulkier groups, the selectivity of the catalyst can be change back to methylpropionate.

This phenomenon was observed by replacement of the phenyl groups in ligands such as dppp (used by Drent for polyketone catalysis) to tertiary butyl groups to yield the ligand 1,3-bis(di-tert-butylphosphino)propane, which gave a selectivity to methyl propionate of 99.6%.[19]

Further improvement in selectivity (99.8%) has been observed at ICI with the ligand 1,2-*bis*(di-*tert*-butylphosphinomethyl)benzene .[20]

Whilst these new bidentate ligands also co-ordinate around the palladium center in a similar fashion to those described by Drent (i.e. with phosphorus atoms cis to one another), it is suggested that the steric bulk of the substituent groups on the phosphorus atoms have a detrimental effect upon the selectivity of the catalyst.

This can be rationalised by consideration of the steric environment created by the substituent groups on each phosphorus atom around the active metal center. The idea of "pocket angle" (Figure 8) may be used to describe the relationship between the steric bulk of the phosphines and the subsequent size of the active metal center available for the co-ordination of further groups (e.g. CO, ethene, solvent, anion).

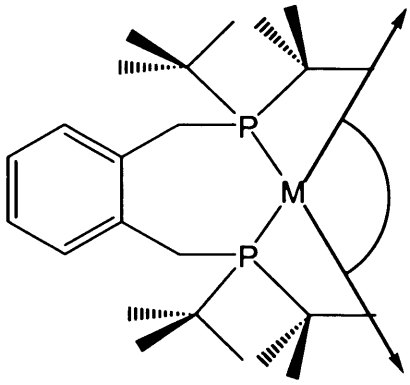


Figure 8. The "pocket angle".

It has been suggested that there is an optimum size for the active site in CO/ethene polymerisation catalysts.[21] It is the size of the pocket angle in the plane of the ligands around the metal center that has a significant effect on selectivity in the case of methyl propionate formation with bidentate ligands.

This observation may be explained when it is considered that the most sterically crowded species formed during the catalytic cycle is the acyl complex, which is formed as an intermediate prior to alkene insertion. In order for chain propagation to occur (in the case of polyketones), it is necessary for ethene to co-ordinate to the metal so that insertion (and therefore propagation) can take place. However, it is apparent that the size of the pocket angle created by the steric bulk of the bidentate phosphine ligand can retard such a reaction. Hence, propagation of the polymer chain becomes unfavourable and methanolysis to give methyl propionate (and regenerate the active catalyst) is observed. Pocket angle and activity data for several *o*-xylene diphosphine ligands with different substituents are collected in Table 3.[22]

R Group	Activity[a]	Selectivity (%) MEP	P-Pd-P Bite angle (°)	Pocket angle[b] (°)
t-Bu	12,000	99.9	103.9	127.7
i-Pr	200	20	104.3	157.9
Cyclohexyl	200	25	103.9	150.5
Ph	400	20	104.6	145.4

a, mol ethylene consumed (mol Pd)$^{-1}$ hr^{-1}. b, pocket angle measured from [(L-L)Pd(DBA)] complex.[22]

Table 3.

The catalytic cycle for the synthesis of methylpropionate with sterically bulky bidentate phosphine ligands is believed to be different from that shown in Figure 7 for the synthesis of polyketones. Work by Eastham has studied the mechanism *via* variable temperature NMR spectroscopy, and implies that only one half of the catalytic cycle depicted in Figure 7, is active in MEP synthesis. It is thought that only the hydride cycle is active in these systems (Figure 9).[23]

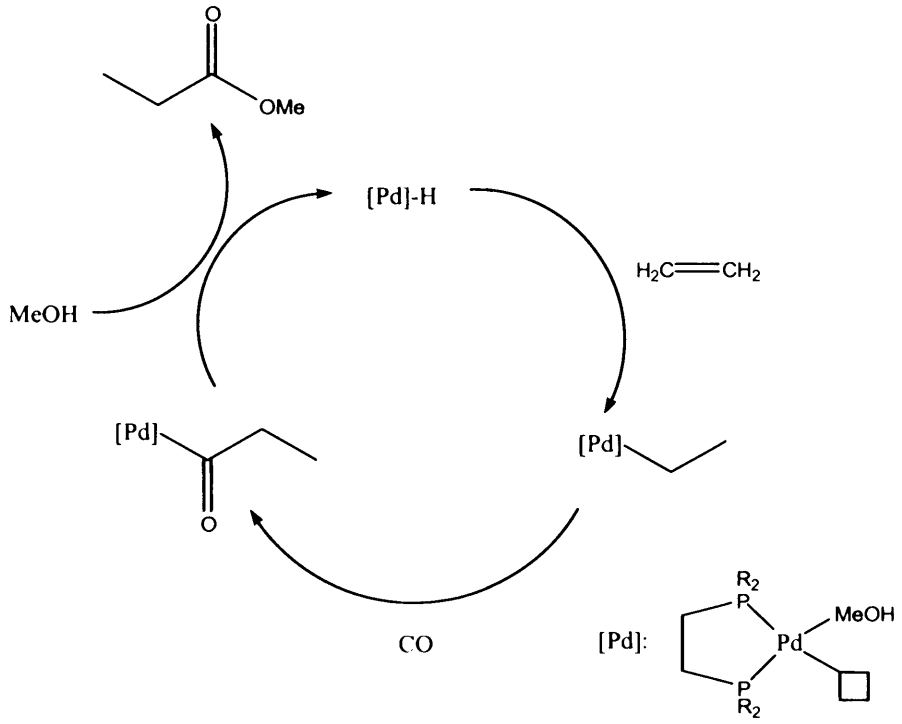


Figure 9. The Hydride cycle

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Chapter Two

2.1 Introduction.

2.1.1 *Tertiary*-butyl substituted phosphines.

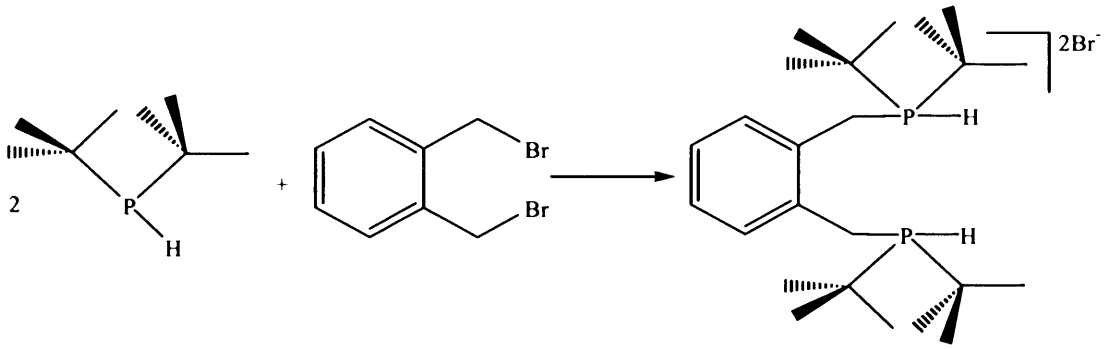
Phosphines substituted with the *tertiary*-butyl functionality have proven to be remarkably successful ligands in a variety of homogeneous catalytic reactions. A pertinent example being the use of *tris*(*t*-butyl)phosphine in the palladium catalysed Heck coupling of arylchlorides with methyl acrylate.[1] Part of the reason for the high reactivity of catalysts derived from this phosphine is the activating effect of the phosphine's high basicity. This criterion can in turn be attributed to the *t*-butyl functionality.

Sterically demanding spectator ligands may also play an important role in the stabilisation of reactive intermediates during catalytic or indeed any other organometallic reaction. The phosphine ligand described in this chapter, namely 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene **1**, has previously been shown to stabilise reactive palladium alkyl and palladium hydride species important in the alkoxycarbonylation of ethylene.[2]

2.1.2 Ligand synthesis.

The first example of the synthesis of an *ortho*-xylene bridged alkyl diphosphine was described by Moulton and Shaw.[3]

In this example, the phosphonium bromide salt of 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene **1** was synthesised *via* the nucleophilic addition of two equivalents of di-*t*-butylphosphine **2** to α,α'dibromo-*ortho*-xylene (Scheme 1). The phosphine was liberated upon subsequent treatment with base.



Scheme 1. Shaw's synthesis of 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene[3]

This strategy, although providing convenient access to these compounds, has limited potential due to its poor yield (typically <40%). The low yield of phosphonium salt is explained by the formation of a second product, where the singly substituted intermediate in the reaction cyclises to give an *iso*-phosphindolinium salt (Figure 1).

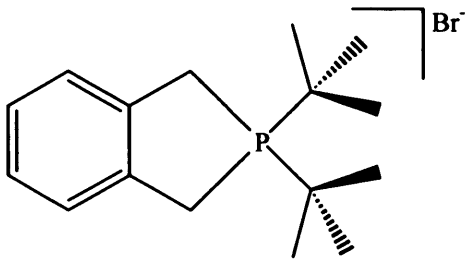
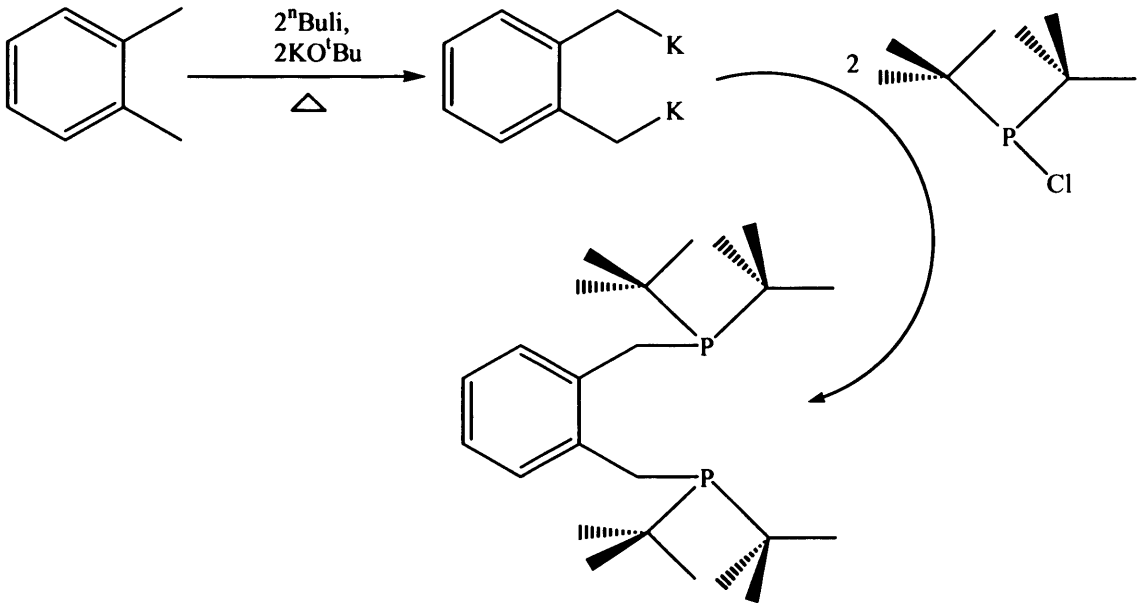


Figure 1. 2,2 di-*t*-butyl *iso*-phosphindolinium bromide

Subsequently, it has become desirable to develop a higher yielding route to **1** and other related *ortho*-xylene bridged diphosphine ligands.

Edwards *et al* (scheme 2)[4] have previously described such a strategy for the synthesis of **1**. A hexane solution of *o*-xylene, ^{n}BuLi and KO^{t}Bu was heated under reflux to afford α,α'dipotassio-*ortho*-xylene as a red pyrophoric solid. Subsequent reaction of the organopotassium with two equivalents of di-*t*-butylchlorophosphine[5] **2** in diethyl ether afforded **1** in 85% yield.



Scheme 2. An alternative synthesis of **1**.[4]

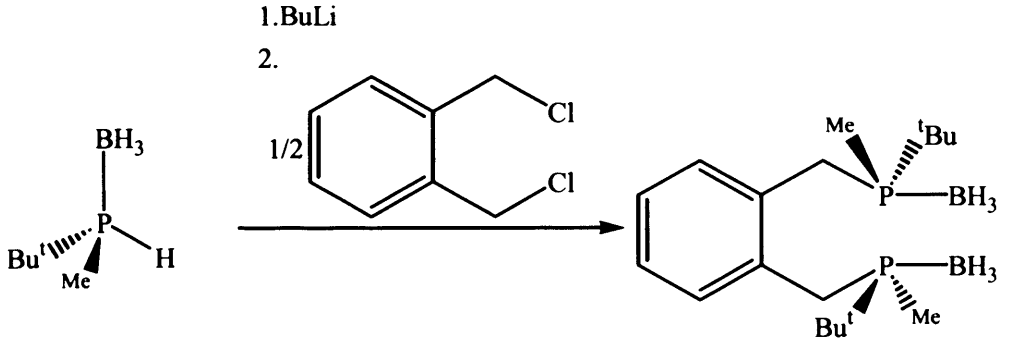
The chemistry described by Edwards *et al*[4] provides an efficient and high yielding route to *ortho*-xylene bridged alkyl diphosphine ligands. However, the synthesis is only applicable to *ortho*-xylene and requires the desired chlorophosphine to be readily available.

2.1.3 Phosphine borane adducts.

Borane adducts of primary and secondary phosphines have proven to be useful in the synthesis of new tertiary phosphine ligands. Their chemistry has recently been reviewed.[6]

Commonly the *tertiary* phosphines that have previously been synthesised *via* a borane adduct carry the diphenyl functionality.[7] Examples of alkyl phosphines synthesised from their borane adducts are less common. Imamoto *et al*[8] have recently described the synthesis of (*S,S*)-1,2-*bis*(*t*-butylmethylphosphinotrihydroboronmethyl)benzene from the corresponding optically active secondary phosphine-borane adduct (Scheme 3). However, there are no examples in the chemical literature of the synthesis of a tertiary phosphine-borane adduct, where the phosphorus carries two *tertiary*-alkyl substituents.

The deprotonation, alkylation procedure described by Imamoto[7] and previous workers,[9,10,11] seemed a pertinent methodology to extend to the ligands of interest in this work.



Scheme 3. Imamoto's synthesis

The chemistry of the borane functionality is such that it aids the deprotonation of the secondary phosphine-borane adduct by inductively removing some of the electron

density from the phosphorus atom to render the P-H proton more acidic. This effect is particularly important in *tertiary*-alkyl substituted species where these groups cause the phosphorus to be particularly electron rich. A second effect of the borane group is that the deprotonated phosphide is less basic than its borane free counterpart. Therefore, their application is advantageous if base catalysed elimination and other undesirable side reactions are to be avoided.[6]

This chapter describes a novel, alternative synthesis of **1**. The methodology is applicable to a wide variety of substrates (both in terms of organophosphorus starting material and backbone) and potentially provides an effective strategy for the synthesis of a wider variety of new *tertiary*-alkyl substituted phosphine ligands. Some novel metal complexes of **1** are also described.

2.2 Results and discussion.

2.2.1 Ligand synthesis.

Di-*tertiary*-butylchlorophosphine **2** was synthesised by the known literature methodology.[5] Di-*tertiary*-butylphosphine **3** was synthesised via the reduction of **2** with $LiAlH_4$ in diethyl ether.

2.2.1.1 Di-*tertiary*-butylphosphinetrihydroboron 4.

Reaction of di-*tertiary*-butylphosphine **3** with an excess of borane-THF adduct afforded di-*tertiary*-butylphosphinetrihydroboron **4** as a white solid in quantitative yield. It was noted that the solid readily sublimed when warmed under vacuum. The structure of **4** was confirmed by $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum displayed a broad quartet with a chemical shift of 48.55 ppm ($^1J_{P\text{-}B}$ 44.65 Hz) as expected for coupling to a nuclei with a spin of 3/2. The $^{11}B\{^1H\}$ NMR spectrum consisted of a doublet with a chemical shift of – 43.31 ppm.

The ^1H NMR Spectrum is dominated by the doublet assigned to the eighteen *tertiary*-butyl protons (δ_H1.25 ppm). A smaller doublet of quartets centred at δ_H 4.07 ppm is also observed for the proton directly bound to the phosphorus atom, the AMX pattern observed being consistent with coupling to both phosphorus and boron. The coupling constant was found to be $^1J_{H\text{-}P}$ 430.74 Hz.

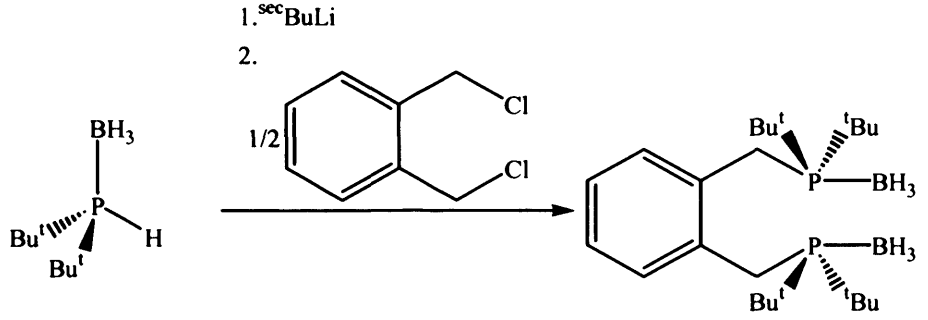
2.2.1.2 1,2-*bis*(di-*tertiary*-butylphosphinotrihydroboronmethyl)benzene **5.**

1,2-*bis*(di-*tertiary*-butylphosphinotrihydroboronmethyl)benzene **5** was synthesised by the method described by Inamoto *et al* [8] for the synthesis of the related compound (*S,S*)-1,2-*bis*(*tertiary*-butylmethylphosphinotrihydroboronmethyl)benzene (scheme 3).

A variety of bases and conditions were investigated for the deprotonation of **4**. When the reaction was carried out with ^{n}BuLi as the base, **5** was obtained in only poor yield (< 20%). $^{31}P\{^{1}H\}$ NMR spectroscopy performed after the addition of the base revealed that **4** was only partially deprotonated with 1.2 equivalents of ^{n}BuLi. Indeed, after the reaction mixture was left to stand at room temperature, the small amount of lithium phosphide in solution rapidly reprotonated to reform **4**.

Further experiments revealed that a stronger base is required to fully deprotonate **4**. The most effective and reproducible was found to be *sec*-BuLi. The dropwise addition of *sec*-BuLi to a cooled (-78° C) THF solution of **4** affords an intensely coloured (yellow) solution of lithium di-*tertiary*-butylphosphidetrihydroboron. The reaction can be followed by $^{31}P\{^{1}H\}$ or $^{11}B\{^{1}H\}$ NMR spectroscopy. The lithium di-*tertiary*-butylphosphidetrihydroboron was observed as a broad quartet with a chemical shift of δ_P 5.73 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum and as a doublet at δ_B –36.59 ppm in its $^{11}B\{^{1}H\}$NMR spectrum.

After stirring the solution at room temperature for 2 hrs and then recooling (-78°C), a THF solution of α,α'dichloro-*ortho*-xylene was added dropwise to afford **5** (Scheme 4) in 93% yield.



Scheme 4. Synthesis of **5**.

The $^{31}P\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{1}H NMR spectra of **5** are fully consistent with the proposed structure. The $^{31}P\{^{1}H\}$ NMR spectrum consists of a broad quartet, with a

chemical shift of δ_P 55.42 ppm ($^1J_{P\text{-}B}$ 68.48 Hz). As would be expected the quartet has shifted downfield by 6.87 ppm upon alkylation of the *secondary* phosphine-borane adduct **4** to form the *tertiary* phosphine-borane adduct **5**. The $^{11}B\{^1H\}$ NMR spectrum shows the expected doublet at δ_B –42.30 ppm.

The ^1H NMR spectrum is again dominated by the *tertiary*-butyl protons that are observed as a doublet centred at δ_H 1.24 ppm ($^3J_{H\text{-}P}$ 12.30 Hz). The methylene protons are also observed as a doublet (δ_H 3.37 ppm, $^2J_{H\text{-}P}$ 11.88 Hz). Two complex resonances are also observed for the two sets of equivalent aromatic protons (δ_H 7.14 and δ_H 7.59 ppm). Colourless crystals of **5** were obtained from a concentrated chloroform solution that was layered with methanol.

The solid-state structure of **5** has been determined by X-ray diffraction (figure 2) and is consistent with the solution structure as determined by NMR spectroscopy. Selected bond lengths and angles are given in Table 1.

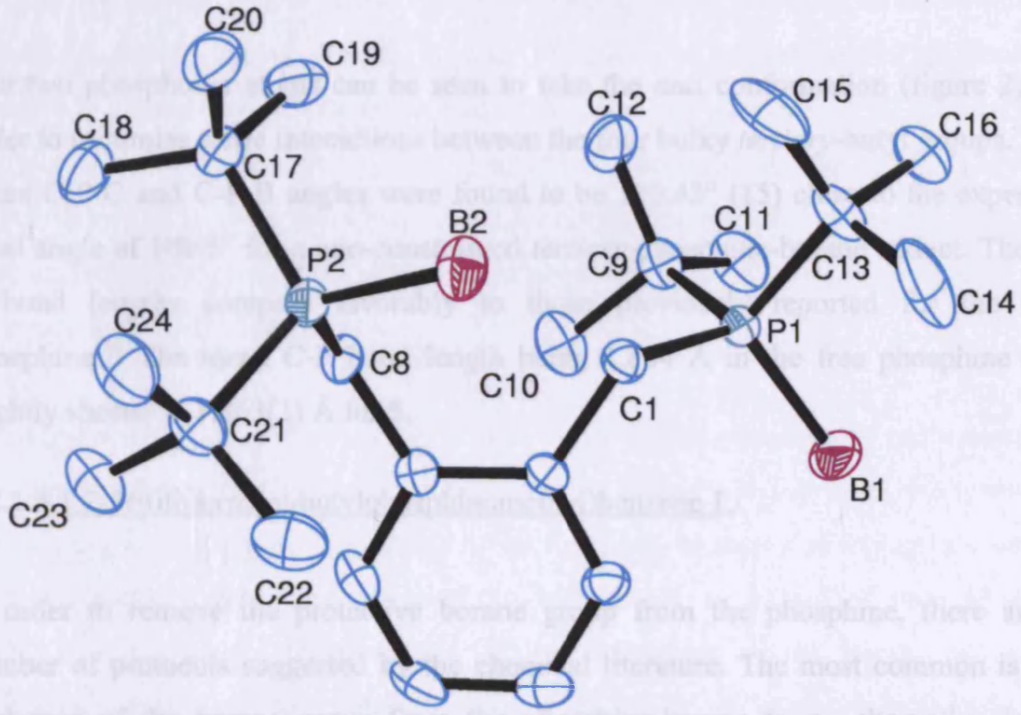


Figure 2. Crystal structure of **5**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Bond	Distance (Å)	Group	Angle (°)
C_1-P_1	1.843(3)	C_7-C_8-P_2	118.69(19)
C_8-P_2	1.854(3)	C_2-C_1-P_1	119.12(19)
P_1-B_1	1.939(4)	C_8-P_2-B_2	114.93(14)
P_2-B_2	1.939(4)	C_1-P_1-B_1	116.27(15)
P_2-C_{21}	1.873(3)	C_{21}-P_2-B_2	109.54(15)
P_2-C_{17}	1.877(3)	C_8-P_2-C_{21}	107.81(13)
P_1-C_{13}	1.867(3)	C_{17}-P_2-C_{21}	112.10(14)
P_1-C_9	1.866(3)	C_{17}-P_2-B_2	109.96(15)
		C_9-P_1-B_1	109.40(19)
		C_1-P_1-C_9	106.71(13)
		C_{13}-P_1-B_1	110.04(19)
		C_9-P_1-C_{13}	112.03(13)

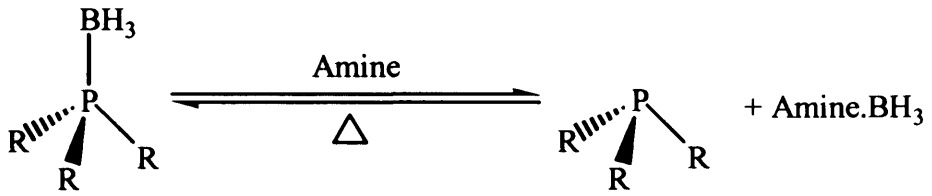
Table 1. Selected bond lengths and angles for 1,2-bis(di-*tertiary*-butylphosphinotrihydroboronmethyl)benzene **5**.

The two phosphorus atoms can be seen to take the *anti* conformation (figure 2), in order to minimise steric interactions between the four bulky *tertiary*-butyl groups. The mean C-P-C and C-P-B angles were found to be 110.43° (15) close to the expected ideal angle of 109.5° for a non-constrained *tertiary*-phosphine-borane adduct. The C-P bond lengths compare favorably to those previously reported for the free phosphine.[12] The mean C-P bond length being 1.884 Å in the free phosphine and slightly shorter at 1.863(3) Å for **5**.

2.2.1.3 1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene **1**.

In order to remove the protective borane group from the phosphine, there are a number of protocols suggested by the chemical literature. The most common is the exchange of the borane group from the phosphine-borane to an alternative lewis base.[7,8] Although phosphine-boranes are more stable than amine-borane adducts, equilibria allow the borane group to migrate to the amine. For this reason and their availability, amines have commonly been employed in deprotection reactions.[9]

To effect deprotection in a "one pot" procedure it is necessary to heat the phosphine-borane under reflux in the presence of a strongly basic amine (*N,N,N,N*-tetramethyldiaminoethane (TMEDA), morpholine, triethylamine) (Scheme 5).



Scheme 5. De-protection of phosphine-borane adducts

Deprotection following this methodology can also be carried out in the presence of "catalytically active" metals, in a deprotection/complexation procedure. The precatalyst Rh(DIOP) has been prepared in this way without loss of activity in subsequent asymmetric hydrogenation reactions when compared to the catalyst precursor prepared by the conventional route.[10]

Samples of **5** were heated under reflux in toluene in the presence of an excess of several different amines (triethylamine, TMEDA, 1,4-diazabicyclo[2.2.2]octane {DABCO}). However, it was found that in all cases this methodology did not afford the complete deprotection of the phosphine (determined *via* $^{31}P\{^{1}H\}$ NMR spectroscopy). Complete exchange of the borane function from **5** was only achieved after several cycles with fresh amine, which was found to be rather inconvenient and gave much-reduced yields of **1**.

In common with Livinghouse *et al*[11] it was found that deprotection of more electron rich phosphine-boranes such as **5** were better achieved *via* treatment with several equivalents of a strong acid ($MeSO_3H$ or $HBF_4.OMe_2$) to form a phosphonium salt of **1**. The phosphine was then liberated on addition of an excess of base (NaOH, $NaHCO_3$). This work highlights one of the limitations of the borane exchange chemistry, where more basic phosphines such as **1** hold the equilibrium towards the left-hand side (Scheme 5), often preventing complete deprotection of the phosphine-borane adduct. It may be for this reason that examples of borane deprotection in the literature *via* the borane exchange methodology are limited to aryl and less basic alkyl phosphines.[7]

The $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra are fully consistent with the proposed structure of **1** and with that previously reported.[3,4,12] As expected the $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet with a chemical shift of δ_P 28.06 ppm indicative of the fact that the two phosphorus atoms are chemically equivalent. Again, as observed with the previously described compounds **4** and **5**, the ^{1}H NMR spectrum is dominated by the resonance assigned to the *t*-butyl protons, which are observed as a sharp doublet with a chemical shift of δ_H 1.14 ppm ($^{3}J_{H\text{-}P}$ 10.77 Hz). As with **5** the methylene protons are also observed as a doublet, and have a chemical shift of δ_H 3.03 ppm ($^{2}J_{H\text{-}P}$ 2.85 Hz). Two multiplets observed at δ_H 7.05 and 7.53 ppm were assigned to the aromatic protons of the *o*-xylene moiety.

2.2.2 Complexation chemistry.

2.2.2.1 [chloro (1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene) silver (I)] 6.

The title compound was synthesised via the reaction of 1.5 equivalents of **1** with silver trifluoromethanesulphonate, and subsequently sodium chloride in dichloromethane to afford **6** as a colourless solid.

The particular interest in the silver (I) system lies in the fact that it can adopt a range of coordination numbers from 2 to 4, and the preference for a particular geometry with chelating ligands is largely ligand dependent and influenced by the length and rigidity of the moiety connecting donor atoms as well as the steric size of other substituents. These parameters are of course, of interest in homogeneous catalysis.

Coordination studies with silver (I) halide ions and chelating diphosphines have previously been performed and a range of structures are observed (Figure 3).[13]

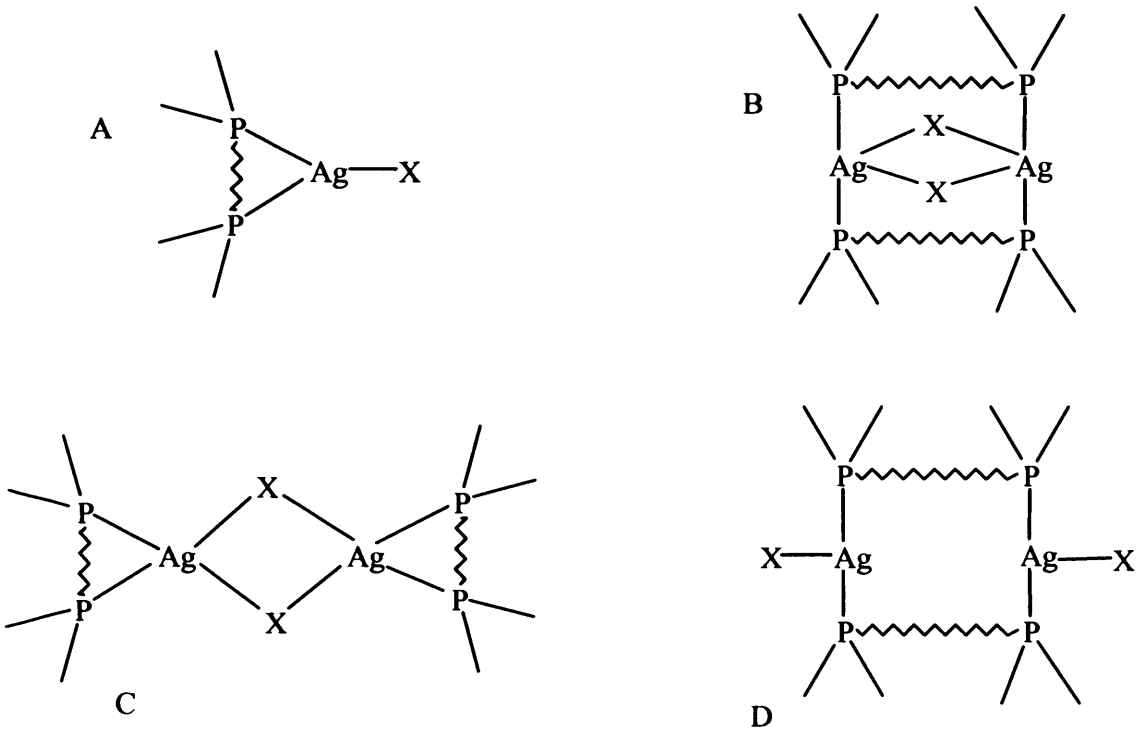


Figure 3. Range of observed structures. (The zig-zag lines represent a range of bridging groups).

Commonly, diphosphine ligands with long chains between the phosphorus atoms and small to medium sized substituents (e.g. phenyl) at phosphorus e.g. 1,5-*bis*(diphenylphosphino) pentane give complexes of type B with the diphosphine bridging two metal centres to give a dimer.[14] The dimer also has two bridging halide ligands.

When the length of the chain between phosphine donors is shortened, structural type C is usually observed. In this case the diphosphine chelates a single metal atom and the dimer is supported only by the bridging halide ions. Interestingly, when the phenyl analogue of **1** (1,2-*bis*(diphenylphosphinomethyl) benzene) is used as the phosphine ligand the structural type observed is C.[13] The dimeric silver atoms are held in a tetrahedral environment with two halide ions bridging between the two metal ions.

The effect of steric bulk from the *t*-butyl groups in **1** is neatly demonstrated by the fact that the silver chloride complex derived from this ligand falls into the trigonal planar motif, A. This appears to be consistent with other bulky *tertiary*-butyl substituted diphosphine ligands (e.g.2,11-*bis*[(di-*tert*-butylphosphino)methyl]

benzophenanthrene) which also gives Ag(I) complexes with the trigonal planar arrangement of ligands.[15] A similar structure is also observed for the related 3-coordinate d^{10} palladium(0) complex described by Bellabarba and Tooze where the same chelating phosphine ligand **1** is coordinated (Figure 4).[31]

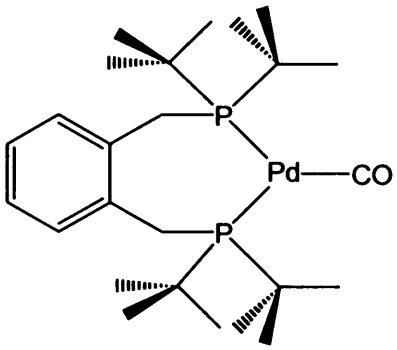


Figure 4. [1,2-*bis*(di-*t*-butylphosphinomethyl)benzene carbonyl palladium (0)][31]

The $^{31}P\{^1H\}$and ^1H NMR spectra of **6** are consistent with the assigned structure of **6**. The $^{31}P\{^1H\}$ NMR spectrum displays the expected two doublets (P-Ag coupling) both having a chemical shift of δ_P 79.80 ppm. Each doublet can be distinguished due to the difference in coupling constant between phosphorus and the two spin ½ isotopes of silver, Ag^{107} and Ag^{109}($^1J_{P\text{-}Ag}$ 407.42 Hz and $^1J_{P\text{-}Ag}$ 541.88 Hz respectively). Again, as observed with the free ligand **1** the ^1H NMR spectrum is dominated by the doublet assigned to the *tertiary*-butyl protons (δ_H 1.32 ppm, $^3J_{H\text{-}P}$ 6.37 Hz). A doublet observed at δ 3.25 ppm can be assigned to the methylene protons, and two multiplets assigned to the aromatic protons δ_H 6.92 and 7.20 ppm.

2.2.2.2 [(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene)tetracarbonyl molybdenum (0)] 7

The title compound **7** was synthesised via the reaction of one equivalent of **1** with *cis*-*bis*(piperidine)tetracarbonylmolybdenum(0)[16] **8** in warm dichloromethane. Initially upon addition of the dichloromethane solution of **1** to **8**, an orange coloured suspension was obtained. Upon heating, the orange solid **8** dissolved to afford a yellow coloured solution. After the solution was allowed to cool, no precipitation of **8** was observed, indicating the reaction had taken place.

Colourless X-ray quality crystals of **7** were grown from a chloroform solution layered with methanol. The X-ray crystal structure of **7** is shown in Figure 5. Selected bond distances and angles are given in Table 2.

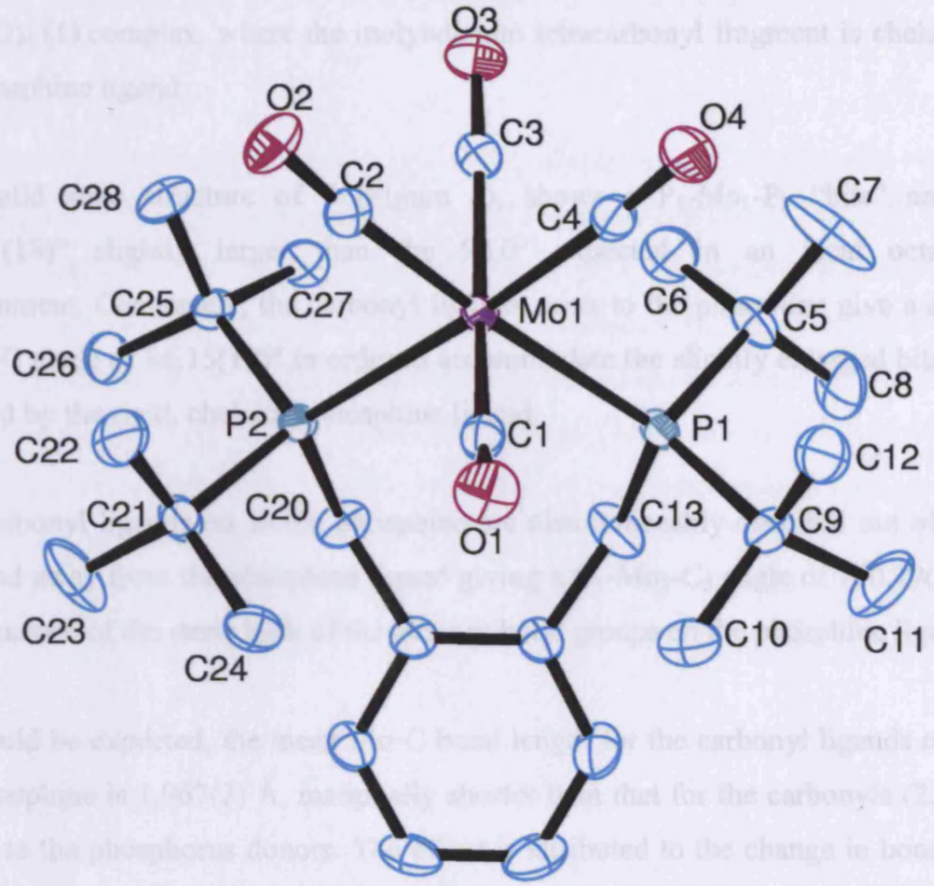


Figure 5. Crystal structure of **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Bond	Length (Å)	Group	Angle (°)
P_1-Mo_1	2.658(6)	P_1-Mo_1-P_2	94.161(18)
P_2-Mo_1	2.658(6)	C_5-P_1-C_9	109.82(11)
P_1-C_{13}	1.879(2)	C_{25}-P_2-C_{21}	109.97(10)
P_2-C_{20}	1.869(2)	C_{13}-P_1-C_5	96.19(11)
Mo_1-C_1	2.035(2)	C_{20}-P_2-C_{25}	97.05(10)
Mo_1-C_2	1.964(2)	C_1-Mo_1-C_3	160.79(10)
Mo_1-C_3	2.035(2)	C_2-Mo_1-C_4	86.15(10)
Mo_1-C_4	1.969(2)		
C_1-O_1	1.144(3)		
C_2-O_2	1.162(3)		
C_3-O_3	1.142(3)		
C_4-O_4	1.157(3)		

Table 2. Selected bond lengths and angles for [(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene)tetracarbonyl molybdenum (0)] **7**.

Reaction via substitution of the two *cis*-piperidine ligands of **8** led to the desired 1:1 $Mo(CO)_4$ (**1**) complex, where the molybdenum tetracarbonyl fragment is chelated by the phosphine ligand.

The solid state structure of **7** (Figure 5), shows a P_1-Mo_1-P_2 "bite" angle of 94.161(18)° slightly larger than the 90.0° expected in an ideal octahedral environment. Conversely, the carbonyl ligands *trans* to the phosphine give a smaller C-Mo-C angle of 86.15(10)° in order to accommodate the slightly enlarged bite angle dictated by the rigid, chelating phosphine ligand.

The carbonyl ligands *cis* to the phosphine are also noticeably distorted out of the *z*-axis and away from the phosphine ligand giving a C_1-Mo_1-C_3 angle of 160.79(10)°, a consequence of the steric bulk of the *tertiary*-butyl groups on the phosphine ligand **1**.

As would be expected, the mean Mo-C bond length for the carbonyl ligands *trans* to the phosphine is 1.967(2) Å, marginally shorter than that for the carbonyls (2.035(2) Å) *cis* to the phosphorus donors. The effect is attributed to the change in bond order resulting from the influence of the relative π acidity of the ligand *trans* to the carbonyl. The bond lengths compare favourably to those previously observed in the related Molybdenum tetracarbonyl complex of the bidentate phosphine, dppm (1,1-*bis*(diphenylphosphino)methane).[17] Again the same trend between Mo-CO bond lengths of the *cis* and *trans* carbonyls is observed. The P-Mo and Mo-C bond lengths observed for **7** are comparable to those previously reported by Cheung *et al.*[17]

The $^{31}P\{^1H\}$ and ^1H NMR spectra are fully consistent with the proposed formulation of **7**. The $^{31}P\{^1H\}$ NMR spectrum shows the expected singlet with a chemical shift of δ_P 57.28 ppm for the two chelating phosphorus atoms in a chemically equivalent environment. The 36 *tertiary*-butyl protons are observed as a doublet with a chemical shift of δ_H 1.42 ppm ($^3J_{H\text{-}P}$ 10.98 Hz) in the ^1H NMR spectrum. The methylene protons are also observed as a doublet (δ_H 3.32 ppm, $^2J_{H\text{-}P}$ 6.36Hz). Two multiplets (δ_H 7.08 ppm, δ_H 7.31 ppm) can be assigned to the two sets of chemically equivalent aromatic protons of the *ortho*-xylene backbone.

The (APCI) mass spectrum of **7** shows the molecular ion (M^+) at *m/z* 604.5. The fragment due to the loss of one carbonyl ligand (M^+, -CO) was also observed at *m/z* 576.5.

The Infrared spectrum of **7** showed four strong absorptions in the carbonyl region (ν_{CO} 2001, 1877, 1871(br, sh) cm^{-1}), which are assigned to the $A_1^{(2)}$, $A_1^{(1)}$, B_1 and B_2 stretching modes of the carbonyl ligands respectively. The infrared spectrum of **7** is consistent with that reported for the related molybdenum tetracarbonyl complex of the C_4 bridged diphosphine dppb (1,4 *bis*(diphenyl phosphino)butane) (Figure 6).[17] The carbonyl stretches were reported at ν_{CO} 2022, 1916, 1900, 1884 cm^{-1},[17] the increase in wave number reflecting the higher π acidity of the phenyl substituted phosphine dppb when compared to **1**.

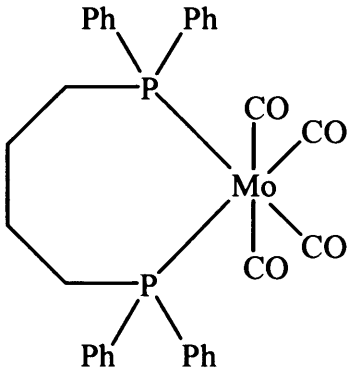


Figure 6.

2.2.2.3 [*bis*(acetonitrile)(1,2-*bis*(di-*tertiary*-butylphosphino methyl)benzene) palladium *bis*(tetrafluoroborate)] **9.**

The title compound **9** was synthesised via the reaction of one equivalent of **1** with [tetrakis(acetonitrile)palladium(II)] *bis*(tetrafluoroborate) **10** in acetonitrile as solvent. After stirring for three hours, the volume of solvent was reduced by half under vacuum. The dropwise addition of diethyl ether to the solution then caused the precipitation of **9** as a crystalline yellow solid.

The compound is observed to be the 1:1 complex. The $^{31}P\{^1H\}$and ^1H NMR spectra are fully consistent with this formulation. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet with a chemical shift of δ_P 50.74 ppm. In common with the previously

described compounds, the *t*-butyl protons are observed as a doublet and have a chemical shift of δ_P 1.52 ppm ($^3J_{H-P}$ 15.18 Hz). The methylene protons are also observed as a doublet (δ_H 3.73 ppm, $^2J_{H-P}$ 9.03 Hz) with the four aromatic protons of the *ortho*-xylene backbone being assigned to two multiplets observed at δ_H 7.33 ppm and δ_H 7.49 ppm. The six protons of the acetonitrile ligands are observed as a singlet with a chemical shift of δ_H 2.18 ppm, slightly downfield from free acetonitrile.

Two peaks in the infra-red spectrum of **9** were observed for the nitrile bonds of the coordinated acetonitrile ligands (ν_{CN} 2312, 2282 cm^{-1}), along with two broader absorptions with lower wavenumber for the BF_4^- counter ions (ν_{BF} 1084, 1028 cm^{-1}). This is consistent with the data reported for the related complex [*bis*(acetonitrile)(1,3-*bis*(di-n-heptylphosphino)propane)palladium *bis*(tetrafluoroborate)][19] (ν_{CN} 2323, 2294 cm^{-1}) and (ν_{BF} 1063 cm^{-1}). The lower wave numbers (ν_{CN}) reflecting the influence of the more π acidic phenyl phosphine ligand *trans* to the acetonitrile ligands when compared to complex **9**.

At first glance the complex **9** appears to be unremarkable. However, it is unusual in the respect that it was synthesised via a source of Pd(II). Often, the reaction of *ortho*-xylene bridged diphosphine ligands with Pd(II) species (and other divalent sources of group X metals), does not lead to a complex where the phosphine is in the usual κ^2 chelating coordination mode.

This observation is neatly demonstrated by the work of Clegg *et al.*[20] Reaction of **1** with the Pd(II) source ($Pd(OAc)_2$) in acetone leads to a dimeric complex (Figure 7). Each of the phosphine donors is coordinated to one of two Pd(OAc) moieties rather than chelating a single metal atom. Both of the Palladium atoms are then *ortho*-metallated to the aromatic ring of the *ortho*-xylene backbone to form two five membered chelate rings.

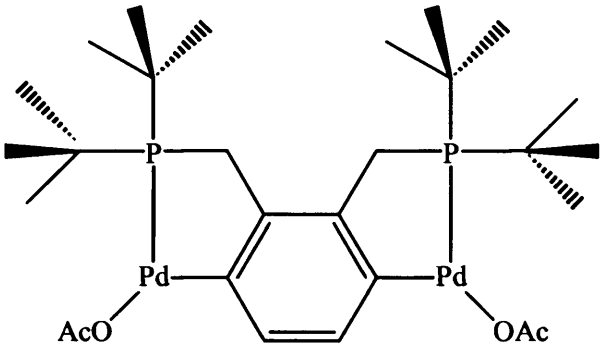


Figure 7. Complex synthesised by Clegg *et al.*[20]

2.2.2.4 [trichloro (1,2-*bis*(di-*t*-butylphosphinomethyl)benzene) nickel (II)] **11.**

An unusual coordination mode was also observed when one equivalent of **1** was reacted with [dichloro(1,2-dimethoxyethane)Ni(II)][21] **12** in dichloromethane. After stirring for three hours, the deep green solution was concentrated under vacuum. Slow vapour diffusion of diethyl ether into the dichloromethane solution gave **11** as a crop of deep blue crystals.

The solid state structure was determined by X-ray diffraction (Figure 8). Selected bond lengths and angles are given in Table 3.

Bond	Length (Å)	Group	Angle (°)
Ni_1-Cl_1	2.258(2)	Cl_1-Ni_1-Cl_2	102.12(11)
Ni_1-Cl_2	2.268(3)	Cl_2-Ni_1-Cl_3	120.12(12)
Ni_1-Cl_3	2.258(3)	Cl_3-Ni_1-Cl_1	111.63(11)
P_1-Ni_1	2.563(3)	C_1-P_1-Ni_1	117.2(3)
C_1-P_1	1.866(9)	P_1-Ni_1-Cl_1	110.79(10)
C_6-P_1	1.885(7)	P_1-Ni_1-Cl_2	110.38(9)
C_2-P_1	1.889(7)	P_1-Ni_1-Cl_3	101.98(12)
C_{16}-P_2	1.831(8)	C_1-P_1-C_2	109.4(4)
C_{17}-P_2	1.855(8)	C_{16}-P_2-C_{17}	108.4(4)
C_{21}-P_2	1.838(8)	C_{21}-P_2-C_{17}	119.3(4)
		C_{16}-P_2-C_{21}	110.4(4)

Table 3. Selected bond lengths and angles for **11**.

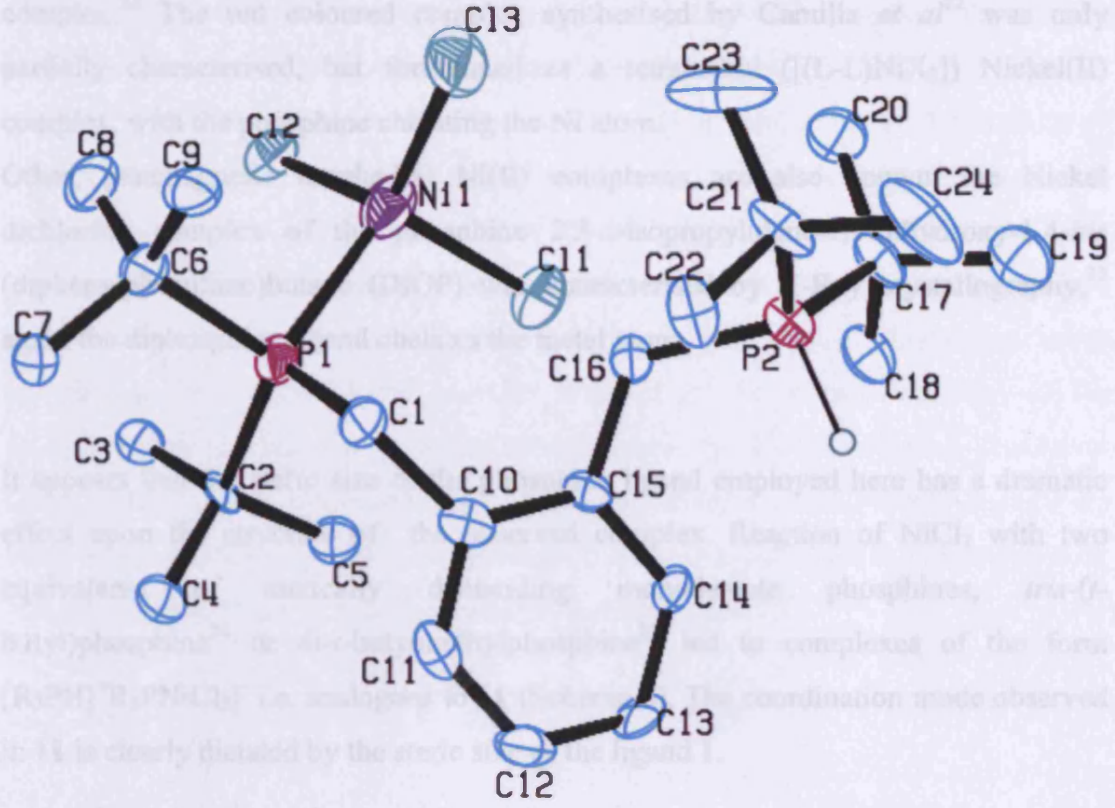


Figure 8.Crystal structure of **11.** Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

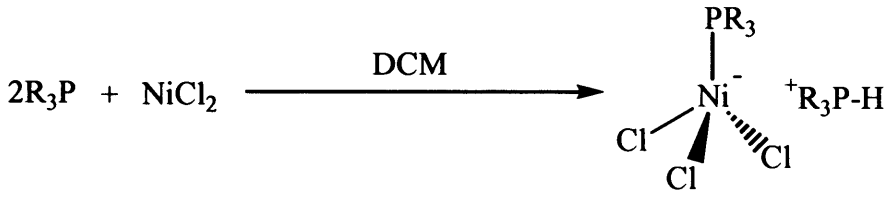
The crystal structure of **11** shows that only one of the phosphines has coordinated to the nickel atom. A third chloride ligand is also coordinated giving an anionic Nickel (II) species. The second phosphorus atom is protonated to form a phosphonium ion and carries a positive charge to become the counter ion for the negatively charged metal fragment. The source of the additional chloride ligand and proton remains unclear, but could be from either the solvent or residual **12** (the yield of 63% may suggest the solvent). The mean bond angle around the nickel (P-Ni-Cl and Cl-Ni-Cl) was found to be 109.50(12)°. The long P-Ni bond (2.563(3) Å) is consistent with that previously measured for other complexes of this type.[24]

The complex was found to be paramagnetic (μ= 4.1 BM in dichloromethane) (Evans method), in common with some other tetrahedral Ni(II) complexes described in the literature.[22, 23, 24, 25] Indeed, reaction of the phenyl analogue of **1** (1,2-*bis*(diphenylphosphinomethyl) benzene) with $NiCl_2$ also gave a paramagnetic

complex.[22] The red coloured complex synthesised by Camilla *et al*[22] was only partially characterised, but formulated as a tetrahedral ([(L-L)NiX_2]) Nickel(II) complex, with the phosphine chelating the Ni atom.

Other, paramagnetic tetrahedral Ni(II) complexes are also known, the Nickel dichloride complex of the phosphine 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-*bis* (diphenylphosphino)butane (DIOP) was characterised by X-Ray crystallography,[23] again the diphosphine ligand chelates the metal atom.

It appears that the steric size of the phosphine ligand employed here has a dramatic effect upon the structure of the observed complex. Reaction of $NiCl_2$ with two equivalents of sterically demanding monodentate phosphines, *tris*-(*t*-butyl)phosphine[24] or di-*t*-butylmethylphosphine[25] led to complexes of the form $[R_3PH]^+R_3PNiCl_3]^-$ i.e. analogous to **11** (Scheme 6). The coordination mode observed in **11** is clearly dictated by the steric size of the ligand **1**.



Scheme 6.

2.2.2.5 [(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene) (*trans, trans* dibenzylideneacetone) palladium (0)] **13.**

This complex has previously been reported by Clegg *et al.*[26] It is included here for completeness, and has been employed in the catalytic studies undertaken for this work.

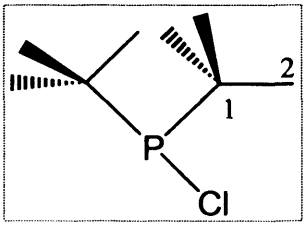
13 was found to have the trigonal planar arrangement of ligands common to complexes of the form[$(R_3P)_2$Pd DBA] or [(P-P)Pd DBA] (where P-P is a chelating diphosphine ligand and DBA is *trans, trans* dibenzylideneacetone).[27] The DBA ligand being coordinated η^2 via only one of its olefinic bonds.

The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra are consistent with this formulation. The $^{31}P\{H\}$ NMR spectrum consists of two broad resonances of equal intensity with chemical shifts of δ_P 49.94 ppm and δ_P 51.57 ppm. This is consistent with the observations of previous workers.[27] The ^{1}H NMR spectrum was again dominated by the resonances assigned to the *tertiary*-butyl protons of the phosphine ligand (δ_H 1.23 ppm, $^{3}J_{H-P}$ 9.66Hz). The methylene protons of the phosphine were observed as a doublet (δ_H 3.06 ppm). Downfield (δ_H 6.89-7.36 ppm) from these well defined resonances are a complex pattern of peaks that can be assigned to the aromatic protons of the phosphine ligand **1**, and those of the phenyl groups of the DBA ligand. The broad nature of the $^{31}P\{^{1}H\}$ NMR spectrum can be rationalised by the dynamic nature of the DBA ligand in solution at room temperature,[28] where the coordinated and free olefinic bonds of the DBA ligand can be exchanged intramolecularly.

2.3 Experimental

All compounds were prepared using standard Schlenk techniques under an atmosphere of dinitrogen or argon. ^{31}P (referenced to H_3PO_4 at $\delta_P = 0$) and ^{11}B (referenced to $Et_2O.BF_3$ at $\delta_B = 0$) NMR data was collected on a Jeol Eclipse 300 MHz spectrometer; ^{1}H and ^{13}C data on a Bruker 400 MHz DPX Avance spectrometer. Mass spectra (ES and APCI) were obtained on a VG Fisons Platform II. Tetrahydrofuran, Diethyl ether and hexane were dried over sodium benzophenone and freshly distilled under N_2 prior to use. Toluene was dried over sodium. Methanol and acetonitrile were dried over calcium hydride. Water used during the work-up of all compounds was carefully deoxygenated by several cycles of heating at reflux and cooling to room temperature under a nitrogen purge. $CDCl_3$, d_6-acetone and d_3-acetonitrile were purchased from Aldrich, dried over 3Å molecular sieves and freeze-thaw degassed before use. C_6D_6 was purchased from Goss scientific and dried over sodium prior to use. Unless stated otherwise all chemicals were purchased from Aldrich and used without further purification.

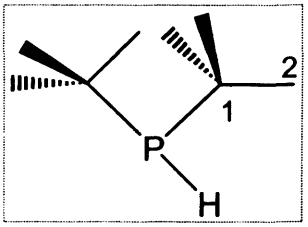
Di-*tertiary*-butylchlorophosphine 2.[4]



Di-*tertiary*-butylchlorophosphine was prepared by the literature method[3] and was found to have the following spectral characteristics.

^{31}P {^{1}H}NMR ($CDCl_3$, 121.65MHz) δ 146.81 (s); ^{1}H NMR ($CDCl_3$, 300MHz) 1.21 (d, $^{3}J_{H\text{-}P}$ 15.71 Hz, **2**); ^{13}C {^{1}H}NMR ($CDCl_3$, 75.56MHz) 27.83 (d, **2**) 39.94 ppm (d, **1**).

Di-*tertiary*-butylphosphine 3.

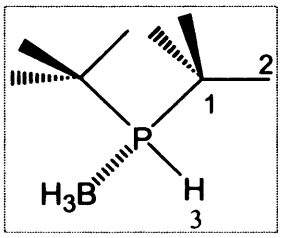


$LiAlH_4$ (2.97g, 66mmol) was slurried in diethyl ether (80 cm^3) and cooled to 0°C in an ice bath. To the stirred slurry was then added (dropwise via cannula) a diethyl ether (40 cm^3) solution of di-*tertiary*-butylchlorophosphine **2** (9.92g, 55mmol) over a one hour period. Upon full addition the solution was allowed to warm to room temperature and was stirred for an additional 20 hrs. The grey suspension was then cooled to 0°C, and a degassed aqueous solution of HCl (110 cm^3, 1M) was added over a 2hr period. Upon full addition the mixture was allowed to stir for an additional 0.5hrs. The stirring was then stopped and the two phases allowed to separate. The organic phase was then removed with a cannula and the aqueous phase extracted with a further two portions of diethyl ether (50 cm^3). The combined diethyl ether washings were then dried over magnesium sulphate and subsequently filtered via cannula. The solvent was then removed by distillation, to give the title compound as a colourless liquid with a strong, unpleasant odour.

Yield: 5.42g, 68%.

^{31}P {^{1}H} NMR ($CDCl_3$, 121.65MHz) δ 20.14 (s); ^{1}H NMR ($CDCl_3$, 300MHz) 1.20 (d, $^{3}J_{H\text{-}P}$ 11.21Hz, **2**); ^{13}C {^{1}H} NMR ($CDCl_3$, 75.56MHz) 29.26 (d, **2**) 31.84 ppm (d, **1**).

Di-*tertiary*-butylphosphinetrihydroboron 4.

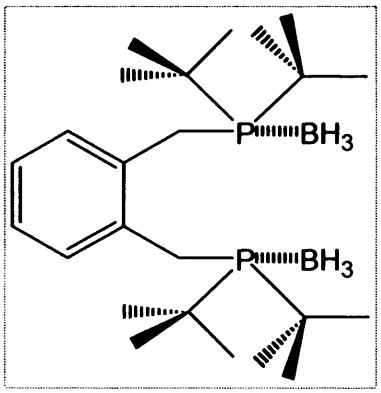


To a cooled (0°C) solution of di-*tertiary*-butylphosphine **3** (5 g, 34 mmol) in THF (50 cm^3), was added a solution of borane.THF (51 mmol) via syringe. A mildly exothermic reaction followed and effervescence was observed. Upon full addition the solution was stirred for a further 1hr at 0°C, allowed to warm to room temperature and then stirred for an additional 4hrs. The solvent was removed in vacuo to yield the title compound as a colourless solid.

Yield: 5.44g, 100%.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65MHz) δ 48.55 (q, $^1J_{P\text{-}B}$ 44.65Hz); ^{11}B $\{^1H\}$ NMR ($CDCl_3$, 96.42MHz) -43.31 (d, br); ^1H NMR ($CDCl_3$, 400MHz) 0.83 (3H, m, br) 1.25 (18H, d, $^3J_{H\text{-}P}$ 13.6Hz, **2**) 4.07 (1H, dq, $^1J_{H\text{-}P}$ 430.74Hz, $^2J_{H\text{-}B}$ 6.36Hz, **3**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 100MHz) 27.88 (d, **2**) 29.60 ppm (d, **1**).

1,2-*bis*(di-*tertiary*-butylphosphinotrihydroboronmethyl)benzene 5.



Di-*tertiary*-butylphosphinetrihydroboron **4** (5.0 g, 31 mmol) was dissolved in THF (50 cm^3) and cooled to -78°C. ^{sec}BuLi (34.4 mmol) was then added gradually via syringe to give an intensely coloured yellow solution. The solution was stirred at -78°C for 0.5hrs, allowed to warm to room temperature, and stirred for an additional 2hrs. The deprotonation can be monitored by both $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy (data given below). The solution was cooled to -78°C and a THF solution (30 cm^3) of α,α'dichloro-*o*-xylene (3.0 g, 17.2 mmol) added dropwise via

cannula. The solution was then allowed to warm to room temperature and was stirred overnight. The solvent was then removed under vacuum and the residues dissolved in DCM (60 cm^3). The solution was washed with two portions of water (50 cm^3) and the organic phase isolated and dried over magnesium sulphate. The solvent was then removed under vacuum to yield **5** as a colourless solid.

Yield: 6.54g, 93%. FW: 421.94

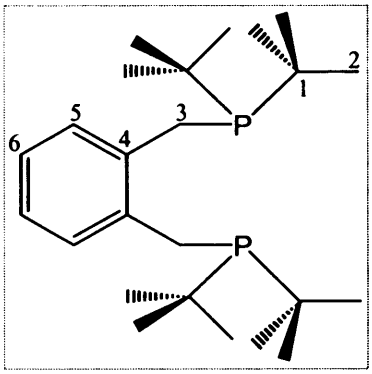
^{31}P {^1H} NMR ($CDCl_3$, 121.65MHz) δ 55.42 (q, $^1J_{P\text{-}B}$ 68.48Hz); ^{11}B {^1H} NMR ($CDCl_3$, 96.42MHz) -42.30 (d); ^1H NMR ($CDCl_3$, 300MHz) 1.243 (36H, d, $^3J_{H\text{-}P}$ 12.30Hz, **2**) 3.373 (4H, d, $^2J_{H\text{-}P}$ 11.88Hz, **3**) 7.139 (2H, m, Ar-**H**) 7.593 (2H, m, Ar-**H**); ^{13}C {^1H} NMR ($CDCl_3$, 100MHz) 24.93 (d, **3**) 28.85 (d, **2**) 33.46 (d, **1**) 126.32 (s, **6**) 132.64 (d, **5**) 134.18 ppm (d, **4**).

MS (APCI): m/z 422 (M^+).

Di-*tertiary*-butyltrihydroboronlithium phosphide.

^{31}P {^1H} NMR (121.65MHz) δ 5.73 (q); ^{11}B {^1H} NMR (96.42MHz) –36.59 ppm (d, $^1J_{B\text{-}P}$ 40.06Hz).

1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene 1.



To a cooled (0°C) DCM (50 cm^3) solution of 1,2-*bis*(di-*tertiary*-butylphosphino trihydroboronmethyl)benzene **1** (4 g, 9 mmol) was added tetrafluoroboric acid dimethyl ether complex (10eq, 90 mmol) via syringe. Upon the initial addition, the evolution of hydrogen gas was noted. Upon full addition the solution was stirred for a further 0.5hrs at 0°C, allowed to warm to room temperature and then stirred for 18hrs. Saturated sodium hydrogen carbonate solution (150 cm^3) was then added and the solution stirred vigorously for 3hrs. The stirring was then stopped, and the two phases allowed to separate. The organic phase was isolated with a cannula and the aqueous phase washed with a further two portions of DCM (30 cm^3). The DCM

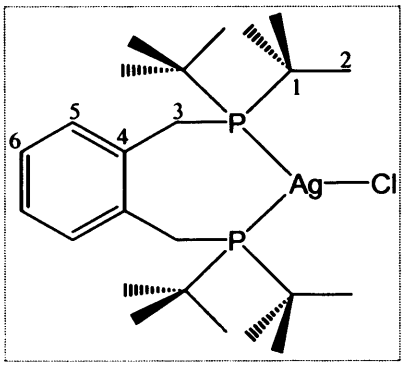
extracts were combined and dried over magnesium sulphate and subsequently filtered via cannula. The solvent was then removed under vacuum to yield **1** as a colourless solid. Further purification was achieved by recrystalisation from hot methanol.

Yield: 2.77 g, 78%

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65MHz) δ 28.06 (s); ^1H NMR ($CDCl_3$, 300MHz) 1.14 (36H, d, $^3J_{H\text{-}P}$ 10.77Hz, **2**) 3.03 (4H, d, $^2J_{H\text{-}P}$ 2.85Hz, **3**) 7.05 (2H, m, Ar-**H**) 7.53 (2H, m, Ar-**H**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56MHz) 26.47 (d, **3**) 29.98 (d, **2**) 31.98 (d, **1**) 125.29 (s, **6**) 131.00 (d, **5**) 138.88 ppm (d, **4**).

MS (APCI): m/z 395 (M, +H).

[chloro (1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene) silver (I)] 6.



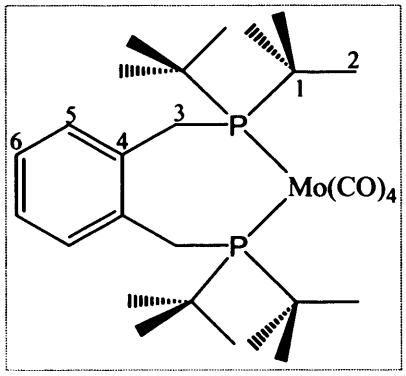
Note: All manipulations were performed with the exclusion of light from the vessels.

Silver trifluoromethanesulphonate (0.22 g, 0.84 mmol) and 1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene (0.40 g, 1.01 mmol) were weighed into a Schlenk flask in a glove box. Dichloromethane (40 cm^3) was then added to the solids and the solution allowed to stir for 18hrs. The solution was then added to sodium chloride (0.35 g, 5.99 mmol) and the mixture stirred for an additional 2hrs, and before filtering through celite to remove the excess sodium chloride. The solvent was removed under vacuum to yield the title compound as a colourless solid.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65MHz) δ 79.80 (d, $^1J_{P\text{-}Ag109}$ 541.88 Hz) 79.80 (d, $^1J_{P\text{-}Ag107}$ 470.42 Hz); ^1H NMR ($CDCl_3$, 300 MHz) 1.32 (36H, d, $^3J_{H\text{-}P}$ 6.37 Hz, **2**) 3.25 (4H, d, br, **3**) 6.92 (2H, m, Ar-**H**) 7.2 (2H, m, Ar-**H**); ^{13}C $\{^1H\}$ ($CDCl_3$, 75.56MHz) 25.72 (d, **3**) 29.87 (d, **2**) 34.92 (d, **1**) 128.87 (s, **6**) 129.64 (d, **5**) 130.87 ppm (d, **4**).

MS (APCI): m/z 501.3 (M^+, -Cl).

[(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene)tetracarbonyl molybdenum (0)] 7.



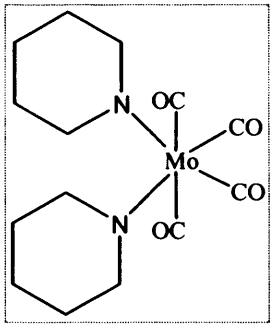
A dichloromethane (50 cm^3) solution of 1,2-*bis*(di-*tertiary*-butylphosphinomethyl) benzene (1.03 g, 2.6 mmol) was added to $[Mo(CO)_4$ (piperidene)$_2]$ **8** (1 g, 2.6 mmol) to give an orange suspension. The solution was then heated at reflux for 0.5 hrs, during which time the solid dissolved to give a yellow solution. The solution was allowed to cool to room temperature and the solvent removed under vacuum. The yellow coloured solid obtained was dissolved in chloroform and was recrystallised upon the addition of methanol. X-ray quality crystals were obtained by layering a concentrated chloroform solution of the complex with methanol.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65) δ 57.28 (s); ^1H NMR ($CDCl_3$, 300MHz) 1.42 (36H, d, $^3J_{H\text{-}P}$ 10.98Hz, **2**) 3.32 (4H, d, $^2J_{H\text{-}P}$ 6.36Hz, **3**) 7.08 (2H, m, Ar-**H**) 7.31 (2H, m, Ar-**H**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 29.85 (d, **3**) 31.30 (d, **2**) 37.65 (d, **1**) 126.33 (s, **6**) 133.29 (d, **5**) 136.91 ppm (d, **4**).

IR (KBr): ν_{CO} 1871, 1877, 2001 cm^{-1}.

MS (APCI): m/z 604.5 (M^+), m/z 576.5 (M^+ - CO).

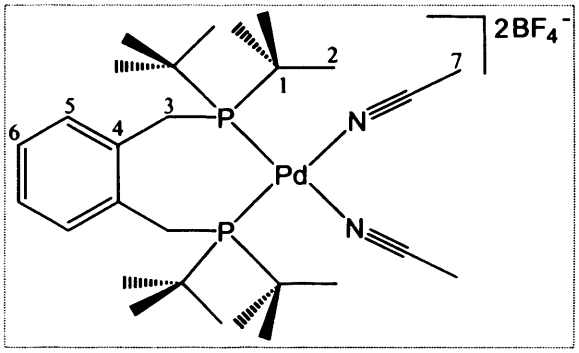
[*cis-bis*(piperidine)tetracarbonylmolybdenum(0)] 8.[16]



A round bottom flask equipped with a reflux condenser was charged with molybdenum hexacarbonyl (5 g, 18.9 mmol) piperidine (10.76 g, 126 mmol) and

hexane (60 cm^3). Upon heating the molybdenum hexacarbonyl dissolved and the solution became yellow in colour. The solution was then heated under reflux for a total of 5 hrs. Upon cooling the product precipitated and was isolated by filtration of the warm solution through a Hersch funnel. The yellow solid was then washed with three portions of hexane (15 cm^3) and was dried under vacuum.

[*bis*(acetonitrile)(1,2-*bis*(di-*tertiary*-butylphosphino methyl)benzene) palladium *bis*(tetrafluoroborate)] 9.



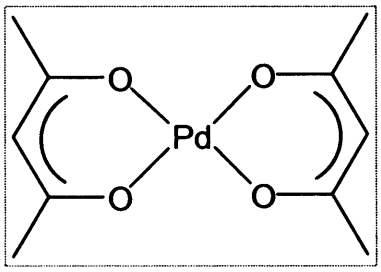
1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene (0.30 g, 0.76 mmol) and [tetrakis(acetonitrile) *bis*(tetrafluoroborate) palladium(II)] (0.33 g, 0.76 mmol) were weighed into a Schlenk in a glove box. Acetonitrile (20 cm^3) was added to afford an orange coloured solution that lightened to yellow. The solution was allowed to stir for 3hrs. The volume of solvent was reduced by half under vacuum. Diethyl ether was added dropwise via syringe to afford the title compound as a crystalline yellow solid. The solid was isolated via cannula filtration and subsequently dried under vacuum.

^{31}P $\{^1H\}$ NMR (CD_3CN, 121.65MHz) δ 50.74 (s); ^1H NMR (CD_3CN, 300MHz) 1.52 (36H, d, $^3J_{H\text{-}P}$ 15.18Hz, **2**) 2.18 (6H, s, **7**) 3.73 (4H, d, $^2J_{H\text{-}P}$ 9.03Hz, **3**) 7.33 (2H, m, Ar-**H**) 7.49 (2H, m, Ar-**H**); ^1H $\{^{31}P\}$ NMR (CD_3CN, 300Hz) 1.52 (36H, s, **2**) 2.18 (6H, s, **7**) 3.73 (4H, s, **3**) 7.33 (2H, m, Ar-**H**) 7.49 (2H, s, Ar-**H**); ^{13}C $\{^1H\}$ NMR (CD_3CN, 75.56MHz) 26.75 (d, **3**) 30.37 (d, **2**) 41.82 (d, **1**) 128.61 (s, **6**) 132.55 (d, **5**) 133.37 ppm (d, **4**).

IR (KBr): ν_{CN} 2312, 2282 cm^{-1}. ν_{BF} 1084, 1028 cm^{-1}.

MS (ES): *m/z* 542.4 (M^+, -MeCN) 501.4 (M^+, -2MeCN).

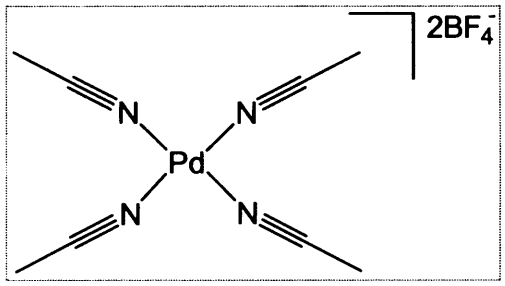
[*bis*(2,4-pentanedionato)palladium(II)].[29]



Palladium chloride (0.89 g, 5.0 mmol) and sodium chloride (2.5eq, 0.73 g, 12.5 mmol) were dissolved in water (14 cm^3) and stirred for 1hr. 2,4-pentanedione (2.5 cm^3) and sodium hydroxide (0.8 g) were added, and the yellow coloured suspension that formed was stirred for an additional 15hrs. The yellow precipitate was isolated on a Buchner funnel and was washed with water, methanol and then diethyl ether. The yellow solid obtained was dissolved in chloroform and filtered to remove a small quantity of palladium black. The solvent was removed under vacuum to yield the title compound as a crystalline yellow solid. Further purification was achieved by recrystallisation from hot benzene.

^1H NMR ($CDCl_3$, 400MHz) δ 2.01 (12H, s) 5.36 (4H, s); ^{13}C {^1H} NMR ($CDCl_3$, 100MHz) 25.86 (s) 101.99 (s) 187.56 ppm (s).

[*bis*(tetrafluoroborate) tetrakis(acetonitrile) palladium(II)] 10.[30]

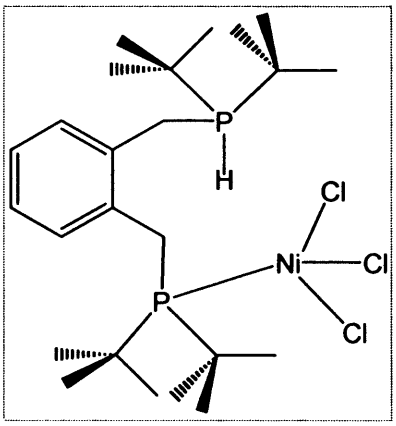


Bis(2,4-pentanedionato)palladium (1.40 g, 4.59 mmol) was dissolved in acetonitrile (20 cm^3). HBF_4 (3eq, 1.21 g, 13.8 mmols) was then added to the solution via syringe, causing the precipitation of finely divided palladium. The solution was then stirred for 18 hrs. During this time the majority of the palladium black was consumed and a yellow coloured solution was obtained. The solution was filtered through a frit and the solvent removed under vacuum to yield the title compound as a crystalline yellow solid.

^1H NMR (CD_3CN, 400MHz) δ 2.66 ppm (s).

IR (KBr): ν_{CN} 2355 cm^{-1}.

[trichloro (1,2-*bis*(di-*t*-butylphosphinomethyl)benzene) nickel (II)] 11



To [dichloro(1,2-dimethoxyethane)nickel(II)] **12** (0.20 g, 0.5 mmol) was added a dichloromethane (30 cm^3) solution of 1,2-*bis*(di-*tertiary*-butylphosphinomethyl) benzene (0.11 g, 0.5 mmol). Upon the addition of the phosphine, there was an instant colour change of the solution from orange to aquamarine. The solution was allowed to stir for 3 hrs and was then concentrated under vacuum to half its initial volume. Slow vapour diffusion of diethyl ether into the solution gave the title complex as blue crystals.

No NMR data was available as the complex was found to be paramagnetic. No EPR data was available as the complex was found to be both EPR and ENDOR silent. The magnetic moment of the complex in solution (Evans method) was found to be μ=4.1 BM.

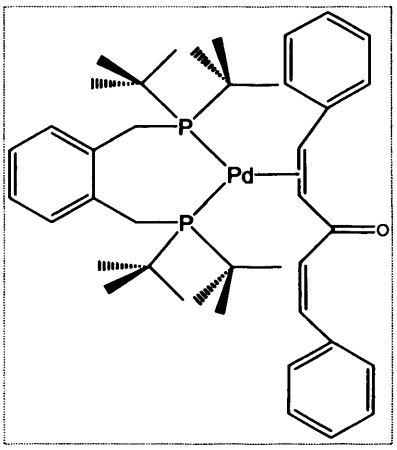
Yield: 0.18g, 63%

[dichloro(1,2-dimethoxyethane) Ni (II)] 12.

A three necked round bottom flask fitted with a reflux condenser was charged with finely ground $Ni.2H_2O^*$ (33.1 g, 0.20 mols), 1,2-dimethoxyethane (100 cm^3) and triethyl orthoformate (65.10 g, 0.44 mols). The slurry was rapidly stirred and heated at reflux for 2 hours. The reaction mixture was allowed to cool and the orange solid collected on a glass frit under N_2. The solid was washed with 1,2dimethoxyethane and pentane and subsequently dried under vacuum.

*$NiCl_2.2H_2O$ was obtained by dehydration of nickel chloride ($NiCl_2.6H_2O$) in a warm oven over several days. The colour of the material was observed to change from the initial deep green colour of $NiCl_2.6H_2O$ to become light yellow. The yellow powder was then stored under a N_2 atmosphere.

[(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene) (*trans, trans* dibenzylidene acetone) Palladium (0)] 13.



THF (60 cm^3) was added to a mixture of 1,2-*bis*(di-*tert*-butylphosphino methyl)benzene (1.34 g, 3.40 mmol) and $[Pd_2(DBA)_3]$ (1.86 g, 1.45 mmol) that had previously been weighed out in a glove box. The turbid red / orange solution was stirred for three hours. The solution was filtered via cannula to yield a red filtrate and a small quantity of residue. The solvent was removed under vacuum to afford a red powdery solid. Hexane (30 cm^3) was added via syringe and trituration performed with a glass rod, resulting in an orange solid separating out. The hexane washings were then removed via cannula filtration and the solid dried under vacuum.

^{31}P $\{^1H\}$ NMR (C_6D_6, 121.65MHz) δ 49.94 (s, br) 51.57 (s, br); ^1H NMR (C_6D_6, 300MHz) 1.231 (36H, d, $^3J_{H\text{-}P}$ 9.66Hz) 3.055 (4H, d, br) 6.885-7.359 (14H, m, Ar-**H**); ^{13}C $\{^1H\}$ NMR (C_6D_6, 75.56MHz) 30.366 (d) 30.472 (d) 36.076 (d) 126.548 (s) 133.267 (d) 137.818 (d) 190.935.

MS (ES): *m/z* 735 (M^+)

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List of Chemicals Chapter 2.

1 1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene

2 Di-*tertiary*-butylchlorophosphine

3 Di-*tertiary*-butylphosphine

4 Di-*tertiary*-butylphosphinetrihydroboron

5 1,2-*bis*(di-*tertiary*-butylphosphinotrihydroboronmethyl)benzene

6 [chloro (1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene) silver (I)]

7 [(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene)tetracarbonyl molybdenum (0)]

8 [(*cis*-*bis*(piperidine) tetracarbonyl molybdenum (0)]

9 [*bis*(acetonitrile)(1,2-*bis*(di-*tertiary*-butylphosphino methyl)benzene)palladium *bis*(tetrafluoroborate)]

10 [*bis*(tetrafluoroborate) tetrakis(acetonitrile) palladium(II)]

11 [trichloro (1,2-*bis*(di-*t*-butylphosphinomethyl)benzene) nickel (II)]

12 [dichloro(1,2-dimethoxyethane) nickel(II)]

13 [(1,2-*bis*(di-*tertiary*-butylphosphinomethyl)benzene) (*trans, trans* dibenzylidene acetone) palladium (0)]

Chapter Three

3.1 Introduction

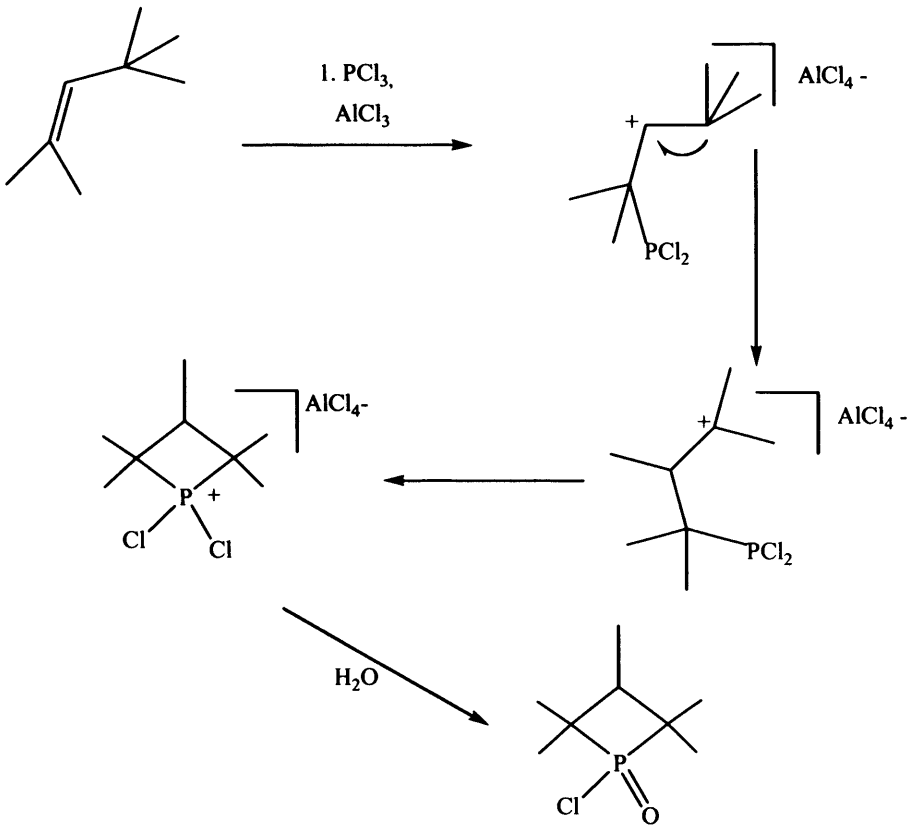
3.1.1 Phosphorus heterocycles

Phosphetanes belong to a larger homologous series of saturated heterocyclic compounds containing a single phosphorus atom. Examples of a wide variety of these compounds are known in the chemical literature, from three membered phosphiranes through to the larger ring compounds, phospholanes (5), phosphinanes (6), phosphepanes (7) and phosphocanes (8).

3.1.2 Synthesis of phosphetanes

The first synthesis of a phosphetane ring was reported by Kosolapoff and Struck in 1957.[1] In this example the phosphetane was prepared in poor yield *via* the Michaelis Arbuzov coupling of triethylphosphite and 1,3-dibromopropane. Since Kosalapoff and Struck's work, two general methods have been devised for the synthesis of phosphetane rings.

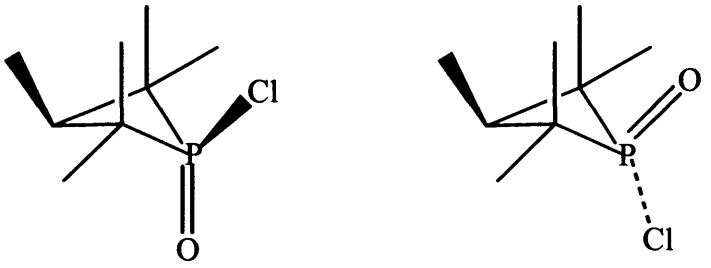
A significant breakthrough came in 1962, when McBride and Jungermann were, for the first time, able to demonstrate the synthesis of a phosphetane ring in high yield.[2] The "McBride" synthesis (Scheme 1), involves the reaction of an electron-rich olefin with PCl_3 in the presence of $AlCl_3$. The attack of an olefinic carbon at a phosphenium cation, followed by a 1,2 shift of a methyl group, and subsequent electrophilic addition to phosphorus affords a phosphetanium ion. Hydrolysis then gives the corresponding phosphinic chloride (1-chloro-2,2,3,4,4-pentamethyl phosphetane-1-oxide **14**).



Scheme 1. The McBride Synthesis

It was later established (via X-ray crystallography)[3] that the synthesis described by McBride was selective for the *trans*-isomer of **14**. Where the methyl group at the C3 position of the phosphetane ring is *trans* across the ring relative to the chlorine at phosphorus (Figure 1). McBride's route is limited by the number of suitable olefins that will cyclise to give the phosphetane ring. Since McBride described the reaction of 2,4,4-trimethylpent-2-ene in 1962, relatively few suitable olefins have been found.[4, 5, 6]

A second methodology has been developed more recently. In this example, the reaction of a di-lithiumphosphide reagent with a 1,3-electrophile has proven to give phosphetanes. A variety of 1,3-electrophiles have been investigated (dihalides, mesylates, tosylates). In common with larger rings in the homologous series, the most successful dielectrophiles in the synthesis of phosphetanes have been cyclic sulphates. Cyclic sulphates can be synthesised from a variety of Diols, not only bringing diversity in the functionality pendant on the phosphetane ring but also providing control over the stereochemistry of these substituents (scheme 2).[7]



Cis Trans

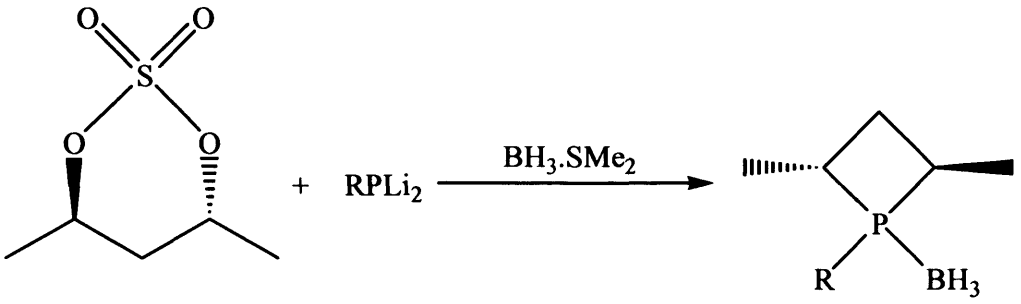
Figure 1. Isomers of **14**

It has been the McBride synthesis that has been of interest during this work. Other methodologies of phosphetane synthesis will not be discussed in further detail.

3.1.3 Structural properties of the phosphetane ring

Initial studies of phosphetanes concentrated upon the stereochemistry of substitution reactions at the phosphorus atom,[8] and the structural properties of the four membered ring. The majority of compounds studied (until recently) have been phosphorus (V) derivatives of the phosphetane ring (oxides, sulphides, borane adducts, phosphonium salts).

It was found that phosphetanes have a folded structure[9] (Figure1), with the fold angle made by the C-C-C and C-P-C plane being between 0-30°. The direction of the fold is usually dictated by the steric size of substituents at phosphorus and the C3 position of the ring.



Scheme 2. Phosphetane synthesis via cyclic sulphates.

P-C bond lengths have been found to be in the range of 1.79-1.96 Å for monocyclic phosphetanes (P-C for classical acyclic phosphines is 1.84 Å). The angles at the ring

carbons being between 84-88° (P-C-C) and 96-102° (C-C-C), this enforces a small C-P-C angle at phosphorus, which commonly falls into the range of 76-86°.

3.1.4 Phosphetanes in homogeneous catalysis

Recent work by Marinetti has described the synthesis of several novel chiral bidentate phosphetane ligands.[10] It was shown that this novel class of ligand can provide active catalysts in the Ruthenium catalysed hydrogenation of carbonyl compounds.[10] The control of chirality in the products having a marked dependence upon the steric size of substituents on the phosphetane ring.

This interesting work by Marinetti also provides insight into the coordination chemistry of phosphetanes.[10] Indeed, up until this point relatively few metal complexes with phosphetane ligands had been described.[14,15]

This chapter describes the synthesis of two novel ligands with the pentamethyl-phosphetane functionality. Several novel transition metal complexes are also described.

3.2 Results and discussion.

3.2.1 Ligand synthesis.

The synthetic protocols outlined in chapter 2 to access *ortho*-xylene bridged diphosphine ligands have been applied to the phosphetane ligands described in this chapter. Importantly, the strategy chosen has provided access to either of the two isomers of the 2,2,3,4,4-pentamethylphosphetane ring.

3.2.1.1 1-chloro-2,2,3,4,4-pentamethylphosphetane-1-oxide **14**

14 was synthesised via a methodology adapted from that described by Jungermann.[2] After several attempts to prepare **14** by Jungermann and McBride's methodology (Scheme 1),[2] it was found that better results (in terms of yield and purity) where achieved by allowing the reaction mixture to stir for a prolonged period of 24 hrs, rather than the 0.5 hr suggested. Both yield and purity where also enhanced by a more cautious work-up procedure where hydrolysis of the phosphetanium salt was carried out at 0°C and over a longer period of time. It was found that samples of **14** should be

stored under a dry nitrogen or argon atmosphere, as **14** was found to gradually hydrolyse when in contact with the air.

The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of **14** were found to be consistent with those previously reported.[8] The $^{31}P\{^{1}H\}$ NMR spectrum consists of a singlet indicative of a single isomer of **14**, with a chemical shift of δ_P 82.93 ppm. The ^{1}H NMR spectrum consists of a doublet (δ_H 0.92 ppm $^{3}J_{HCCH}$ 7.11 Hz), assigned to the protons of the methyl group at the 3 position of the ring coupled to the adjacent proton. Two doublets were observed that integrated to the 12 protons of the methyl groups at the 2 and 4 positions of the ring (δ_H 1.31 ppm, $^{3}J_{H\text{-}P}$ 10.95 Hz and δ_H 1.38 $^{3}J_{H\text{-}P}$ 9.30 Hz). A multiplet (δ_H 1.78 ppm) was also observed for the single proton at C3 of the phosphetane ring.

3.2.1.2 2,2,3,4,4-Pentamethylphosphetane **15**

The title compound was synthesised in 80% yield *via* the reduction of **14** with $LiAlH_4$. **15** was isolated as a volatile clear liquid with a strong unpleasant odour. The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra were fully consistent with that previously reported.[4,8] In common with previous workers, **15** was isolated as a 9:1 mixture of *trans:cis* isomers.

3.2.1.3 2,2,3,4,4-pentamethylphosphetane-trihydroboron **16**

Reaction of 2,2,3,4,4-pentamethylphosphetane **15** with an excess of borane-THF adduct afforded **16** as a colourless low-melting solid in near quantitative yield. The structure of **16** was confirmed by $^{31}P\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{1}H NMR spectroscopy. In common with **15** the $^{31}P\{^{1}H\}$ NMR spectrum consisted of two resonances (δ_P 57.99 ppm, (q), $^{1}J_{P\text{-}B}$ 29.78Hz, 9eq and δ_P 55.73 ppm, (q), $^{1}J_{P\text{-}B}$ 32.75Hz, 1eq), again the 9:1 ratio of isomers (*trans:cis*) was observed. The $^{11}B\{^{1}H\}$ NMR spectrum was concordant with the $^{31}P\{^{1}H\}$ NMR spectrum, in that two doublets were observed in the 9:1 ratio (δ_B –44.62 ppm, 9eq and δ_B –43.79, 1eq). The ^{1}H NMR spectrum consisted of a complex pattern of peaks due to the mixture of two isomers. However, the resonances due to the *trans* isomer could be assigned. In common with **14**, the protons of the C3 methyl group were observed as a doublet with a chemical shift of δ_H 0.92ppm ($^{3}J_{H\text{-}H}$ 7.26 Hz). The methyl groups at the 2 and 4 position of the ring were also observed as a doublet (δ_H 1.320, $^{3}J_{H\text{-}P}$ 11.64 Hz). The final ring proton at C3 was

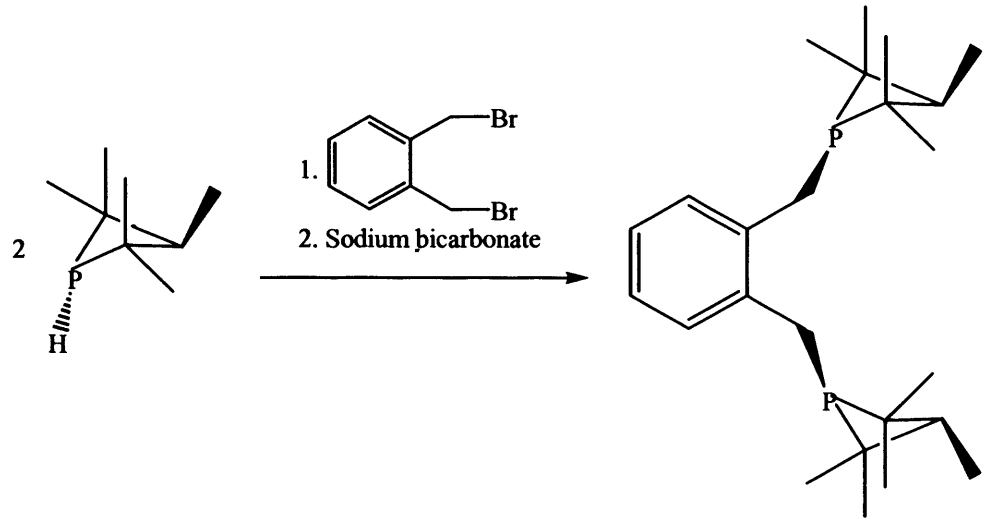
observed as a quartet with a chemical shift of δ_H 2.603 ($^3J_{H-H}$ 7.26 Hz). In common with **4** (see chapter 2), the P-H proton could be assigned to a doublet of quartets δ_H 5.169 ($^1J_{H-P}$ 331.92Hz, $^2J_{H-B}$ 6.15Hz) the AMX pattern being consistent with coupling to both phosphorus and boron. Partial NMR spectroscopy data for the *cis* isomer of **14** is given in the experimental section.

3.2.1.4 1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene **17**

17 was prepared via a reaction analogous to that described by Moulton and Shaw (Scheme 3).[11] Reaction of **16** (as a 9:1 mixture of *trans* and *cis* isomers) with α,α'-dibromo-*o*-xylene in acetone led to the dihydrobromide-phosphonium salt **18**.

18 was characterised *via* $^{31}P\{^1H\}$, ^{31}P and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum consisted of four singlets, three of which integrate to give a ratio of 16:4:1. Each peak can be assigned to a diphosphonium salt that contains two phosphetane rings, which can be in one of two possible isomeric forms.

Since the electrophilic addition to phosphorus(III) in the phosphetane system is known to invert the configuration of the substituents at phosphorus,[8] and from the statistical distribution of products likely to be observed from the 9:1 mixture of isomers in the starting materials, the peaks can be assigned to diphosphonium salts where both rings are the *cis* isomer (δ_P 49.7 ppm, 16 equivalents), the mixed form where one ring is the *trans* isomer and the other *cis* (δ_P 39.54 ppm, 4 equivalents) and the all *trans* form (δ_P 35.9 ppm, 1 equivalent). The formation of a phosphonium salt in this reaction was confirmed by ^{31}P NMR spectroscopy, where the coupling to the P-H proton gave the familiar double multiplet pattern of a phosphonium salt. The P-H coupling constant was found to be 467 Hz.



Scheme 3. Synthesis of **17**

A fourth resonance in the $^{31}P\{^{1}H\}$ NMR spectrum (δ_P 92.2 ppm) was assigned to the formation of a phospholanium salt **19** (Figure 2) similar to that described in the analogous reaction of di-*t*-butylphosphine **3** (Chapter 2).[11]

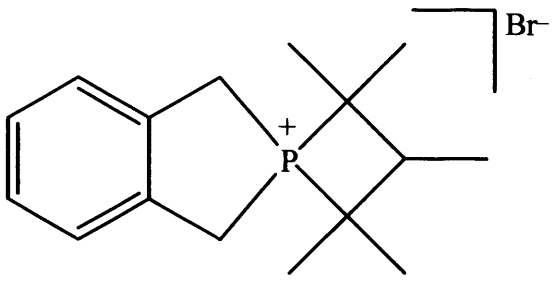


Figure 2. Phospholanium salt **19**

The full characterisation of **19** is given in the experimental section.

In common with that observed in Chapter 2, reaction of the phosphonium salts with a base (sodium bicarbonate) led to the corresponding (16:4:1) mixture of phosphines in modest yield (38%). Subsequent recrystalisation of this mixture from hot methanol gave the single isomer (shown to be **17**) as a crop of colourless crystalline needles. The solid-state structure was determined by X-ray crystallography and is shown in Figure 3. Selected bond lengths and angles are given in Table 1.

The $^{31}P\{^{1}H\}$, ^{1}H NMR spectra and mass spectra are consistent with the proposed structure of **17** and that determined by X-Ray crystallography. The $^{31}P\{^{1}H\}$ NMR spectrum consists of a singlet with a chemical shift of δ_P 29.31 ppm, as expected for two chemically and magnetically equivalent phosphorus atoms. The ^{1}H NMR spectrum showed the basic pattern of resonances now familiar to the pentamethylphosphetane functionality.[4,8] The methyl protons adjoining the 3 position of the ring where observed as a doublet with a chemical shift of δ_H 0.842 ppm ($^{3}J_{HCCH}$ 7.05 Hz). The twelve protons of the methyl groups at the 2 and 4 position of the ring were observed as a set of two doublets with chemical shifts of δ_H 1.20 and δ_H 1.24 ppm. The methine proton at the 3 position of the ring was observed as the familiar quartet with a chemical shift of δ_H 2.26 ($^{3}J_{HCCH}$ 7.05 Hz).

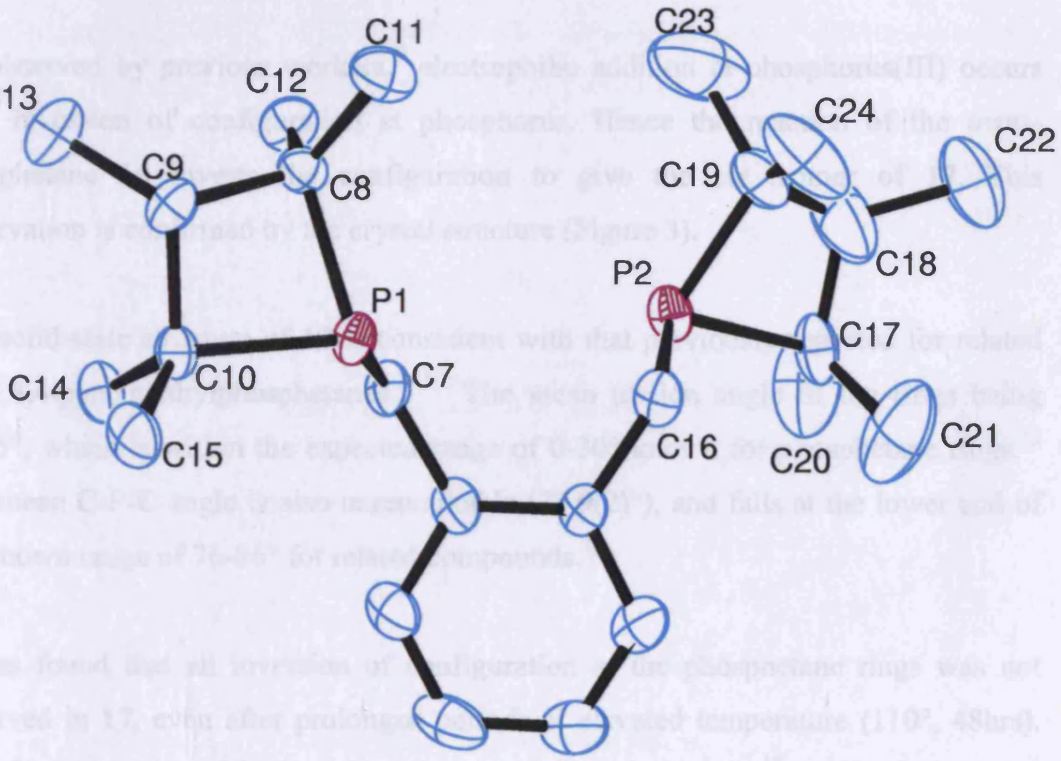


Figure 3. X-Ray Crystal structure of **17**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability

Bond	Length (Å)	Group	Angle (°)
C_7-P_1	1.864(4)	C_{10}-P_1-C_8	78.2(2)
C_{16}-P_2	1.862(4)	C_{10}-C_9-C_8	99.0(3)
P_1-C_8	1.882(5)	C_{19}-P_2-C_{17}	77.5(2)
P_1-C_{10}	1.887(4)	C_{19}-C_{18}-C_{17}	101.1(5)
P_2-C_{17}	1.899(5)	C_8-P_1-C_7	107.0(2)
P_2-C_{19}	1.888(5)	C_{10}-P_1-C_7	108.6(2)
C_9-C_8	1.565(6)	C_{19}-P_2-C_{16}	104.9(2)
C_9-C_{10}	1.562(6)	C_{17}-P_2-C_{16}	107.8(2)
C_{18}-C_{19}	1.525(10)		
C_{18}-C_{17}	1.546(10)		

Table 1. Selected bond lengths and angles for **17**

As observed by previous workers,[8] electrophilic addition at phosphorus(III) occurs with inversion of configuration at phosphorus. Hence the reaction of the *trans*-phosphetane **15** inverts the configuration to give the *cis* isomer of **17**. This observation is confirmed by the crystal structure (Figure 3).

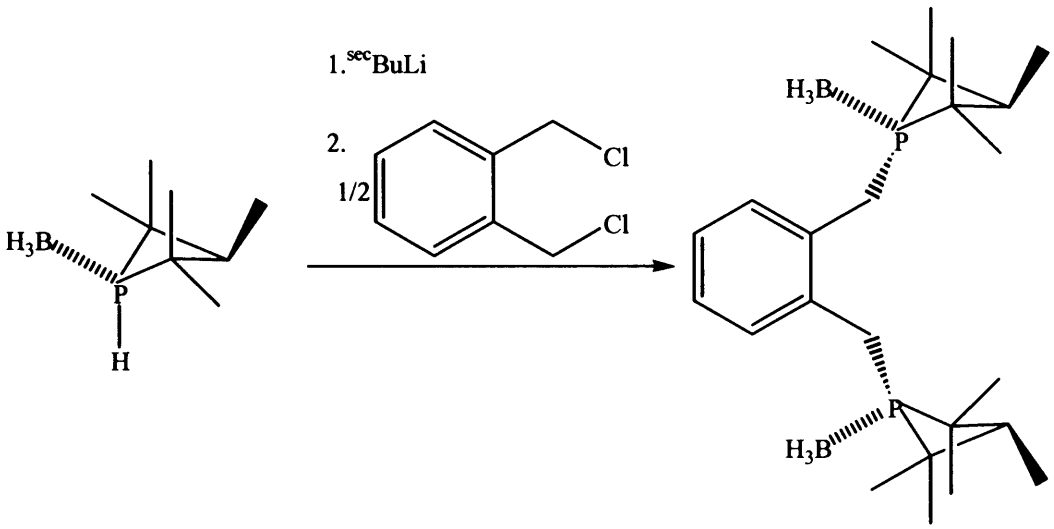
The solid state structure of **17** is consistent with that previously reported for related 2,2,3,4,4-pentamethylphosphetanes.[3,12] The mean torsion angle of the rings being 21.25°, which is within the expected range of 0-30° known for phosphetane rings.[13] The mean C-P-C angle is also unremarkable (77.9(2)°), and falls at the lower end of the known range of 76-86° for related compounds.[13]

It was found that an inversion of configuration at the phosphetane rings was not observed in **17**, even after prolonged periods at elevated temperature (110°, 48hrs). This is consistent with the observations of Cremer *et al*, [19] where the related 1,2,2,3,4,4-hexamethylphosphetane was also found to be configurationally stable. However, The configuration of the 1-phenyl and 1-*tert*-butyl analogues was found to invert under similar conditions.[19]

3.2.1.5 1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene-trihydroboron **20**

The title compound was synthesised *via* a methodology analogous to that described for **5** (see Chapter 2). A THF solution of a 9:1 mixture of *trans*:*cis* isomers of **16** was cooled to -78°C and 1.2 equivalents of *sec*-BuLi where added gradually *via* syringe. The resulting highly coloured solution (yellow) was then allowed to warm to room temperature and was stirred for an additional 1 hr. The deprotonation can be monitored *via* $^{31}P\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectroscopy. The lithium phosphetanides are observed as two quartets with chemical shifts of δ_P 23.89 ppm ($^{1}J_{P\text{-}B}$ 29.77 Hz, *trans* isomer) and δ_P 30.12 ppm ($^{1}J_{P\text{-}B}$ 29.78Hz, *cis* isomer) *via* $^{31}P\{^{1}H\}$ NMR spectroscopy. Two doublets were observed in the $^{11}B\{^{1}H\}$ NMR spectrum with chemical shifts of δ_B –37.310 ppm (*trans* isomer) and δ_B -35.840 ppm (*cis* isomer). Again the 9:1 ratio of *trans*:*cis* isomers is maintained.

Upon re-cooling (-78°C), a THF solution of 0.5 equivalents of α,α'-dichloro-*o*-xylene was added drop wise *via* cannula to afford **20** in 89% yield (Scheme 4).



Scheme 4. Synthesis of **20**

The $^{31}P\{^{1}H\}$ NMR spectrum of **20** revealed a broad resonance with a chemical shift of δ_P 66.36 ppm. As expected, upon alkylation of the 2°-phosphetane-borane adduct to form the 3° phosphetane-borane adduct, a downfield shift of 8.37 ppm is observed. The $^{11}B\{^{1}H\}$ NMR spectrum consisted of a broad resonance at δ_B –43.03 ppm. The ^{1}H NMR spectrum was also found to be consistent with the proposed structure of **20**.

A doublet observed at δ_H 0.91 ppm could be assigned to the methyl protons at the 3 position of the phosphetane ring. The twelve protons of the methyl groups at the 2 and 4 positions of the phosphetane ring were observed as a doublet at δ_H 1.35 ($^3J_{HCCP}$ 9.90Hz). The final ring proton at the 3 position of the phosphetane ring was observed as a quartet with a chemical shift of δ_H 2.56 ppm ($^3J_{HCCH}$ 7.27 Hz). The methylene protons of the *o*-xylene moiety, in common with that observed previously, could be assigned to a doublet at δ_H 3.51 ppm ($^2J_{H\text{-}P}$ 11.85Hz). Finally, two multiplets with chemical shifts of δ_H 7.15 ppm and δ_H 7.36 ppm were assigned to each of the two sets of chemically equivalent aromatic protons of the *o*-xylene backbone.

3.2.1.6 1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene **21**

In common with **5**, compound **20** was deprotected using the methodology described in Chapter 2 to give **21**. Reaction of **20** with 10 equivalents of HBF_4.OMe2 and subsequent reaction with base gave the free phosphine **21** in a mixture with the other ring isomers. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture revealed three peaks, again in a ratio of 16:4:1 analogous to those observed in the synthesis of **17**. However, the distribution of products was different to that previously observed. The resonance corresponding to the compound with both phosphetane rings in the *trans* form (δ_P 42.55 ppm) was now the major product of the reaction. This observation is consistent with previous work.[8] It was found that addition reactions of the phosphetane system involving phosphorus(V), led to the retention of the configuration at phosphorus.**21** was purified by recrystallisation from hot methanol to give fine colourless needles. The crystals were subsequently found to be unsuitable for determination of the solid-state structure by X-ray diffraction.

The $^{31}P\{^1H\}$ and ^1H NMR spectra and the mass spectrum are consistent with the proposed formulation of **21**. The $^{31}P\{^1H\}$ NMR spectrum consists of a single peak (δ_P 42.55 ppm), highlighting the chemical equivalence of the two phosphorus atoms. The ^1H NMR spectrum has the familiar pattern of peaks seen for the compounds previously described. The six protons of the methyl groups at the 3 position of the rings were observed as a doublet at δ_H 0.81 ppm ($^3J_{HCCH}$ 9.66 Hz). The twelve methyl protons adjoining the 2 and 4 positions are observed as two doublets with chemical shifts of δ_H 1.14 ppm ($^3J_{HCCP}$ 7.26Hz) and δ_H 1.24 ppm ($^3J_{HCCP}$ 18.48 Hz). The final two ring protons at the 3 position of the rings being observed as a quartet at δ_H 2.71

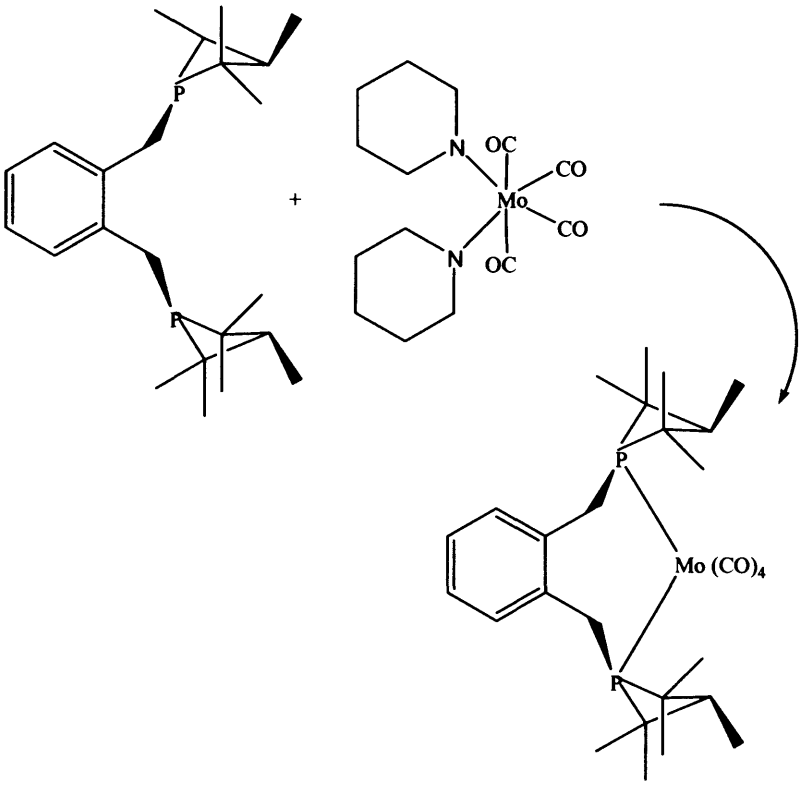
ppm ($^3J_{HCCH}$ 7.26 Hz). The methylene protons of the *o*-xylene backbone are observed as a broad doublet at δ_H 3.34 ppm. Two multiplets at δ_H 7.06 ppm and δ_H 7.16 ppm were observed for the aromatic protons of the *o*-xylene moiety.

The APCI mass spectrum of **21** was consistent with that previously observed for **17**, with the ion corresponding to the singly protonated species being observed at *m/z* 391.2.

3.2.2 Complexation Chemistry.

3.2.2.1 1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene tetracarbonyl molybdenum(0) 22

In a reaction analogous to that described for **7**, one equivalent of **17** was reacted with **8** in warm dichloromethane (Scheme 5). Subsequent recrystalisation *via* layering a chloroform solution of the buff coloured solid with methanol, led to a crop of colourless crystals of **22**. The solid state structure of **22** was determined by X-Ray diffraction and is shown in Figure 4. Selected bond lengths and angles are given in Table 2.



Scheme 5. Synthesis of **22**

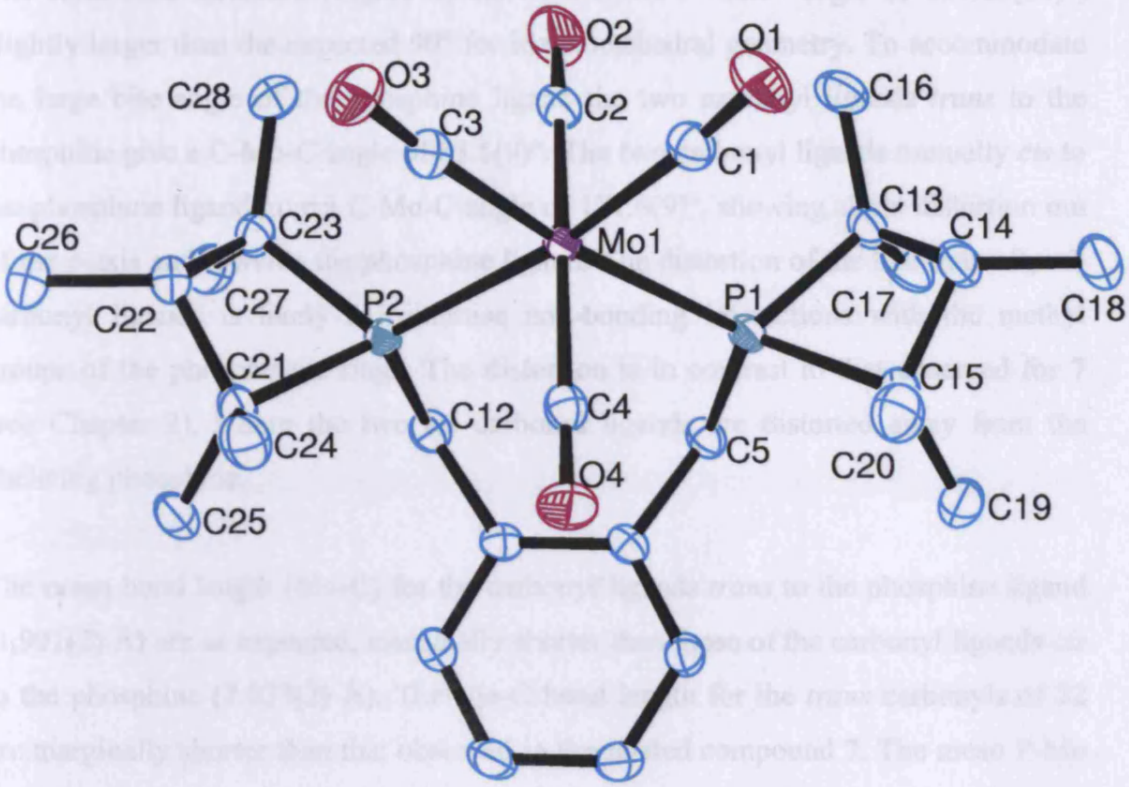


Figure 4. X-Ray Crystal structure of **22**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability

Bond	Length (Å)	Group	Angle (°)
P_1-Mo_1	2.543(5)	C_{13}-P_1-C_{15}	77.82(10)
P_2-Mo_1	2.545(6)	C_{13}-C_{14}-C_{15}	100.57(15)
Mo_1-C_1	1.993(2)	C_{21}-P_2-C_{23}	77.80(9)
Mo_1-C_2	2.028(2)	C_{12}-C_{22}-C_{23}	100.01(17)
Mo_1-C_3	1.988(2)	P_1-Mo_1-P_2	100.68(18)
Mo_1-C_4	2.038(2)	C_1-Mo_1-C_3	83.5(9)
P_1-C_{13}	1.906(2)	C_2-Mo_1-C_4	171.60(9)
P_1-C_{15}	1.911(2)	C_1-Mo_1-C_4	91.58(9)
P_2-C_{21}	1.908(2)	C_3-Mo_1-C_4	94.10(9)
P_2-C_{23}	1.904(2)		

Table 2. Selected bond lengths and angles for **22**

The solid state structure (Figure 4) shows a P-Mo-P "bite" angle of 100.68(18)°, slightly larger than the expected 90° for ideal octahedral geometry. To accommodate the large bite angle of the phosphine ligand the two carbonyl ligands *trans* to the phosphine give a C-Mo-C angle of 83.5(9)°. The two carbonyl ligands mutually *cis* to the phosphine ligand give a C-Mo-C angle of 171.6(9)°, showing slight distortion out of the *z*-axis and towards the phosphine ligand. The distortion of the two mutually *cis* carbonyl ligands is likely to minimise non-bonding interactions with the methyl groups of the phosphetane rings. The distortion is in contrast to that observed for **7** (see Chapter 2), where the two *cis* carbonyl ligands are distorted away from the chelating phosphine.

The mean bond length (Mo-C) for the carbonyl ligands *trans* to the phosphine ligand (1.991(2) Å) are as expected, marginally shorter than those of the carbonyl ligands *cis* to the phosphine (2.033(2) Å). The Mo-C bond length for the *trans* carbonyls of **22** are marginally shorter than that observed in the related compound **7**. The mean P-Mo bond length is of interest in **22** (2.544(6) Å) as it appears to differ significantly from that in **7** (2.658(6) Å). It is however, difficult to rationalise this observation in terms of the σ-basicity and π-acidity of the phosphine ligand employed.

The mean fold angle of the rings was found to be 20.20°, similar to that observed in the free phosphine (21.25°). The mean C-P-C angle in the phosphetane rings (77.81(10)°) also remained relatively unchanged upon coordination, when compared to the free ligand **17** (77.90(2)°). Both observations are indicative of the rigid and constrained structure of the phosphetane ring.

The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra are fully consistent with the proposed structure of **22**. A singlet (δ_P 69.863 ppm) is observed in the $^{31}P\{^{1}H\}$ NMR spectrum, indicating that the two phosphorus atoms are chemically equivalent. The familiar pattern of resonances previously observed for the pentamethylphosphetane and *o*-xylene functionalities were observed in the ^{1}H NMR spectrum.

The APCI mass spectrum of **22** was also consistent with that previously observed for **7**. The molecular ion was observed at *m/z* 598 (M^+). The fragment due to the loss of

one carbonyl ligand was also observed at *m/z* 570 (M^+ -CO). Both showing the isotopic pattern expected for a molybdenum complex.

The infra-red spectrum was recorded from a KBr disc of **22**. Four bands were observed in the carbonyl region of the infrared (ν_{CO} 1847.7 (sh), 1914.6, 2013.6 cm^{-1}) consistent with that previously described for **7**. The A_1 band for **22** (2013.6 cm^{-1}) seems to imply lower σ-basicity for the phosphetane **17** when compared to that of the analogous complex of **1** (2001 cm^{-1}) (see Chapter 2).

3.2.2.2[1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene tetracarbonyl molybdenum(0)] **23**

23 was synthesised *via* a reaction analogous to that for **22** (Scheme 5). Similarly, a crop of colourless crystals of **23** was obtained by layering a chloroform solution of **23** with methanol. The X-Ray crystal structure of **23** is shown in Figure 5. Selected bond lengths and angles are given in Table 3.

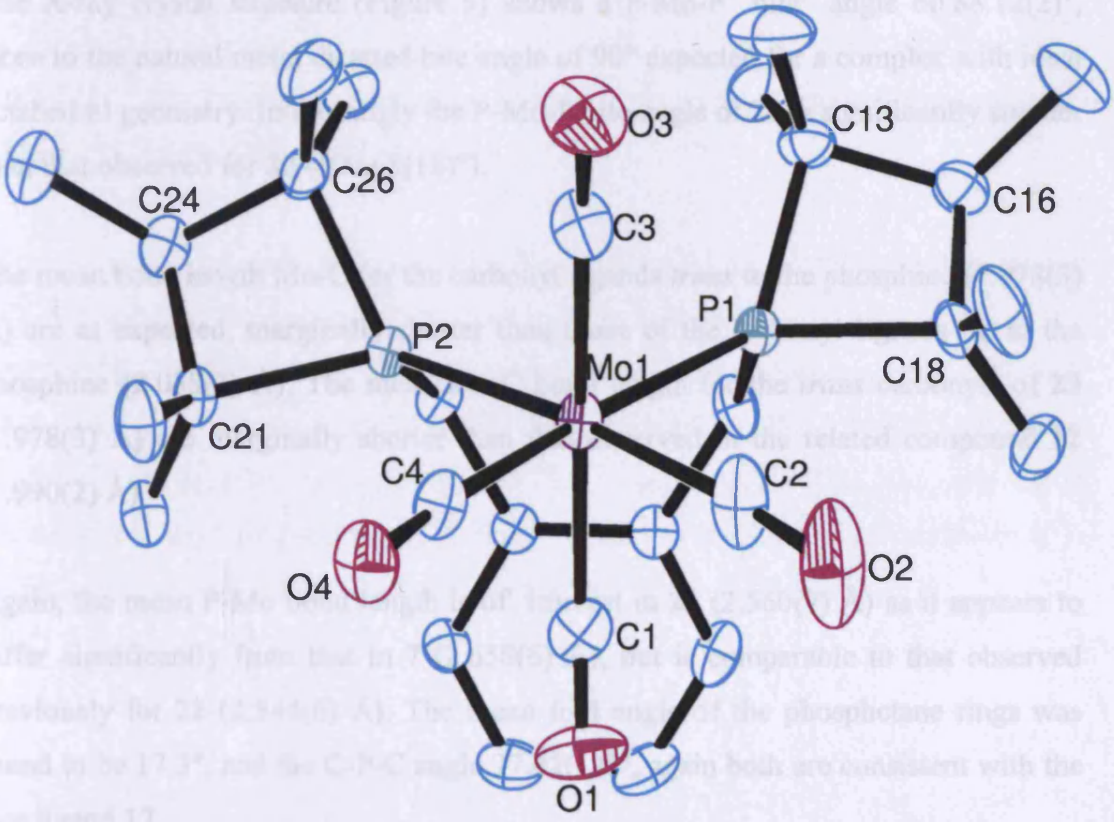


Figure 5. X-Ray Crystal structure of **23**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability

Bond	Length (Å)	Group	Angle (°)
P_1-Mo_1	2.559(7)	C_{13}-P_1-C_{18}	77.12(12)
P_2-Mo_1	2.560(6)	C_{13}-C_{16}-C_{18}	99.1(2)
Mo_1-C_2	1.968(3)	C_{21}-P_2-C_{26}	77.71(12)
Mo_1-C_4	1.988(3)	C_{21}-C_{24}-C_{26}	99.8(2)
Mo_1-C_1	2.055(3)	P_1-Mo_1-P_2	88.12(2)
Mo_1-C_3	2.021(3)	C_2-Mo_1-C_4	84.13(11)
P_1-C_{13}	1.903(3)	C_1-Mo-C_4	84.92(11)
P_1-C_{18}	1.908(3)	C_1-Mo_1-C_2	82.86(12)
P_2-C_{21}	1.900(3)	C_1-Mo_1-C_3	168.30(10)
P_2-C_{26}	1.899(3)		

Table 3. Selected bond lengths and angles for **23**.

The X-ray crystal structure (Figure 5) shows a P-Mo-P "bite" angle of 88.12(2)°, close to the natural metal dictated bite angle of 90° expected for a complex with ideal octahedral geometry. Interestingly the P-Mo-P bite angle of **23** is significantly smaller than that observed for **22** (100.68(18)°).

The mean bond length Mo-C for the carbonyl ligands *trans* to the phosphine (1.978(3) Å) are as expected, marginally shorter than those of the carbonyl ligands *cis* to the phosphine (2.038(3) Å). The mean Mo-C bond length for the *trans* carbonyls of **23** (1.978(3) Å) are marginally shorter than that observed in the related compound **22** (1.990(2) Å).

Again, the mean P-Mo bond length is of interest in **23** (2.560(7) Å) as it appears to differ significantly from that in **7** (2.658(6) Å), but is comparable to that observed previously for **22** (2.544(6) Å). The mean fold angle of the phosphetane rings was found to be 17.3°, and the C-P-C angle 77.42(12)°, again both are consistent with the free ligand **17**.

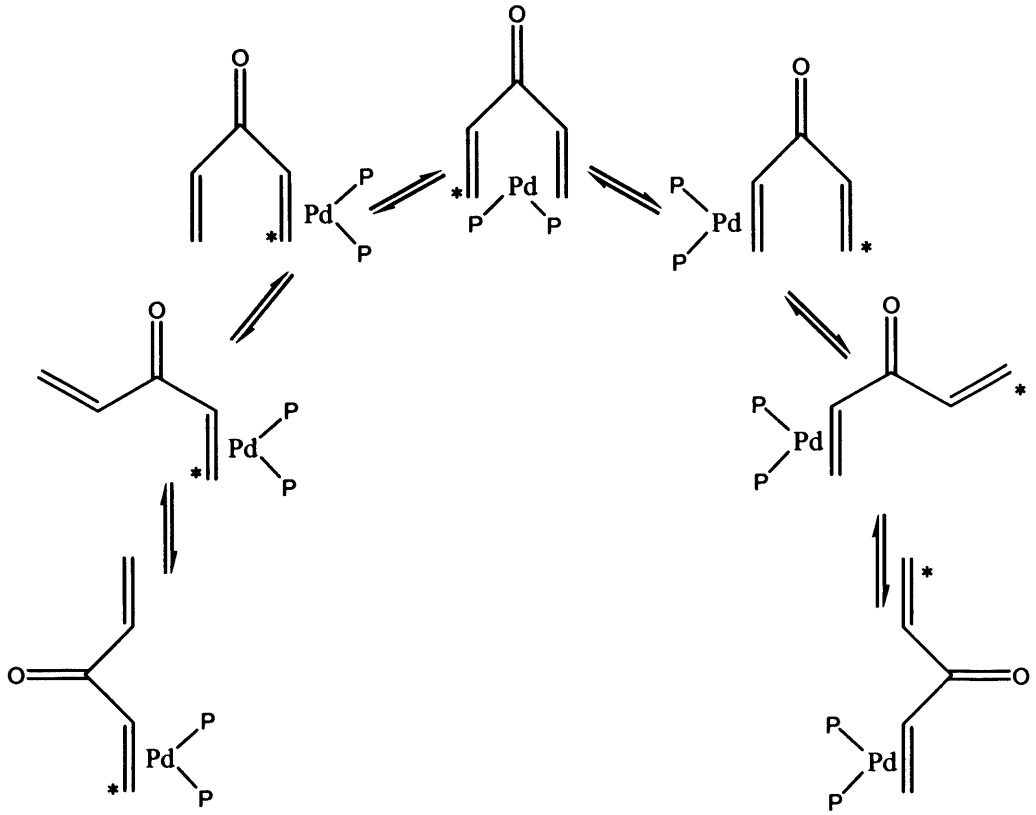
The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra are fully consistent with the proposed structure of **23**. A singlet (δ_P 84.058 ppm) is observed in the $^{31}P\{^{1}H\}$ NMR spectrum, indicating that the two phosphorus atoms are chemically equivalent. The now familiar pattern of resonances previously observed for the pentamethylphosphetane and *o*-xylene functionalities were observed in the ^{1}H NMR Spectrum.

The APCI mass spectrum of **23** was similar to that previously observed for **22**. The molecular ion was observed at *m/z* 598 (M^+). The fragment due to the loss of one carbonyl ligand was also observed at *m/z* 570 (M^+ -CO). Both showing the isotopic pattern expected for a molybdenum complex.

The IR spectrum was recorded from a KBr disc of **23**. Four bands were observed in the carbonyl region of the infrared (ν_{CO} 1857, 1877, 1912, 2016 cm^{-1}) consistent with that previously described for **22**. Again, the A_1 band for **22** (2016 cm^{-1}) seems to infer lower σ-basicity for the phosphine **21** when compared to that of the analogous complex of **1** (2001 cm^{-1}).

3.2.2.3 [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (*trans, trans* dibenzylideneacetone) palladium (0)] **24**

24 was synthesised *via* reaction of **17** with $[Pd(DBA)_2]$ in THF to afford an orange coloured solution. Subsequent work up gave **24** in 76% yield.
The $^{31}P\{^{1}H\}$ NMR spectrum (298K) consisted of two broad resonances (δ_P 58.3 and 64.4 ppm), resulting from the dynamic behaviour of the DBA ligand. When the $^{31}P\{^{1}H\}$ NMR spectra was recorded at low temperature (248K), the two broad resonances where resolved into a complex pattern of peaks, each corresponding to complexes with one of the possible conformations of the DBA ligand.[19]



Scheme 6. Fluxional nature of the DBA ligand (where * distinguishes between the two double bonds)

The ^{1}H NMR spectrum of **24** recorded at low temperature, also revealed resonances due to the protons of the coordinated and uncoordinated olefinic bonds of the DBA ligand (δ_H 5.03 and 7.65 ppm respectively), this being consistent with that observed by previous workers.[23]

3.2.2.4 [Dichloro (1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) palladium (II)] **25**

25 was synthesised *via* displacement of the DBA ligand in complex **24** with 1,4-*p*-benzoquinone and subsequent oxidation with anhydrous HCl in diethyl ether. Upon standing the complex was precipitated as a yellow solid. Crystals of **25** were grown by the slow vapour diffusion of diethyl ether into a concentrated THF solution of the complex to give **25** as a crop of yellow to orange coloured crystals. A small amount of red crystals were also isolated, and subsequently found to be the THF solvate. The solid state structure was determined *via* X-ray diffraction, and is shown in Figure 6. Selected bond lengths and angles are given in Table 4.

The most striking feature of the structure is the deviation from the perfect square-planar geometry commonly observed in d^8 Pd(II) halide complexes. The two chloride ligands being twisted out of the *x-y* plane by 22.5°. The distortion is also carried through into the *o*-xylene unit bridging between the two phosphetane donors.

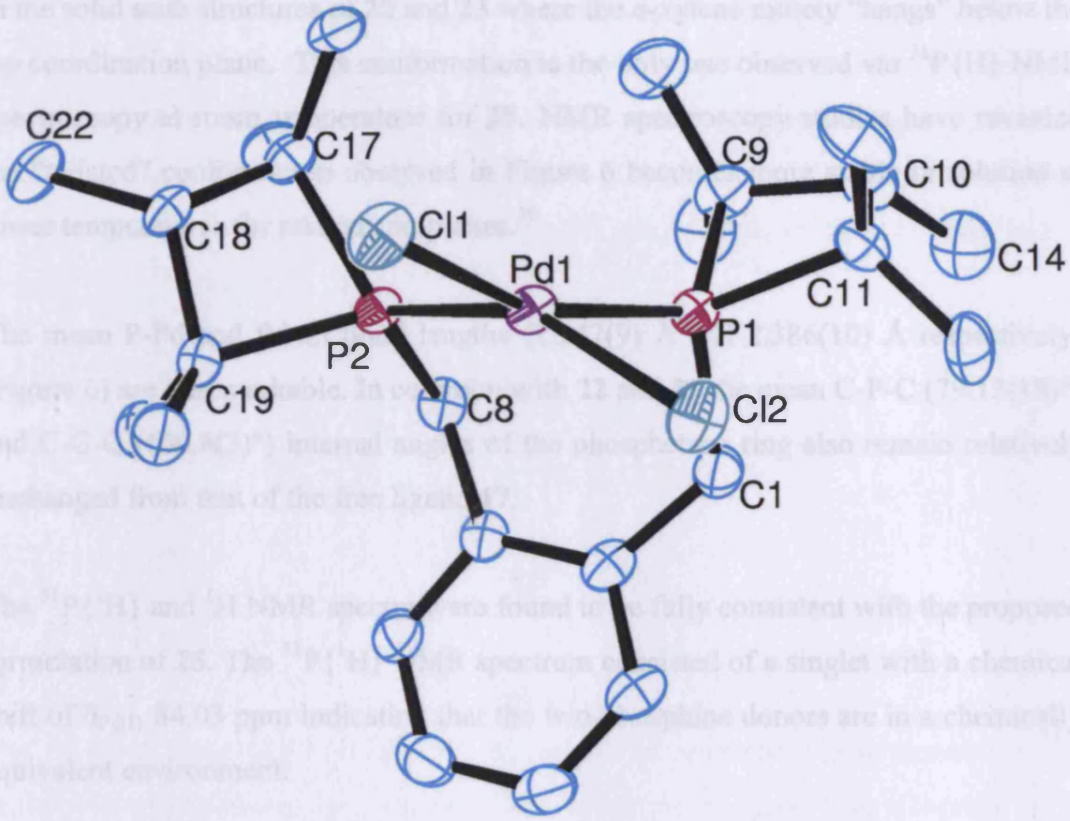


Figure 6. X-Ray Crystal structure of **25**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability

Bond	Length (Å)	Group	Angle (°)
P_1-Pd_1	2.242(9)	C_9-P_1-C_{11}	79.11(18)
P_2-Pd_1	2.252(9)	C_9-C_{10}-C_{11}	99.2(3)
Pd_1-Cl_1	2.379(10)	C_{17}-P_2-C_{19}	79.15(16)
Pd_1-Cl_2	2.392(9)	C_{17}-C_{18}-C_{19}	101.5(3)
		P_1-Pd_1-P_2	92.17(3)
		Cl_1-Pd_1-Cl_2	92.58(3)
		P_1-Pd_1-Cl_2	85.37(3)
		P_2-Pd_1-Cl_1	97.75(3)

Table 4. Selected bond lengths and angles for **25**

This has previously been observed in solution , where it is believed that the *o*-xylene moiety can adopt different conformations.[20] The most stable conformation of the ligand being the C_2 symmetrical "scorpionate" arrangement, similar to that observed in the solid state structures of **22** and **23** where the *o*-xylene moiety "hangs" below the *x-y* coordination plane. This conformation is the only one observed *via* $^{31}P\{H\}$ NMR spectroscopy at room temperature for **25**. NMR spectroscopy studies have revealed the "twisted" conformation observed in Figure 6 becomes more stable in solution at lower temperatures for related complexes.[20]

The mean P-Pd and Pd-Cl bond lengths (2.247(9) Å and 2.386(10) Å respectively) (Figure 6) are unremarkable. In common with **22** and **23** the mean C-P-C (79.13(18)°) and C-C-C (100.4(3)°) internal angles of the phosphetane ring also remain relatively unchanged from that of the free ligand **17**.

The $^{31}P\{^1H\}$ and ^1H NMR spectra were found to be fully consistent with the proposed formulation of **25**. The $^{31}P\{^1H\}$ NMR spectrum consisted of a singlet with a chemical shift of $\delta_{P\{H\}}$ 84.03 ppm indicating that the two-phosphine donors are in a chemically equivalent environment.

The ^1H NMR spectrum showed the pattern of peaks expected for the 2,2,3,4,4-pentamethylphosphetane functionality. The resonance for the methylene protons of the *o*-xylene backbone were observed as two doublets (δ_H 3.55 ppm and 3.59 ppm), rather than the expected doublet observed in previous complexes. The multiplicity of these resonances suggesting the distorted structure observed *via* X-ray diffraction (figure 6) may occur in solution.

3.2.2.5 [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (η^2 ethylene) palladium (0)] 26

26 was synthesised via the reaction of **17** with [(η^5-cyclopentadiene)(η^2-allyl) palladium(II)] **28** ,[16] in cold (-40 °C) diethyl ether under an atmosphere of high purity ethylene. Addition of **17** to **28** presumably causes the reductive elimination of the cyclopentadienyl and allyl ligands to give a coordinatively unsaturated phosphine

Pd(0) complex in common with that observed by previous workers with bulky monodentate phosphine ligands.[21] Coordination of ethylene to this intermediate complex then gave **26**, which was isolated as a red/orange coloured solid.

The $^{31}P\{^{1}H\}$ NMR spectrum of **26** when recorded at room temperature consisted of a single broad resonance ($\delta_{P\{H\}}$ 54.79) due to the propeller like rotation of the ethylene ligand around the metal-ethylene σ-bond. However, at low temperature (258K) the broad resonance was resolved into a doublet of doublets, consistent with coupling between phosphorus and each of the inequivalent protons of the ethylene ligand (Figure 7).

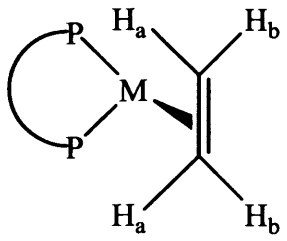


Figure 7.

The ^{1}H NMR Spectrum consisted of the pattern of resonances now familiar to the pentamethylphosphetane functionality. The η^2-ethylene ligand was observed as a broad resonance (δ_H 2.39 ppm) at both room and lower temperature.

3.2.2.6 [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (η^1-ethyl) palladium (II) tetrafluoroborate] **27**

The gradual addition of a diethyl ether solution of HBF_4 to a cooled diethyl ether solution of **26** caused the immediate precipitation of **27** as an orange coloured solid. The reaction being analogous to that previously demonstrated by Conroy-Lewis *et al.*[22]

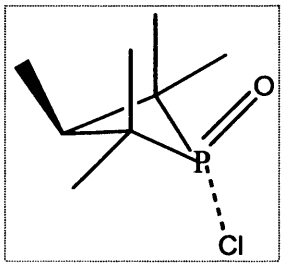
The $^{31}P\{^{1}H\}$ NMR spectrum consisted of two resonances ($\delta_{P\{H\}}$ 49.11 and 62.59 ppm), each corresponding to one of the inequivalent phosphorus atoms. Again the ^{1}H NMR spectrum showed the familiar pattern of resonances for the

pentamethylphosphetane functionality. The most striking feature of the ^{1}H NMR spectrum was the complex resonance observed at high field (δ_H –8.34ppm), corresponding to the proton of the ethyl ligand that is interacting with the palladium atom. The resonance assigned to the five remaining protons of the ethyl ligand was partially obscured by resonances due to the methyl groups at the 2 and 4 positions of the phosphetane ring.

3.3 Experimental

All compounds were prepared using standard Schlenk techniques under an atmosphere of dinitrogen or argon. ^{31}P (referenced to H_3PO_4 at $\delta_P = 0$) and ^{11}B (referenced to $Et_2O.BF_3$ at $\delta_B = 0$) NMR data was collected on a Jeol Eclipse 300 MHz spectrometer; ^{1}H and ^{13}C data on a Bruker 400 MHz DPX Avance. Mass spectra (ES and APCI) were obtained on a VG Fisons Platform II. Tetrahydrofuran, Diethyl ether and hexane were dried over sodium benzophenone. Toluene was dried over sodium. Methanol and acetonitrile were dried over calcium hydride. Water used during the work-up of all compounds was carefully deoxygenated by several cycles of heating at reflux and cooling to room temperature under a nitrogen purge. $CDCl_3$ and d_3-acetonitrile were purchased from Aldrich, dried over 3Å molecular sieves and freeze-thaw degassed before use. C_6D_6 was purchased from Goss scientific and dried over sodium prior to use. Unless otherwise stated all chemicals were purchased from Aldrich and used without further purification. [(η^5-cyclopentadiene)(η^3-allyl)Pd(II)] and [Pd(η^3-allyl)Cl]$_2$ were prepared as detailed in the literature.[17]

1-chloro-2,2,3,4,4-pentamethylphosphetane-1-oxide 14
(Adapted from the method of Jungermann).[2]



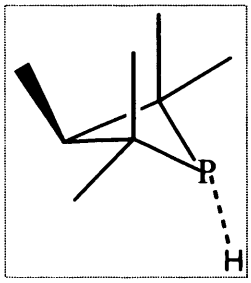
To a cooled (0° C) dichloromethane (250 cm^3) suspension of PCl_3 (0.134 mols, 18.4 g) and $AlCl_3$ (0.168 mols, 22.33 g) was gradually added (over 1hr) *via* cannula a DCM solution (50 cm^3) of 2,4,4 trimethylpent-2-ene. During the addition of the alkene the amount of suspended $AlCl_3$ noticeably decreased until the solution became clear and yellow in colour. The reaction was stirred for 24 hrs, where upon the solution darkened to a deep orange colour. Methanol (110 cm^3) was then added to the cooled (0° C) reaction mixture over 3 hrs. The addition was performed cautiously at first due to the exothermic nature of the reaction. After the full addition of the methanol, the reaction was stirred at 0° C for a further 0.5 hr. Ice cooled water (200 cm^3) was then added to the cooled reaction mixture. The organic layer was removed *via* cannula and dried over Na_2SO_4. The solution was filtered *via* cannula and the solvent removed under reduced pressure to yield the product as fine off-white crystals that were dried carefully under vacuum.

Yield: 21.6 g, 82%.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 82.93 (s); ^1H NMR ($CDCl_3$, 300 MHz) 0.92 (3H, d, $^3J_{HCCH}$ 7.11 Hz) 1.31 (6H, d, $^3J_{H\text{-}P}$ 10.95 Hz) 1.38 (6H, d, $^3J_{H\text{-}P}$ 9.30 Hz) 1.778 (1H, m); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 7.31 (d) 18.23 (d) 25.96 (d) 42.29 (d) 56.87 ppm (d).

MS (APCI): *m/z* 159.1 (M, -Cl).

2,2,3,4,4-Pentamethylphosphetane 15



To a slurry of $LiAlH_4$ (2.83 mmol, 0.11 g) in Et_2O (20 cm^3) was slowly added a Et_2O solution (20 cm^3) of 1-chloro 2,2,3,4,4 pentamethylphospetane-1-oxide (2.57 mmol, 0.5 g). The solution was stirred for a further 1 hr at 0° C and then allowed to warm to room temperature before stirring for a further 24hrs. Water (1 cm^3) was added to the cooled (0° C) reaction mixture cautiously *via* cannula. 4 cm^3 of 15% NaOH solution was then added and the solution was stirred at 0° C for a further 0.5 hrs. The Et_2O layer was removed *via* cannula and dried over anhydrous Na_2SO_4. The Et_2O was then removed by distillation to yield the 2,2,3,4,4 pentamethylphosphetane as a clear liquid, with a strong unpleasant odour.

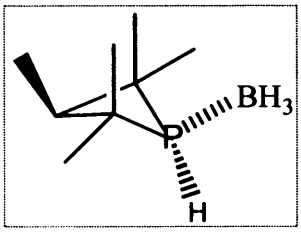
Yield: 0.28 g, 80%.

9:1 mixture of *trans:cis* isomers.

(*trans* **15**) ^{31}P $\{^1H\}$ NMR ($CDCl_3$,121.65 MHz) δ 16.95 (s); ^1H NMR ($CDCl_3$, 300 MHz) 0.79 (3H, d, $^3J_{HCCH}$ 7.02 Hz) 1.22 (12H, d, $^3J_{H\text{-}P}$ 7.92 Hz) 2.68 (1H, q, $^3J_{HCCH}$ 7.02 Hz) 3.78 (1H, d, $^1J_{H\text{-}P}$ 176.06 Hz); ^1H $\{^{31}P\}$ NMR ($CDCl_3$, 300 MHz) 0.79 (3H, d, $^3J_{HCCH}$ 7.02 Hz) 1.23 (12H, s) 2.68 (1H, q $^3J_{HCCH}$ 7.05 Hz); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 10.24 (s) 23.16 (d) 31.75 (d) 56.64 ppm (d).

Partial data for *cis* **15**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 14.722 (s); ^1H NMR ($CDCl_3$, 300 MHz) 0.87 (3H, d, $^3J_{HCCH}$ 7.23 Hz) 1.18 (12H, d, br); ^1H $\{^{31}P\}$ ($CDCl_3$, 300 MHz) 1.21 ppm (12H, s).

2,2,3,4,4-pentamethylphosphetane-trihydroboron 16



To a solution of 2,2,3,4,4-pentamethylphosphetane (0.28 g, 1.95 mmol) in THF (20 cm^3), was added a solution of borane THF adduct (1 M, 1.5 eq, 2.93 mmol). The solution was stirred for 2.5 hrs, and the solvent removed under vacuum to yield the product as a white low melting solid.

Yield: 0.30 g, 99%

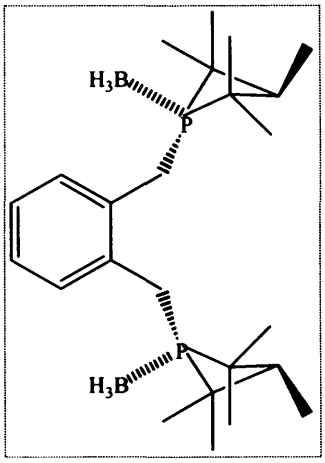
9:1 mixture of *trans:cis* isomers.

trans **16** ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 57.99 (q, $^1J_{P\text{-}B}$ 29.78 Hz); ^{11}B $\{^1H\}$ NMR ($CDCl_3$, 96.42 MHz) –44.618 (d); ^1H NMR ($CDCl_3$, 300 MHz) 0.92 (3H. d, $^3J_{HCCH}$ 7.26 Hz) 1.32 (12H, d, $^3J_{H\text{-}P}$ 11.64 Hz) 2.60 (1H, q, $^3J_{HCCH}$ 7.26 Hz) 5.17 (1H. dq, $^1J_{H\text{-}P}$ 331.92 Hz, $^2J_{H\text{-}B}$ 6.15 Hz); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 9.14 (s) 18.76 (d) 32.77 (d) 53.77 ppm (d).

Partial data for *cis* **16**: ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 55.73 (q, $^1J_{P\text{-}B}$ 32.75 Hz); ^{11}B $\{^1H\}$ NMR ($CDCl_3$, 96.42 MHz) –43.787 (d); ^1H NMR ($CDCl_3$, 300 MHz) 0.97 (3H, d, $^3J_{HCCH}$ 7.23 Hz) 1.27 (12H, d, $^3J_{H\text{-}P}$ 14.07 Hz); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 23.97 (s) 29.92 (d) 31.67 (d) 51.73 ppm (d).

MS (APCI): *m/z* 158.9 (M, $+H^+$)

1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene-trihydroboron 20



To a cooled (-78° C) THF solution (25 cm^3) of 2,2,3,4,4-pentamethylphosphetane-trihydroboron (0.31 g, 1.95 mmol) was added, *via* syringe, *sec*-BuLi (2.10 mmol) upon full addition of the *sec*-BuLi the solution became bright yellow. The solution was stirred for 2 hrs at -78° C and then a further 0.5 hr at room temperature to give 1-lithio-2,2,3,4,4-pentamethylphosphetanide-trihydroboron. The deprotonation can monitored by either $^{31}P\{H\}$ or $^{11}B\{H\}$ NMR spectroscopy (data given below). The solution was cooled to –78 °C and a THF solution (10 cm^3) of α,α'-dichloro-o-xylene (0.17 g, 0.97 mmol) was added slowly *via* cannula. The solution was allowed to stir for 1 hr at –78 °C and then allowed to warm to room temperature before being left to stir for a further 18hrs. During this time the solution became cloudy as LiCl precipitated. The solvent was removed under vacuum, and dichloromethane (30 cm^3) and water (30 cm^3) added to give a two-phase system. The organic phase was then removed *via* cannula and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield the product as a white solid.

Yield: 0.36 g, 89%

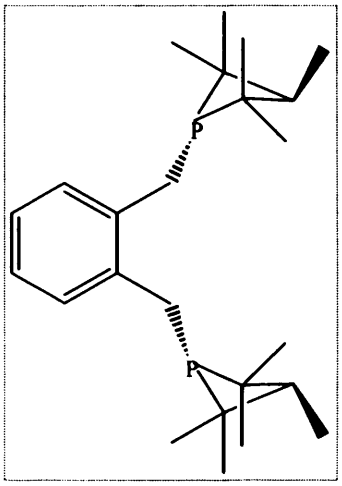
$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 66.36 (m, br); $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96.42 MHz) –43.029 (d, br); ^1H NMR ($CDCl_3$, 300 MHz) 0.91 (6H, d, $^3J_{HCCH}$ 7.26 Hz) 1.35 (24H, d, $^3J_{H\text{-}P}$ 9.90 Hz) 2.56 (2H, q, $^3J_{HCCH}$ 7.27 Hz) 3.51 (4H, d, $^2J_{H\text{-}P}$ 11.85 Hz) 7.15-7.36 (4H, m, Ar-**H**); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 9.00 (s) 20.98 (d) 35.04 (d) 52.22 (d) 126.97 (d) 129.49 (s) 130.75 ppm (d).

MS (APCI): *m/z* 419.1 ($M+H^+$).

2,2,3,4,4 pentamethyl lithiumphosphetanide

^{31}P {^{1}H} NMR (121.65MHz) (*trans* isomer) δ 23.89 (q, $^{1}J_{P-B}$ 29.768 Hz) (*cis* isomer) 30.12 (q, $^{1}J_{P-B}$ 29.780 Hz); ^{11}B {^{1}H} (96.42 MHz) (*trans* isomer) –37.31 (d) (*cis* isomer) –35.84 ppm (d).

1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene 21



To a stirred cooled (0°C) solution of 1,2-*bis*(2,2,3,4,4pentamethylphosphetane methyl)benzene-trihydroboron (0.40 g, 0.97 mmol) in DCM (40 cm^3) was added, *via* syringe, tetrafluoroboric acid dimethylether complex (10 eq, 9.70 mmol). The solution was stirred at 0 °C for 30 minutes and then allowed to warm to room temperature. After stirring for 6 hrs at room temperature, 80 cm^3 of saturated sodium bicarbonate solution was added and the solution stirred rapidly for 16hrs. The stirring was stopped and the two phases allowed to separate. The organic phase was removed *via* cannula and the aqueous phase washed with a 30 cm^3 portion of DCM. The combined organic phases were dried over $MgSO_4$ and subsequently filtered *via* cannula. The solvent was removed under reduced pressure to yield 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl)benzene as a white solid.

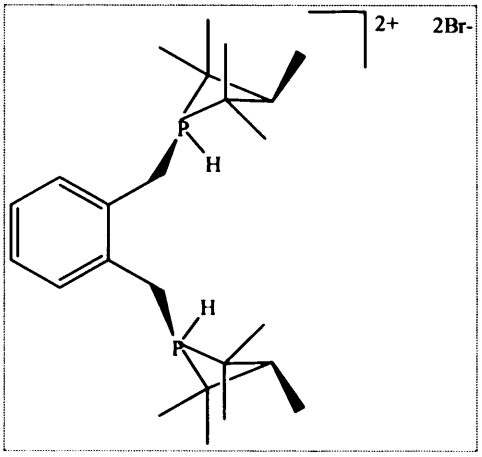
Yield; 0.32 g , 86%

NMR data (reaction mixture): ^{31}P {^{1}H} NMR (121.65 MHz) 42.55 (s, 1 eq) 59.97 (s, 4 eq) 29.31 (s, 16 eq).

^{31}P {^{1}H} NMR ($CDCl_3$, 121.65 MHz) δ 42.55 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) 0.81 (6H, d, $^{3}J_{HCCH}$ 9.66 Hz) 1.14 (12H, d, $^{3}J_{H-P}$ 7.26 Hz) 1.24 (12H, d, $^{3}J_{H-P}$ 18.48 Hz) 2.71 (2H, q, $^{3}J_{HCCH}$ 7.26 Hz) 3.34 (4H, d, br) 7.06 (2H, m, Ar-**H**) 7.16 (2H, m, Ar-**H**); ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) 9.80 (s, 1C) 21.08 (d) 25.62 (d) 27.64 (d) 29.49 (d) 53.15 (d) 126.31 (s) 130.47 (d) 139.746 ppm (d).

MS (APCI): *m/z* 391.2 ($M+H^+$).

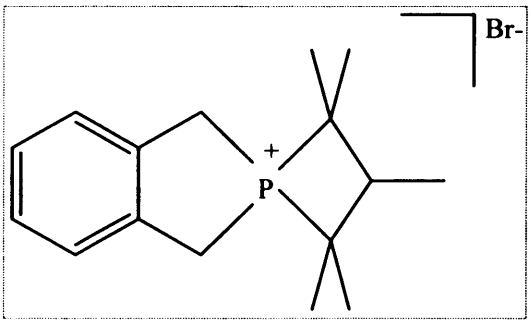
1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl)benzene-dihydrobromide 18



An acetone (20 cm^2) solution of α,α'-dibromo-o-xylene (0.21 g 0.8 mmol) was added *via* cannula to 2,2,3,4,4-pentamethylphosphetane (0.23 g, 1.6 mmol). The solution was then allowed to stir for 24 hours. The volume of solvent was reduced by 80 % until a white solid precipitated from solution (cyclic impurity **19**). The solution was then filtered *via* cannula and the solvent removed under vacuum to yield the title compound as a mixture of isomers.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 49.70 (s, 16eq) 39.52 (s, 4eq) 35.97 (s, 1eq); ^{31}P NMR ($CDCl_3$, 121.65 MHz) 49.65 (dm, $^1J_{P-H}$ 467 Hz); ^1H NMR ($CDCl_3$, 300 MH_z) 0.82 (6H, d) 1.45 - 1.67 (24H, m), 2.44 (2H, q), 3.56 (4H, d, $^2J_{H-P}$ 17.37 Hz) 7.27 (2H, m, Ar-**H**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 8.37 (m) 20.29 (d) 21.00 (d) 25.60 (d) 32.27-33.31 (m) 48.67 (d) 50.43 (d) 58.81 (d) 126.01 (s) 129.78 (d) 137.60 ppm (d).

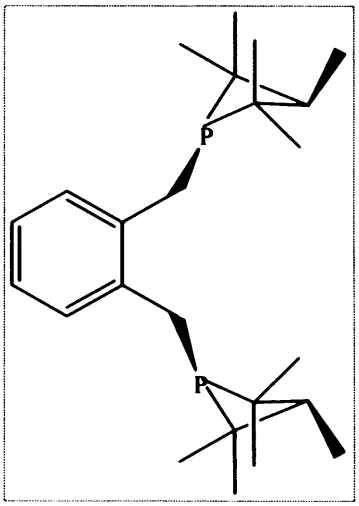
2,2,3,4,4 pentamethyl *iso*-1-phosphatindolium bromide 19



^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 92.23 (s); ^{31}P NMR ($CDCl_3$, 121.65 MHz) 92.23 (m); ^1H NMR ($CDCl_3$, 300 MH_z), 1.02 (3H, d, $^3J_{HCCH}$ 6.15 Hz) 1.47 (6H, d, $^3J_{H-P}$ 3.75 Hz) 1.54 (6H, d, $^3J_{H-P}$ 3.75 Hz) 2.84 (1H, q, $^3J_{HCCH}$ 3.51 Hz) 4.33 (4H, d, $^2J_{H-P}$ 13.4 Hz) 7.23-7.27 (m, Ar-**H**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 9.32 (d) 19.92 (s) 25.86 (d) 27.25 (d) 40.15 (d) 52.00 (d) 127.42 (d) 129.03 (d) 130.27 ppm (d).

MS (APCI): *m/z* 247.1(M^+).

1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene 17



17 can also be conveniently synthesised, without isolation of the intermediate phosphonium salt, by employing the following procedure.

An acetone solution (70 cm^3) of α,α'-dibromo-*o*-xylene (16 mmols, 4.10 g) was added via cannula to a stirred acetone solution (25 cm^3) of 2,2,3,4,4-Pentamethylphosphetane (31 mmols, 4.47 g). The solution was allowed to stir for 16 hrs. An aqueous solution (100 cm^3) of sodium bicarbonate (2.6 g, 31 mmols) was then added to the solution and the mixture vigorously stirred for 1 hr. The organic layer was removed *via* cannula, dried over anhydrous Na_2SO_4 and subsequently filtered via cannula. The solvent was removed under reduced pressure to yield 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanium methyl) benzene as a white solid. The crude product was then recrystallised from hot methanol to give a mixture of the *cis-cis* and *trans-trans* isomers in a ratio of 9:1.

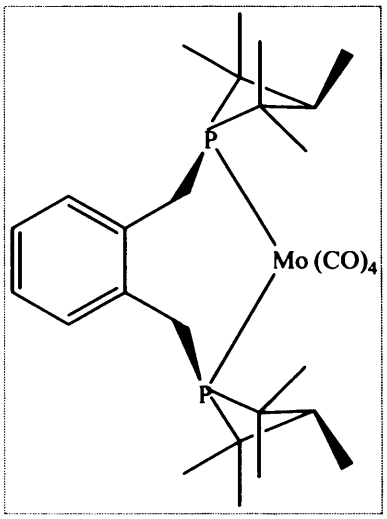
Yield: 2.30 g ,38%

NMR data (crude reaction mixture): ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 29.31 (s, 16 eq) 42.549 (s, 4 eq) 59.972 ppm (s, 1 eq).

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 29.31 (s); ^1H NMR ($CDCl_3$, 300 MHz) 0.84 (6H, d, $^3J_{HCCH}$ 7.05 Hz) 1.20 (12H, d, $^3J_{H\text{-}P}$ 18.03 Hz) 1.24 (12H, d, $^3J_{H\text{-}P}$ 5.28 Hz) 2.26 (2H, q, $^3J_{HCCH}$ 7.05 Hz) 3.07 (4H, d, br) 7.05 (2H, m, Ar-**H**) 7.19 (2H, m, Ar-**H**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 8.485 (d) 20.35 (d) 26.58 (d) 31.56 (d) 32.50 (d) 50.48 (d) 126.06 (s) 129.79 (d) 137.60 ppm (d).

MS (APCI): *m/z* 391.2 ($M + H^+$).

1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene tetracarbonyl molybdenum(0) 22



A DCM solution (15 cm^3) of 1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphatane methyl)benzene (0.21 g, 0.53 mmol) was added to [*cis*(piperidine)$_2$(CO)$_4$Mo] (0.20 g, 0.53 mmol) to give an orange coloured suspension. Upon heating under reflux (0.25 hrs), the suspended material dissolved to give a yellow coloured solution. The solution was allowed to cool to room temperature and the solvent removed under vacuum to leave a buff coloured solid, which was recrystallised by layering a chloroform solution of the solid with methanol.

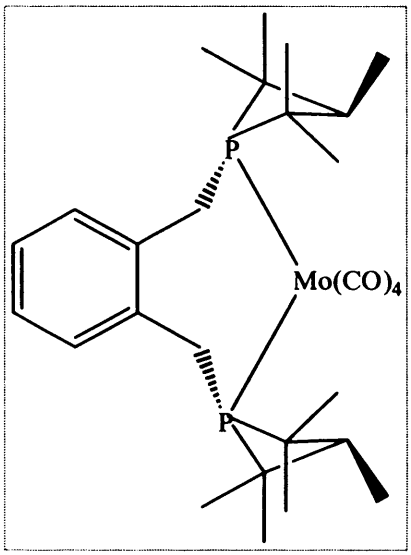
Yield: 0.16 g, 52%

^{31}P {^1H} NMR ($CDCl_3$, 121.65 MHz) δ 69.86 (s); ^1H NMR ($CDCl_3$, 300 MHz) 0.86 (6H, d, $^3J_{HCCH}$ 6.72 Hz) 1.34 (12H, d, $^3J_{H\text{-}P}$ 17.46 Hz) 1.49 (12H, d, $^3J_{H\text{-}P}$ 9.69 Hz) 2.49 (2H, q, $^3J_{HCCH}$ 6.06 Hz) 3.39 (4H, d, $^2J_{H\text{-}P}$ 5.70 Hz) 7.12 (2H, m, Ar-**H**) 7.31 (2H, m, Ar-**H**); ^{13}C {^1H} ($CDCl_3$, 75.56 MHz) 8.76 (s) 21.91 (d) 26.93 (d) 30.90 (d) 33.66 (d) 49.12 (d) 126.64 (s) 131.77 (d) 135.37 ppm (d).

MS (APCI): *m/z* 598 (M^+), 570 (M^+ -CO).

IR (KBr): ν_{CO} 1847, 1914, 2013 cm^{-1}.

[1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene tetracarbonyl molybdenum(0)] 23



The title compound was synthesised by an identical procedure to that described for **22** (see above). Except that 1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetane methyl)benzene (0.9 g, 2.2 mmol) and 0.89 g (2.2 mmol) of [*cis* (piperidine)$_2$(CO)$_4$Mo] were employed.

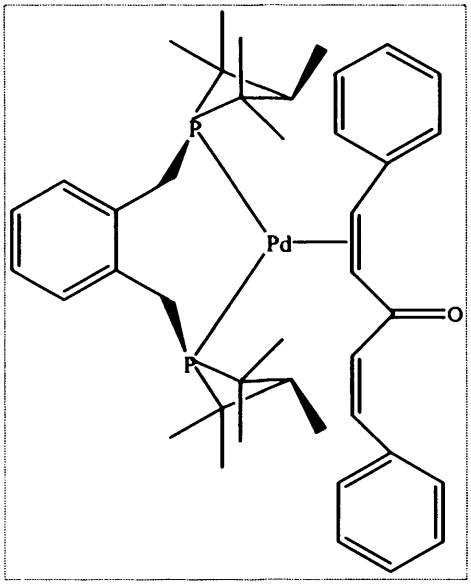
Yield: 0.78 g, 59%

^{31}P {^{1}H} NMR ($CDCl_3$, 121.65 MHz) δ 84.06 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) 0.86 (6H, d, $^3J_{HCCH}$ 7.05 Hz) 1.28 (12H, d, $^3J_{H\text{-}P}$ 11.43 Hz) 1.39 (12H, d, $^3J_{H\text{-}P}$ 18.24 Hz) 2.74 (2H, q, $^3J_{HCCH}$ 7.02 Hz) 3.40 (4H, d, $^2J_{H\text{-}P}$ 7.68Hz) 7.16 (2H, m, Ar-**H**) 7.25 (2H, m, Ar-**H**); ^{13}C {^{1}H} ($CDCl_3$, 75.56 MHz) 9.49 (s) 25.39 (d) 26.94 (d) 30.89 (d) 36.59 (d) 53.13 (d) 127.40 (s) 130.78 (d) 137.71 ppm (d).

MS (APCI): *m/z* 598 (M^+), 570 (M^+ -CO).

IR (KBr): ν_{CO} 1857, 1877, 1912, 2016 cm^{-1}.

[(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (*trans, trans* dibenzylideneacetone) palladium (0)] 24



To $[Pd_2(DBA)_3]$ (0.28 g, 0.30 mmols) was added, *via* cannula, a THF (20 cm^3) solution of 1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphatanemethyl)benzene (0.190 g, 0.48 mmols). The solution was stirred for 2hrs whereupon a gradual colour change from deep violet to red/orange was observed. The solvent was removed under reduced pressure and the remaining red solid dissolved in three $30cm^3$ portions of hexane to remove any residual $[Pd_2(DBA)_3]$. After filtering *via* cannula the hexane was reduced in volume under reduced pressure and the orange complex precipitated from solution, the remaining hexane was removed via filter cannula and the orange complex washed with three 5 cm^3 portions of cold (-15° C) diethyl ether.

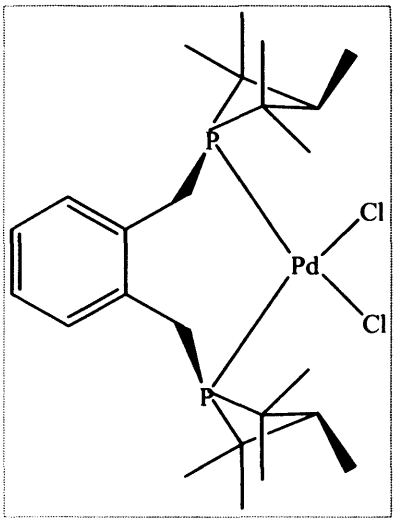
Yield: 0.27 g, 76%

^{31}P $\{^1H\}$ NMR (C_6D_6, 121.65 MHz, 298K) δ 58.3 (s,br), 64.4 (s, br); ^{31}P $\{^1H\}$ NMR (Toluene-d_3, 121.65 MHz, 248K) 52.82-57.06 (m) 66.87-69.84 (m); ^1H NMR (C_6D_6, 300 MHz) 0.62 (6H, d, $^3J_{HCCH}$ 7.23 Hz) 0.98 (24H, m, br) 2.15 (2H, q, $^3J_{HCCH}$ 6.39 Hz) 2.91 (4H, d, $^2J_{H\text{-}P}$ 7.92 Hz) 5.29 (2H, br) 7.247 (12H, m); ^{13}C $\{^1H\}$ (C_6D_6, 75.45 MHz) 1.14 (s) 8.77 (m) 20.99 (m) 28.88 (d) 29.29 (d) 31.40 (d) 37.50 (m) 49.08 (s) 50.521 (s) 125.521 (s) 128.790 (s) 135.188 ppm (s).

^{31}P $\{^1H\}$ NMR (Toluene-d_3, 121.65 MHz, 248K) δ 52.82-57.06 (m) 66.87-69.84 (m); ^1H NMR (Toluene-d_3, 300 MHz, 248K) 0.67 (6H, d, br) 0.84-0.94 (12H, m, br) 2.565 (4H, d, br) 5.03 (2H, m, br, C=C coordinated) 7.65 ppm (2H, d, ^3J 15.36 Hz, C=C free).

MS (ES): *m/z* 496 (M, -DBA).

[Dichloro (1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) palladium (II)] 25



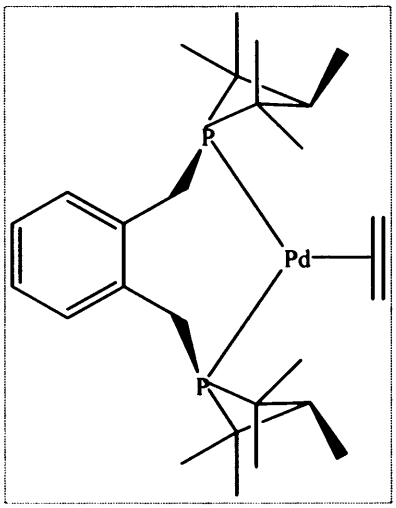
A solution of [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphatane methyl)benzene) (*trans, trans*-dibenzylidene acetone) Palladium(0)] (0.1 g, 0.14 mmol) in diethyl ether (8 cm^3) was added to 1,4-*p*-benzoquinone (0.01 g, 0.14 mmols). The solution was stirred for 1 hr during which time it gradually darkened to a red colour. An anhydrous diethyl ether solution of HCl (0.28 mmols) was then added *via* syringe to the solution and an instant colour change to yellow was observed. At this point the stirring was stopped and, over 2.5 hrs a yellow solid precipitated. The supernatant was removed *via* cannula filtration and the solid dried under vacuum. X-ray quality crystals were obtained *via* the slow vapour diffusion of diethyl ether into a concentrated solution of the complex in THF.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 84.03 (s); ^1H NMR ($CDCl_3$, 300 MHz) 0.96 (6H, d, $^3J_{HCCH}$ 7.26 Hz) 1.45 (12H, d, $^3J_{HCCP}$ 14.94 Hz) 1.66 (12H, d, $^3J_{HCCP}$ 20.43 Hz) 3.026 (2H, q, br) 3.554 (2H, d, $^2J_{HCP}$ 4.17 Hz) 3.590 (d, 2H) 7.249 (m, Ar-**H**) 7.290 ppm (m, Ar-**H**).

(Found: C, 49.97 ; H 6.89%. Calc. For complex: C, 50.76; H, 7.10; Cl, 12.48; P, 10.90%).

MS (APCI): *m/z* 531.8 (M, -Cl).

[(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (η^2-ethylene) palladium (0)] 26

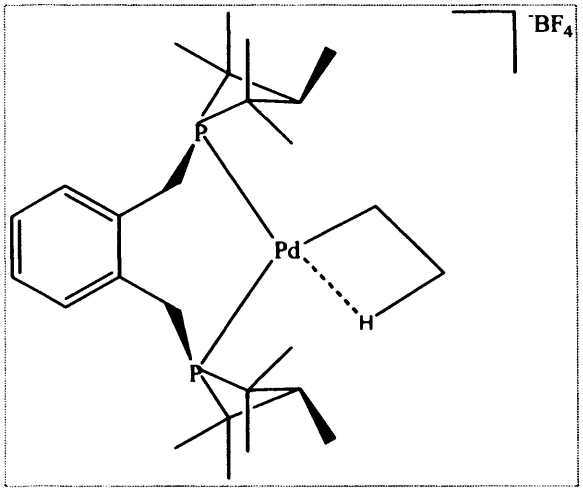


A diethyl ether (20 cm^3) solution of 1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphatane methyl)benzene was added gradually *via* cannula to a cooled (-40°C) diethyl ether (15 cm^3) solution of [(η^3-allyl)(η^5-cyclopentadiene)palladium(II)] (0.12 g, 0.54 mmols) under a ethylene atmosphere, to give an orange solution. A small portion of the solution was removed *via* cannula and the solvent removed under vacuum to give an orange coloured solid.

^{31}P {^1H} NMR (d_6-acetone, 298K, 121.65 MHz) δ 54.79 (br)

^{31}P {^1H} NMR (d_6-acetone, 258K, 121.65 MHz) δ 53.47 (dd, J 23.82 Hz, J 190.55 Hz); ^1H NMR (d_6-acetone, 300 MHz) 0.89 (6H, d, $^3J_{HCCH}$ 6.36 Hz) 1.19 (12H. d, br) 1.44 (12H, d, br) 2.39-2.61 (2H, q, br) 3.36 (4H, d, br) 6.91 (2H, m, Ar-**H**) 7.18 (2H, m, Ar-**H**); ^{13}C {^1H} NMR (d_6-acetone, 75.56 MHz) 7.42 (d) 20.64 (m) 31.16 (d) 48.99 (d) 125.95 (s) 129.61 (s) 137.89 ppm (s).

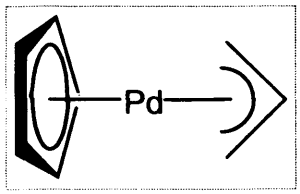
[(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (η^1-ethyl) palladium (II) tetrafluoroborate] 27



To the cooled (-40°C) diethyl ether solution of [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphatanemethyl)benzene) (η^2ethylene)Palladium(0)] (see above **26**) was added a diethyl ether solution of HBF_4 (0.54 mmols) *via* syringe. Upon addition there was an instant precipitation of the title compound as an orange coloured solid. The supernatant was then removed *via* cannula filtration and the solid was then dried under vacuum.

^{31}P {^1H} NMR (d_2-DCM, 121.65 MHz) δ 49.11 (s, br) 62.59 (s, br); ^{11}B {^1H} NMR (d_2-DCM, 96.42 MHz) -2.01 (s); ^1H NMR (d_2-DCM, 300 MHz) –8.34 (1H, m) 0.97 (6H, d, $^3J_{HCCH}$ 6.90 Hz) 1.23 (12H, d, br) 1.39 (12H. d, br) 1.44 (4H, m, br) 2.74 (2H, q, $^3J_{HCCH}$ 6.90 Hz) 3.65 (4H, d, br) 7.15 (2H, m, Ar-**H**) 7.44 (2H, m, Ar-**H**); ^{13}C {^1H} NMR (d_2-DCM, 75.56 MHz) 8.31 (d) 17.49 (Et) 20.23 (s) 22.96 (s) 27.13 (d) 29.24 (s) 30.30 (s) 127.96 (s) 130.07 (s) 133.23 ppm (s).

[(η^5-cyclopentadiene)(η^3-allyl)palladium(II)] 28.[17]

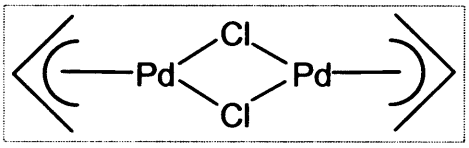


[μ^2dichloro (η^3allyl)$_2$ dipalladium(II)] **29** (1 g, 2.73 mmol) was degassed in a Schlenk vessel and then dissolved in THF (10 cm^3). Benzene (10 cm^3) was then added to give a yellow coloured solution. The solution was cooled (-20°C) and a THF solution of sodium cyclopentadiene (5.46 mmol) was added dropwise over a 0.5hr period, *via* a

cannula, during the addition the solution gradually became deep red in colour. The solution was stirred at -20°C for a further 1hr and allowed to warm to room temperature and stirred for an additional 0.5 hrs. The solvent was then removed under vacuum whilst cooling the flask to prevent any product subliming. The red solid obtained was then extracted with 20 cm^3 of hexane and filtered *via* cannula. The solvent was then removed under a mild vacuum (40-60 Tor) whilst being stirred slowly in order to prevent sublimation of the product. The product was isolated as a deep red solid with an unusual odour.

Sodium cyclopentadienide was prepared by the gradual addition of freshly distilled cyclopentadiene dimer to a cooled (0°) THF solution of finely divided sodium metal to give a light pink coloured solution. After filtration, the concentration of sodium cyclopentadiene was found by the reaction of 1 cm^3 of the solution with water and titration against standard acid.

[$\mu_2$dichloro (η^3-allyl)$_2$ dipalladium(II)] 29[17]



A 200 cm^3 flask fitted with a condenser topped with a gas outlet and oil bubbler was charged with palladium chloride (2.22 g, 12.5 mmol) NaCl (1.5 g, 25.9 mmol) and H_2O (5 cm^3) and allowed to stir for 0.5 hrs. A MeOH (30 cm^3) solution of allylchloride (3.0 g, 33.5 mmol) was then added to the flask and carbonmonoxide bubbled into the solution by means of a glass tube for a 1 hr period. The yellow suspension obtained from the reaction was poured into water (150 cm^3) and extracted with two portions of $CHCl_3$ (50 cm^3). The $CHCl_3$ solution was dried over calcium chloride and subsequently filtered on a buchner funnel. Slow evaporation of the solvent under vacuum yielded the title compound as a crystalline yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (1H, s) 2.98 (2H, d, ^3J 12.06 Hz) 4.05 (2H, d, ^{3}J 6.64 Hz) 5.38 ppm (1H. m, ^{3}J 1.24 Hz).

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List of Chemicals, Chapter 3.

14 1-chloro-2,2,3,4,4-pentamethylphosphetane-1-oxide
15 2,2,3,4,4-Pentamethylphosphetane
16 2,2,3,4,4-pentamethylphosphetane-trihydroboron
17 1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene
18 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl)benzene-dihydrobromide
19 2,2,3,4,4 pentamethyl *iso*-1-phosphatindolium bromide
20 1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene-trihydroboron
21 1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene
22 [1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene tetracarbonyl molybdenum(0)]
23 [1,2-*bis*(2,2,*trans*-3,4,4-pentamethylphosphetanemethyl)benzene tetracarbonyl molybdenum(0)]
24 [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (*trans, trans* dibenzylideneacetone) palladium (0)]
25 [Dichloro (1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) palladium (II)]
26 [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (η_2 ethylene) palladium (0)]
27 [(1,2-*bis*(2,2,*cis*-3,4,4-pentamethylphosphetanemethyl)benzene) (η_1 ethyl) palladium (II) tetrafluoroborate]
28 [($\eta_5$cyclopentadiene)($\eta_2$allyl) palladium(II)]
29 [$\mu_2$dichloro ($\eta_3$allyl)$_2$ dipalladium(II)]

Chapter Four

4.1 Introduction.

An efficient synthesis of di-1-adamantylphosphine was first described by Goerlich and Schmutzler in 1995.[1] Their work providing access to the precursors required to synthesise a range of di-1-adamantyl substituted phosphine ligands. Since this point, di-1-adamantyl phosphines have been implied in the chemical literature to provide an effective alternative to *t*-butyl substituted phosphine ligands in a number of catalysed reactions.

Buchwald has described the use of 2-[di(1-adamantyl)phosphino)]biphenyl (Figure 1) in the palladium catalysed formation of diaryl ethers (Scheme 1).[3]

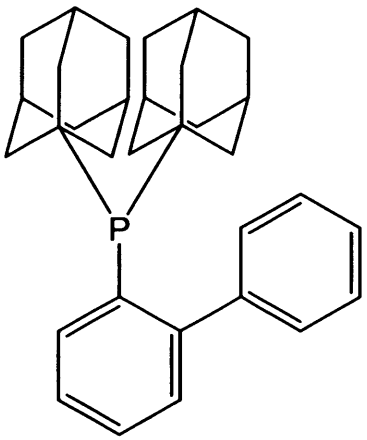
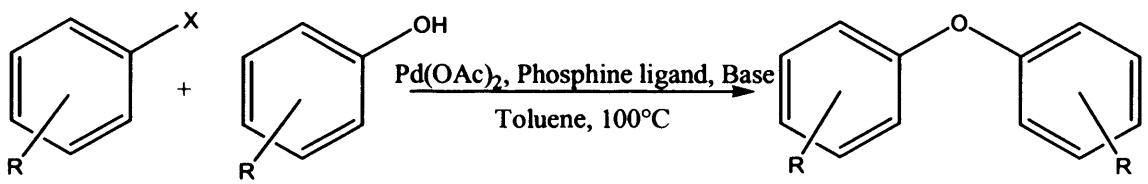


Figure 1. 2-[di(1-adamantyl)phosphino)]biphenyl

Buchwald noted that there was a difference in catalytic activity between the adamantyl substituted ligand when compared to the *t*-butyl analogue. The difference was most apparent in coupling of electron rich aryl-chlorides, with the adamantyl substituted ligand giving higher yields of the coupled product. The authors imply that the difference in catalyst activity is due to the differing steric influence of the adamantyl groups.



Scheme 1. Catalytic formation of diarylethers[3]

Bulky monodentate phosphine ligands have also been established as effective ligands in the heck coupling of arylchlorides, tri-*t*-butylphosphine being a well established example.[4] Di-1-adamantyl substituted phosphines have also recently been examined in this reaction by Beller.[5]

Beller was able to demonstrated that di-1-adamantyl-*n*-butylphosphine provided catalysts with similar and sometimes higher activity than those formed with tri-*t*-butylphosphine. The difference in activity being most apparent with coupling reactions with non-activated arylchlorides.

4.1.2 Phosphorylation reactions

Phosphorylation reactions performed in the presence of aluminium chloride are well known in the chemical literature. Some of the earliest examples were described by Clay.[6] A number of different substrates have been phosphorylated under these conditions.

Kinnear and Perren[7] described the phosphorylation of alkyl chlorides in the presence of aluminium chloride in DCM solution. The reactions gave compounds of the form $RP(O)Cl_2$ (phosphonic dichlorides) after aqueous work-up. The reaction proved to be applicable to a variety of alkyl chlorides (R: Me, Et, *i*-Pr, *t*-Bu) and gave good yields of product in most cases.

Olah,[8] employed a number of cyclic and polycyclic hydrocarbons, and again isolated compounds with the general form $RP(O)Cl_2$. It was found that adamantane, alkyl adamantanes and diamantane gave reasonable yields (64, 40-46 and 60% respectively). However, in reactions with bicyclic, monocyclic and acyclic hydrocarbons the yield was significantly lower (10-20%).
The reactions described by Perren[7] and Olah[8] are selective for the singly alkylated phosphonic dichlorides. Examples of selective reactions were the major product is doubly alkylated are more unusual. Indeed, the example described by Goerlich[1] appears to unique in this respect.

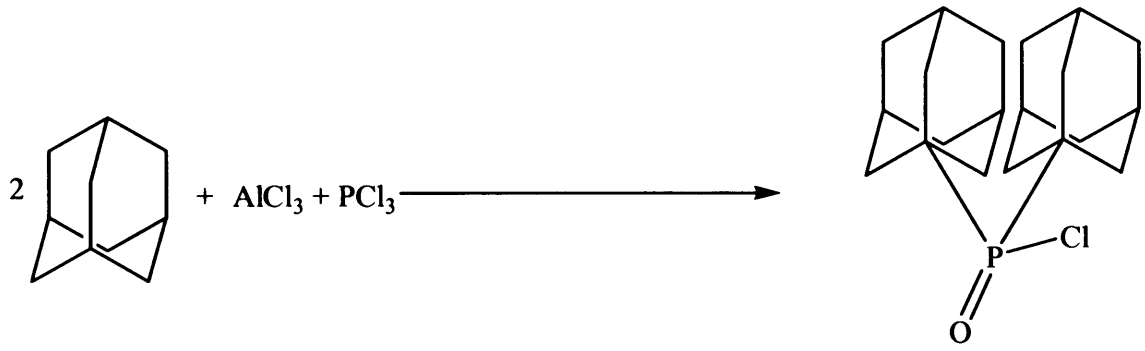
4.2 Results and discussion

4.2.1 Ligand synthesis.

The synthetic strategies outlined in chapter 2 to access *ortho*-xylene bridged diphosphine ligands have been applied to the novel phosphines described in this chapter. Both ligands could have been accessed *via* the xylene metallation chemistry described previously. However, because of the nature of the organophosphorus starting materials (i.e. phosphinic chlorides) (**30, 37**), it is more convenient to utilise the phosphino-borane chemistry previously described in chapters 2 and 3.

4.2.1.1 Di-1-Adamantylphosphinic chloride 30

30 was synthesised *via* a methodology (Scheme 1) modified from that of Goerlich *et al.*[1] Adamantane, aluminium chloride (1.5 equivalents) and a large excess of phosphorus trichloride where slurried together in a round-bottomed flask to give a buff coloured suspension. Upon heating under reflux, a bright orange coloured suspension was afforded. Subsequent work up gave **30** as an off white crystalline solid in 99% yield. Unlike **14**, it was found that **30** did not rapidly hydrolyse in air.



Scheme 1. Goerlich's synthesis of **30**

The $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **30** where found to be fully consistent with those previously reported.[1]

4.2.1.2 Di-1-Adamantylphosphine 31

31 was synthesised *via* a methodology adapted from that described previously by Goerlich.[1] The reduction of **30** with lithium aluminium hydride afforded **31** as a

colourless solid in 67% yield. The ^{31}P $\{^1H\}$, ^1H and ^{13}C $\{^1H\}$ NMR Spectra of **31** were found to be fully consistent with those previously reported.[1]

4.2.1.3 Di-1-Adamantylchlorophosphine 32

The title compound was prepared *via* an adaptation of the methodology of Goerlich *et al.*[1] The phosgene solution employed by Goerlich, was replaced by triphosgene for reasons of safety and ease of handling. **32** was isolated as a yellow solid in moderate yield (47%). The NMR Spectra of **32** were fully consistent with those previously described.[1]

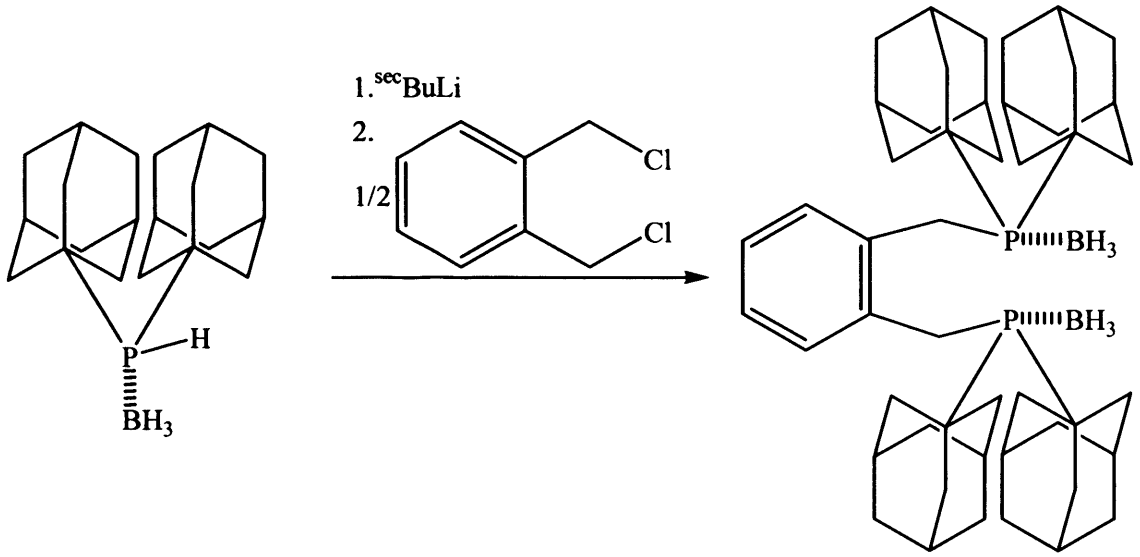
4.2.1.4 Di-1-Adamantylphosphine trihydroboron 33

Reaction of **32** with borane THF adduct, afforded **33** as a colourless solid in near quantitative yield. The structure of **33** was confirmed *via* $^{31}P\{^1H\}$, ^1H and $^{11}B\{^1H\}$ NMR Spectroscopy. As would be expected, the $^{31}P\{^1H\}$ NMR spectrum consisted of a single broad quartet (δ_P 41.37 ppm, $^1J_{P\text{-}B}$ 64.45 Hz) indicative of a phosphine-borane adduct seen in previous compounds. The $^{11}B\{^1H\}$ NMR spectrum reflected that observed in the $^{31}P\{^1H\}$ NMR spectrum, and consisted of a single sharp doublet (δ_B – 43.78 ppm). In common with related compounds described in the chemical literature,[1] the ^1H NMR spectrum consisted of a broad resonance (δ_H 1.74-2.02 ppm) that could be assigned to the 30 adamantyl protons. A smaller double quartet (δ_H 3.72 ppm, $^1J_{H\text{-}P}$ 350.58 Hz, $^2J_{H\text{-}B}$ 6.64 Hz) was also observed for the phosphorus bound proton.

4.2.1.5 1,2-*bis*(di-1-adamantylphosphinotrihydroboronmethyl)benzene 34[10]

34 was synthesised *via* the methodology previously described for the synthesis of **5** and **20** (scheme 2). To a cooled (-78°C) THF solution of **33** was gradually added 1.1 equivalents of ^{sec}BuLi, to afford a intensely coloured solution (yellow). The solution was stirred for 0.5 hr and then allowed to warm to room temperature and stir for an additional 1 hr. The deprotonation was monitored by $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy. The lithium phosphide being observed as a broad quartet, with a chemical shift of δ_P 9.67 ppm *via* $^{31}P\{^1H\}$ NMR spectroscopy and a doublet with a chemical shift of δ_B –39.00 ppm in the $^{11}B\{^1H\}$ NMR spectrum.

Upon recooling (-78°C), a THF solution of 0.5 equivalents of α,α'-dichloro-*ortho*-xylene was added drop wise via cannula. After subsequent work-up, **34** was isolated as a colourless solid in 92% yield.



Scheme 2. Synthesis of **34**

The $^{31}P\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{1}H NMR spectra of **33** are fully consistent with the proposed structure. The $^{31}P\{^{1}H\}$ NMR spectrum consisted of a broad quartet with a chemical shift of δ_P 41.37 ppm. Conversely the $^{11}B\{^{1}H\}$ NMR spectrum consisted of a sharp doublet with a chemical shift of δ_B –46.35 ppm ($^{1}J_{B\text{-}P}$ 51.84 Hz), both being indicative of a phosphine-borane adduct. The ^{1}H NMR spectrum displayed two broad resonance's (δ_H 1.722 and 1.9-2.2 ppm) that integrate and can be assigned to the 60 protons of the adamantyl groups. The methylene protons of the *ortho*-xylene backbone were observed as a doublet (δ_H 3.29 ppm, $^{2}J_{H\text{-}P}$ 12.0 Hz) with the aromatic protons being assigned to two multiplets (δ_H 7.11 and 7.61ppm respectively).

4.2.1.6 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene **35**

In common with **5** and **20**, **34** was deprotected to give the free phosphine **35** upon reaction with 10 equivalents of tetrafluoroboric acid dimethylether complex, and subsequent reaction with sodiumbicarbonate. Attempts to grow crystals of **35** were unsuccessful. However, it was found that **35** could be precipitated from a saturated DCM solution upon cooling at -40°C for a prolonged period.

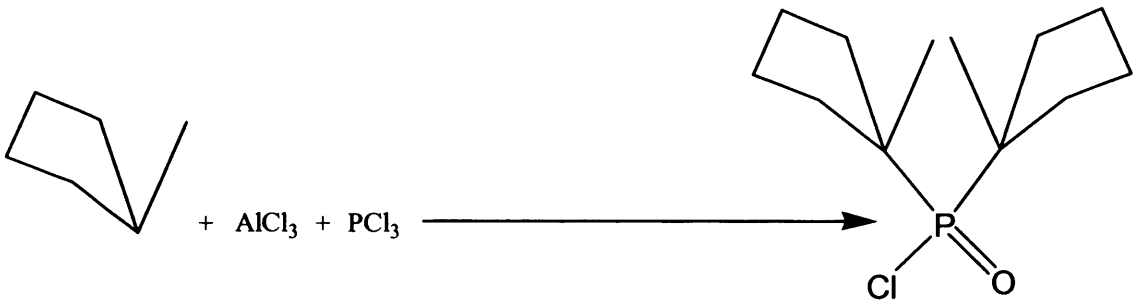
The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra were consistent with the proposed structure of **35**. The $^{31}P\{^{1}H\}$ NMR spectrum consisted of a singlet with a chemical shift of δ_P 26.37 ppm. A chemical shift similar to that previously observed for the *t*-butyl analogue **1** (δ_P 28.06 ppm). The ^{1}H NMR spectrum consisted of the now familiar pattern of resonances. Two multiplets (δ_H 1.70 and 1.91 ppm) were assigned to the 60 protons of the adamantyl groups. The methylene protons of the *o*-xylene backbone were observed as a doublet (δ_H 3.01 ppm, $^{2}J_{H\text{-}P}$ 3.00 Hz), and each set of chemically equivalent aromatic protons were observed as a multiplet (δ_H 7.036 and 7.544 ppm). The APCI mass spectra showed a peak for the molecular ion of **35** at *m/z* 707.5.

4.2.1.7 Di (1-methylcyclopentyl)phosphinic chloride **36**

36 was synthesised *via* a methodology similar to that employed for **30** (Scheme 3). Methylcyclopentane, $AlCl_3$ and PCl_3 were slurried together, unlike the previous reaction with adamantane there was no initial colour change. Upon the suspension being heated to reflux, the suspension became bright orange in colour, as observed previously. After work-up **36** was isolated as a viscous colourless oil.

The $^{31}P\ \{^{1}H\}$ NMR spectrum of **36** consisted of a singlet with a chemical shift of δ_P 95.51 ppm, and is similar to that observed for the related compound **30** (δ_P 86.80 ppm).

The ^{1}H NMR spectrum of **36** was also found to be consistent with the proposed structure. A doublet was observed at δ_H 1.26 ppm and can be assigned to the six methyl protons of the methylcyclopentyl groups. A double multiplet with chemical shifts of δ_H 1.55 and δ_H 2.27 ppm could be assigned to the eight protons at the 2 position of the cyclopentyl rings. The final eight protons were assigned to a multiplet observed at δ_H 1.69 ppm.



Scheme 3. Synthesis of **36**

The APCI mass spectrum further supports the proposed structure of **36**, with the molecular ion being observed at *m/z* 249.

Further investigation into the scope of this reaction was also carried out. When methylcyclohexane was employed as the hydrocarbon substrate, a viscous oil similar to **36** was isolated. The ^{31}P $\{^1H\}$ NMR spectrum of the oil revealed a complicated pattern of resonances. The largest two resonances having chemical shifts consistent with the mono and dialkylated species (δ_P 58.80 and 96.44 ppm respectively) in a 1:1 ratio. Attempts to isolate either of these compounds were unsuccessful.

Norbornane was also trialed as the substrate under the conditions used in previous reactions. Again, a viscous colourless oil was isolated from the reaction. The $^{31}P\{^1H\}$ NMR spectrum of the oil showed a mixture of compounds, with the major component having a chemical shift of δ_P 56.40 ppm, consistent with a monoalkylated phosphonic dichloride.

4.2.1.8 Di(1-methylcyclopentyl)phosphine 37

37 was synthesised *via* the reduction of **36** with $LiAlH_4$ in diethyl ether. **37** was isolated as a colourless, unpleasant smelling oil in 78% yield.

The structure of **37** was confirmed by ^{31}P $\{^1H\}$, ^1H and ^{13}C $\{^1H\}$ NMR spectroscopy. The ^{31}P $\{^1H\}$ NMR spectrum consisted of a singlet with a chemical shift of δ_P 15.63 ppm, this being similar to that of the other secondary alkyl phosphines previously described (**3, 32**). The ^1H NMR spectrum was also consistent with the proposed structure of **37**. A doublet with a chemical shift of δ_H 1.28 ppm could be assigned to

the six methyl protons of the methylcyclopentyl groups. The eight ring protons at the 2 position were assigned to a double multiplet with chemical shifts of δ_H 1.65 and 2.30 ppm. The remaining eight ring protons were then assigned to a broad multiplet with a chemical shift of δ_H 1.72 ppm.

4.2.1.9 Di(1-methylcyclopentyl)phosphine trihydroboron **38**

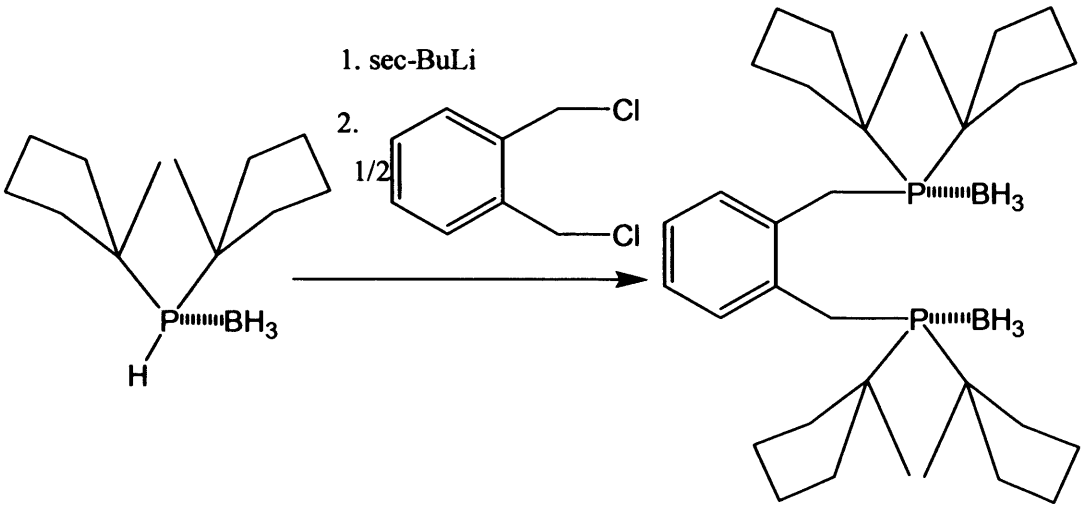
Reaction of a THF solution of **37** with 1.5 equivalents of borane THF adduct, yielded the phosphine-borane adduct **38** as a low melting solid in almost quantitative yield.

As would be expected for a phosphine-borane adduct, the ^{31}P $\{^1H\}$ NMR spectrum consisted of a broad quartet which had a chemical shift of δ_P 48.59 ppm. In common with the phosphine-borane adducts previously described, the ^{11}B $\{^1H\}$ NMR spectrum consisted of a doublet with a chemical shift of δ_B –44.28 ppm.

4.2.1.10 1,2-*bis*(di-1-methylcyclopentylphosphinotrihydroboronmethyl)benzene **39**

Synthesis of **39** (Scheme 4) was carried out *via* the methodology previously described for the related compounds **5**, **20** and **34**.

Di(1-methylcyclopentyl)phosphine trihydroboron **38** was deprotonated with sec-BuLi in THF solution at -78° C to give the corresponding lithium phosphide. The solution becomes a distinctive yellow colour and can be monitored by either ^{31}P $\{^1H\}$ or ^{11}B $\{^1H\}$ NMR spectroscopy. The lithium phosphide of **38** having a chemical shift of δ_P 12.37 ppm in the ^{31}P $\{^1H\}$ and δ_B –37.52 ppm in the ^{11}B $\{^1H\}$ NMR spectrum.



Scheme 4. Synthesis of **39**

The synthesis of **39** was then completed upon the addition of 0.5 equivalents of α,α'dichloro-*o*-xylene as a THF solution.

The ^{31}P $\{^1H\}$, ^{11}B $\{^1H\}$ and ^1H NMR spectrum of **39** were found to be consistent with the proposed structure. The ^{31}P $\{^1H\}$ NMR spectrum consisted of a broad quartet with a chemical shift of δ_P 52.70 ppm, and is in agreement with that observed for the related compounds **5**, **20** and **34**. The ^{11}B $\{^1H\}$ NMR spectrum consisted of a doublet with a chemical shift δ_B –43.35 ppm.

The ^1H NMR spectrum of **39** exhibited the now familiar pattern of resonances due to the methylcyclopentyl groups. A doublet with a chemical shift of δ_H 3.33 ppm could also be assigned to the four methylene protons of the *o*-xylene backbone. The two sets of chemically equivalent aromatic protons were observed as two multiplets with chemical shifts of δ_H 7.06 and 7.37 ppm

4.2.1.11 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene **40**

The phosphine borane adduct **39** was deprotected upon reaction with ten equivalents of tetrafluoroboric acid dimethyl ether complex, and subsequently sodium bicarbonate solution to give the phosphine **40**.

It was found that **40** could also be synthesised by the addition of two equivalents of di(1-methylcyclopentyl)phosphine to α,α'dibromo-*o*-xylene, to give the hydrobromide diphosphonium salt (not isolated). Reaction with sodium hydroxide then gave the free phosphine. In common with that observed previously (**19**) the major product of the addition reaction was an *iso*-phosphindolinium salt (**41**) (Figure 2), the full characterisation of this compound is given in the experimental section.

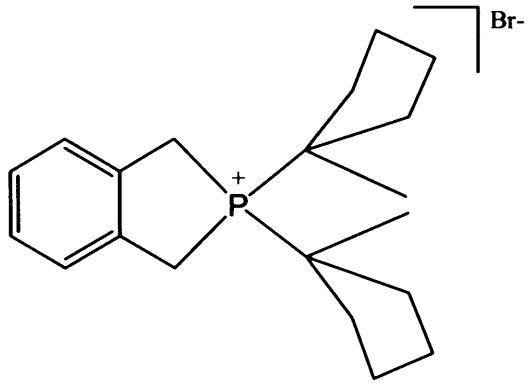


Figure 2. *iso*-phosphindolinium salt **41**

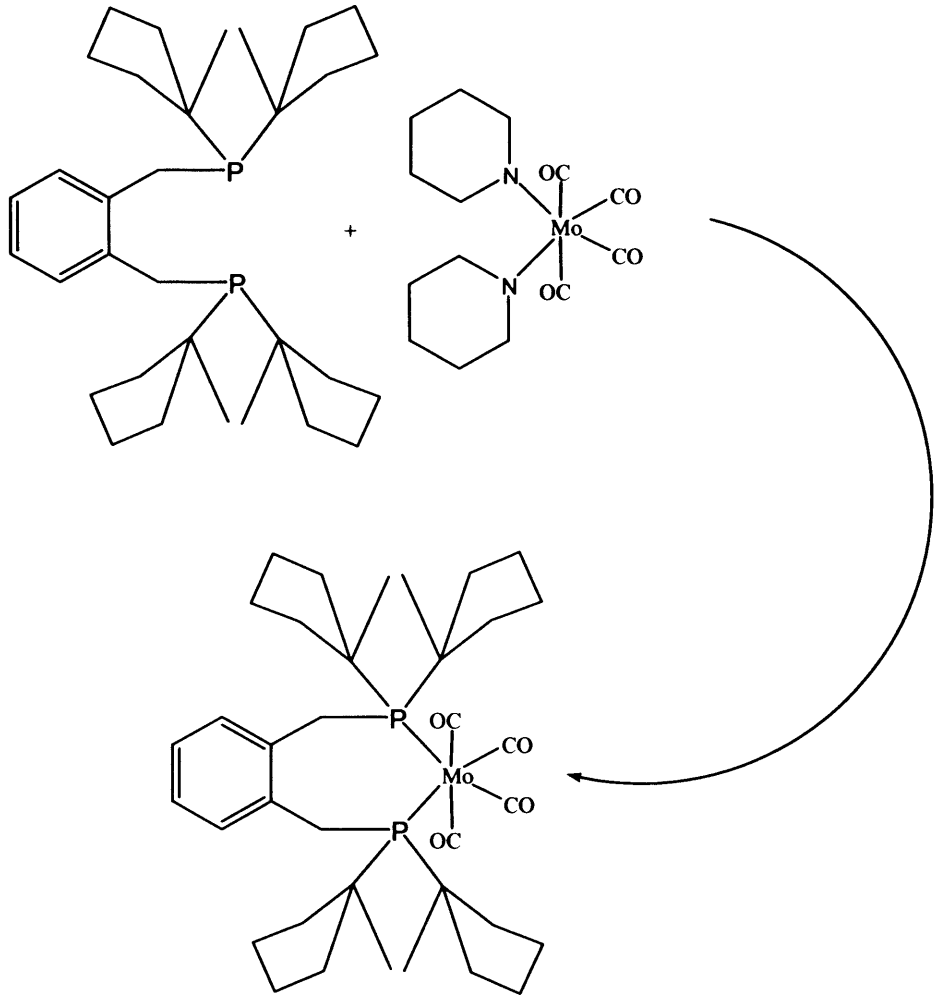
The NMR data generated with the material isolated from either route was found to be identical. The ^{31}P $\{^1H\}$ NMR spectrum was found to consist of a singlet with a chemical shift of δ_P 33.84 ppm. The ^1H NMR spectrum consisted of a doublet with a chemical shift of δ_H 1.16 ppm that could be assigned to the twelve methyl protons of the methylcyclopentyl groups. The remaining ring protons of the methylcyclopentyl groups were observed as a broad complex multiplet, with a chemical shift of δ_H 1.54 ppm. The four methylene protons of the *o*-xylene backbone were observed as a doublet with δ_H 3.08 ppm, and the remaining aromatic protons were observed as two multiplets δ_H 7.01 and 7.40 ppm.

4.2.2 Complexation chemistry

4.2.2.1 [(1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene) tetracarbonyl molybdenum (0)] 42

In a reaction analogous to that described for the synthesis of **7**, **22** and **23**, **42** was synthesised by reaction of the phosphine ligand **40** with one equivalent of [*cis*-*bis*(piperidine)tetracarbonylmolybdenum(0)] **8** in hot DCM solution (Scheme 5). Initially an orange coloured suspension of material was obtained. However, after heating the solution at reflux for 0.75 hrs, the suspended material dissolved and the

solution became yellow in colour. After work-up, **42** was isolated as a buff coloured solid. Further purification was achieved by recrystalisation from a chloroform solution layered with methanol. The crystals obtained were found to be slightly too small for determination of the solid state structure by X-ray diffraction.



Scheme 5. Synthesis of **42**.

The ^{31}P $\{^1H\}$, ^1H and ^{13}C $\{^1H\}$ NMR spectra of **42** are consistent with the proposed structure. The ^{31}P $\{^1H\}$ NMR spectrum shows the expected singlet with a chemical shift of δ_P 56.69 ppm for the two chemically equivalent, chelating phosphorus donors. The twelve methyl protons of the methylcyclopentyl groups are observed as a sharp doublet in the ^1H NMR spectrum (δ_H 1.40 ppm) due to three bond H-P coupling. The remaining ring protons of the methylcyclopentyl groups are observed as a broad multiple resonance (δ_H 1.74 ppm). The four methylene protons are observed as a

doublet (δ_H 3.31 ppm), the remaining two multiplets (δ_H 7.08 and 7.15 ppm) could each be assigned to one of the two chemical equivalent sets of aromatic protons.

The $^1H\{^{31}P\}$ NMR spectrum of **42** was also recorded, and provided further confidence in the assignment of resonances observed in the ^1H NMR spectrum. The doublet observed for the methyl protons of the methylcyclopentyl groups in the ^1H NMR spectrum, is observed as a singlet (δ_H 1.40 ppm) in the phosphorus decoupled spectrum. Similarly, the doublet due to the methylene protons of the *o*-xylene backbone in the ^1H NMR also collapses to a singlet in the phosphorus decoupled spectrum (δ_H 1.74 ppm). Little effect is observed with the ring protons of the methylcyclopentyl groups, which are again observed as a complex broad resonance.

The FAB mass spectrum further confirms the structure of **42**, and shows the molecular ion (M^+) at *m/z* 706.7. Further ions are also observed with masses that correspond to the sequential loss of the carbonyl ligands (678.7 (M^+, -CO), 650.2 (M^+, -2CO), 622.7 (M^+, -3CO)).

The infra-red spectrum of **42** is consistent with that observed previously for the related compounds **7**, **22** and **23**.

4.2.2.2 [(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) tetracarbonyl molybdenum (0) **43**

43 was synthesised by the same methodology as **42**. The buff coloured solid isolated from the reaction was then further purified by precipitation upon the addition of methanol to a chloroform solution of the title compound.

The $^{31}P\{^1H\}$ and ^1H NMR spectra are fully consistent with the proposed structure of **43**. A singlet (δ_P 51.84 ppm) is observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating that the two phosphorus atoms are chemically equivalent. The ^1H NMR spectrum of **43** showed the pattern of resonances familiar to the adamantyl functionality. The methylene protons of the *o*-xylene backbone were observed as a doublet with a chemical shift of δ_H 3.30 ppm. The two sets of chemically equivalent aromatic

protons were observed as two multiplets with a chemical shift of δ_H 7.05 and 7.32 ppm.

The FAB mass spectrum of **43** is also in agreement with the proposed structure. The molecular ion being observed at *m/z* 810. A further ion due to the loss of two of the carbonyl ligands was also observed at *m/z* 754.

4.2.2.3[(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene)(*trans,trans*dibenzylidene acetone) palladium (0)] **44**

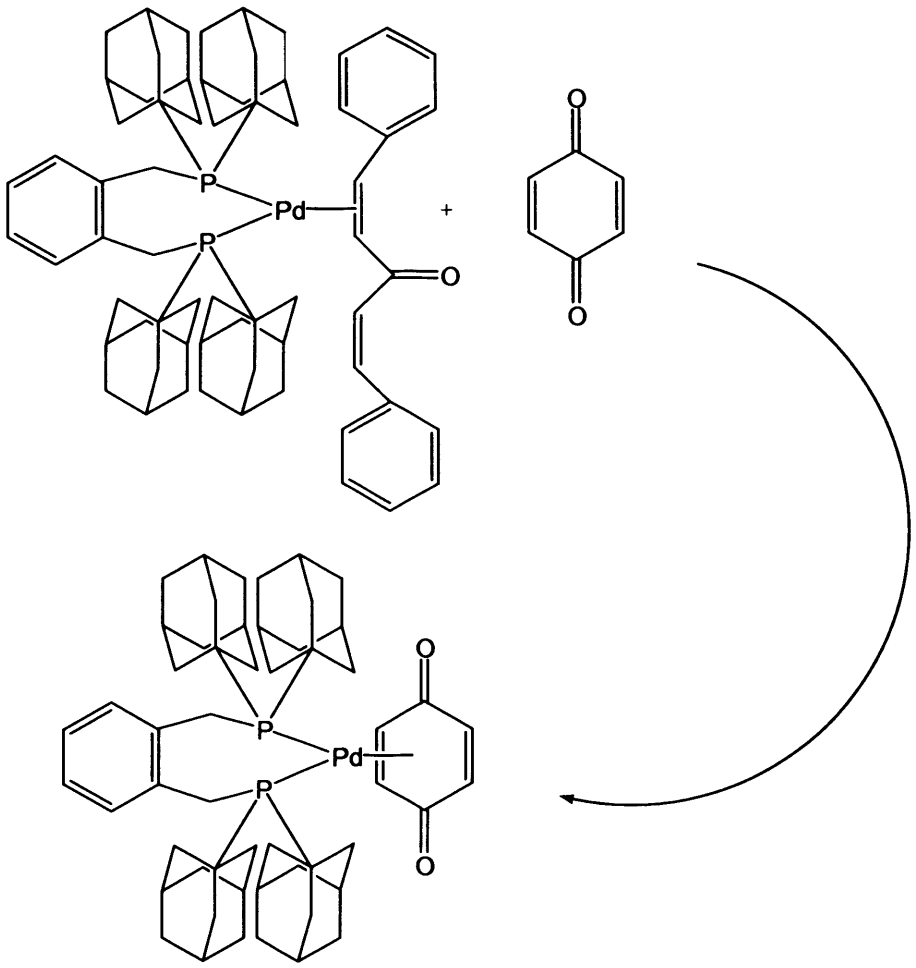
44 was synthesised *via* the reaction of one equivalent of phosphine **35**, with $[Pd(DBA)_2]$ in THF solution. The complex **44** was isolated as a orange solid in 88% yield.

In common with complex **24**, the ^{31}P $\{^1H\}$ NMR spectrum of **44** consisted of two complex broad resonances (δ_P 43.94 and 47.90 ppm). These being due to the dynamic behaviour of the DBA ligand, as the coordinated and uncoordinated double bond is exchanged.[9] The ^1H NMR spectrum further confirmed the structure of **24**, with the now familiar pattern of resonances due to the adamantyl groups and the methylene protons of the *o*-xylene backbone. The DBA ligand was also observed with a complex pattern of resonances being observed for the aromatic groups (δ_H 7.03 – 7.23 ppm) and smaller resonances for the coordinated and uncoordinated double bonds (δ_H 5.31 and 6.93-7.79 ppm respectively. The pattern of resonances in the aromatic region of the ^1H NMR spectrum is further complicated by the presence of peaks due to the aromatic protons of the phosphines backbone.

The FAB mass spectrum of **44** shows the molecular ion with *m/z* 1047, further supporting the proposed formulation.

4.2.2.4 [(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene)(1,4-*para*-benzoquinone) palladium (0)] **45**

Reaction of complex **44** with one equivalent of 1,4-*para*-benzoquinone resulted in a ligand exchange reaction. The DBA ligand of **44** being replaced by 1,4-*para*-benzoquinone to give complex **45** (Scheme 6).



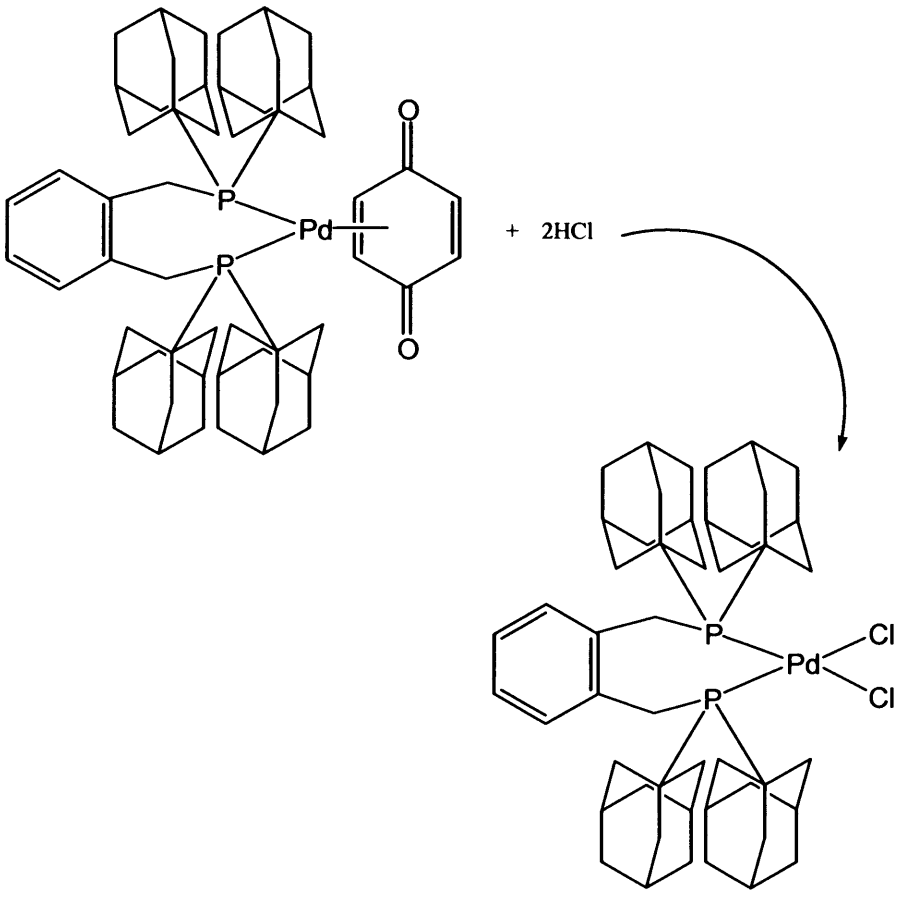
Scheme 6. Synthesis of **45**

The ^{31}P $\{^1H\}$ NMR spectrum of **45** confirms the ligand exchange with a sharp singlet (δ_P 50.48 ppm) observed rather than the broad resonances of **44**. The ^1H NMR spectrum of **45** confirms the coordination of the benzoquinone ligand, with a singlet observed (δ_H 5.91 ppm). The ^1H NMR spectrum is dominated by the broad resonances that can be assigned to the sixty protons of the four adamantyl groups. The methylene

protons of the *o*-xylene backbone were observed as a doublet (δ_H 3.00 ppm) and the aromatic protons as two multiplets (δ_H 6.95 and 7.35 ppm).

4.2.2.5 [Dichloro (1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) palladium (II)]**46**

Complex **46** was synthesised by the oxidation of the palladium (0) complex **45** with an anhydrous diethylether solution of HCl (Scheme 7). Upon addition of the HCl solution, there was an instant colour change from red to yellow.



Scheme 7. Synthesis of **46**

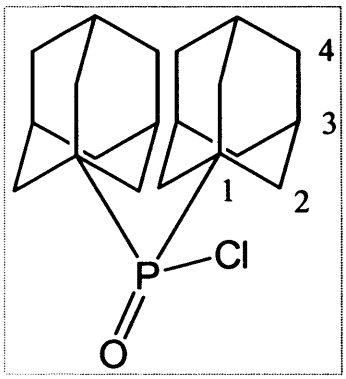
The $^{31}P\{^1H\}$ NMR Spectrum consists of a singlet with a chemical shift of δ_P 31.46 ppm. Again the ^1H NMR spectrum is dominated by the broad resonances due to the sixty protons of the adamantyl groups (δ_H 1.34-2.35 ppm). The methylene protons of the *o*-xylene backbone are observed as a doublet (δ_H 2.55 ppm). The ^1H NMR

spectrum is completed by the two multiplets due to the two chemically equivalent sets of aromatic protons of the *o*-xylene backbone (δ_H 7.15 and 7.45 ppm).

4.3 Experimental.

All compounds were prepared using standard Schlenk techniques under an atmosphere of dinitrogen or argon. ^{31}P (referenced to H_3PO_4 at $\delta_P = 0$) and ^{11}B (referenced to $Et_2O.BF_3$ at $\delta_B = 0$) NMR data was collected on a Jeol Eclipse 300 MHz spectrometer; ^{1}H and ^{13}C data on a Bruker 400 MHz DPX Avance. Mass spectra (ES and APCI) were obtained on a VG Fisons Platform II. Tetrahydrofuran, Diethyl ether and hexane were dried over sodium benzophenone. Toluene was dried over sodium. Methanol and acetonitrile were dried over calcium hydride. Water used during the work-up of all compounds was carefully deoxygenated by several cycles of heating at reflux and cooling to room temperature under a nitrogen purge. $CDCl_3$, d_6-acetone and d_3-acetonitrile were purchased from Aldrich, dried over 3Å molecular sieves and freeze-thaw degassed before use. C_6D_6 was purchased from Goss scientific and dried over sodium prior to use. Unless otherwise stated all chemicals were purchased from Aldrich and used without further purification.

Di-1-Adamantylphosphinic chloride 30[1]



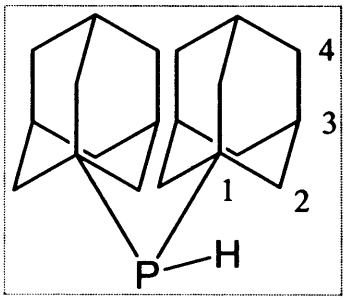
Adapted from the method of Goerlich[1].

Phosphorus trichloride (83 cm^3, 0.98 mol) was added rapidly via cannula to a mixture of (freshly sublimed) $AlCl_3$ (26.66 g, 0.2 mol) and adamantane (27.2 g, 0.20 mol) to afford a buff coloured suspension. Upon reflux and stirring of the solution a tangerine coloured suspension was obtained. Upon further reflux the suspension darkened to reach a deep orange colour. The suspension was refluxed for a total of 18 hrs. Excess phosphorus trichloride was then removed via distillation (BP: 75 °C) to afford an orange solid. Upon cooling to ambient temperature, chloroform (250 cm^3) was added to regenerate the orange suspension. This was then cooled to 0 °C and water (150 cm^3) was added gradually via syringe. From this point onward it was unnecessary to employ an inert atmosphere. The orange suspension was Buchner filtered (with celite) to remove the orange solid impurity. The lower (chloroform) phase of the filtrate was then separated with a separating funnel and dried with magnesium sulphate. After a second Buchner filtration (with celite) the solvent was removed from the suspension via rotary evaporation, to afford the title compound as an off white solid.

Yield: 36.28 g, 99%.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65MHz): δ 86.8 (s); ^1H NMR($CDCl_3$, 400MHz) 1.670 (6H, br, **4**), 1.972 (3H, br, **3**), 2.068 (6H, br, **2**); ^{13}C $\{^1H\}$ ($CDCl_3$, 75.56 MHz) 27.922 (d, ^3J 10.38Hz, **3**), 36.397 (d, **4**), 36.931 (d, **2**), 46.077 ppm (d).

Di-1-Adamantylphosphine 31[1]



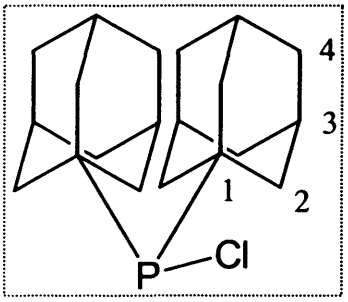
$LiAlH_4$ (3.5 g, 74 mmol) was added over 2 hrs to a cooled solution (0 °C) of di-1-adamantyl phosphinic chloride (16 g, 45 mmol) in THF (250 cm^3). The reaction was then allowed to warm to ambient temperature and was stirred for 20 hrs. The grey

suspension was then cooled (0 °C) and HCl (75 cm^3, 1 M) was slowly added via syringe, to afford a two-phase system with some solid present in the lower phase. Conc. HCl (8 cm^3, 11 M) was then added to improve the separation of the two layers. The (upper) organic phase was removed *via* cannula and dried over magnesium sulphate. After filtration via cannula, the volatiles were removed under vacuum to afford the product as a white solid.

Yield: 9.1 g, 67%.

^{31}P {^1H} NMR ($CDCl_3$, 121.65 MHz) δ 18.0 (s); ^1H NMR ($CDCl_3$, 300 MHz) 1.58-1.89 (30H, m, br), 2.72 (1H, d, $^1J_{H-P}$ 210.3 Hz); $^{13}C\{^1H\}$ ($CDCl_3$,75.56 MHz) 29.13 (d, **3**) 33.98 (d, **1**) 36.73 (d, **4**) 43.54 ppm (d, **2**).

Di-1-Adamantylchlorophosphine 32[1]

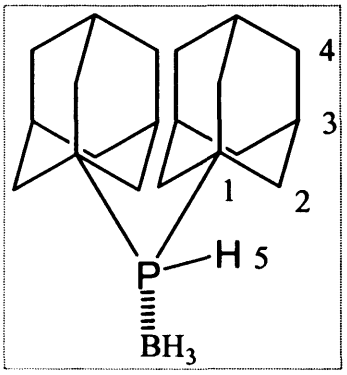


Triphosgene (4.0 g, 13 mmol) solution (60 cm^3 toluene) was added gradually via cannula to a stirred, cooled (0 °C) solution of DBU (6 cm^3, 40 mmol) and di-1-adamantylphosphine (5.65 g, 19 mmol) (170 cm^3 toluene). Full addition of the triphosgene afforded a viscous, bright yellow suspension. Further toluene (100 cm^3) was added to lower the viscosity and ease the stirring. The suspension was stirred at ambient temperature for 24hrs. The suspension was then filtered via cannula to afford a yellow solid. The solid was then washed with (4 * 100 cm^3) toluene, which was combined with the original filtrate. The volatiles were then removed in-vacuo to afford the product as a yellow solid. The product was then washed with pentane (2 * 30 cm^3) and dried under vacuum.

Yield: 3.25 g, 47%.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 139.55 (s); ^1H NMR ($CDCl_3$, 300MHz) 1.72-2.03 (m, br); ^{13}C {^1H} NMR ($CDCl_3$, 75.56 MHz) 26.97 (d, **3**) 36.09 (d, **2**) 36.30 (d, **4**) 40.13 ppm (d, **1**).

Di-1-Adamantylphosphine trihydroboron 33

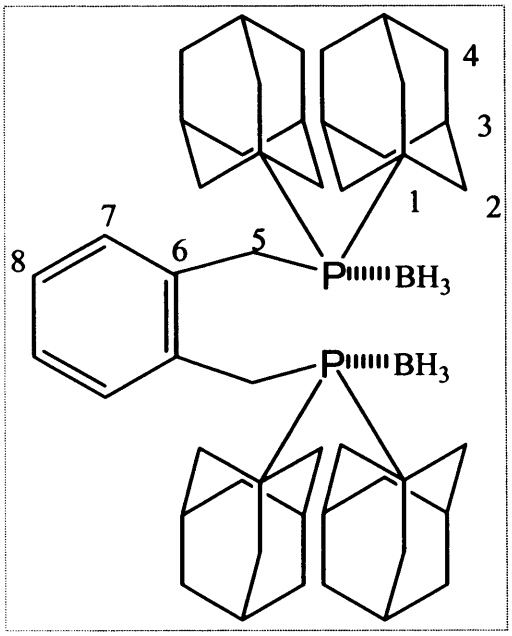


Borane (THF adduct) (10 cm^3, 10 mmol) was added to stirred solution of di-1-adamantyl phosphine (1.5 g, 4.5 mmol) in THF (30 cm^3). Stirring for a further 5 hrs afforded a slightly turbid solution. The volatiles were then removed in-vacuo to yield the product as a white solid.

Yield: 1.55 g, 99%

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 41.374 (q, $^1J_{P-B}$ 64.45 Hz); $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96.42MHz) –43.787 (d); ^1H NMR ($CDCl_3$, 300 MHz) 1.741-2.005 (30H, m, br) 3.720 (1H, dq, $^1J_{H-P}$ 350.58 Hz, $^2J_{H-B}$ 6.6 Hz, **5**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 28.176 (d, **3**), 34.687 (d, **1**), 36.462 (d, **4**), 40.035 ppm (d, **2**).

1,2-*bis*(di-1-adamantylphosphinotrihydroboronmethyl)benzene 34



Di-1-Adamantylphosphine trihydroboron (5 g, 15 mmol) was dissolved in 40 cm^3 THF and cooled to –78 °C. *sec*-BuLi (16.5 mmol) was then added to the cooled solution via syringe to give an intensely coloured yellow solution. The solution was then allowed to stir at –78 °C for 0.5 hr and allowed to warm to room temperature and was stirred for an additional two hours. The deprotonation can be monitored by $^{31}P\{^1H\}$ or $^{11}B\{^1H\}$ NMR spectroscopy (data given below). The THF solution of di-1-adamantyltrihydroboronlithium phosphide was then recooled to –78 °C and regained its yellow colouration, a THF solution (30 cm^3) of α,α'dichloro-*o*-xylene (1.44 g, 8.25 mmol) was then added drop wise via cannula. The solution was then allowed to warm to room temperature and stir overnight. The solvent was then removed under vacuum and the white solid washed with Et_2O (two 20 cm^3 portions) and dried under vacuum to give the title compound as a white solid.

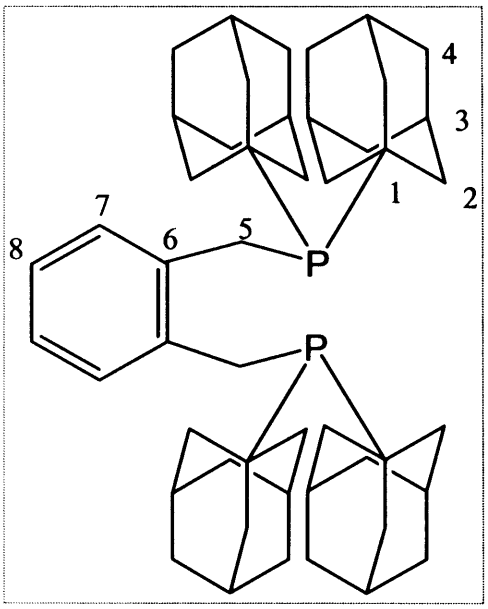
Yield: 5.57 g, 92%

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz): δ 41.374 (q, br); $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96.42 MHz) –46.353 (d, $^1J_{B\text{-}P}$ 51.84 Hz); ^1H NMR ($CDCl_3$, 300 MHz) 1.722 (24H, br, **4**) 1.9-2.2 (36H, br, **3,2**) 3.287 (4H, d, $^2J_{H\text{-}P}$ 12.0 Hz, **5**) 7.110 (2H, m, Ar-H) 7.612 (2H, m, Ar-H); $^{13}C\{^1H\}$ ($CDCl_3$, 75.57 MHz) 21.319 (d, **5**) 28.372 (d, **3**) 36.616 (d, **4**) 38.250 (d, **2**) 40.036 (d, **1**) 126.372 (s, **7**) 129.783 (d, **8**) 132.434 ppm (d, **6**).

APCI MS: *m/z* 734.8 (M^+).

Di-1-adamantyltrihydroboronlithium phosphide. $^{31}P\{^1H\}$ NMR (121.65MHz) δ 9.667 (q, $^1J_{P\text{-}B}$ 38.71 Hz); $^{11}B\{^1H\}$ NMR (96.42MHz) –39.008 ppm (d).

1,2-*bis*(di-1-adamantylphosphinomethyl)benzene 35



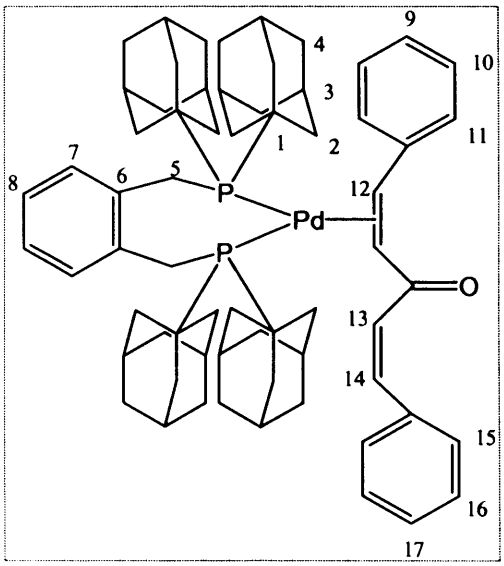
To a cooled (0 °C) DCM (80 cm^3) solution of 1,2-*bis*(di-1-adamantylphosphino trihydroboronmethyl)benzene (5 g, 6.8 mmol) was added tetrafluoroboric acid dimethyl ether complex (10 eq, 68 mmol) via syringe. Upon the addition of the acid the evolution of hydrogen gas was noted. Upon full addition the solution was allowed to stir at 0 °C for an additional one hour and then allowed to warm to room temperature and was stirred overnight. 150 cm^3 of saturated sodium bicarbonate solution was then added and the two-phase system was stirred rapidly for 9 hrs. The stirring was stopped and the two phases allowed to separate. The organic phase was then removed via cannula and the aqueous phase washed with a further 30 cm^3 portion of dichloromethane. The combined portions of DCM were then dried over magnesium sulphate and subsequently filtered via cannula. The solvent was then removed under reduced pressure to yield the title compound as a white solid. 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene could be further purified by precipitation from a concentrated DCM solution by cooling at –40 °C.

Yield: 3.41 g, 71%

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 26.371 (s); ^1H NMR ($CDCl_3$, 300 MHz) 1.703 (24H, d, br, **4**) 1.914 (36H, m, br, **2,3**) 3.005 (4H, d, $^2J_{H\text{-}P}$ 3.0 Hz, **5**) 7.036 (2H, m, Ar-H) 7.544 (2H, m, Ar-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 25.685 (d, **5**) 28.777 (d, **3**) 36.678 (d, **4**) 37.120 (d, **6**) 41.032 (d, **1**) 124.218 (s, **7**) 130.846 (d, **8**) 135.312 ppm (d, **7**).

APCI MS: *m/z* 707.5 (M^+).

[(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene)(*trans*,*trans*dibenzylidene acetone) palladium (0)] 44

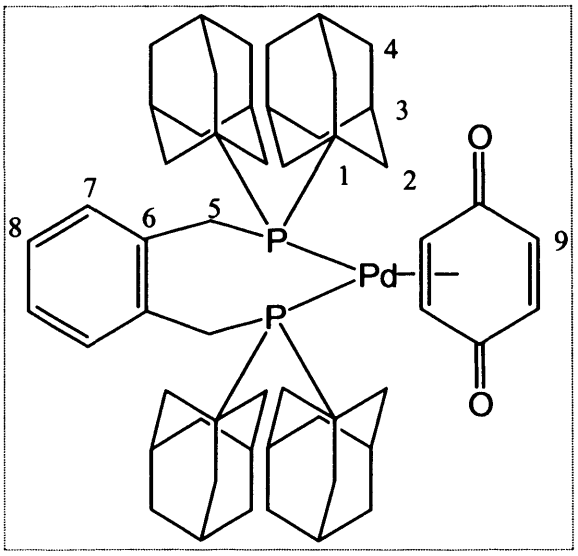


THF (40 cm^3) was added to a combination of 1,2-*bis*(di-1-adamantyl phosphinomethyl)benzene (1.05 g, 1.45 mmol) and [$Pd(DBA)_2$] (0.8 g, 1.45 mmol) that had previously been weighed out in a glove box. The red / orange turbid solution was stirred for three hours. The solution was then filtered via cannula to yield a red filtrate and a small quantity of residue. The solvent was then removed under vacuum to afford a red powdery solid. Hexane (30 cm^3) was added via syringe and trituration performed with a glass rod, resulting in an orange solid separating out. The hexane washings were then removed via cannula filtration and the solid dried under vacuum. Yield 1.34 g, 88%.

^{31}P {^1H} NMR (C_6D_6, 121.65 MHz) δ 43.944 (br) 47.900 (br) (1:1 ratio); ^1H NMR (C_6D_6, 300 MHz) 1.251-2.312 (60H, m, br, **2/3/4**) 3.396 (4H, d, $^2J_{H\text{-}P}$ 7.02Hz, **5**) 5.307 (2H, m, br, **12**) 6.928 (1H, d, $^3J_{H\text{-}H}$ 15.00 Hz, **13/14**) 7.798 (1H, d, **13/14**) 7.027-7.230 ppm (14H, m, Ar-H); ^{13}C {^1H} (C_6D_6, 75.56 MHz) 27.84 (d) 29.71 (d) 34.65 (d) 32.72 (d) 39.49 (d) 118.26-139.81 ppm (m).

MS (FAB) : *m/z* 1047 (M^+).

[(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene)(1,4-*para*-benzoquinone) palladium (0)] 45

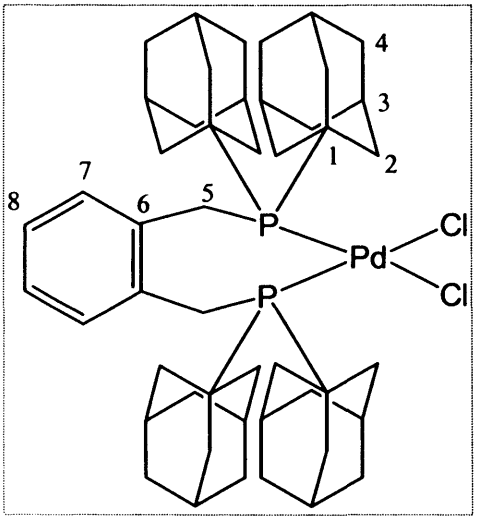


To degassed 1,4-para-benzoquinone (38 mg, 0.35 mmol) was added (*via* cannula) a toluene solution (20 cm^3) of [(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) (*trans, trans* dibenzylideneacetone)palladium(0)] (0.34 g, 0.32 mmol). The solution was allowed to stir for 3 hours. The solvent was then removed under vacuum to yield a red solid. The solid was washed with diethylether (3*10 cm^3) at –15 °C and filtered via cannula to yield the red complex and a yellow solution of DBA and excess 1,4-para-benzoquinone.

^{31}P $\{^1H\}$ NMR (C_6D_6, 121.65 MHz) δ 50.48 (s); ^1H NMR (C_6D_6, 300 MHz) 1.532-2.181 (60H, m, **2,3**) 3.006 (4H, d, $^2J_{H-P}$ 5.28Hz, **5**) 5.913 (4H, s, **9**) 6.951 (2H, m, Ar-H) 7.346 (2H, m, Ar-H); ^{13}C $\{^1H\}$ NMR (C_6D_6, 75.56 MHz) 26.65 (d) 29.41 (d) 35.91 (d) 37.01 (d) 41.23 (d) 124.67 (s) 130.53 (d) 134.07 ppm (d).

MS (FAB): *m/z* 921.3 (M^+).

[Dichloro (1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) palladium (II)] 46

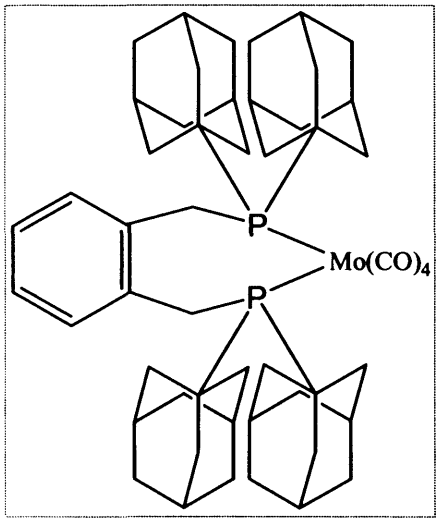


To a diethylether solution ($60cm^3$) of [(1,2-*bis*(di-1-adamantylphosphinomethyl) benzene)(1,4-*para*-benzoquinone) palladium (0)] (0.5 g, 0.47 mmol) was added (*via* syringe) anhydrous HCl (diethylether solution) (1 cm^3, 0.95 mmol). An instant change in the colour of the solution from red to yellow was observed. The solution was allowed to stir for 1.5 hrs and was then allowed to stand for 2 hrs, during which time a yellow solid precipitated from the solution. The yellow coloured complex was isolated by cannula filtration and was dried under vacuum.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 31.46 (s); ^1H NMR ($CDCl_3$, 300 MHz) 1.34-2.35 (60H, m, **2,3,4**) 2.55 (4H, d, **5**) 7.15 (2H, m, Ar-H) 7.45 (2H, δm, Ar-H); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 26.34 (d) 29.98 (d) 34.74 (d) 38.02 (d) 43.09 (d) 124.17 (s) 130.92 (d) 135.71 ppm (d).

MS (FAB): *m/z* 884.4 (M^+)

[(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) tetracarbonyl molybdenum (0)] 43



A DCM solution (40 cm^3) of 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene (0.24 g, 0.34 mmol) was added to [*cis*(piperidine)$_2$(CO)$_4$Mo] **8** (0.13 g, 0.53 mmol) to give an orange coloured suspension. Upon heating under reflux (0.25 hrs), the suspended material dissolved to give a yellow coloured solution. The solution was allowed to cool to room temperature and the solvent removed under vacuum to leave a buff coloured solid. Further purification was achieved by precipitation of the title compound from chloroform upon the addition of methanol.

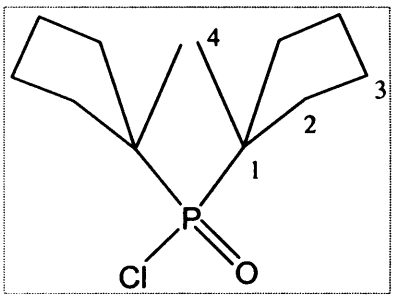
Yield: 0.20 g, 65%

^{31}P {^1H} NMR ($CDCl_3$, 121.65 MHz) δ 51.84 (s); ^1H NMR ($CDCl_3$, 300 MHz) 1.57-2.32 (60H, m, br) 3.30 (4H, d, br) 7.05 (2H, m, Ar-H) 7.32 (2H, m, Ar-H); ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz) 29.09 (d) 36.82 (d) 37.03 (d) 40.52 (d) 128.57 (s) 133.73 (d) 136.42 ppm (d).

IR (KBr): ν_{CO} 1988, 1886, 1864 cm^{-1}.

MS (FAB): m/z 914 (M^+), 858 (M^+, -2CO).

Di(1-methylcyclopentyl)phosphinic chloride 36



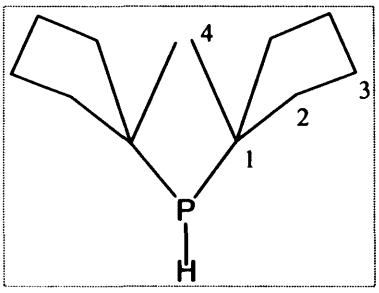
A two neck round bottom flask fitted with a condenser topped with a gas inlet was charged with $AlCl_3$ (7.88 g, 59 mmol) and methylcyclopentane (5.00 g, 59 mmol). Phosphorus trichloride (32.5 cm^3) was then added rapidly via cannula. The solution was then heated to reflux and became bright orange after 0.5 hrs. The solution was heated under reflux for a total time of 24 hrs. The orange suspension was then allowed to cool and the excess PCl_3 was then removed via distillation. The orange coloured oil obtained was then poured cautiously onto crushed ice (200 g). The reaction flask was washed with chloroform (250 cm^3), and the washings added to the previously decanted material. The two phase system was filtered through celite to remove the solid orange impurity. The two phases were then separated and the organic phase dried over magnesium sulphate. After filtration, the chloroform was removed via distillation to afford the title compound as a viscous clear oil.

Yield: 7.34 g, 74%.

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 95.513 (s); ^1H NMR ($CDCl_3$, 400 MHz) 1.267 (3H, d, $^3J_{H\text{-}P}$ 19.07Hz, **4**) 1.553 (2H, m, **3**) 1.690 (4H, m, **2**) 2.272 (2H, m, **3**); ^1H $\{^{31}P\}$ NMR ($CDCl_3$, 300 MHz) 1.313 (3H, s, **4**) 1.612 (2H, m, **3**) 1.734 (4H, m, **2**) 2.335 (2H, m, **3**); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 24.788 (d, **4**) 25.474 (d, **3**) 25.784 (d, **3**) 36.846 (d, **2**) 50.469 ppm (d, **1**).

MS (APCI): *m/z* 249 (M^+); 250 ($M\text{-}H^+$).

Di(1-methylcyclopentyl)phosphine 37

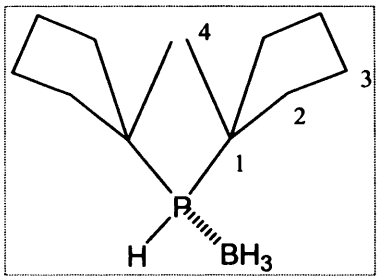


$LiAlH_4$ (1.09 g, 28.8 mmols) was slurried in diethylether (50 cm^3) and cooled in an ice bath. A diethylether (50 cm^3) solution of Di(1-methylcyclopentyl)phosphinic chloride (6.20 g, 25.0 mmol) was then added to the slurry via cannula over a 2hr period to prevent overheating. The solution was then stirred for a further 1 hr at 0 °C and then allowed to warm to room temperature and stir for an additional 18 hrs. The solution was then cooled in an ice bath and 4 cm^3 of 15% aqueous NaOH was gradually added via cannula until the remaining grey solid became granular in appearance. The solution was then filtered via cannula to remove the grey solid, and was dried over magnesium sulphate. After cannula filtration the solvent was removed by distillation to leave the title compound as a colourless oil with a strong, unpleasant odour.

Yield: 3.85 g, 78%

^{31}P $\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 15.627 (s); ^1H NMR ($CDCl_3$, 300 MHz) 1.284 (3H, d, $^3J_{H\text{-}P}$ 10.77 Hz, **2**) 1.654 (2H, m, **4**) 1.719 (4H, m, **3**) 2.300 (2H, m, **4**); ^1H $\{^{31}P\}$ NMR ($CDCl_3$, 300 MHz) 1.298 (3H, s) 1.661 (2H, m) 1.725 (4H, m) 2.325 (2H, m); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75.56 MHz) 23.693 (d, **2**) 25.346 (d, **4**) 27.892 (d, **3**) 41.420 ppm (d, **1**).

Di(1-methylcyclopentyl)phosphine trihydroboron 38

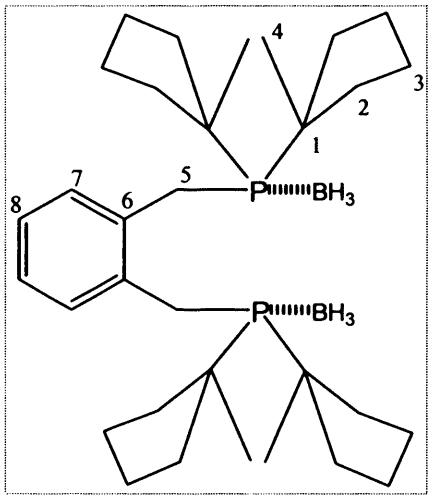


Di(1-methylcyclopentyl)phosphine (3.85 g, 19.5 mmols) was dissolved in THF (40 cm^3) and cooled in an ice bath. Borane THF adduct (1.50 eq, 29.25 mmol) was then added to the cooled solution via syringe. The solution was stirred for 0.5 hrs and then allowed to warm to room temperature and was stirred for an additional 3 hrs. The solvent was removed under vacuum to give the title compound as a colourless solid.

Yield: 4.05 g, 98%

^{31}P {^1H} NMR ($CDCl_3$, 121.65 MHz) δ 48.595 (q, $^1J_{P\text{-}B}$ 53.599 Hz); ^{11}B {^1H} NMR ($CDCl_3$, 96.42 MHz) –44.276 (d); ^1H NMR ($CDCl_3$, 300 MHz) 1.173-1.778 (m); ^{13}C {^1H} ($CDCl_3$, 75.56 MHz) 23.738 (d, **4**) 24.457 (d, **3**) 38.321 ppm (d, **1**).

1,2-*bis*(di-1-methylcyclopentylphosphinotrihydroboronmethyl)benzene 39



To a cooled (-78 °C) THF solution (60 cm^3) of Di(1-methylcyclopentyl) phosphine trihydroboron (6.5 g, 30.6 mmol) was added, *via* syringe, sec-BuLi (33.66 mmol) upon full addition of the sec-BuLi the solution became bright yellow. The solution was stirred for 1.5 hrs at –78 °C and then a further 0.5 hr at room temperature to give lithio-di(1-methylcyclopentyl)phosphide-trihydroboron. The deprotonation can monitored by either $^{31}P\{^1H\}$ or $^{11}B\{^1H\}$ NMR spectroscopy (data given below). The

solution was cooled to -78° and a THF solution (30 cm^3) of α,α'-dichloro-o-xylene (2.66 g, 15.2 mmol) was added slowly *via* cannula. The solution was allowed to stir for 1 hr at –78 °C and then allowed to warm to room temperature before being left to stir overnight. During this time the solution became cloudy as LiCl precipitated. The solvent was removed under vacuum, and dichloromethane (60 cm^3) and water (40 cm^3) added to give a two-phase system. The organic phase was then removed *via* cannula and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield the product as a white solid.

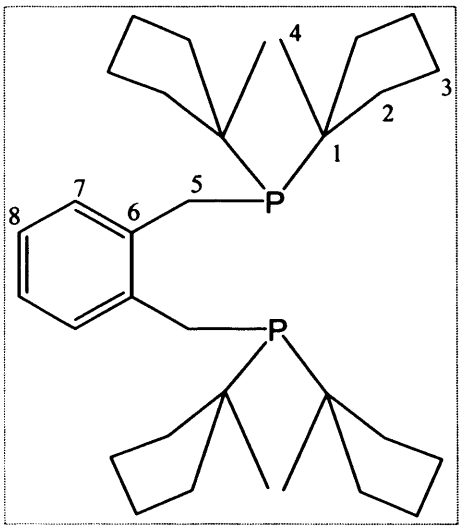
Yield: 6.08 g, 76%

^{31}P $\{^1H\}$ ($CDCl_3$, 121.65 MHz) δ 52.70 (m, br); ^{11}B $\{^1H\}$ (96.42 MHz) –43.35 (d, br); ^1H NMR($CDCl_3$, 400 MHz) 1.25 (12H, d, $^3J_{H-P}$ 11.86 Hz) 1.38 (8H, m, br) 1.56 (16H, br) 1.96 (8H, m, br) 3.33 (4H, d, $^2J_{H-P}$ 6.82Hz) 7.06 (2H, m, Ar-H) 7.37 (2H, m, Ar-H); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 23.39 (d) 24.26 (d) 40.05 (d) 125.30 (s) 131.34 (s) 132.69 ppm (s).

lithio-di(1-methylcyclopentyl)phosphide-trihydroboron

^{31}P $\{^1H\}$ (121.65MHz) δ 12.37 (q, $^1J_{P-B}$ 41.689 Hz); ^{11}B $\{^1H\}$ (96.42MHz) -37.518 ppm (d).

1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene 40

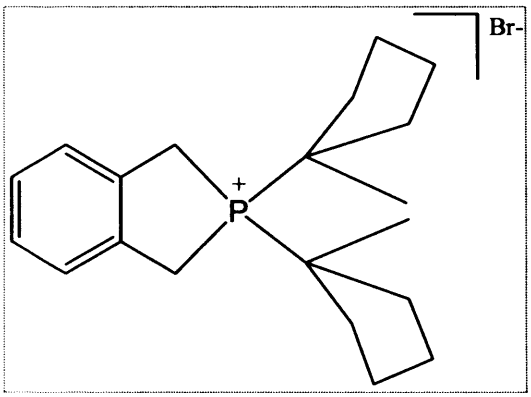


To a cooled (0 °C) DCM (75 cm^3) solution of 1,2-*bis*(di-1-methylcyclopentylphosphinotrihydroboronmethyl)benzene (6.05 g, 11.55 mmol) was added tetrafluoroboric acid dimethyl ether complex (10 eq, 115.5 mmol) via syringe. Upon the addition of the acid the evolution of a gas was noted. Upon full addition the solution was allowed to stir at 0 °C for an additional one hour and then allowed to warm to room temperature and was stirred overnight. 250 cm^3 of saturated sodium bicarbonate solution was then added and the two-phase system was stirred rapidly for 9 hrs. The stirring was stopped and the two phases allowed to separate. The organic phase was then removed via cannula and the aqueous phase washed with a further 40 cm^3 portion of dichloromethane. The combined portions of DCM were then dried over magnesium sulphate and subsequently filtered via cannula. The solvent was then removed under reduced pressure to yield the title compound as a white solid.

Yield. 3.91 g, 68%

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.65 MHz) δ 33.84 (s); 1H NMR ($CDCl_3$, 300 MHz) 1.16 (12H, $^3J_{H\text{-}P}$ 11.80 Hz) 1.54 (32H, m, br) 3.08 (4H, d, $^2J_{H\text{-}P}$ 2.1Hz) 7.01 (2H, m, Ar-H) 7.40 (2H, m, Ar-H); $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz) 23.29 (s) 38.37 (d) 39.45 (d) 40.30 (s) 44.45 (d) 124.36 (d) 130.09 (s) 137.28 ppm (d).

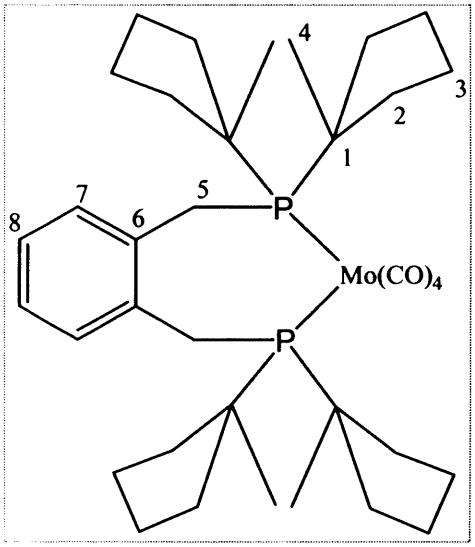
2,2 di-methylcyclopentyl *iso*-phosphindolinium bromide 41



^{31}P {^{1}H} NMR (d_6-acetone, 121.65 MHz) δ 73.29 (s); ^{1}H NMR (d_6-acetone, 300 MHz) 1.61 (6H, d, $^{3}J_{H-P}$ 17.4 Hz) 1.83 (8H, m, br) 1.98 (8H, m, br) 4.20 (4H, d, $^{2}J_{H-P}$ 9.0 Hz) 7.32 (2H, m, Ar-H) 7.46 (2H, m, Ar-H); ^{1}H {^{31}P} NMR (d_6-acetone, 300 MHz) 1.61 (6H, s) 1.79 (8H, m, br) 1.96 (8H, m, br) 4.20 (4H, s) 7.33 (2H, m, Ar-H) 7.45 (2H, m, Ar-H); ^{13}C {^{1}H} NMR (d_6-acetone, 100 MHz) 23.88 (s) 25.32 (d) 26.55 (d) 37.58 (s) 41.92 (d) 128.79 (d) 129.40 (s) 137.34 ppm (d).

MS (ESI): *m/z* 301.1 (M^+), 218.9 (M, - Mecyclopent), 136.6 (M, -2Mecyclopent).

[(1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene)tetracarbonyl molybdenum (0)] 42



A dichloromethane (50 cm^3) solution of 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene (0.45 g, 0.90 mmol) was added to [*cis*(piperidene)$_2$Mo(CO)$_4$] **8** (0.35 g, 0.90 mmol) to give a orange coloured suspension. The solution was then heated at reflux for 0.75 hrs, upon heating the suspended material dissolved to give a yellow coloured solution. The solution was allowed to cool to room temperature and the solvent was then removed under vacuum.

The yellow coloured solid obtained was dissolved in chloroform and was recrystallised upon the addition of methanol. The title compound was further purified by layering a concentrated chloroform solution of the complex with methanol.

Yield: 0.34 g, 55%

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.65 MHz) 56.69 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) 1.40 (12H, d, $^{3}J_{H\text{-}P}$ 12.0 Hz) 1.74 (32H, m, br) 3.31 (4H, d, $^{2}J_{H\text{-}P}$ 4.8 Hz) 7.08 (2H, m, Ar-H) 7.15 (2H, m, Ar-H); $^{1}H\{^{31}P\}$ ($CDCl_3$, 300 MHz) 1.40 (12H, s) 1.74 (32H, m, br) 3.31 (4H, s) 7.08 (2H, m, Ar-H) 7.17 (2H, m, Ar-H); $^{13}C\{^{1}H\}$ ($CDCl_3$, 75.56 MHz) 24.12 (d) 29.86 (s) 38.90 (s) 40.82 (d) 47.13 (s) 126.04 (d) 132.91 (s) 136.41 ppm (d).

MS (FAB): *m/z* 706.7 (M^+), 678.7 (M^+, -CO), 650.2 (M^+, -2CO), 622.7 (M^+, -3CO).

IR (KBr): ν_{CO} 2007, 1894 (sh), 1846 cm^{-1}

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List of Chemicals, Chapter 4

30 Di-1-Adamantylphosphinic chloride
31 Di-1-Adamantylphosphine
32 Di-1-Adamantylchlorophosphine
33 Di-1-Adamantylphosphine trihydroboron
34 1,2-*bis*(di-1-adamantylphosphinotrihydroboronmethyl)benzene
35 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene
36 Di (1-methylcyclopentyl)phosphinic chloride
37 Di (1-methylcyclopentyl) phosphine
38 Di (1-methylcyclopentyl) phosphine trihydroboron
39 1,2-*bis*(di-1-methylcyclopentylphosphinotrihydroboronmethyl)benzene
40 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene
41 2,2 di-methylcyclopentyl *iso*-phosphindolinium bromide
42[(1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene)tetracarbonyl molybdenum (0)]
43 [(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) tetracarbonyl molybdenum (0)]
44[(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene)(*trans,trans*dibenzylidene acetone) palladium (0)]
45[(1,2-*bis*(di-1-adamantylphosphinomethyl)benzene)(1,4-*para*-benzoquinone) Palladium (0)]
46 [Dichloro (1,2-*bis*(di-1-adamantylphosphinomethyl)benzene) palladium (II)]

Chapter Five

5.1 Introduction

The catalytic reactions described in this chapter were carried out in the semi-technical area at Lucite international, Wilton. Four, two litre mechanically stirred hastelloy autoclaves (A, B, E and F) were used to carry out the catalysis with 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene and 1,2-*bis*(2,2,3,4,4-pentamethyl phosphetanemethyl)benzene. Catalysis with 1,2-*bis*(di-1-adamantyl phosphinomethyl)benzene was carried out in a magnetically stirred 300ml glass Buchi autoclave.

Each autoclave was standardised by performing a catalytic run with 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene **1**. The properties and catalytic activity of complexes derived from this ligand being well understood in the methoxycarbonylation of ethylene.[1, 2, 6]

Each of the novel phosphine ligands previously described (**17**, **21**, **35** and **40**), was tested in the methoxycarbonylation of ethylene under standard conditions established for **1**. Two palladium sources ($Pd(OAc)_2$ and $Pd(DBA)_2$) were employed under differing conditions. Each test acting as a screen for either activity or catalyst robustness.

The palladium species used as catalysts in the hastelloy autoclaves were formed *in-situ*. Reactions were carried out with a 1:1 mixture of carbon monoxide:ethylene maintained at a pressure of 10 bar above vapour pressure (100 °C (hastelloy autoclave), 80 °C (Buchi autoclave)). The rate of reaction was monitored by measurement of the amount of the gaseous mixture consumed by the reaction (Hastelloy autoclave). Reaction commences upon the introduction of the carbon monoxide / ethylene mixture to the autoclave. After the reaction is complete, the solution isolated was analysed *via* gas chromatography and the weight gain recorded.

Catalysis carried out with $Pd(OAc)_2$ was performed in methanol with a Pd loading of 0.0014 mol%. The initial rate of the reaction under these conditions is a good measure of the catalyst systems activity.

Reactions carried out with $Pd(DBA)_2$ as the palladium source (ligand **1, 40**), were run with a palladium loading of 0.00031 mol% in a methylpropionate / methanol (70 wt% MeP) solution (Hastelloy autoclave). This alternative solvent system provides a higher ratio of methanol : Pd. However, the reactants are diluted with MeP. Under these conditions the Pd catalyst isn't dissolved solely in methanol, which also acts as a reactant in the catalytic cycle. Therefore the catalytic species are more likely to be involved in side reactions which may remove intermediates from the catalytic cycle. This provides conditions were the stability of the catalytic system can be assessed. 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene was used with $Pd(DBA)_2$ as the palladium source in neat methanol, as a test for activity.

5.2 Results and Discussion

A summary of the weight gain from each catalytic run where $Pd(OAc)_2$ was used as the palladium source is given in Table 1.

Reaction	Ligand	Autoclave	Ratio	Wt gain (g)	Average wt gain (g)
			Pd:Lig:Acid		
1	1,2-*bis*(di-*t*-butylphosphino methyl)benzene	E	1:5:100	251.56	224.46
2	1,2-*bis*(di-*t*-butylphosphino methyl)benzene	F	1:5:100	197.37	-
3	1,2-*bis*(di-1-methylcyclo pentylphosphinomethyl)benzene	A	1:5:100	242.90	218.54
4	1,2-*bis*(di-1-methylcyclo pentylphosphinomethyl)benzene	B	1:5:100	194.19	-

Table 1. Catalysis performed with $Pd(OAc)_2$

Each ligand was run twice to give the average weight gain. The standard ligand **1** was also run on each of the autoclaves to ensure the reliability of the results, representative data is given in Table 1.

Table 2 gives that data obtained from catalytic reactions carried out with $Pd(DBA)_2$ used as the palladium source.

Reaction	Ligand	Autoclave	Ratio	Wt gain (g)	Average wt gain (g)
			Pd:Lig:Acid		Gain (g)
5	1,2-*bis*(di-1-adamantyl phosphinomethyl)benzene	Buchi	1:1:10	-	75.7
6	1,2-*bis*(di-*t*-butylphosphino methyl)benzene	Buchi	1:1:10	-	29.6
7	1,2-*bis*(di-*t*-butylphosphino methyl)benzene	B	1:5:100	42.42	47.89
8	1,2-*bis*(di-*t*-butylphosphino methyl)benzene	B	1:5:100	53.37	-
9	1,2-*bis*(di-1-methylcyclo pentylphosphinomethyl)benzene	A	1:5:100	42.45	42.45

Table 2. Catalysis performed with $Pd(DBA)_2$

5.2.1 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene

When $Pd(OAc)_2$ was used as the palladium source, the catalyst system derived from 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene (**40**) gave a weight gain comparable to that seen with the 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene (**1**) standard (Table 1). **40** was found to give a catalyst system selective for methylpropionate.

Reaction rate and turnover data for the reactions carried out with $Pd(OAc)_2$ with phosphine ligand **1** and **40** is shown in Figure 1 and 2.

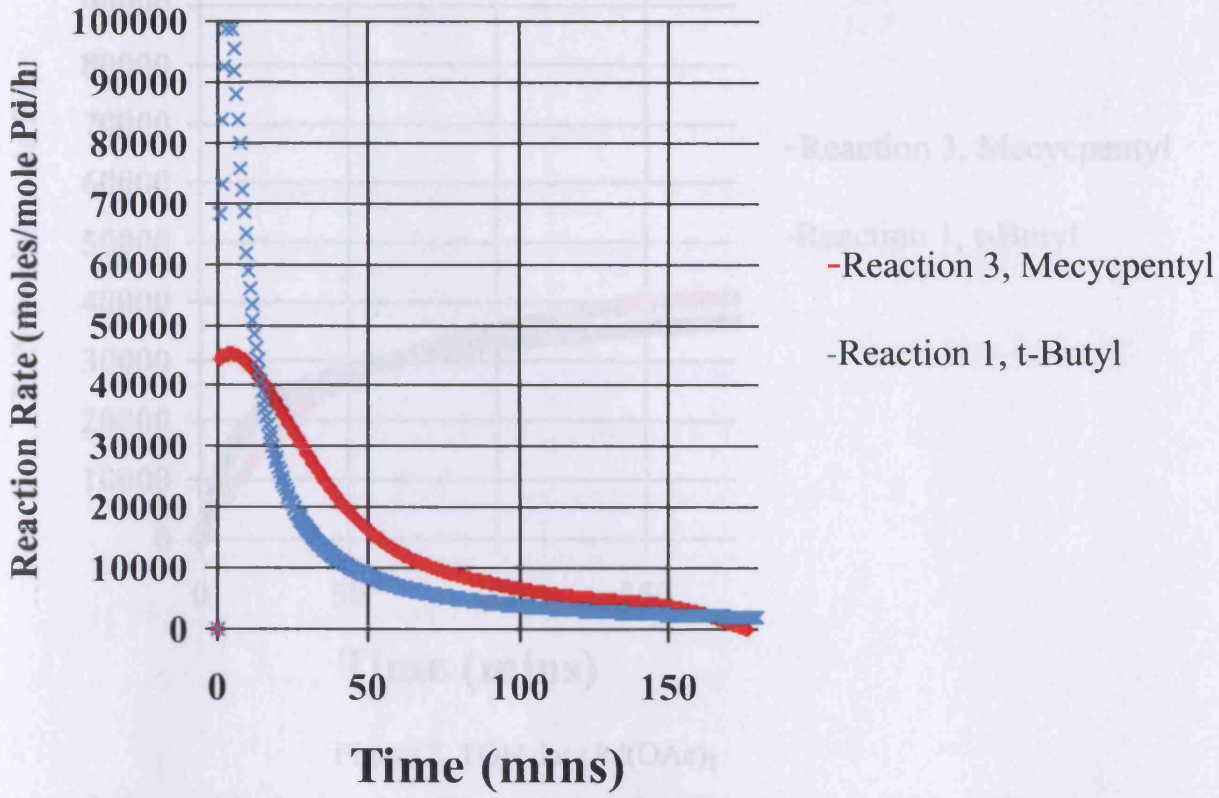

Figure 1. Reaction rate data $Pd(OAc)_2$

The initial reaction rate (Figure 1) of the reaction with 1,2-*bis*(di-1-methylcyclopentyl phosphinomethyl)benzene (**40**) is considerably lower than that with 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene (**1**). However, as the reaction progresses the rate of reaction observed with **1** decreases sharply in the early stages. A similar drop in the reaction rate is not observed with **40**, rather a gradual decline in the rate is observed.

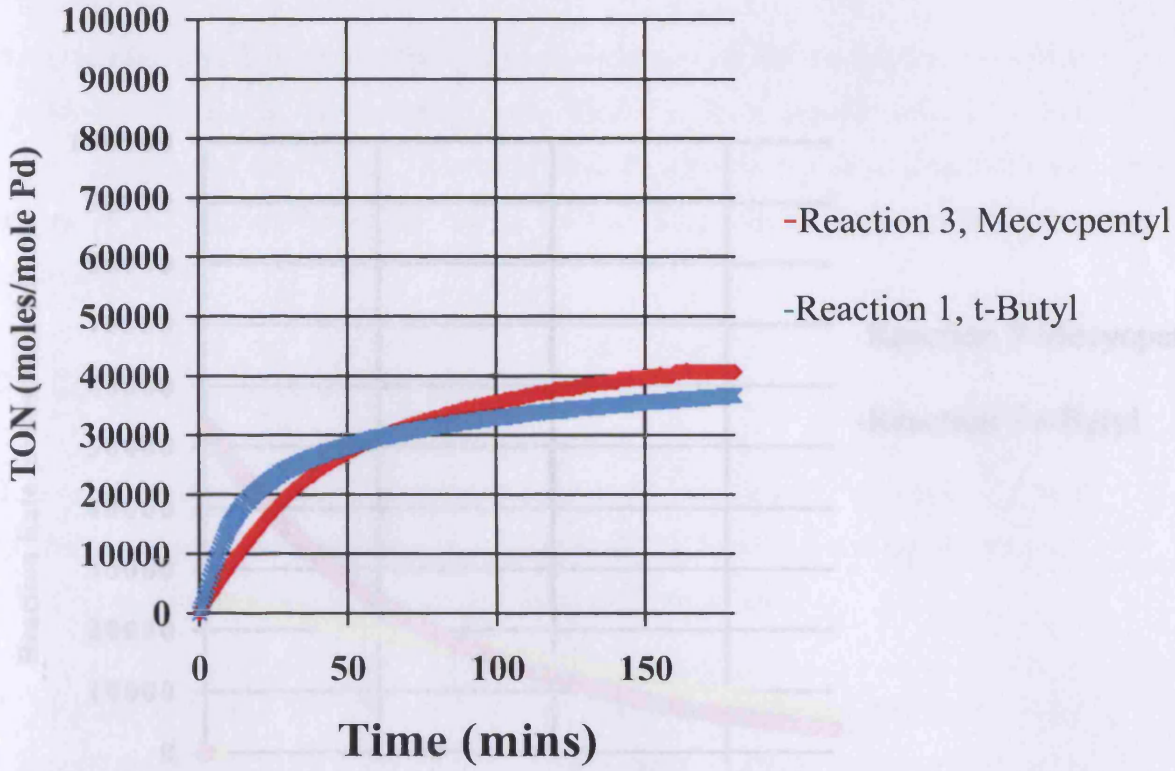

Figure 2. TON data $Pd(OAc)_2$

The trend observed in the rate data (Figure 1) is reflected in the turnover data (Figure 2), with the lower but more stable rate of **40** giving approximately equal turnover number when compared to **1** after 3 hrs.

Reaction rate and turn over data for the reactions carried out with $Pd(DBA)_2$ is shown in Figure 3 and 4. Catalytic runs with **40** were found to give a weight gain comparable to those observed with **1** (Table 2). The catalyst system derived from **40** was again found to be selective for methylpropionate.

When rate of reaction is compared to that of the standard, it can be seen that the initial rate of reaction with **1** is approximately double that of **40**. As the reaction proceeds the rate decreases in both cases. The decrease in rate being attributed to the consumption of methanol in the reaction.

Interestingly, the drop in reaction rate for **40** appears to be linear, as would be expected if the change in reaction rate were due to methanol consumption. However, the drop in reaction rate observed for **1** is non-linear. The deviation being attributed to the decay of the catalyst.

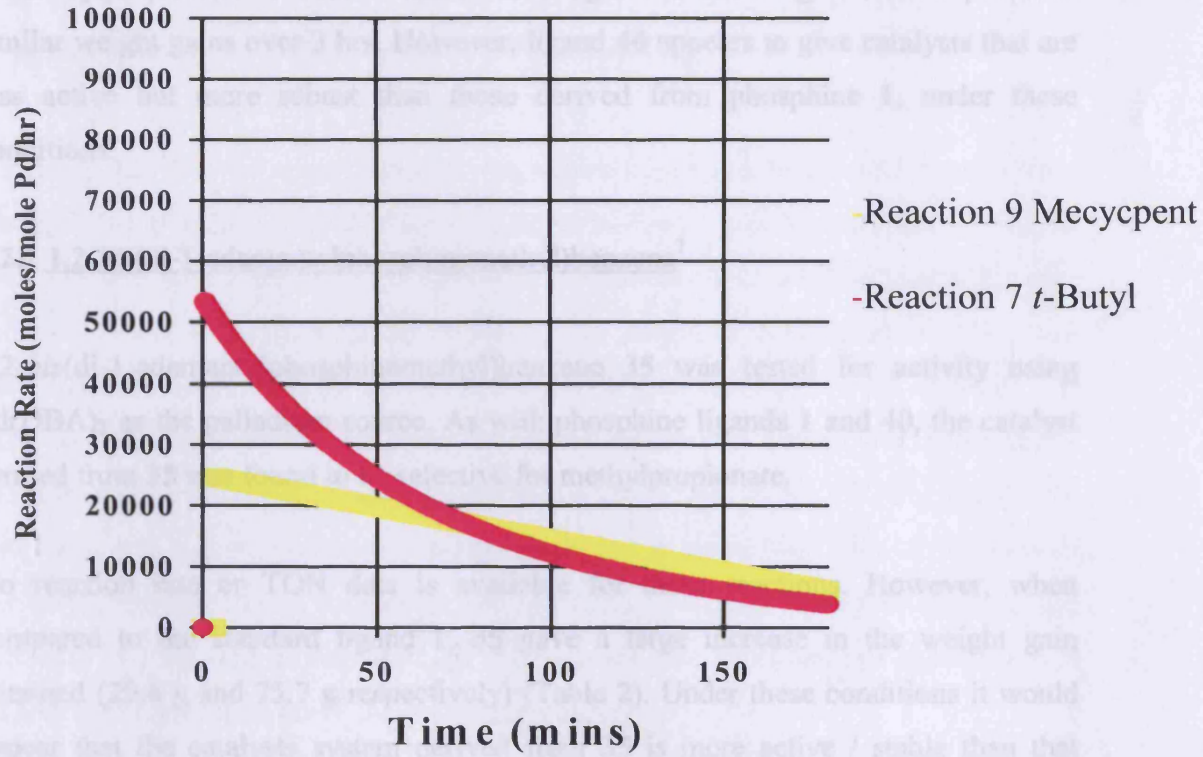

Figure 3. Reaction rate data $Pd(DBA)_2$

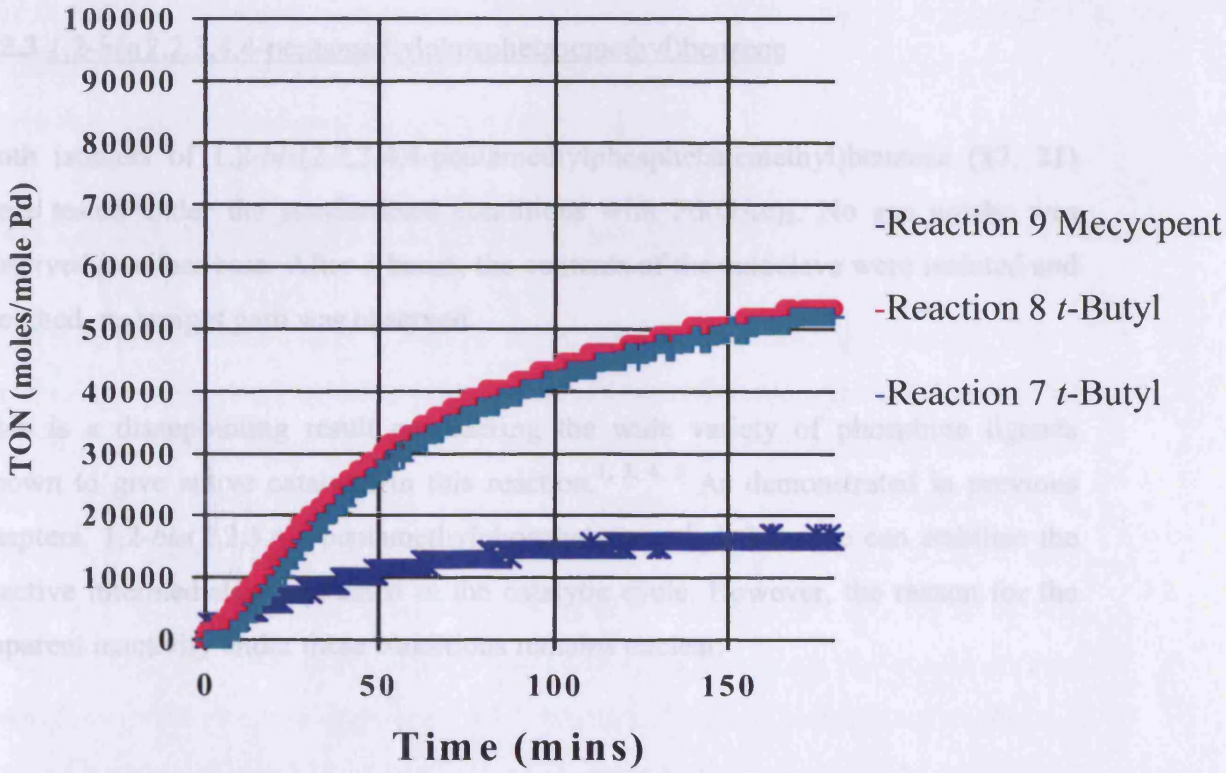

Figure 4. TON data $Pd(DBA)_2$

The results suggest that catalyst formed from phosphine **40** have a similar selectivity to methylpropionate as those formed from ligand **1**. Both ligands have provided similar weight gains over 3 hrs. However, ligand **40** appears to give catalysts that are less active but more robust than those derived from phosphine **1**, under these conditions.

5.2.2 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene[7]

1,2-*bis*(di-1-adamantylphosphinomethyl)benzene **35** was tested for activity using $Pd(DBA)_2$ as the palladium source. As with phosphine ligands **1** and **40**, the catalyst formed from **35** was found to be selective for methylpropionate.

No reaction rate or TON data is available for these reactions. However, when compared to the standard ligand **1**, **35** gave a large increase in the weight gain obtained (29.6 g and 75.7 g respectively) (Table 2). Under these conditions it would appear that the catalysts system derived from **35** is more active / stable than that derived from **1**.

5.2.3 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl)benzene

Both isomers of 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl)benzene (**17**, **21**) were tested under the standardised conditions with $Pd(OAc)_2$. No gas uptake was observed in either case. After 3 hours, the contents of the autoclave were isolated and weighed, no weight gain was observed.

This is a disappointing result considering the wide variety of phosphine ligands known to give active catalysts in this reaction.[1, 3, 4, 5] As demonstrated in previous chapters, 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl) benzene can stabilise the reactive intermediates implicated in the catalytic cycle. However, the reason for the apparent inactivity under these conditions remains unclear.

5.3 Experimental

Standard procedure ($Pd(OAc)_2$ (Hastelloy autoclave)

$Pd(OAc)_2$ (22 mg, 0.1 mmol) and the respective phosphine ligand (0.5 mmol) were weighed out in a glove box into a 500 ml three necked round bottom flask. Methanol (300 ml) was added and the mixture allowed to stir for 1 hr. Methanesulphonic acid (10 mmol) was then added to the solution. The weight of the catalyst solution was taken and it was charged to the autoclave and heated to 100 °C with stirring. The reaction was started by the introduction of carbon monoxide / ethylene 1:1 mixture to the autoclave. The total pressure was controlled at 12.3 bar by a TESCOM valve. The autoclave was maintained at this temperature and pressure for 3 hrs during which period the amount of gas consumed was recorded. The gases were then isolated and the autoclave allowed to cool to room temperature. The depressurised autoclave was then emptied and the mass of the solution recorded.

Mass of ligand charged: 1,2-*bis*(di-*t*-butylphosphinomethyl)benzene (201 mg), 1,2-*bis*(di-1-methylcyclopentylphosphinomethyl)benzene (200 mg), 1,2-*bis*(di-1-adamantylphosphinomethyl)benzene (360 mg), 1,2-*bis*(2,2,3,4,4-pentamethylphosphetanemethyl)benzene (200 mg).

Standard procedure ($Pd(DBA)_2$) (Hastelloy autoclave)

A mechanically stirred 2 litre Hastelloy autoclave was evacuated and charged with a previously weighed out solution comprising of: Methylpropionate : Methanol (300 ml, 70 wt% MeP), Pd(as DBA salt) (0.014 mmols), appropriate phosphine ligand (0.076 mmols), methanesulphonic acid (2.25 mmols). The autoclave was heated to 100 °C and when at temperature, 8 bar of ethylene was added on top of the vapour pressure of the solvents and immediately a further 2 bar of a 1:1 mixture of carbon monoxide and ethylene was added to the system. At this point the autoclave was opened up to the reservoir containing a 1:1 mixture of carbon monoxide and ethylene and the reaction allowed to proceed. The temperature and pressure were maintained for 3 hours during which time the volume of gas consumed was recorded. The

autoclave was isolated and vented, and then allowed to cool to room temperature. The depressurised autoclave was emptied and the final weight of the solution recorded.

Procedure ($Pd(DBA)_2$) (Buchi autoclave)

The catalyst system was prepared by reacting one equivalents of the appropriate phosphine ligand with $Pd(DBA)_2$ (50 mg) in methanol (100 ml) followed by reaction with methanesulphonic acid (10 eq). The solution was then charged to the autoclave under an inert atmosphere. The solution was heated to 80 °C, before the addition of carbon monoxide / ethylene (1:1 mixture) at 10 bar above vapour pressure. The reaction was allowed to proceed for 2hrs before the solution was isolated and the weight gain calculated.

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Crystal Data

Table 1. Crystal data and structure refinement for compound **5** (02DENNIS2).

Identification code	C24H50B2P2
Empirical formula	C24 H50 B2 P2
Formula weight	422.20
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 14.1750(3) A alpha = 90 deg. b = 15.0620(4) A beta = 90 deg. c = 25.4500(6) A gamma = 90 deg.
Volume	5433.7(2) A^3
Z	8
Density (calculated)	1.032 Mg/m^3
Absorption coefficient	0.168 mm^-1
F(000)	1872
Crystal size	0.12 x 0.08 x 0.06 mm
Theta range for data collection	2.98 to 25.02 deg.
Index ranges	-16<=h<=16, -17<=k<=17, -30<=l<=30
Reflections collected	45277
Independent reflections	4785 [R(int) = 0.1765]
Max. and min. transmission	0.9900 and 0.9801
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4785 / 0 / 290
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1141
R indices (all data)	R1 = 0.0967, wR2 = 0.1295
Extinction coefficient	0.0027(4)
Largest diff. peak and hole	0.274 and -0.335 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for S92.

P(1)-C(1)	1.843(3)	P(1)-C(9)	1.866(3)
P(1)-C(13)	1.867(3)	P(1)-B(1)	1.939(4)
P(2)-C(8)	1.854(3)	P(2)-C(21)	1.873(3)
P(2)-C(17)	1.877(3)	P(2)-B(2)	1.939(4)
C(1)-C(2)	1.516(4)	C(2)-C(3)	1.387(4)
C(2)-C(7)	1.405(4)	C(3)-C(4)	1.384(4)
C(4)-C(5)	1.379(4)	C(5)-C(6)	1.383(4)
C(6)-C(7)	1.398(4)	C(7)-C(8)	1.518(4)
C(9)-C(12)	1.530(4)	C(9)-C(10)	1.540(4)
C(9)-C(11)	1.544(4)	C(13)-C(15)	1.527(5)
C(13)-C(16)	1.535(4)	C(13)-C(14)	1.550(4)
C(17)-C(18)	1.532(4)	C(17)-C(20)	1.534(4)
C(17)-C(19)	1.546(4)	C(21)-C(23)	1.534(4)
C(21)-C(24)	1.536(4)	C(21)-C(22)	1.545(4)
C(1)-P(1)-C(9)	106.71(13)	C(1)-P(1)-C(13)	102.25(13)
C(9)-P(1)-C(13)	112.03(13)	C(1)-P(1)-B(1)	116.27(15)
C(9)-P(1)-B(1)	109.40(19)	C(13)-P(1)-B(1)	110.04(19)
C(8)-P(2)-C(21)	107.81(13)	C(8)-P(2)-C(17)	102.38(13)
C(21)-P(2)-C(17)	112.10(14)	C(8)-P(2)-B(2)	114.93(14)
C(21)-P(2)-B(2)	109.54(15)	C(17)-P(2)-B(2)	109.96(15)
C(2)-C(1)-P(1)	119.12(19)	C(3)-C(2)-C(7)	118.3(2)
C(3)-C(2)-C(1)	118.7(2)	C(7)-C(2)-C(1)	122.9(2)
C(4)-C(3)-C(2)	122.3(3)	C(5)-C(4)-C(3)	119.1(3)
C(4)-C(5)-C(6)	119.6(3)	C(5)-C(6)-C(7)	121.6(3)
C(6)-C(7)-C(2)	118.6(3)	C(6)-C(7)-C(8)	118.4(2)
C(2)-C(7)-C(8)	123.0(2)	C(7)-C(8)-P(2)	118.69(19)
C(12)-C(9)-C(10)	108.4(3)	C(12)-C(9)-C(11)	109.7(2)
C(10)-C(9)-C(11)	107.9(2)	C(12)-C(9)-P(1)	113.9(2)
C(10)-C(9)-P(1)	107.1(2)	C(11)-C(9)-P(1)	109.7(2)
C(15)-C(13)-C(16)	109.3(3)	C(15)-C(13)-C(14)	108.3(3)
C(16)-C(13)-C(14)	107.2(3)	C(15)-C(13)-P(1)	114.6(2)
C(16)-C(13)-P(1)	111.1(2)	C(14)-C(13)-P(1)	105.9(2)
C(18)-C(17)-C(20)	110.1(2)	C(18)-C(17)-C(19)	108.0(3)
C(20)-C(17)-C(19)	107.2(3)	C(18)-C(17)-P(2)	113.7(2)
C(20)-C(17)-P(2)	109.6(2)	C(19)-C(17)-P(2)	108.0(2)
C(23)-C(21)-C(24)	109.2(3)	C(23)-C(21)-C(22)	108.1(3)
C(24)-C(21)-C(22)	107.7(3)	C(23)-C(21)-P(2)	114.8(2)
C(24)-C(21)-P(2)	110.2(2)	C(22)-C(21)-P(2)	106.6(2)

Table 1. Crystal data and structure refinement for S92. Compound **17**.

Identification code	02DENNIS3
Empirical formula	C24 H40 P2
Formula weight	390.50
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.0343(3) A b = 13.2316(8) A c = 15.4746(10) A alpha = 83.084(3) deg. beta = 79.072(3) deg. gamma = 87.465(3) deg.
Volume	1204.02(12) A^3
Z	2
Density (calculated)	1.077 Mg/m^3
Absorption coefficient	0.186 mm^-1
F(000)	428
Crystal size	0.15 x 0.04 x 0.04 mm
Theta range for data collection	3.92 to 25.32 deg.
Index ranges	-7<=h<=7, -15<=k<=15, -18<=l<=18
Reflections collected	13420
Independent reflections	4369 [R(int) = 0.1640]
Absorption correction	SORTAV
Max. and min. transmission	0.9926 and 0.9726
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4369 / 30 / 245
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0900, wR2 = 0.2117
R indices (all data)	R1 = 0.1273, wR2 = 0.2368
Largest diff. peak and hole	1.293 and -0.568 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for S92.

P(1)-C(7)	1.864(4)	P(1)-C(8)	1.882(5)
P(1)-C(10)	1.887(4)	P(2)-C(16)	1.862(4)
P(2)-C(19)	1.888(5)	P(2)-C(17)	1.899(5)
C(1)-C(6)	1.380(7)	C(1)-C(2)	1.412(6)
C(1)-C(7)	1.507(7)	C(2)-C(3)	1.411(7)
C(2)-C(16)	1.494(6)	C(3)-C(4)	1.370(7)
C(4)-C(5)	1.372(8)	C(5)-C(6)	1.388(8)
C(8)-C(11)	1.523(6)	C(8)-C(12)	1.528(6)
C(8)-C(9)	1.565(6)	C(9)-C(13)	1.518(6)
C(9)-C(10)	1.562(6)	C(10)-C(15)	1.536(6)
C(10)-C(14)	1.540(6)	C(17)-C(21)	1.493(10)
C(17)-C(20)	1.503(8)	C(17)-C(18)	1.546(10)
C(18)-C(19)	1.525(10)	C(18)-C(22)	1.534(9)
C(19)-C(24)	1.502(8)	C(19)-C(23)	1.526(10)
C(7)-P(1)-C(8)	107.0(2)	C(7)-P(1)-C(10)	108.6(2)
C(8)-P(1)-C(10)	78.2(2)	C(16)-P(2)-C(19)	104.9(2)
C(16)-P(2)-C(17)	107.8(2)	C(19)-P(2)-C(17)	77.5(2)
C(6)-C(1)-C(2)	119.3(5)	C(6)-C(1)-C(7)	119.9(4)
C(2)-C(1)-C(7)	120.6(4)	C(3)-C(2)-C(1)	117.6(4)
C(3)-C(2)-C(16)	120.4(4)	C(1)-C(2)-C(16)	122.0(4)
C(4)-C(3)-C(2)	121.7(5)	C(3)-C(4)-C(5)	120.4(5)
C(4)-C(5)-C(6)	119.0(5)	C(1)-C(6)-C(5)	122.0(5)
C(1)-C(7)-P(1)	110.5(3)	C(11)-C(8)-C(12)	109.3(4)
C(11)-C(8)-C(9)	113.5(4)	C(12)-C(8)-C(9)	114.2(4)
C(11)-C(8)-P(1)	114.3(3)	C(12)-C(8)-P(1)	115.8(3)
C(9)-C(8)-P(1)	88.6(3)	C(13)-C(9)-C(10)	118.5(4)
C(13)-C(9)-C(8)	118.0(4)	C(10)-C(9)-C(8)	99.0(3)
C(15)-C(10)-C(14)	109.3(4)	C(15)-C(10)-C(9)	112.2(4)
C(14)-C(10)-C(9)	114.7(4)	C(15)-C(10)-P(1)	113.7(3)
C(14)-C(10)-P(1)	117.2(3)	C(9)-C(10)-P(1)	88.5(3)
C(2)-C(16)-P(2)	113.3(3)	C(21)-C(17)-C(20)	109.4(6)
C(21)-C(17)-C(18)	118.5(6)	C(20)-C(17)-C(18)	109.1(6)
C(21)-C(17)-P(2)	117.4(4)	C(20)-C(17)-P(2)	114.5(4)
C(18)-C(17)-P(2)	86.4(4)	C(19)-C(18)-C(22)	119.5(7)
C(19)-C(18)-C(17)	101.1(5)	C(22)-C(18)-C(17)	117.1(8)
C(24)-C(19)-C(18)	121.8(6)	C(24)-C(19)-C(23)	105.9(6)
C(18)-C(19)-C(23)	110.3(7)	C(24)-C(19)-P(2)	117.9(4)
C(18)-C(19)-P(2)	87.4(4)	C(23)-C(19)-P(2)	112.9(5)

Table 1. Crystal data and structure refinement for compound **11** DENNIS5.

Identification code	s92
Empirical formula	C24 H45 Cl3 Ni P2
Formula weight	560.60
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	Pca2(1)
Unit cell dimensions	a = 17.1927(5) A alpha = 90 deg. b = 10.6519(9) A beta = 90 deg. c = 15.6082(9) A gamma = 90 deg.
Volume	2858.4(3) A^3
Z	4
Density (calculated)	1.303 Mg/m^3
Absorption coefficient	1.081 mm^-1
F(000)	1192
Crystal size	0.20 x 0.18 x 0.16 mm
Theta range for data collection	3.05 to 25.33 deg.
Index ranges	-20<=h<=20, -12<=k<=12, -18<=l<=18
Reflections collected	40734
Independent reflections	5190 [R(int) = 0.1590]
Max. and min. transmission	0.8460 and 0.8128
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5190 / 2 / 287
Goodness-of-fit on F^2	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0760, wR2 = 0.1646
R indices (all data)	R1 = 0.1278, wR2 = 0.1836
Absolute structure parameter	0.09(4)

Largest diff. peak and hole 0.910 and -0.835 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for DENNIS5. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni(1)	816(1)	2613(1)	2103(1)	67(1)
Cl(1)	2137(1)	2548(2)	2100(2)	63(1)
Cl(2)	548(1)	2951(2)	3507(2)	52(1)
Cl(3)	299(2)	941(3)	1419(2)	87(1)
P(1)	319(1)	4446(2)	1191(2)	42(1)
P(2)	2158(1)	1164(2)	-760(2)	42(1)
C(1)	468(4)	4340(7)	9(6)	43(2)
C(2)	727(4)	5984(6)	1594(6)	37(2)
C(3)	460(5)	6156(7)	2496(5)	42(2)
C(4)	519(5)	7131(7)	1053(6)	45(2)
C(5)	1623(4)	5822(8)	1610(6)	45(2)
C(6)	-774(4)	4386(8)	1263(6)	43(2)
C(7)	-1160(4)	5664(7)	1006(6)	43(2)
C(8)	-1017(5)	4052(9)	2158(8)	59(3)
C(9)	-1071(5)	3397(8)	667(7)	54(3)
C(10)	1269(4)	4593(7)	-383(5)	38(2)
C(11)	1403(5)	5753(7)	-747(6)	46(2)
C(12)	2120(5)	6060(8)	-1087(6)	49(2)
C(13)	2703(4)	5239(8)	-1065(6)	42(2)
C(14)	2578(4)	4035(7)	-730(6)	37(2)
C(15)	1860(4)	3694(7)	-393(5)	33(2)

C(16)	1776(5)	2381(7)	-46(6)	39(2)
C(17)	2833(5)	156(7)	-137(6)	46(2)
C(18)	3436(5)	1028(8)	280(7)	56(3)
C(19)	3286(6)	-659(9)	-804(7)	65(3)
C(20)	2424(6)	-642(8)	516(7)	62(3)
C(21)	1364(5)	430(7)	-1369(6)	50(2)
C(22)	931(5)	1539(8)	-1796(6)	53(2)
C(23)	803(6)	-313(10)	-789(8)	91(4)
C(24)	1701(7)	-365(9)	-2106(8)	83(4)

Table 3. Bond lengths [A] and angles [deg] for DENNIS5.

Ni(1)-Cl(3)	2.258(3)
Ni(1)-Cl(2)	2.268(3)
Ni(1)-Cl(1)	2.272(2)
Ni(1)-P(1)	2.563(3)
P(1)-C(1)	1.866(9)
P(1)-C(6)	1.885(7)
P(1)-C(2)	1.889(7)
P(2)-C(16)	1.831(8)
P(2)-C(21)	1.838(8)
P(2)-C(17)	1.855(8)
C(1)-C(10)	1.531(11)
C(2)-C(3)	1.491(11)
C(2)-C(4)	1.528(12)
C(2)-C(5)	1.551(10)
C(6)-C(9)	1.495(12)
C(6)-C(8)	1.501(14)
C(6)-C(7)	1.567(11)
C(10)-C(11)	1.379(11)
C(10)-C(15)	1.395(11)
C(11)-C(12)	1.383(12)
C(12)-C(13)	1.329(11)
C(13)-C(14)	1.402(11)
C(14)-C(15)	1.391(10)
C(15)-C(16)	1.506(10)
C(17)-C(20)	1.502(13)
C(17)-C(18)	1.536(12)
C(17)-C(19)	1.564(13)
C(21)-C(24)	1.542(15)
C(21)-C(23)	1.542(14)
C(21)-C(22)	1.547(11)
Cl(3)-Ni(1)-Cl(2)	120.12(12)
Cl(3)-Ni(1)-Cl(1)	111.63(11)
Cl(2)-Ni(1)-Cl(1)	102.08(11)
Cl(3)-Ni(1)-P(1)	101.98(12)
Cl(2)-Ni(1)-P(1)	110.38(9)

Cl(1)-Ni(1)-P(1)	110.79(10)
C(1)-P(1)-C(6)	101.2(4)
C(1)-P(1)-C(2)	109.4(4)
C(6)-P(1)-C(2)	112.3(4)
C(1)-P(1)-Ni(1)	117.2(3)
C(6)-P(1)-Ni(1)	105.8(3)
C(2)-P(1)-Ni(1)	110.6(3)
C(16)-P(2)-C(21)	110.4(4)
C(16)-P(2)-C(17)	108.4(4)
C(21)-P(2)-C(17)	119.3(4)
C(10)-C(1)-P(1)	120.5(6)
C(3)-C(2)-C(4)	110.6(6)
C(3)-C(2)-C(5)	107.7(7)
C(4)-C(2)-C(5)	109.3(7)
C(3)-C(2)-P(1)	107.9(5)
C(4)-C(2)-P(1)	115.0(6)
C(5)-C(2)-P(1)	106.1(5)
C(9)-C(6)-C(8)	108.5(7)
C(9)-C(6)-C(7)	107.9(7)
C(8)-C(6)-C(7)	109.1(7)
C(9)-C(6)-P(1)	109.1(6)
C(8)-C(6)-P(1)	109.9(6)
C(7)-C(6)-P(1)	112.2(5)
C(11)-C(10)-C(15)	119.3(7)
C(11)-C(10)-C(1)	118.1(7)
C(15)-C(10)-C(1)	122.6(7)
C(10)-C(11)-C(12)	121.2(7)
C(13)-C(12)-C(11)	120.4(8)
C(12)-C(13)-C(14)	119.8(7)
C(15)-C(14)-C(13)	121.0(7)
C(14)-C(15)-C(10)	118.1(7)
C(14)-C(15)-C(16)	117.6(7)
C(10)-C(15)-C(16)	124.3(7)
C(15)-C(16)-P(2)	113.9(6)
C(20)-C(17)-C(18)	111.7(8)
C(20)-C(17)-C(19)	111.8(7)
C(18)-C(17)-C(19)	106.3(7)
C(20)-C(17)-P(2)	113.0(6)
C(18)-C(17)-P(2)	107.1(5)
C(19)-C(17)-P(2)	106.5(6)
C(24)-C(21)-C(23)	113.0(8)
C(24)-C(21)-C(22)	106.1(8)
C(23)-C(21)-C(22)	110.1(8)
C(24)-C(21)-P(2)	110.0(7)
C(23)-C(21)-P(2)	112.3(7)
C(22)-C(21)-P(2)	104.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for DENNIS5.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ni(1)	50(1)	81(1)	71(1)	-28(1)	13(1)	-17(1)
Cl(1)	54(1)	87(2)	49(1)	-3(1)	8(2)	3(1)
Cl(2)	40(1)	63(2)	53(1)	7(1)	3(1)	-5(1)
Cl(3)	72(2)	71(2)	118(3)	-35(2)	6(2)	-7(1)
P(1)	27(1)	40(1)	58(2)	-13(1)	3(1)	-6(1)
P(2)	48(1)	32(1)	46(1)	0(1)	-3(1)	3(1)
C(1)	30(4)	41(5)	59(6)	-3(4)	3(4)	-2(4)
C(2)	36(4)	10(4)	65(6)	-17(4)	6(4)	-3(3)
C(3)	44(5)	34(5)	46(6)	-2(4)	2(4)	-3(4)
C(4)	47(5)	30(4)	57(6)	-10(4)	2(4)	-5(4)
C(5)	41(5)	42(5)	53(6)	-4(4)	1(4)	-6(4)
C(6)	30(4)	46(5)	54(6)	1(5)	-3(4)	-1(4)
C(7)	35(4)	39(5)	56(6)	0(4)	3(4)	4(4)
C(8)	36(5)	68(6)	71(7)	9(6)	7(5)	0(4)
C(9)	33(5)	45(6)	83(7)	14(5)	-6(5)	-6(4)
C(10)	44(5)	37(5)	32(5)	-1(4)	-12(4)	-7(4)
C(11)	58(5)	35(5)	44(5)	-4(5)	-3(5)	15(4)
C(12)	61(6)	31(5)	56(6)	8(4)	4(5)	-11(4)
C(13)	25(4)	47(5)	53(6)	-7(4)	9(4)	-21(4)
C(14)	22(4)	39(5)	50(5)	-6(4)	7(4)	-2(3)
C(15)	38(4)	26(4)	34(4)	7(4)	-5(4)	0(4)
C(16)	40(4)	35(5)	41(5)	1(4)	9(4)	6(4)

C(17)	53(5)	29(5)	57(6)	6(4)	-15(4) 17(4)
C(18)	61(6)	42(6)	65(7)	3(5)	-8(5) 16(5)
C(19)	65(6)	58(6)	72(8)	1(6)	-14(6) 6(5)
C(20)	67(6)	52(6)	67(7)	24(5)	5(5) 11(5)
C(21)	68(6)	24(5)	60(7)	-4(4)	-29(5) 4(4)
C(22)	59(6)	53(6)	45(6)	-9(5)	-6(5) 21(5)
C(23)	94(8)	81(7)	99(10)	56(8)	-45(8) -56(6)
C(24)	114(9)	44(6)	89(9)	-22(6)	-63(8) 18(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for DENNIS5.

	x	y	z	U(eq)
H(2)	2620(30)	1820(40)	-1340(30)	12(15)
H(1A)	310	3485	-169	52
H(1B)	98	4931	-262	52
H(3A)	770	6817	2770	62
H(3B)	526	5368	2812	62
H(3C)	-90	6397	2499	62
H(4A)	-38	7308	1109	68
H(4B)	642	6963	451	68
H(4C)	818	7857	1252	68
H(5A)	1809	5625	1032	68
H(5B)	1761	5137	2000	68
H(5C)	1865	6603	1808	68
H(7A)	-1698	5515	823	65
H(7B)	-867	6044	534	65
H(7C)	-1158	6232	1499	65
H(8A)	-1584	4098	2205	88
H(8B)	-780	4641	2563	88
H(8C)	-844	3197	2291	88
H(9A)	-810	2599	790	81
H(9B)	-964	3646	74	81
H(9C)	-1633	3298	747	81
H(11)	994	6352	-764	55
H(12)	2198	6863	-1337	59
H(13)	3201	5468	-1276	50
H(14)	2991	3442	-734	44
H(16A)	1218	2213	61	47
H(16B)	2051	2329	510	47
H(18A)	3181	1548	715	84
H(18B)	3667	1569	-159	84

H(18C)	3844	522	550	84
H(19A)	3673	-1175	-506	98
H(19B)	3550	-108	-1215	98
H(19C)	2921	-1204	-1110	98
H(20A)	2810	-1054	883	93
H(20B)	2111	-1280	223	93
H(20C)	2085	-112	868	93
H(22A)	514	1213	-2162	79
H(22B)	1297	2025	-2144	79
H(22C)	707	2079	-1352	79
H(23A)	581	250	-357	137
H(23B)	1087	-992	-504	137
H(23C)	384	-670	-1138	137
H(24A)	2021	-1042	-1869	124
H(24B)	2021	168	-2477	124
H(24C)	1274	-727	-2441	124

Crystal data and structure refinement for compound **25.** (DENNIS6 (RED CRYSTAL)).

Empirical formula	C24 H40 Cl2 P2 Pd
Formula weight	567.80
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 8.7462(2) A alpha = 90 deg. b = 16.7335(3) A beta = 103.4470(19) deg. c = 8.9946(4) A gamma = 90 deg.
Volume	1280.31(7) A^3
Z	2
Density (calculated)	1.473 Mg/m^3
Absorption coefficient	1.068 mm^-1
F(000)	588
Crystal size	0.18 x 0.16 x 0.12 mm
Theta range for data collection	2.93 to 27.44 deg.
Index ranges	-11<=h<=11, -21<=k<=21, -11<=l<=11
Reflections collected	22112
Independent reflections	5738 [R(int) = 0.1095]
Max. and min. transmission	0.8825 and 0.8310
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5738 / 1 / 272
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0810
R indices (all data)	R1 = 0.0419, wR2 = 0.0849
Absolute structure parameter	-0.03(2)
Largest diff. peak and hole	0.496 and -0.874 e.A^-3

Table 3.

Bond lengths (A) and angles [deg] for DENNIS6 (RED CRYSTAL).

Pd(1)-P(1)	2.2415(9)	Pd(1)-P(2)	2.2519(9)
Pd(1)-Cl(1)	2.3791(10)	Pd(1)-Cl(2)	2.3917(9)
P(1)-C(1)	1.823(4)	P(1)-C(11)	1.872(4)
P(1)-C(9)	1.901(4)	P(2)-C(8)	1.856(4)
P(2)-C(17)	1.884(4)	P(2)-C(19)	1.906(4)
C(1)-C(2)	1.508(6)	C(2)-C(3)	1.394(5)
C(2)-C(7)	1.405(5)	C(3)-C(4)	1.378(6)
C(4)-C(5)	1.378(6)	C(5)-C(6)	1.383(6)
C(6)-C(7)	1.398(5)	C(7)-C(8)	1.528(5)
C(9)-C(12)	1.518(6)	C(9)-C(13)	1.525(6)
C(9)-C(10)	1.571(6)	C(10)-C(14)	1.519(6)
C(10)-C(11)	1.584(5)	C(11)-C(16)	1.523(6)
C(11)-C(15)	1.523(6)	C(17)-C(21)	1.519(6)
C(17)-C(20)	1.539(6)	C(17)-C(18)	1.557(5)
C(18)-C(22)	1.528(5)	C(18)-C(19)	1.562(5)
C(19)-C(23)	1.515(5)	C(19)-C(24)	1.524(5)

P(1)-Pd(1)-P(2)	92.17(3)	P(1)-Pd(1)-Cl(1)	160.54(4)
P(2)-Pd(1)-Cl(1)	97.75(3)	P(1)-Pd(1)-Cl(2)	85.37(3)
P(2)-Pd(1)-Cl(2)	154.49(4)	Cl(1)-Pd(1)-Cl(2)	92.58(3)
C(1)-P(1)-C(11)	108.16(18)	C(1)-P(1)-C(9)	108.41(19)
C(11)-P(1)-C(9)	79.11(18)	C(1)-P(1)-Pd(1)	111.23(14)
C(11)-P(1)-Pd(1)	116.96(13)	C(9)-P(1)-Pd(1)	128.24(13)
C(8)-P(2)-C(17)	116.12(16)	C(8)-P(2)-C(19)	109.23(16)
C(17)-P(2)-C(19)	79.15(16)	C(8)-P(2)-Pd(1)	108.98(12)
C(17)-P(2)-Pd(1)	120.30(13)	C(19)-P(2)-Pd(1)	120.28(11)
C(2)-C(1)-P(1)	118.0(3)	C(3)-C(2)-C(7)	119.0(4)
C(3)-C(2)-C(1)	117.2(3)	C(7)-C(2)-C(1)	123.6(3)
C(4)-C(3)-C(2)	122.0(4)	C(5)-C(4)-C(3)	118.9(4)
C(4)-C(5)-C(6)	120.4(4)	C(5)-C(6)-C(7)	121.2(4)
C(6)-C(7)-C(2)	118.2(4)	C(6)-C(7)-C(8)	118.4(3)
C(2)-C(7)-C(8)	123.4(3)	C(7)-C(8)-P(2)	111.6(2)
C(12)-C(9)-C(13)	108.0(4)	C(12)-C(9)-C(10)	114.8(4)

C(13)-C(9)-C(10)	111.4(4)	C(12)-C(9)-P(1)	121.4(3)
C(13)-C(9)-P(1)	111.5(3)	C(10)-C(9)-P(1)	88.7(2)
C(14)-C(10)-C(9)	116.2(4)	C(14)-C(10)-C(11)	115.0(4)
C(9)-C(10)-C(11)	99.2(3)	C(16)-C(11)-C(15)	109.2(4)
C(16)-C(11)-C(10)	117.0(3)	C(15)-C(11)-C(10)	111.8(3)
C(16)-C(11)-P(1)	115.9(3)	C(15)-C(11)-P(1)	112.4(3)
C(10)-C(11)-P(1)	89.4(2)	C(21)-C(17)-C(20)	110.8(3)
C(21)-C(17)-C(18)	110.9(3)	C(20)-C(17)-C(18)	115.3(4)
C(21)-C(17)-P(2)	117.6(3)	C(20)-C(17)-P(2)	113.5(3)
C(18)-C(17)-P(2)	86.9(2)	C(22)-C(18)-C(17)	116.5(3)
C(22)-C(18)-C(19)	116.9(3)	C(17)-C(18)-C(19)	101.5(3)
C(23)-C(19)-C(24)	108.5(3)	C(23)-C(19)-C(18)	112.8(3)
C(24)-C(19)-C(18)	114.7(3)	C(23)-C(19)-P(2)	114.7(3)
C(24)-C(19)-P(2)	118.8(3)	C(18)-C(19)-P(2)	86.0(2)

Table 1. Crystal data and structure refinement for Compound **7**.

Identification code	02Dennis10
Empirical formula	C28 H44 Mo O4 P2
Formula weight	602.51
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 11.17300(10) A alpha = 90 deg. b = 20.0465(3) A beta = 98.2020(5) deg. c = 13.1725(2) A gamma = 90 deg.
Volume	2920.19(7) A^3
Z	4
Density (calculated)	1.370 Mg/m^3
Absorption coefficient	0.589 mm^-1
F(000)	1264
Crystal size	0.30 x 0.25 x 0.22 mm
Theta range for data collection	3.02 to 27.48 deg.
Index ranges	-14<=h<=14, -26<=k<=26, -17<=l<=17
Reflections collected	41366
Independent reflections	6672 [R(int) = 0.0894]
Max. and min. transmission	0.8814 and 0.8431
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6672 / 0 / 328
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0818
R indices (all data)	R1 = 0.0471, wR2 = 0.0870
Largest diff. peak and hole	0.457 and -0.834 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s92. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	2062(1)	1718(1)	3007(1)	16(1)
P(1)	2545(1)	657(1)	1924(1)	20(1)
P(2)	-310(1)	1505(1)	2730(1)	17(1)
O(1)	2769(2)	1088(1)	5213(1)	35(1)
O(2)	1726(2)	3028(1)	4220(1)	32(1)
O(3)	2162(2)	2880(1)	1401(2)	40(1)
O(4)	4792(2)	2112(1)	3439(2)	37(1)
C(1)	2433(2)	1258(1)	4393(2)	22(1)
C(2)	1811(2)	2527(1)	3790(2)	23(1)
C(3)	2050(2)	2413(1)	1880(2)	27(1)
C(4)	3795(2)	1942(1)	3260(2)	24(1)
C(5)	3217(2)	875(1)	704(2)	30(1)
C(6)	2348(3)	1351(2)	60(2)	43(1)
C(7)	4444(3)	1221(2)	977(3)	68(1)
C(8)	3382(3)	279(2)	-2(2)	48(1)
C(9)	3575(2)	40(1)	2734(2)	31(1)
C(10)	2862(2)	-256(1)	3544(2)	34(1)
C(11)	4041(4)	-540(2)	2144(3)	58(1)
C(12)	4684(2)	404(2)	3320(2)	42(1)
C(13)	1291(2)	123(2)	1279(2)	37(1)
C(14)	402(2)	-234(1)	1846(2)	26(1)
C(15)	537(2)	-924(1)	1986(2)	38(1)
C(16)	-267(3)	-1303(1)	2436(2)	39(1)

	C(17)	-1256(2)	-1001(1)	2742(2)
34(1)				
	C(18)	-1432(2)	-327(1)	2584(2)
30(1)				
	C(19)	-613(2)	73(1)	2149(2)
23(1)				
	C(20)	-933(2)	793(1)	1907(2)
29(1)				
	C(21)	-969(2)	1387(1)	3973(2)
26(1)				
	C(22)	-600(3)	1971(2)	4704(2)
45(1)				
	C(23)	-2347(2)	1295(2)	3850(3)
58(1)				
	C(24)	-397(2)	758(1)	4495(2)
30(1)				
	C(25)	-1159(2)	2200(1)	1931(2)
22(1)				
	C(26)	-2546(2)	2163(1)	1801(2)
32(1)				
	C(27)	-781(2)	2162(1)	851(2)
28(1)				
	C(28)	-777(2)	2888(1)	2387(2)
32(1)				

Table 3. Bond lengths [A] and angles [deg] for s92.

Mo(1)-C(2)	1.964(2)
Mo(1)-C(4)	1.969(2)
Mo(1)-C(1)	2.035(2)
Mo(1)-C(3)	2.035(2)
Mo(1)-P(2)	2.6578(6)
Mo(1)-P(1)	2.6581(6)
P(1)-C(13)	1.869(2)
P(1)-C(9)	1.909(3)
P(1)-C(5)	1.919(2)
P(2)-C(20)	1.867(2)
P(2)-C(21)	1.903(2)
P(2)-C(25)	1.914(2)
O(1)-C(1)	1.144(3)
O(2)-C(2)	1.162(3)
O(3)-C(3)	1.146(3)
O(4)-C(4)	1.157(3)
C(5)-C(6)	1.528(4)
C(5)-C(7)	1.532(4)
C(5)-C(8)	1.543(4)
C(9)-C(11)	1.531(4)
C(9)-C(10)	1.538(4)
C(9)-C(12)	1.546(4)
C(13)-C(14)	1.506(3)
C(14)-C(19)	1.399(3)
C(14)-C(15)	1.401(4)
C(15)-C(16)	1.374(4)
C(16)-C(17)	1.370(4)
C(17)-C(18)	1.378(4)
C(18)-C(19)	1.400(3)
C(19)-C(20)	1.508(3)

C(21)-C(24)	1.532(3)
C(21)-C(22)	1.535(4)
C(21)-C(23)	1.536(3)
C(25)-C(26)	1.536(3)
C(25)-C(28)	1.541(3)
C(25)-C(27)	1.542(3)
C(2)-Mo(1)-C(4)	86.15(10)
C(2)-Mo(1)-C(1)	85.94(9)
C(4)-Mo(1)-C(1)	83.26(9)
C(2)-Mo(1)-C(3)	80.22(10)
C(4)-Mo(1)-C(3)	82.59(10)
C(1)-Mo(1)-C(3)	160.79(10)
C(2)-Mo(1)-P(2)	89.44(7)
C(4)-Mo(1)-P(2)	175.56(7)
C(1)-Mo(1)-P(2)	96.99(6)
C(3)-Mo(1)-P(2)	96.13(7)
C(2)-Mo(1)-P(1)	176.11(7)
C(4)-Mo(1)-P(1)	90.23(7)
C(1)-Mo(1)-P(1)	95.06(7)
C(3)-Mo(1)-P(1)	97.91(7)
P(2)-Mo(1)-P(1)	94.161(18)
C(13)-P(1)-C(9)	103.65(13)
C(13)-P(1)-C(5)	96.19(11)
C(9)-P(1)-C(5)	109.82(11)
C(13)-P(1)-Mo(1)	120.43(9)
C(9)-P(1)-Mo(1)	111.74(8)
C(5)-P(1)-Mo(1)	113.61(9)
C(20)-P(2)-C(21)	104.27(12)
C(20)-P(2)-C(25)	97.05(10)
C(21)-P(2)-C(25)	109.97(10)
C(20)-P(2)-Mo(1)	118.97(8)
C(21)-P(2)-Mo(1)	113.74(8)
C(25)-P(2)-Mo(1)	111.41(7)
O(1)-C(1)-Mo(1)	168.5(2)
O(2)-C(2)-Mo(1)	175.1(2)
O(3)-C(3)-Mo(1)	166.3(2)
O(4)-C(4)-Mo(1)	175.5(2)
C(6)-C(5)-C(7)	108.9(3)
C(6)-C(5)-C(8)	105.6(2)
C(7)-C(5)-C(8)	108.2(3)
C(6)-C(5)-P(1)	108.27(17)
C(7)-C(5)-P(1)	110.57(18)
C(8)-C(5)-P(1)	115.00(19)
C(11)-C(9)-C(10)	107.9(2)
C(11)-C(9)-C(12)	107.8(2)
C(10)-C(9)-C(12)	107.0(2)
C(11)-C(9)-P(1)	115.4(2)
C(10)-C(9)-P(1)	107.87(17)
C(12)-C(9)-P(1)	110.44(18)
C(14)-C(13)-P(1)	123.44(18)
C(19)-C(14)-C(15)	118.3(2)
C(19)-C(14)-C(13)	123.4(2)
C(15)-C(14)-C(13)	117.9(2)
C(16)-C(15)-C(14)	122.6(3)
C(17)-C(16)-C(15)	119.1(3)
C(16)-C(17)-C(18)	119.5(2)
C(17)-C(18)-C(19)	122.5(2)
C(14)-C(19)-C(18)	117.9(2)
C(14)-C(19)-C(20)	122.6(2)
C(18)-C(19)-C(20)	119.1(2)

C(19)-C(20)-P(2)	123.44(17)
C(24)-C(21)-C(22)	106.7(2)
C(24)-C(21)-C(23)	107.2(2)
C(22)-C(21)-C(23)	109.4(2)
C(24)-C(21)-P(2)	107.52(16)
C(22)-C(21)-P(2)	110.06(17)
C(23)-C(21)-P(2)	115.47(19)
C(26)-C(25)-C(28)	107.7(2)
C(26)-C(25)-C(27)	107.41(19)
C(28)-C(25)-C(27)	107.9(2)
C(26)-C(25)-P(2)	116.06(16)
C(28)-C(25)-P(2)	110.44(15)
C(27)-C(25)-P(2)	107.02(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s92.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mo(1)	13(1)	16(1)	18(1)	0(1)	1(1)	-1(1)
P(1)	18(1)	21(1)	22(1)	-3(1)	7(1)	-4(1)
P(2)	13(1)	17(1)	20(1)	1(1)	0(1)	0(1)
O(1)	39(1)	42(1)	22(1)	4(1)	-3(1)	2(1)
O(2)	37(1)	25(1)	32(1)	-8(1)	-7(1)	7(1)
O(3)	47(1)	32(1)	44(1)	15(1)	16(1)	-2(1)
O(4)	19(1)	36(1)	53(1)	0(1)	-1(1)	-6(1)
C(1)	19(1)	22(1)	26(1)	-3(1)	3(1)	1(1)
C(2)	19(1)	25(1)	23(1)	3(1)	-4(1)	2(1)
C(3)	23(1)	28(1)	29(1)	1(1)	6(1)	-1(1)
C(4)	22(1)	21(1)	28(1)	-1(1)	2(1)	1(1)
C(5)	25(1)	41(2)	26(1)	-3(1)	12(1)	-7(1)
C(6)	58(2)	45(2)	29(1)	6(1)	19(1)	5(1)
C(7)	50(2)	121(4)	36(2)	2(2)	12(2)	-53(2)
C(8)	55(2)	60(2)	34(2)	-3(1)	24(1)	13(2)
C(9)	36(1)	21(1)	39(1)	4(1)	12(1)	6(1)
C(10)	44(2)	26(1)	33(1)	1(1)	5(1)	-5(1)
C(11)	91(3)	33(2)	56(2)	3(1)	28(2)	28(2)
C(12)	25(1)	42(2)	58(2)	17(1)	3(1)	6(1)
C(13)	37(1)	44(2)	32(1)	-17(1)	15(1)	-18(1)
C(14)	25(1)	24(1)	29(1)	-10(1)	6(1)	-9(1)
C(15)	29(1)	26(1)	59(2)	-16(1)	7(1)	-3(1)

C(16)	44(2)	20(1)	50(2)	-2(1)	-5(1)	-7(1)
C(17)	44(2)	30(1)	30(1)	-2(1)	8(1)	-18(1)
C(18)	28(1)	29(1)	34(1)	-11(1)	10(1)	-10(1)
C(19)	21(1)	21(1)	24(1)	-5(1)	-2(1)	-6(1)
C(20)	25(1)	23(1)	36(1)	-3(1)	-9(1)	-2(1)
C(21)	20(1)	31(1)	28(1)	8(1)	8(1)	2(1)
C(22)	73(2)	31(2)	38(2)	-2(1)	33(2)	6(2)
C(23)	21(1)	99(3)	58(2)	38(2)	15(1)	9(2)
C(24)	32(1)	32(1)	24(1)	8(1)	1(1)	-4(1)
C(25)	19(1)	20(1)	26(1)	4(1)	-2(1)	2(1)
C(26)	20(1)	36(2)	39(2)	8(1)	-1(1)	7(1)
C(27)	28(1)	33(1)	24(1)	8(1)	-1(1)	3(1)
C(28)	36(1)	20(1)	36(1)	4(1)	-6(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s92.

	x	y	z	U(eq)
H(6A)	2684	1474	-562	64
H(6B)	2238	1753	459	64
H(6C)	1566	1130	-131	64
H(7A)	5021	910	1354	103
H(7B)	4351	1613	1404	103
H(7C)	4743	1362	346	103
H(8A)	3730	435	-602	72
H(8B)	2595	71	-227	72
H(8C)	3926	-49	374	72
H(10A)	2352	-622	3239	51
H(10B)	2353	91	3785	51
H(10C)	3428	-425	4124	51
H(11A)	4393	-882	2629	87
H(11B)	4660	-377	1747	87
H(11C)	3369	-734	1677	87
H(12A)	5206	81	3729	63
H(12B)	4410	741	3775	63
H(12C)	5137	622	2829	63
H(13A)	808	407	759	44
H(13B)	1674	-223	895	44

H(15)	1210	-1139	1760	46
H(16)	-139	-1769	2533	47
H(17)	-1816	-1255	3061	41
H(18)	-2135	-126	2778	36
H(20A)	-1824	824	1848	35
H(20B)	-723	879	1213	35
H(22A)	-909	1895	5354	67
H(22B)	-938	2386	4394	67
H(22C)	284	2004	4832	67
H(23A)	-2570	1090	4472	87
H(23B)	-2607	1006	3260	87
H(23C)	-2743	1730	3741	87
H(24A)	479	766	4486	44
H(24B)	-744	362	4127	44
H(24C)	-559	743	5207	44
H(26A)	-2823	2262	2458	48
H(26B)	-2810	1714	1576	48
H(26C)	-2888	2490	1287	48
H(27A)	-954	2589	498	42
H(27B)	-1237	1806	457	42
H(27C)	86	2067	910	42
H(28A)	-1169	3239	1940	47
H(28B)	103	2935	2442	47
H(28C)	-1022	2928	3070	47

Table 1. Crystal data and structure refinement for Compound **22** (02DENNIS12).

Empirical formula	C28 H40 Mo O4 P2
Formula weight	598.48
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 12.5960(2) A alpha = 90 deg. b = 17.2901(3) A beta = 105.5887(7) deg. c = 13.8362(2) A gamma = 90 deg.
Volume	2902.49(8) A^3
Z	4
Density (calculated)	1.370 Mg/m^3
Absorption coefficient	0.592 mm^-1
F(000)	1248
Crystal size	0.20 x 0.06 x 0.06 mm
Theta range for data collection	3.05 to 27.49 deg.
Index ranges	-16<=h<=15, -22<=k<=22, -17<=l<=17
Reflections collected	39770
Independent reflections	6638 [R(int) = 0.0761]
Max. and min. transmission	0.9653 and 0.8907
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6638 / 0 / 326
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0707
R indices (all data)	R1 = 0.0432, wR2 = 0.0748
Largest diff. peak and hole	0.537 and -0.567 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for 02DENNIS12.

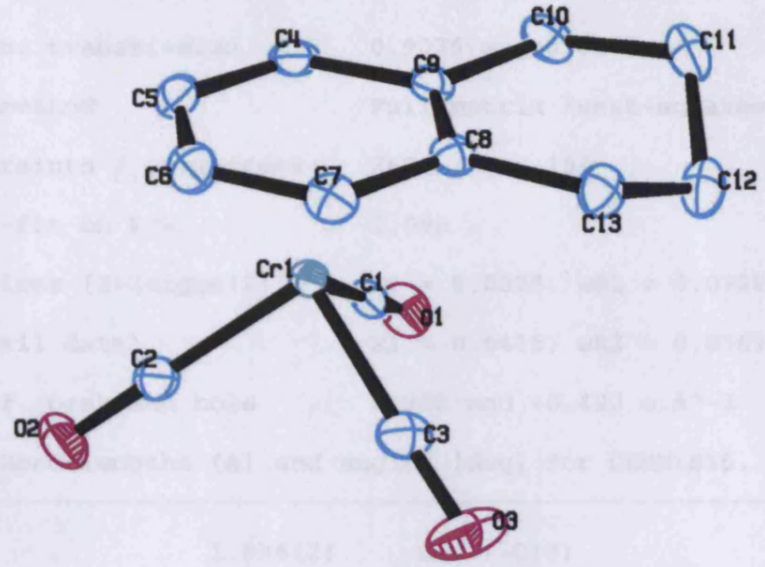
Mo(1)-C(3)	1.988(2)	Mo(1)-C(1)	1.993(2)
Mo(1)-C(2)	2.028(2)	Mo(1)-C(4)	2.038(2)
Mo(1)-P(1)	2.5427(5)	Mo(1)-P(2)	2.5451(6)
P(1)-C(5)	1.856(2)	P(1)-C(13)	1.906(2)
P(1)-C(15)	1.911(2)	P(2)-C(12)	1.856(2)
P(2)-C(23)	1.904(2)	P(2)-C(21)	1.908(2)
O(1)-C(1)	1.155(3)	O(2)-C(2)	1.152(3)
O(3)-C(3)	1.156(3)	O(4)-C(4)	1.144(3)
C(5)-C(6)	1.515(3)	C(6)-C(7)	1.397(3)
C(6)-C(11)	1.402(3)	C(7)-C(8)	1.387(3)
C(8)-C(9)	1.384(3)	C(9)-C(10)	1.378(3)
C(10)-C(11)	1.397(3)	C(11)-C(12)	1.516(3)
C(13)-C(16)	1.520(3)	C(13)-C(17)	1.524(3)
C(13)-C(14)	1.562(3)	C(14)-C(18)	1.534(3)
C(14)-C(15)	1.554(3)	C(15)-C(19)	1.523(3)
C(15)-C(20)	1.533(3)	C(21)-C(24)	1.527(3)
C(21)-C(25)	1.529(3)	C(21)-C(22)	1.562(3)
C(22)-C(26)	1.523(3)	C(22)-C(23)	1.563(3)
C(23)-C(28)	1.526(3)	C(23)-C(27)	1.534(3)
C(3)-Mo(1)-C(1)	83.35(9)	C(3)-Mo(1)-C(2)	91.96(9)
C(1)-Mo(1)-C(2)	91.58(9)	C(3)-Mo(1)-C(4)	94.10(9)
C(1)-Mo(1)-C(4)	94.89(9)	C(2)-Mo(1)-C(4)	171.60(9)
C(3)-Mo(1)-P(1)	171.42(6)	C(1)-Mo(1)-P(1)	88.07(6)
C(2)-Mo(1)-P(1)	88.07(7)	C(4)-Mo(1)-P(1)	86.81(6)
C(3)-Mo(1)-P(2)	87.89(6)	C(1)-Mo(1)-P(2)	170.98(7)
C(2)-Mo(1)-P(2)	86.59(7)	C(4)-Mo(1)-P(2)	87.82(6)
P(1)-Mo(1)-P(2)	100.682(18)	C(5)-P(1)-C(13)	106.64(9)
C(5)-P(1)-C(15)	109.36(10)	C(13)-P(1)-C(15)	77.82(10)
C(5)-P(1)-Mo(1)	116.50(7)	C(13)-P(1)-Mo(1)	119.48(7)
C(15)-P(1)-Mo(1)	120.60(7)	C(12)-P(2)-C(23)	107.61(10)
C(12)-P(2)-C(21)	110.64(10)	C(23)-P(2)-C(21)	77.80(9)
C(12)-P(2)-Mo(1)	116.29(7)	C(23)-P(2)-Mo(1)	118.78(7)
C(21)-P(2)-Mo(1)	119.53(7)	O(1)-C(1)-Mo(1)	175.0(2)
O(2)-C(2)-Mo(1)	177.4(2)	O(3)-C(3)-Mo(1)	175.11(19)
O(4)-C(4)-Mo(1)	177.53(19)	C(6)-C(5)-P(1)	116.14(14)
C(7)-C(6)-C(11)	118.05(19)	C(7)-C(6)-C(5)	118.43(18)
C(11)-C(6)-C(5)	123.28(19)	C(8)-C(7)-C(6)	122.2(2)
C(9)-C(8)-C(7)	119.5(2)	C(10)-C(9)-C(8)	118.9(2)
C(9)-C(10)-C(11)	122.4(2)	C(10)-C(11)-C(6)	118.86(19)
C(10)-C(11)-C(12)	117.69(19)	C(6)-C(11)-C(12)	123.42(18)
C(11)-C(12)-P(2)	113.71(14)	C(16)-C(13)-C(17)	108.75(19)
C(16)-C(13)-C(14)	111.83(19)	C(17)-C(13)-C(14)	115.4(2)
C(16)-C(13)-P(1)	118.38(15)	C(17)-C(13)-P(1)	113.92(15)
C(14)-C(13)-P(1)	87.44(13)	C(18)-C(14)-C(15)	117.6(2)
C(18)-C(14)-C(13)	116.7(2)	C(15)-C(14)-C(13)	100.57(17)
C(19)-C(15)-C(20)	107.5(2)	C(19)-C(15)-C(14)	114.90(19)
C(20)-C(15)-C(14)	113.15(19)	C(19)-C(15)-P(1)	116.72(16)
C(20)-C(15)-P(1)	116.30(16)	C(14)-C(15)-P(1)	87.48(14)
C(24)-C(21)-C(25)	108.00(19)	C(24)-C(21)-C(22)	113.07(19)
C(25)-C(21)-C(22)	113.60(19)	C(24)-C(21)-P(2)	116.55(15)
C(25)-C(21)-P(2)	117.39(15)	C(22)-C(21)-P(2)	87.15(13)
C(26)-C(22)-C(21)	117.77(19)	C(26)-C(22)-C(23)	117.9(2)
C(21)-C(22)-C(23)	100.01(17)	C(28)-C(23)-C(27)	107.90(19)
C(28)-C(23)-C(22)	112.21(19)	C(27)-C(23)-C(22)	114.86(18)
C(28)-C(23)-P(2)	119.17(15)	C(27)-C(23)-P(2)	114.45(16)
C(22)-C(23)-P(2)	87.29(13)		

Table 1. Crystal data and structure refinement for Compound **23** (DENNIS16).

Empirical formula	C28 H40 Mo O4 P2
Formula weight	598.48
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 37.8437(7) A alpha = 90 deg. b = 8.7185(2) A beta = 109.0023(10) deg. c = 18.4939(4) A gamma = 90 deg.
Volume	5769.4(2) A^3
Z	8
Density (calculated)	1.378 Mg/m^3
Absorption coefficient	0.596 mm^-1
F(000)	2496
Crystal size	0.22 x 0.20 x 0.18 mm
Theta range for data collection	3.22 to 27.45 deg.
Index ranges	-48<=h<=48, -9<=k<=11, -20<=l<=23
Reflections collected	26788
Independent reflections	6561 [R(int) = 0.0891]
Max. and min. transmission	0.9003 and 0.8801
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6561 / 0 / 326
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0836
R indices (all data)	R1 = 0.0644, wR2 = 0.0915
Largest diff. peak and hole	0.661 and -0.964 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for DENNIS16.

Mo(1)-P(1)	2.5588(7)	Mo(1)-P(2)	2.5599(6)
Mo(1)-C(2)	1.968(3)	Mo(1)-C(4)	1.988(3)
Mo(1)-C(3)	2.021(3)	Mo(1)-C(1)	2.055(3)
P(1)-C(5)	1.867(2)	P(1)-C(13)	1.903(3)
P(1)-C(18)	1.908(3)	P(2)-C(12)	1.857(2)
P(2)-C(26)	1.899(3)	P(2)-C(21)	1.900(3)
O(1)-C(1)	1.148(3)	O(2)-C(2)	1.158(3)
O(3)-C(3)	1.152(3)	O(4)-C(4)	1.153(3)
C(5)-C(6)	1.502(4)	C(6)-C(7)	1.397(3)
C(6)-C(11)	1.405(3)	C(7)-C(8)	1.386(4)
C(8)-C(9)	1.386(4)	C(9)-C(10)	1.384(4)
C(10)-C(11)	1.385(4)	C(11)-C(12)	1.523(3)
C(13)-C(14)	1.534(4)	C(13)-C(15)	1.536(4)
C(13)-C(16)	1.556(4)	C(16)-C(17)	1.524(4)
C(16)-C(18)	1.567(4)	C(18)-C(20)	1.514(4)
C(18)-C(19)	1.526(4)	C(21)-C(23)	1.518(4)
C(21)-C(22)	1.522(3)	C(21)-C(24)	1.565(4)
C(24)-C(25)	1.519(4)	C(24)-C(26)	1.550(4)
C(26)-C(27)	1.533(3)	C(26)-C(28)	1.534(4)
C(2)-Mo(1)-C(4)	84.13(11)	C(2)-Mo(1)-C(3)	88.68(12)
C(4)-Mo(1)-C(3)	86.19(11)	C(2)-Mo(1)-C(1)	82.86(12)
C(4)-Mo(1)-C(1)	84.92(11)	C(3)-Mo(1)-C(1)	168.30(10)
C(2)-Mo(1)-P(1)	91.69(8)	C(4)-Mo(1)-P(1)	175.79(7)
C(3)-Mo(1)-P(1)	94.15(8)	C(1)-Mo(1)-P(1)	94.16(8)
C(2)-Mo(1)-P(2)	173.44(10)	C(4)-Mo(1)-P(2)	95.99(7)
C(3)-Mo(1)-P(2)	97.88(8)	C(1)-Mo(1)-P(2)	90.61(7)
P(1)-Mo(1)-P(2)	88.12(2)	C(5)-P(1)-C(13)	100.78(12)
C(5)-P(1)-C(18)	105.07(12)	C(13)-P(1)-C(18)	77.12(12)
C(5)-P(1)-Mo(1)	116.05(9)	C(13)-P(1)-Mo(1)	128.64(9)
C(18)-P(1)-Mo(1)	121.63(8)	C(12)-P(2)-C(26)	102.09(11)
C(12)-P(2)-C(21)	105.41(12)	C(26)-P(2)-C(21)	77.71(12)
C(12)-P(2)-Mo(1)	113.01(8)	C(26)-P(2)-Mo(1)	127.03(8)
C(21)-P(2)-Mo(1)	125.25(8)	O(1)-C(1)-Mo(1)	168.7(2)
O(2)-C(2)-Mo(1)	174.1(3)	O(3)-C(3)-Mo(1)	172.6(2)
O(4)-C(4)-Mo(1)	173.7(2)	C(6)-C(5)-P(1)	117.3(2)
C(7)-C(6)-C(11)	118.5(3)	C(7)-C(6)-C(5)	119.5(2)
C(11)-C(6)-C(5)	121.9(2)	C(8)-C(7)-C(6)	121.6(3)
C(9)-C(8)-C(7)	119.5(3)	C(10)-C(9)-C(8)	119.3(3)
C(9)-C(10)-C(11)	121.8(3)	C(10)-C(11)-C(6)	119.2(2)
C(10)-C(11)-C(12)	119.3(2)	C(6)-C(11)-C(12)	121.5(2)
C(11)-C(12)-P(2)	115.4(2)	C(14)-C(13)-C(15)	108.3(2)
C(14)-C(13)-C(16)	114.7(3)	C(15)-C(13)-C(16)	111.8(2)
C(14)-C(13)-P(1)	111.7(2)	C(15)-C(13)-P(1)	119.7(2)
C(16)-C(13)-P(1)	89.8(2)	C(17)-C(16)-C(13)	118.1(2)
C(17)-C(16)-C(18)	117.3(2)	C(13)-C(16)-C(18)	99.1(2)
C(20)-C(18)-C(19)	108.8(2)	C(20)-C(18)-C(16)	113.9(2)
C(19)-C(18)-C(16)	113.6(2)	C(20)-C(18)-P(1)	118.1(2)
C(19)-C(18)-P(1)	112.2(2)	C(16)-C(18)-P(1)	89.3(2)
C(23)-C(21)-C(22)	108.6(2)	C(23)-C(21)-C(24)	113.6(2)
C(22)-C(21)-C(24)	114.6(2)	C(23)-C(21)-P(2)	119.0(2)
C(22)-C(21)-P(2)	111.0(2)	C(24)-C(21)-P(2)	89.2(2)
C(25)-C(24)-C(26)	117.0(2)	C(25)-C(24)-C(21)	118.1(2)
C(26)-C(24)-C(21)	99.8(2)	C(27)-C(26)-C(28)	108.5(2)
C(27)-C(26)-C(24)	114.6(2)	C(28)-C(26)-C(24)	113.0(2)
C(27)-C(26)-P(2)	111.4(2)	C(28)-C(26)-P(2)	118.9(2)
C(24)-C(26)-P(2)	89.7(2)		



Dennis 15.

Table 1. Crystal data and structure refinement for DENNIS15.

Empirical formula	C13 H12 Cr O3
Formula weight	268.23
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 8.1008(2) A alpha = 90 deg. b = 11.0168(4) A beta = 103.840(2) deg. c = 13.2324(3) A gamma = 90 deg.
Volume	1146.64(6) A^3
Z	4
Density (calculated)	1.554 Mg/m^3
Absorption coefficient	0.989 mm^-1
F(000)	552
Crystal size	0.15 x 0.12 x 0.10 mm
Theta range for data collection	3.18 to 27.48 deg.
Index ranges	-10<=h<=10, -13<=k<=14, -15<=l<=16
Reflections collected	10621

Independent reflections	2606 [R(int) = 0.0445]
Max. and min. transmission	0.9076 and 0.8658
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2606 / 0 / 154
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0726
R indices (all data)	R1 = 0.0415, wR2 = 0.0767
Largest diff. peak and hole	0.352 and -0.427 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for DENNIS15.

Cr(1)-C(1)	1.836(2)	Cr(1)-C(3)	1.838(2)
Cr(1)-C(2)	1.839(2)	Cr(1)-C(4)	2.208(2)
Cr(1)-C(5)	2.216(2)	Cr(1)-C(7)	2.216(2)
Cr(1)-C(6)	2.220(2)	Cr(1)-C(8)	2.247(2)
Cr(1)-C(9)	2.258(2)	O(1)-C(1)	1.158(2)
O(2)-C(2)	1.160(2)	O(3)-C(3)	1.155(3)
C(4)-C(5)	1.398(3)	C(4)-C(9)	1.429(3)
C(5)-C(6)	1.410(3)	C(6)-C(7)	1.395(3)
C(7)-C(8)	1.427(3)	C(8)-C(9)	1.403(3)
C(8)-C(13)	1.507(3)	C(9)-C(10)	1.515(3)
C(10)-C(11)	1.531(3)	C(11)-C(12)	1.520(3)
C(12)-C(13)	1.520(3)		

C(1)-Cr(1)-C(3)	89.13(9)	C(1)-Cr(1)-C(2)	88.20(8)
C(3)-Cr(1)-C(2)	90.71(9)	C(1)-Cr(1)-C(4)	90.40(8)
C(3)-Cr(1)-C(4)	152.26(8)	C(2)-Cr(1)-C(4)	117.00(8)
C(1)-Cr(1)-C(5)	117.36(8)	C(3)-Cr(1)-C(5)	153.46(8)
C(2)-Cr(1)-C(5)	91.56(8)	C(4)-Cr(1)-C(5)	36.85(8)
C(1)-Cr(1)-C(7)	152.42(7)	C(3)-Cr(1)-C(7)	89.74(8)
C(2)-Cr(1)-C(7)	119.37(8)	C(4)-Cr(1)-C(7)	78.14(7)
C(5)-Cr(1)-C(7)	66.26(8)	C(1)-Cr(1)-C(6)	154.41(8)
C(3)-Cr(1)-C(6)	116.42(9)	C(2)-Cr(1)-C(6)	92.62(8)
C(4)-Cr(1)-C(6)	66.50(8)	C(5)-Cr(1)-C(6)	37.06(8)
C(7)-Cr(1)-C(6)	36.65(7)	C(1)-Cr(1)-C(8)	115.13(7)
C(3)-Cr(1)-C(8)	88.94(8)	C(2)-Cr(1)-C(8)	156.66(8)
C(4)-Cr(1)-C(8)	66.29(7)	C(5)-Cr(1)-C(8)	78.76(7)
C(7)-Cr(1)-C(8)	37.30(7)	C(6)-Cr(1)-C(8)	66.86(7)
C(1)-Cr(1)-C(9)	89.47(7)	C(3)-Cr(1)-C(9)	114.95(8)
C(2)-Cr(1)-C(9)	154.19(8)	C(4)-Cr(1)-C(9)	37.30(7)
C(5)-Cr(1)-C(9)	66.89(7)	C(7)-Cr(1)-C(9)	66.20(7)

C(6)-Cr(1)-C(9)	78.79(7)	C(8)-Cr(1)-C(9)	36.30(7)
O(1)-C(1)-Cr(1)	179.30(16)	O(2)-C(2)-Cr(1)	178.09(17)
O(3)-C(3)-Cr(1)	178.30(19)	C(5)-C(4)-C(9)	121.46(18)
C(5)-C(4)-Cr(1)	71.91(11)	C(9)-C(4)-Cr(1)	73.25(11)
C(4)-C(5)-C(6)	119.68(18)	C(4)-C(5)-Cr(1)	71.25(11)
C(6)-C(5)-Cr(1)	71.63(11)	C(7)-C(6)-C(5)	119.45(18)
C(7)-C(6)-Cr(1)	71.51(11)	C(5)-C(6)-Cr(1)	71.31(11)
C(6)-C(7)-C(8)	121.38(18)	C(6)-C(7)-Cr(1)	71.83(11)
C(8)-C(7)-Cr(1)	72.51(10)	C(9)-C(8)-C(7)	119.36(17)
C(9)-C(8)-C(13)	121.21(16)	C(7)-C(8)-C(13)	119.43(17)
C(9)-C(8)-Cr(1)	72.28(10)	C(7)-C(8)-Cr(1)	70.19(10)
C(13)-C(8)-Cr(1)	129.33(13)	C(8)-C(9)-C(4)	118.64(17)
C(8)-C(9)-C(10)	122.26(17)	C(4)-C(9)-C(10)	119.10(17)
C(8)-C(9)-Cr(1)	71.42(10)	C(4)-C(9)-Cr(1)	69.44(10)
C(10)-C(9)-Cr(1)	130.14(13)	C(9)-C(10)-C(11)	113.29(16)
C(12)-C(11)-C(10)	111.28(16)	C(11)-C(12)-C(13)	109.96(17)
C(8)-C(13)-C(12)	112.07(16)