The Synthesis of Aminomethylphosphines, Their Metal Complexes and Their Use in Homogeneous Catalysis

A Thesis submitted
by

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Dedicated to Mum and Dad
for all their support

ABSTRACT

Chapter 1 reviews the literature concerning synthetic routes to aminomethylphosphines and studies of their reactivity together with a brief review of related aminoethylphosphines and isostructural tertiary phosphine analogues to aminomethylphosphines.

The preparation and characterisation of the phosphonium salts $[R_2P(CH_2OH)_2]^+X^-$ (R = Ph, Cy, C_8H_{14}; X^- = Cl^-, HSO_4^-) and the preparation and characterisation of aminomethylphosphines are presented in Chapter 2. Treatment of the mixed isomers of the salt $[C_8H_{14}P(CH_2OH)_2]^+X^-$ in boiling sulphuric acid gives the 3,3,1 isomer by decomposition of the 4,2,1 isomer. The X-ray crystal structure of $[Ph_2P(CH_2OH)_2]^+Cl^-$ shows hydrogen bonding between the hydroxyl groups and chlorine anion. Treatment of the reported phosphonium salts with triethylamine and a primary or secondary amine gave aminomethylphosphines in good yields. The ^1H, ^{13}C and ^{31}P n.m.r. spectra are reported for all important aminomethylphosphines. The novel nature of the ^1H n.m.r. signals for the methylene protons, in the PCH_2N link of these phosphines have been investigated using two-dimensional (^{31}P-^1H) (HSC) n.m.r. and variable temperature n.m.r. spectra. The X-ray crystal structure of $(Cy_2PCH_2)_2NCHMePh$ reveals the bulky nature of the phosphine and the relationship between the methylene protons and phosphorus in the solid state.

In Chapter 3 a variety of transition metal complexes have been prepared using aminomethylphosphines of the type $(R_2PCH_2)_2NR'$ reported in Chapter 2. The preparation and characterisation of cis platinum(II), palladium(II) and nickel(II) dichloride complexes is described together with the X-ray crystal structure of cis-$[PdCl_2(Ph_2PCH_2)_2NCH_2CH_2OH]$ which shows the phosphine in a six-membered chelate chair conformation. Cobalt(II) dichloride, and molybdenum(0) and tungsten(0) tetracarbonyl complexes of the bis-aminomethylphosphines are also prepared and characterised. Treatment of $[Rh(COD)Cl]_2$ with a phosphine in the presence of KPF_6 gave hydrogenation catalyst precursors of the type $[Rh(COD)(R_2PCH_2)_2NR']PF_6$ in good yields. Treatment of the cis-Pt(II) aminomethylphosphine complexes with $SnCl_2$ gave $[PtCl(SnCl_3)(R_2PCH_2)_2NR']$ complexes which displayed poor solubility. Reactions of the phosphine $(Cy_2PCH_2)_2NCHMePh$ with various metal complexes have been investigated, as have some reactions of Pt(II) dichloride, diphosphine complexes.

The last Chapter investigates the use of Rh(I) and Pt(II) aminomethylphosphine complexes in catalytic hydrogenation and hydroformylation. The catalytic hydrogenation of α-acetamidocinnamic acid using $[Rh(COD)(R_2PCH_2)_2NR']^+PF_6^-$ catalyst precursors at 1.1 atmospheres of H_2, gave N-acetylphenylalanine in good yields but only as racemic mixtures. The hydroformylation of styrene at 100 atmospheres of CO/H_2 and at 60°C using a $[PtCl_2(R_2PCH_2)_2NR'] + SnCl_2$ catalyst system gave low yields of 2-phenylpropanal with optical inductions of up to 31% and high branched to chain product ratios, up to 36:1. Phosphines with R = Cy showed no reaction and phosphines with R = C_8H_{14} gave better yields but higher ratios of 3-phenylpropanal (chain product).

ACKNOWLEDGEMENTS

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1986 and December 1989, under the supervision of Dr. R. D. W. Kemmitt.

The work has not been, and is not concurrently being presented for any other degree.

Date: 11th July 1990 Signed: D. J. Lees

ABBREVIATIONS AND SYMBOLS

General and Physical

Å	-	Angström unit
atm	-	Atmospheres (pressure)
br	-	Broad
°C	-	Centigrade
δ	-	Chemical shift
cm^3	-	Cubic centimetres
(°)	-	Degrees
d	-	Doublet
g	-	Gramme
Hz	-	Hertz
h	-	Hour
i.r.	-	Infrared
K	-	Kelvin
M^+	-	Molecular ion (Mass spec.)
m	-	Multiplet (n.m.r.)
MHz	-	Megahertz
M.p.	-	Melting point
mmole	-	Millimole
mmHg	-	Millimetres of mercury
Min	-	Minute
n.m.r.	-	Nuclear magnetic resonance
p.p.m.	-	Parts per million
p.s.i.	-	Pounds per square inch
$\{^1H\}$	-	Proton decoupled
q	-	Quartet
sh	-	Shoulder
s	-	Singlet
t	-	Triplet
cm^{-1}	-	Wavenumber

ABBREVIATIONS AND SYMBOLS (Continued) ....

Chemical

Ar	-	Aryl
^{t}Bu	-	tertiary-Butyl
Cy	-	Cyclohexyl
COD	-	cis,cis-Cyclo-octa-1,5-diene
D	-	Deuterium
DBA	-	Dibenzylideneacetone (1,5-diphenyl-1,4-pentadien-3-one)
dppe	-	1,2 Bis-(diphenylphosphino)ethane
dppp	-	1,3 Bis-(diphenylphosphine)propane
Et	-	Ethyl
DIOP	-	2,3-O-Isopropylidene-2,3-dihydroxy-1,4 bis(diphenylphosphino)-butane
DBP-DIOP	-	2,3-O-Isopropylidene-2,3-dihydroxy-1,4 bis(dibenzophosphole)-butane
Me	-	Methyl
NBD	-	2,5 Norbornadiene; (Bicyclo[2,2,1] hepta-2,5 diene)
Ph	-	Phenyl
pip	-	Piperidine
Py	-	Pyridine
^{i}Pr	-	iso-Propyl
THF	-	Tetrahydrofuran

CONTENTS

CONTENTS (Continued) ....

CHAPTER 1

Synthesis and Reactions of Aminomethylphosphines

1.1 Introduction

Aminomethylphosphines have been known for some 30 years since the discovery by Coates and Hoye[1] that hydroxymethylphosphines react with primary and secondary amines to give aminomethylphosphines. These compounds were being investigated at this time with a view to utilising them as flame retardants for fabrics, and there is a report that in the early 1950's[2] Reeves and Guthrie reacted a tetrahydroxymethylphosphonium salt, $P^{+}(CH_2OH)_4Cl^{-}$ (THPC) with an aminoethylated cotton fabric, thus creating a P-C-N linkage by elimination of water.

Scheme 1

$$\text{Cotton-OCH}_2\text{CH}_2\text{NH}_2 + \text{HOCH}_2\text{P}^{+}(\text{CH}_2\text{OH})_3\text{Cl}^{-} \xrightarrow{-\text{H}_2\text{O}} \text{Cotton-OCH}_2\text{CH}_2\text{NH-CH}_2\text{P}^{+}(\text{CH}_2\text{OH})_3\text{Cl}^{-}$$

Being chemically bonded to the fabric, this compound acted as a flame retardant that could not be removed even when boiled in water. Interest in this area has continued,[3] and more recently aminomethylphosphines with hydrophilic substituents on nitrogen have also been used successfully as metal sequestrants,[4,5] particularly with a view to water treatment.

Since the early 1960's aminomethylphosphine chemistry has been studied mainly from a synthetic aspect and a large range of compounds,[6] over 200 to date, have been reported. From the synthetic routes available it has been shown that many varied compounds can be prepared with the possibility of incorporating a multitude of functional groups. Variations of substituents at phosphorus, nitrogen, and carbon, in the P-C-N 'backbone', have all been investigated. Mono, bi, tri and tetradentate aminomethylphosphine ligands have been prepared,[7] and also cage structure compounds have been reported.[8]

A wide range of optically active derivatives have been synthesised with chiral centres at phosphorus[9] and various substituents on nitrogen.[10,11] The main two contributors in the latter area, Markl & Jin, and Kellner & Tzshach, have prepared nearly 50% of the aminomethylphosphine compounds reported in the literature. A review by Kellner & Tzshach[12] summarises

some of the developments in aminoalkylphosphine chemistry, and contains many references. However, details of the characterisation of many aminomethylphosphines remains sketchy, with rarely more than a m.p or b.p and a proton n.m.r. spectrum being reported.

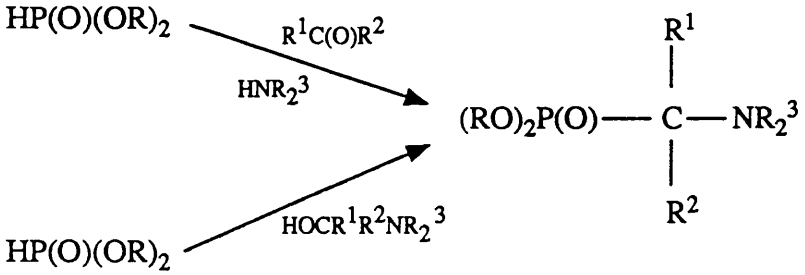
Aminomethylphosphines as ligands in transition-metal complexes is an area that has hardly been investigated, with only a few metal carbonyl-phosphine complexes being reported. Again characterisation details are few and only two crystal structures have appeared to date.[13,41]

This first chapter covers the development of aminomethylphosphine chemistry, reviewing different synthetic routes, reactivity studies, and also novel and analogous compounds. Metal complexes of aminomethylphosphines will be discussed independently in Chapter 3.

1.2 Synthesis of Aminomethylphosphines by a Modified Mannich Reaction

Aminomethylphosphines have the general formula $R_{(4-n)}P(CH_2NR'R'')_{(n-1)}$ (R' and R = alkyl or aryl; R'' = H, alkyl or aryl). An early reported synthesis[14] of aminoalkylphosphorus compounds involved the treatment of a phosphorus acid diester with an α-alkanolamine or an aldehyde or ketone plus an amine. These give the corresponding substituted aminophosphonic acids *(1)*, Scheme 2.

Scheme 2



R = Me, Et; R^1 = H, Me; R^2 = H, Me, Et, Ph, Pr; R^3 = Me, Et, Bu, ^{i}Pr, Cy.

This was the first report of a reaction of a P-H bond with a carbonyl group and an amine in a modified Mannich reaction to form a P-C-N linkage.

The first reported synthesis of aminomethylphosphines by Coates and Hoye[1] involved treating tetrahydroxymethylphosphonium chloride (THPC) *(2)* with four mole equivalents of a secondary amine to give a tris-(dialkylaminomethylphosphine). Average yields reported were around 76-83% showing this to be an efficient route to a variety of tertiary phosphines, Scheme 3.

Scheme 3

$$P^+(CH_2OH)_4Cl^- + 4R_2NH \longrightarrow P(CH_2NR_2)_3 \ (3) + 3H_2O + HCHO + R_2\overset{+}{N}H_2Cl^-$$

R = Et, yield = 82%

Simple modifications involve the use of a non-nucleophilic base such as triethylamine to remove the HCl and liberate the hydroxymethylphosphine from the phosphonium salt. This route is still regarded as the most simple and effective synthetic route into aminomethylphosphines.

Aminomethylphosphines may also be prepared by reaction of PH_3, RPH_2 or R_2PH in a single pot reaction with formaldehyde and a primary or secondary amine,[15] Scheme 4.

Scheme 4

$$RR^1NH + HCHO \xrightarrow[+H^+]{-H_2O} RR^1N^+ = CH_2 \xrightarrow{PH_3} P(CH_2NRR^1)_3 \quad (4)$$

R = H, Alkyl, Aryl; R^1 = H, Alkyl, Aryl

The first reported ^1H n.m.r. spectrum of an aminomethylphosphine was obtained for $P(CH_2NEt_2)_3$ *(3)* by Mavel and Martin.[16] Much of the work by Coates and Hoye concentrated on synthesis of phosphines of the formula $P(CH_2NR_2)_3$ using THPC *(2)* as the starting material. This work was extended to Petrov[17] who reacted diethylamine with $P(CH_2OH)_3$, $PrP(CH_2OH)_2$ and $Pr_2P(CH_2OH)$ respectively to yield the corresponding phosphines, $P(CH_2NEt_2)_3$ *(5)*, $PrP(CH_2NEt_2)_2$ *(6)* and $Pr_2PCH_2NEt_2$ *(7)*. Petrov also treated $PhPH_2$ with $CH_2(NEt_2)_2$ at 140° for 1.5h to give $PhP(CH_2NEt_2)_2$ *(8)* in an 80% yield, previously reported by Coates and Hoye.[15]

The first bis(aminomethylphosphine) reported came from Maier at Monsanto.[18] Diprimary α,ω-bis-phosphinoalkanes were treated with four moles of formaldehyde and a secondary amine to give α,ω-bis (bis-dialkyl-aminomethylphosphiroalkanes) with yields of 63-93%, Scheme 5. Infrared, ^{1}H n.m.r. and ^{31}P n.m.r. spectra were reported, but in the ^{1}H n.m.r. spectrum the signal in the P-CH_2 region was too broad to be interpreted.

Scheme 5

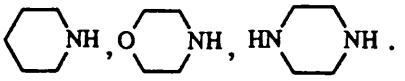
$$H_2P(CH_2)_nPH_2 + HCHO + HNEt_2 \xrightarrow{-H_2O} (Et_2NCH_2)_2P(CH_2)_nP(CH_2NEt_2)_2 \quad (9)$$

$n = 1$ to 4

Maier then extended this work with reaction of hypophosphorus acid with formaldehyde and a secondary amine.[19] A variety of amines were used and some novel compounds were made, Scheme 6.

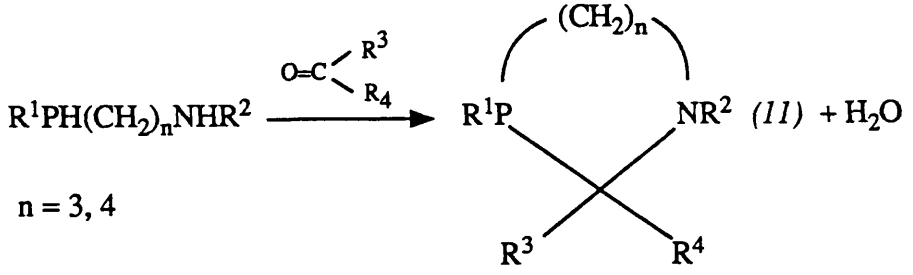
Scheme 6

$$R_2NH + HCHO \xrightarrow[+H^+]{-H_2O} R_2N^+{=}CH_2 \xrightarrow{H_3PO_2} R_2NCH_2P(O)(H)(OH) \quad (10)$$

$R_2NH = Et_2NH,$  .

Work by Issleib showed that β-aminoethylphosphines and γ-aminopropyl-phosphines could be reacted with aldehydes or ketones to form 5- and 6-membered heterocycles containing a P-C-N linkage,[20,21] Scheme 7.

Scheme 7



$n = 3, 4$

$R^1, R^4 = H$, alkyl, aryl; $R^2, R^3 = H$, alkyl

The incorporation of aminoacids into aminomethylphosphines was first investigated by Carlson for the Hooker Chemical Corporation.[4] Glycine and other aminocarboxylic acids were treated with THPC *(2)* under alkaline

conditions. The reaction was carried out at a pH range of 10.5 to 11.5 to ensure complete ionisation of the aminocarboxylic acid. At lower pH values the reaction terminates due to protonation of the amino acid. Two examples of these compounds are shown in Scheme 8.

Scheme 8

$$P\left(CH_2N\begin{matrix}CH_2CO_2R\\CH_2CO_2R\end{matrix}\right)_3 \quad (12) \qquad P(CH_2NHCH_2CO_2R)_3 \quad (13) \qquad R = H, Na$$

These compounds, as mentioned previously, were shown to be successful sequestering reagents for metals, typically, iron, copper, aluminium, tin and lead.

Acetoxymethylphosphines have been reported as precursors for hydroxymethylphosphines used in the preparation of aminomethylphosphines.[22] Action of potassium hydroxide in aqueous alcohol on acetoxymethylphosphines gives the corresponding hydroxymethylphosphines which react *in situ* with secondary amines (3-4h, 70°C) to give aminomethylphosphines, Scheme 9.

Scheme 9

$$R_nP(CH_2OCOMe)_{(3-n)} \xrightarrow[R_2NH]{KOH,\ MeOH/H_2O} R_nP(CH_2NR_2)_{(3-n)}$$

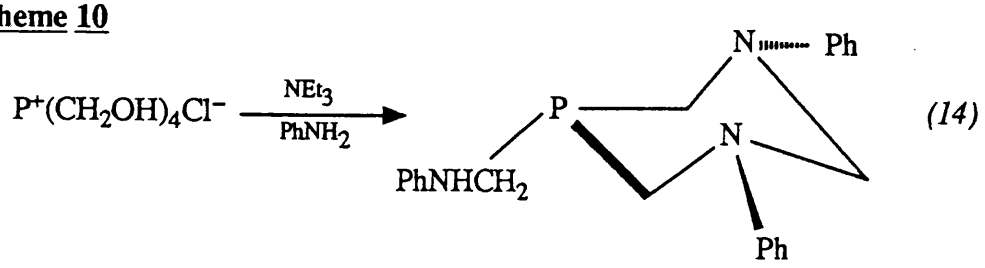
$n = 0, 1, 2;\quad R = Me, Et, Pr, Bu.$

The reaction of THPC *(2)* with aniline in the presence of triethylamine reported by Frank and Drake,[23] gave a novel 6-membered heterocycle *(14)*, Scheme 10. The formaldehyde released by the neutralisation of *(2)* with triethylamine evidently proceeds to react and link two secondary amino groups of the tris (aminomethylphosphine). This was confirmed when isolated tris (hydroxymethylphosphine treated with aniline gave only the tris (aminomethylphosphine).

Rapid inversion of the ring and at the N atoms allows two stable chair conformations of *(14)* to exist. This allows the substituent on phosphorus to be axial or equatorial. ^1H n.m.r. studies of the $PC\underline{H}_2N$ protons

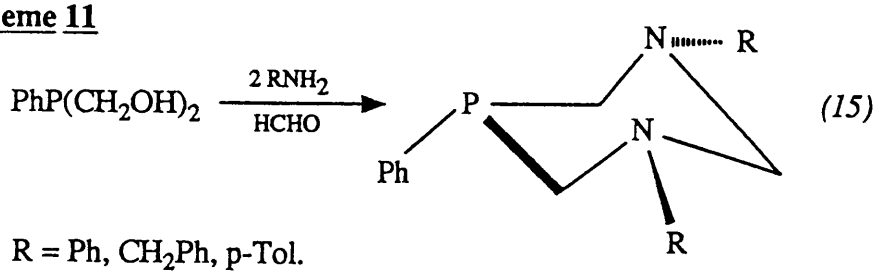
suggested that the substituent was equatorial and the lone pair axial. This was confirmed by studies of the ^1H n.m.r. spectra of similar compounds by Arbuzov, Erastov and Nikonov.[24] They had taken bis (hydroxymethyl)-phenylphosphine and treated it with primary aryl and benzyl-amines in the presence of formaldehyde,[25] Scheme 11.

Scheme 10



(14)

Scheme 11

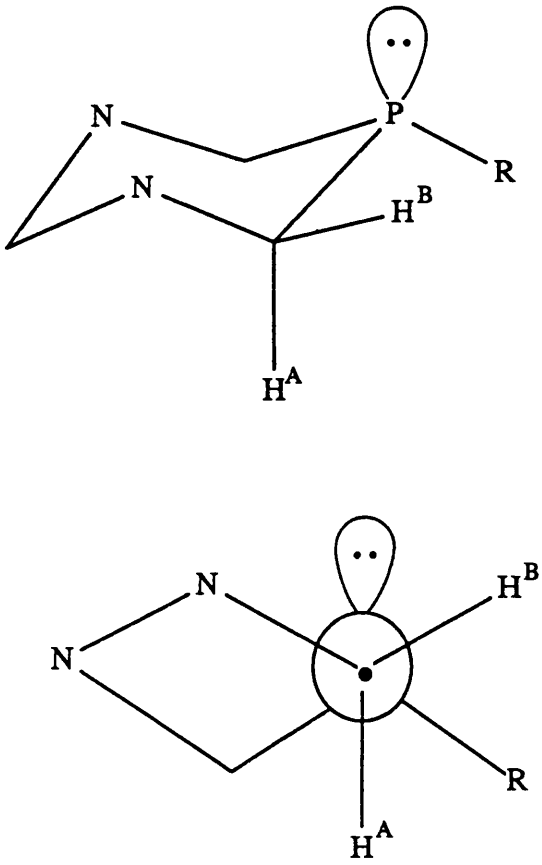


(15)

R = Ph, CH_2Ph, p-Tol.

The analysis of the $PC\underline{H}_2N$ signal in the ^1H n.m.r. spectrum by Arbuzov *et al.*, showed an ABX pattern in which there was a significant difference in the J(PH) coupling between the A and B protons, Figure 1. The low value for the $J(PH^A)$ coupling indicated that a lone pair to H^A eclipsing angle of a 180° was required, and this could only be satisfied if the lone pair was axial. The stable conformation of these heterocycles was therefore confirmed.

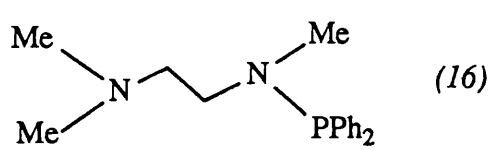
Aminomethylphosphines have been prepared as polydentate phosphorus-nitrogen ligands by Grim and Matienzo.[26,27] The reaction of N and/or N′, mono, bi or tri, methylenediamine or ethylenediamine with formaldehyde and diphenylphosphine at 60° for 1½ hours yields four different polydentate aminomethylphosphine ligands *(16)*, *(17)*, *(18)*, *(19)*, Figure 2. Later work[7] on the coordination chemistry of these ligands in Mo, W and Cr



R = CH_2NHPh, Ph

If the P lone pair was in the position of R (equatorial) then the reported coupling constants would not be observed.

Figure 1



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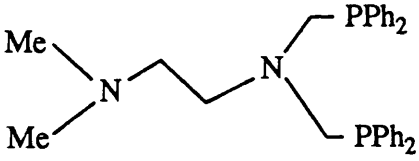
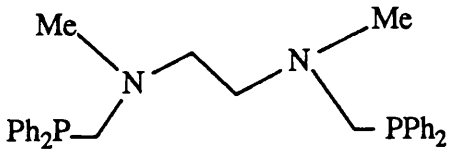
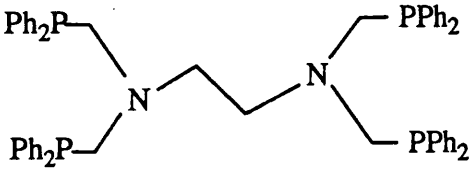


(17)



(18)



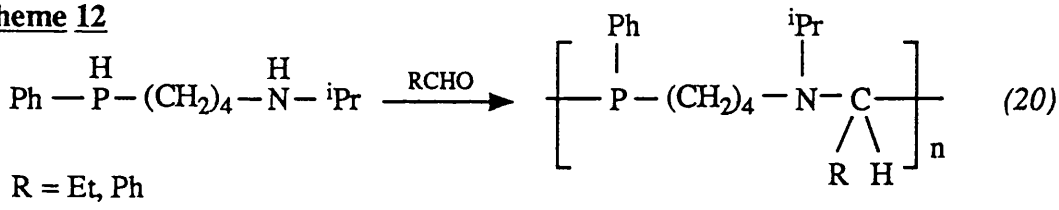
(19)

Figure 2

carbonyl complexes showed that only phosphorus coordination took place.

Extension of earlier work on aminoalkylphosphine-heterocycles by Issleib *et al.*[28] has shown that high molecular weight polymers can be formed depending on the starting materials and the stoichiometry. The reaction of aminobutyl-phenylphosphines with aldehydes or ketones generally give 7-membered heterocycles in low yield from an intramolecular Mannich reaction. However, reaction of isopropylaminobutylphenylphosphine with propionaldehyde or benzaldehyde gives an intermolecular polycondensation product *(20)*, Scheme 12.

Scheme 12



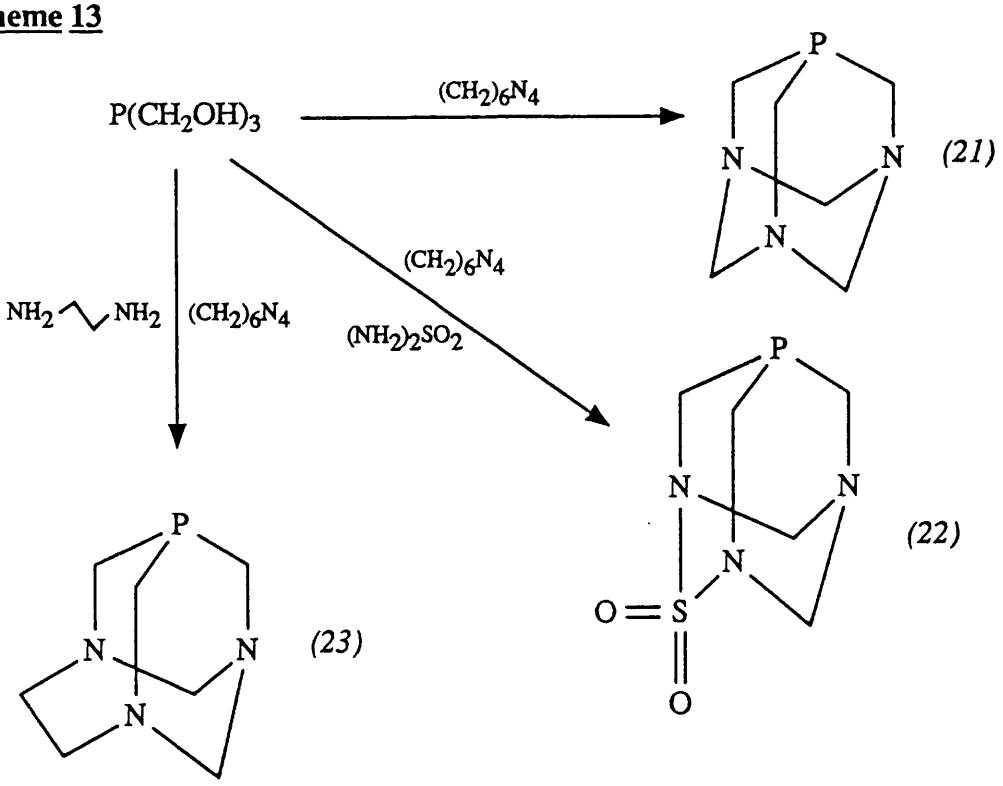
(20)

Novel tricyclic compounds have been synthesised[29-31] by the reaction of neutralised THPC *(2)* with hexamethylenetetramine, or an ammonia/ formaldehyde mixture. Addition of primary amines allowed the introduction of various substituents into the tricyclic-heterocycle. It is not surprising that polymeric materials were also isolated from these reactions, since there is the possibility of intermolecular condensations taking place. However, yields of the heterocycles of up to 66% were reported, Scheme 13.

The potential of the Mannich reaction as a good synthetic route to a variety of tertiary phosphines was fully recognised by the work of Markl and Yu Jin.[9,32-35] A large range of primary and secondary phosphines, and primary, secondary, and bis amines as starting materials have been covered. No attempt is made here to describe all the compounds made, but a number of interesting aminomethylphosphines are illustrated in Scheme 14.

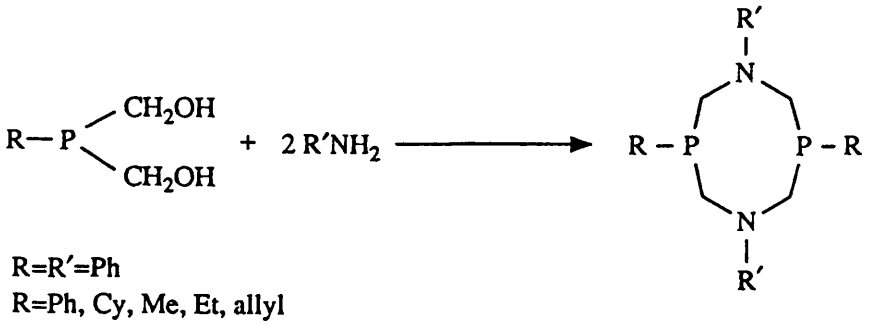
In many of the compounds reported, chiral centres have been incorporated at both phosphorus, using phosphines of the type R^1R^2PH, and by using

Scheme 13



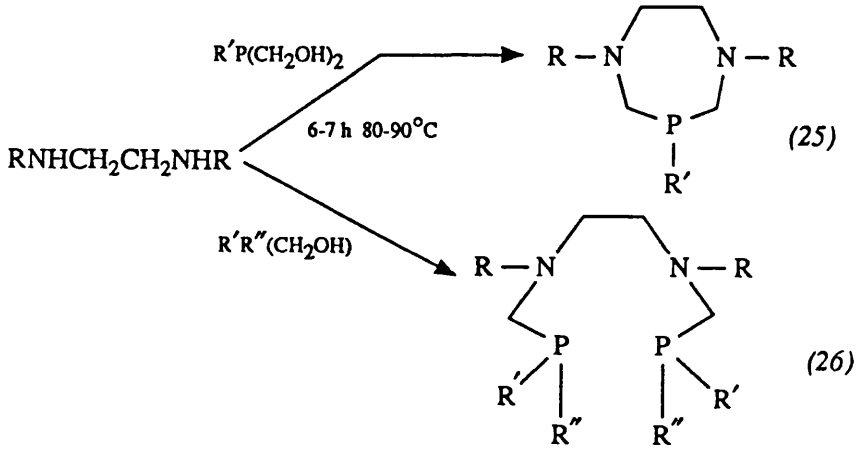
chiral amines, and aminoacid esters, e.g. (+) or (-) α-methylbenzylamine or L(-) alanine ethylester. Many of the bis-phosphines, such as *(24)*, *(26)*, *(27)*, *(28)* and *(29)*, have had their coordination chemistry investigated briefly with Mo and Ni carbonyl complexes. Actual experimental details of the phosphine synthesis are notable by their absence, but long reaction times and high temperatures, (up to 10h and 120°) were required. Most of the compounds were obtained as solids in 26-93% yield with melting points of 130-200°C.

No ^{31}P n.m.r. spectra or elemental analysis are given but ^{1}H n.m.r. data for many of the compounds were quoted. The $PC\underline{H}_2N$ signal in the ^{1}H n.m.r. spectra proved to be of interest. In heterocycles such as *(24)*, *(25)* and *(27)*, the protons appear as an ABX pattern, generally with $J(PH^A) > J(PH^B)$. Interpretation of these results has led to conformational assignments being made for the different possible invertomers of these compounds. The ABX pattern for the $PC\underline{H}_2N$ signal is also found in non-cyclic compounds, e.g. *(28)*, where there is a chiral carbon centre

1. 

(24)

R=R′=Ph
R=Ph, Cy, Me, Et, allyl
R′=p-Tol, Ph, (+) and (-) CHMePh

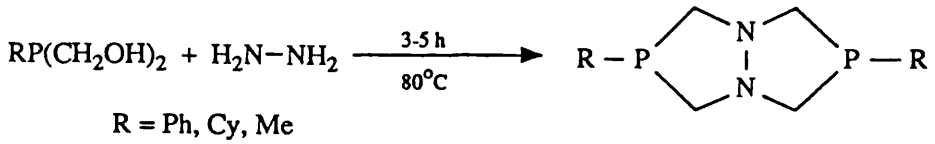
2. 

(25)

R = (+) or (-) CHMePh
R′ = Ph, Cy, Et, Me

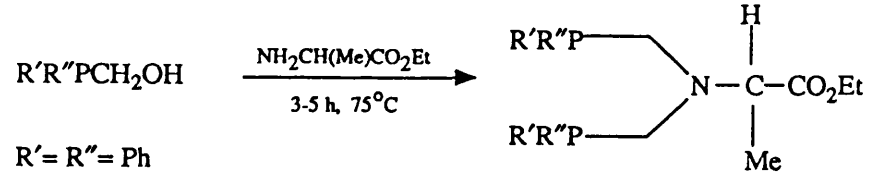
(26)

R = (+) or (-) CHMePh
R′ = Ph
R″= p-Cl-Ph, p-F-Ph

3. 

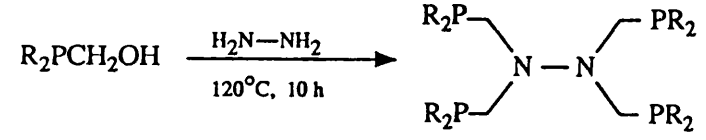
(27)

R = Ph, Cy, Me

4. 

(28)

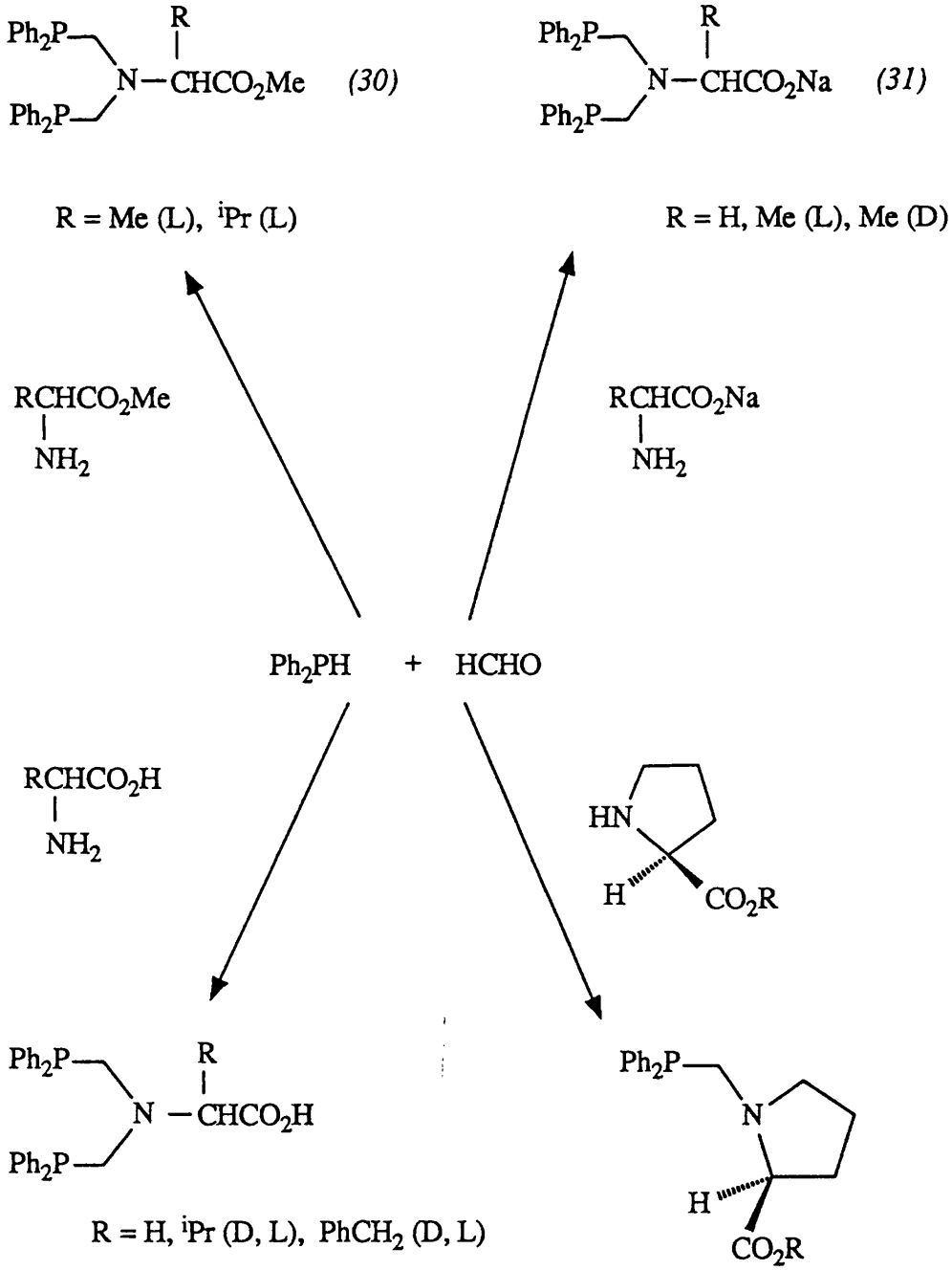
R′= R″= Ph
R′= Ph; R″= p-F-Ph, p-Tol

5. 

Scheme 14

attached to nitrogen, although values for J(PH) couplings were not reported.

The reactions of chiral amines with formaldehyde and secondary phosphines were extended by Kellner and Tzshach.[10,36,37] A range of amino acid derivatives were taken, e.g. sodium salts, free acids, esters and hydrochloride salts, to produce a series of N,N-bis(phosphinomethyl)amino acid derivatives, shown in Scheme 15.

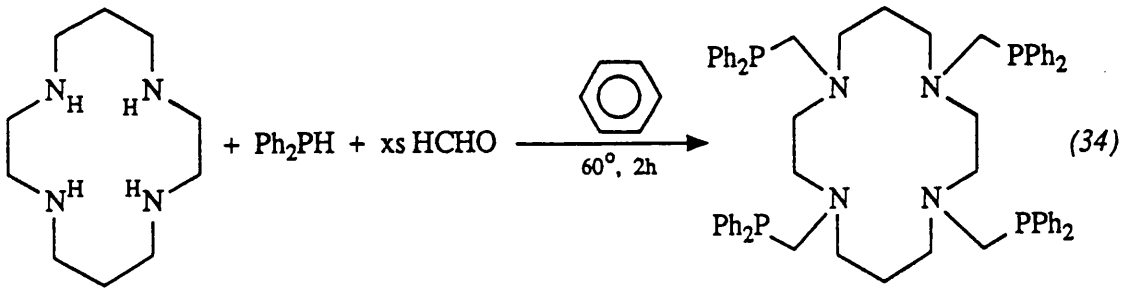


Scheme 15

Amino acids used included glycine, valine, alanine and phenylalanine. Purification of the products was difficult as they formed highly viscous undistillable oils, although it was proposed that preparation of silylester hydrochloride derivatives would give crystallisable products. These bis-phosphine ligands were then investigated with rhodium catalysts in asymmetric hydrogenation reactions with poor success. Asymmetric induction was observed but the optical yields were found to be independent of the aminoacid substituents present.[38]

The first crystal structure of an aminomethylphosphine came from the work of Power *et al.*[39] In their investigation of macrocyclic polyhetero ligand systems, the macrocycle cyclam was refluxed in benzene with excess formaldehyde and diphenylphosphine to give *(34)* in a 70% yield, Scheme 16.

Scheme 16



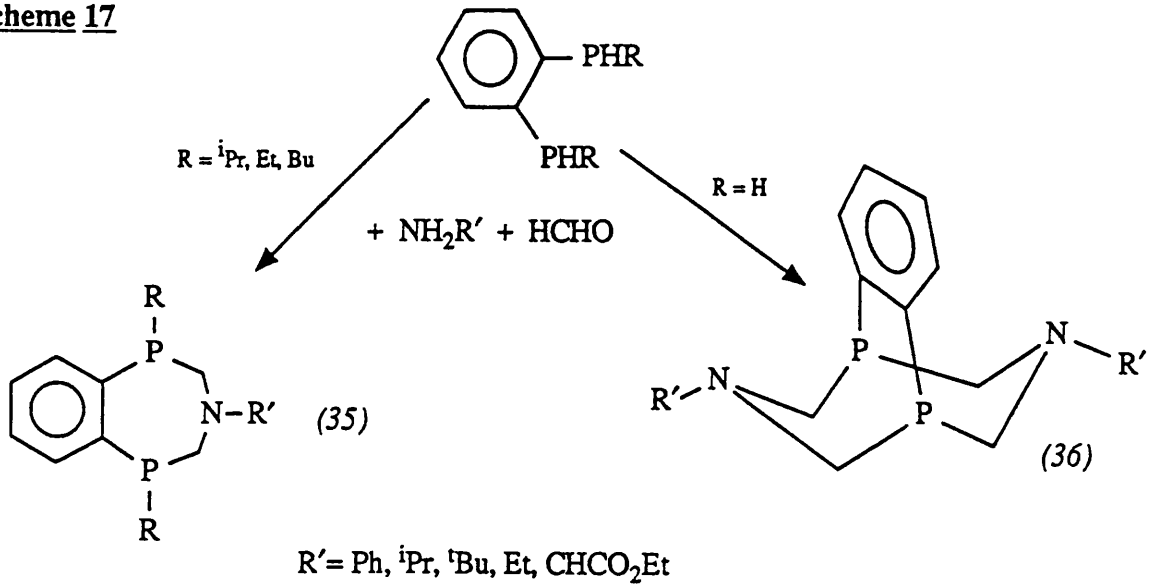
(34)

Compound *(34)* was isolated as colourless, air stable crystals when cooled at -20°C in ethanol. It was noted that this preparation could be extended to a number of other macrocycles containing N-H bonds.

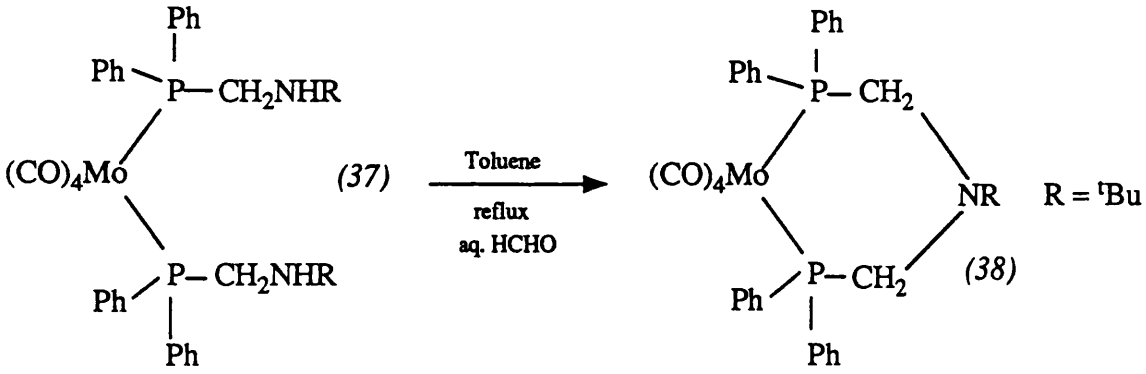
The aminomethylation of o-phenylenediphosphines has been studied by Issleib[40] to give a range of novel heterocycles in 52-78% yields, *(35)*, *(36)*, Scheme 17.

Very recently a bis-aminomethylphosphine has been synthesised, from metal coordinated mono-aminomethylphosphines, in quantitative yield,[41] Scheme 18.

Scheme 17



Scheme 18

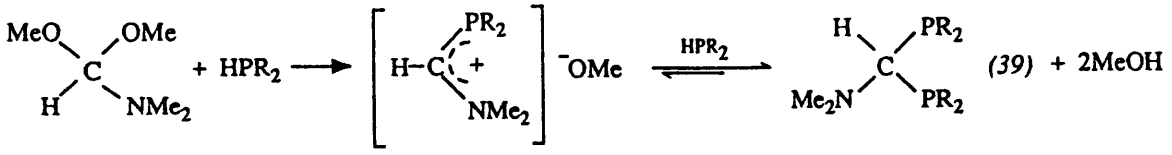


1.3 Synthesis of Aminoalkylphosphines by Other Condensation Reactions

Other simple condensation reactions leading to P-C-N type tertiary phosphines can be generally regarded as pseudo Mannich reactions. Issleib[42] treated a phosphine RPH_2 with N-hydroxymethyl(diethylamine) to give $RP(CH_2NEt_2)_2$ as the condensation product. This showed that reaction *via* hydroxymethylphosphines was not the only efficient route to amino alkylphosphines. This reaction and variations of it were also investigated by Maier[43] using both diphenylphosphine and diphenylphosphine oxide as the starting materials.

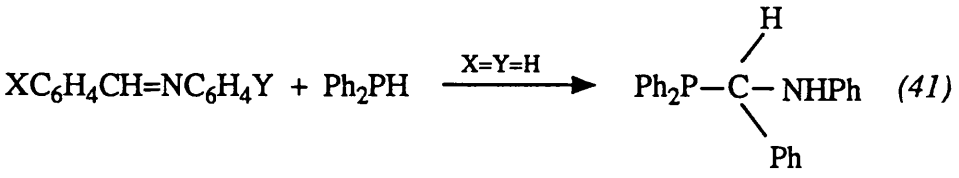
An extension of this previous work has shown that acetals could also be used, *via* elimination of alcohols,[44] to give compounds such as *(39)*, Scheme 19.

Scheme 19



Phosphines with active P-H bonds can react directly with imines to form aminomethylphosphines. Thus Issleib[45] found that treatment of diethylphosphine with N-methylidene-t-butylamine gave $Et_2PCH_2NH^tBu$ *(40)* in an 82% yield. In this example the product was treated with formaldehyde and further diethylphosphine to give the bis-phosphine $(Et_2PCH_2)_2N^tBu$. This reaction was also investigated by Pudovick *et al.*[46] using N-benzylidene-methylamine and various N-aryl substituted imines. Further investigation of this work[47] utilising Schiff bases of the general formula $XC_6H_4CH{=}NC_6H_4Y$ led to a series of α-aminobenzylphosphines *(41)*, Scheme 20, but no reference to any preferred chirality at the P-C-N carbon was made. Thus it must be assumed that only racemic mixtures were synthesised.

Scheme 20



Routes to aminomethylphosphines, *via* the Mannich reaction using hydroxymethylphosphonium salts, hydroxymethylphosphines or phosphines and formaldehyde, generally all require aqueous or protic reaction media. However, it has been shown that diphenylhydroxymethyl phosphine can be isolated as a solid and will react rapidly with amines in non-aqueous solvents.[48] Soviet workers[49,50] have extended earlier work by Issleib[44]

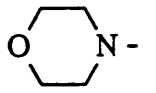
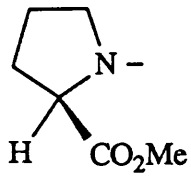
with some success to provide a non-aqueous route to aminomethylphosphines. These compounds have been synthesised in good yields, 63-95%, by the direct reaction of tetraalkyldiaminomethanes or alkoxymethylamines with secondary phosphines, without solvent, Scheme 21.

Scheme 21

$$(Me_2N)_2CH_2 + HPRR' \xrightarrow[CF_3CO_2H\ (cat)]{80^\circ C} Me_2NCH_2PRR'\ (42) + Me_2NH$$

$R = {}^{i}Pr, {}^{t}Bu;\ R' = {}^{i}Pr, PhCH_2, Ph$

$$R_2NCH_2OMe + HPRR' \xrightarrow[-MeOH]{125^\circ} R_2NCH_2PRR'\ (43)$$

$R_2N =$  ; 

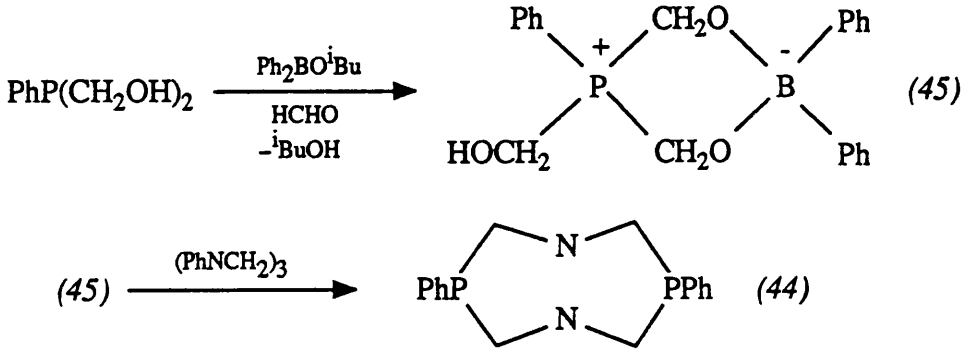
$R = R' = {}^{i}Pr;\ R = {}^{i}Pr, {}^{t}Bu;\ R' = {}^{t}Bu, {}^{i}Pr, CH_2Ph, Ph$

The products were characterised by their ^1H n.m.r. spectra and by mass spectroscopy. Fully assigned ABX patterns for the PCH_2N protons in the ^1H n.m.r. spectra were reported, where either phosphorus or the amine substituent was chiral.

Synthesis of 1,5-diaza-3,7 diphosphacyclooctanes *(44)* have been described by treating hydroxymethylphosphines and diphenyl boric acids with amines.[51] These synthetic routes and similar routes to 1,3,5-diazaphosphorinanes have appeared in a review.[52] The diphenylboric acids were made by treatment of a hydroxymethylphosphine with formaldehyde and isobutyldiphenylborate.[53]

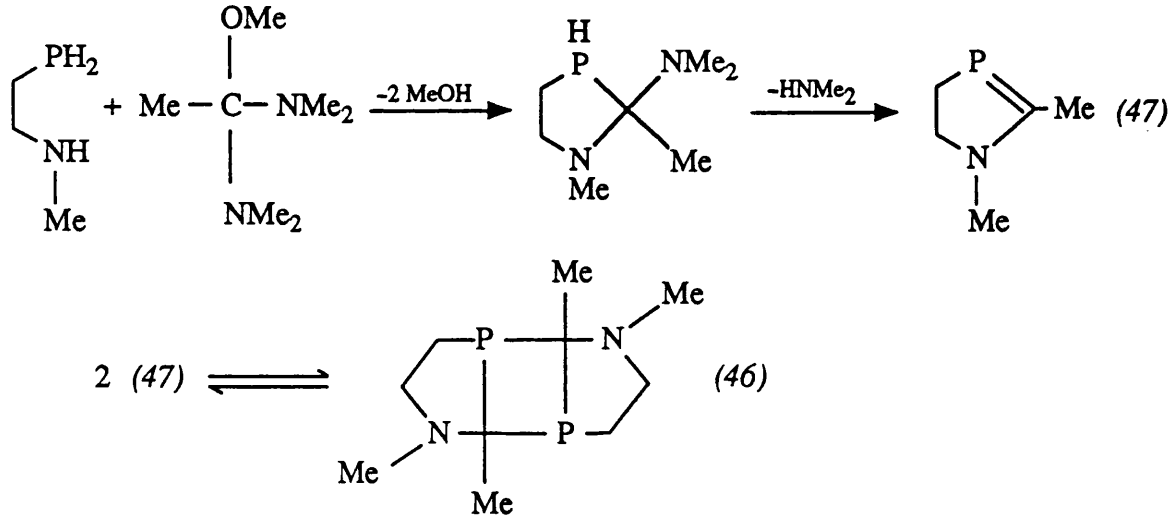
The reaction of 2-aminoethylphosphines with dimethylacetamide-dimethylacetal has yielded some interesting aminoalkylphosphines containing P-C-N

Scheme 22



linkages.[54] In the case of the reaction of 2(N-methylamino)ethylphosphine with dimethylacetamide-dimethylacetal, elimination of 2 moles of methanol followed by one mole of dimethylamine gave a novel heterocycle with a 5-4-5 ring combination *(46)*.

Scheme 23



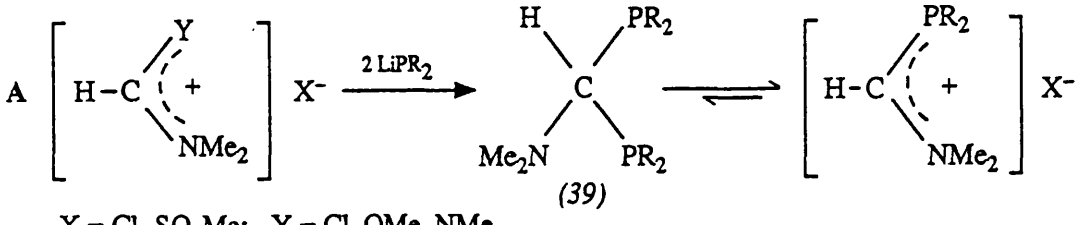
In the X-ray crystal structure of *(46)* the C-P-C bond angles were reported as 91°, and also its ^{31}P n.m.r. spectrum showed a large down-field shift at +60 p.p.m. This indicates the effect that bond strain has on ^{31}P n.m.r. chemical shifts.

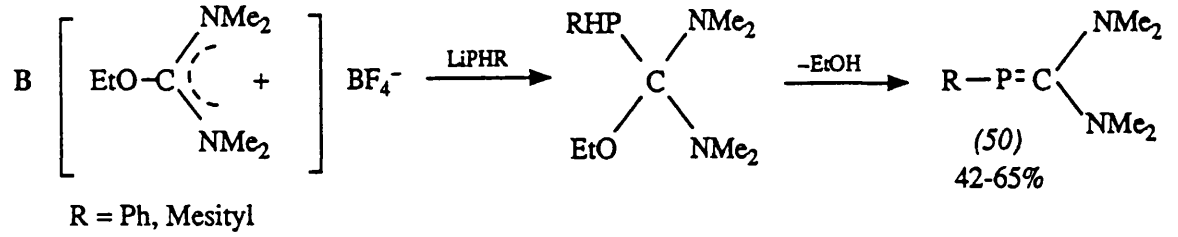
1.4 Synthesis of Aminomethylphosphines using Alkalimetal-phosphides $R_2P^-M^+$

Two preparations have been reported where α-chloromethyl(dimethylamine) has been treated with lithium-diphenylphosphide[55] or lithium-dimethylphosphide.[56] In the first example the product, $Ph_2PCH_2NMe_2$ *(48)* was isolated in a 66% yield after vacuum distillation. The product from the second example, $Me_2PCH_2NMe_2$ *(49)* was characterised by adduct formation. The most obvious drawback of this synthetic route are the extra preparative steps required to make the starting materials, e.g. α-chloromethylamines and phosphides.

Work by Issleib[44,57] has shown that reaction of various dialkylaminocarbenium cations with phosphides give compounds such as *(39)*, Scheme 24 (A), as described in Section 1.3. Yields of these compounds range from 25 to 65%. Depending on the substituents on carbon and phosphorus, compounds similar to *(39)* can decompose to give bis(dimethylamino)methylidenephosphines *(50)*, Scheme 24 (B).[58,59]

Scheme 24



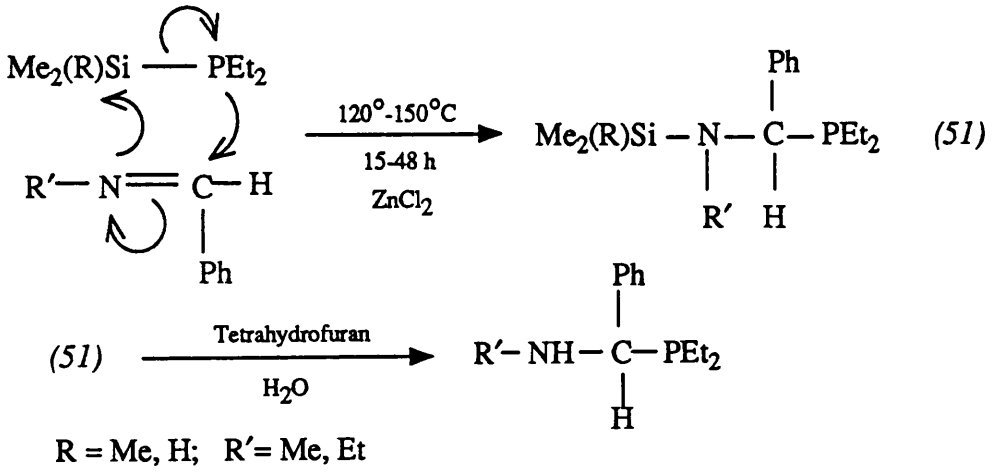


1.5 Miscellaneous Routes to Aminomethylphosphines

French workers[60] have shown that silylphosphines of the type R_3SiPR_2 react with imines to give N-silylaminomethylphosphines in yields of 53-80%.

Hydrolysis of these compounds gave the corresponding aminomethylphosphines, Scheme 25.

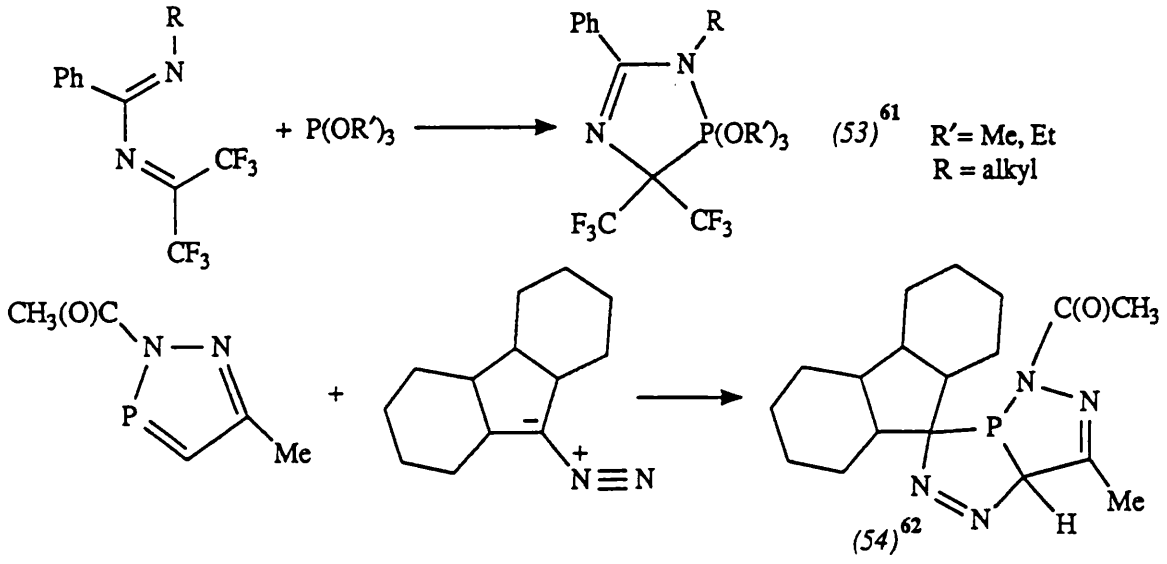
Scheme 25



The chiral centre, generated at carbon in the P–C–N link in these compounds, must be assumed to be racemic.

Some novel compounds containing P–C–N linkages have appeared over the past 15 years, and they have been prepared by various electrocyclic addition reactions. Many of these compounds bear little or no resemblance to conventional aminomethylphosphines so two brief examples, from Burger[61] and Arbuzov[62] respectively, are given to illustrate this point, Scheme 26.

Scheme 26



Aminomethylphosphine oxides have been prepared by Van der Gen *et al.*[63] by the reaction of chlorodiphenylphosphine with aminomethylethers or by the reaction of diphenylethylphosphite with aminomethylene chlorides. The latter reaction was reported to give better products. An 88% yield of the phosphine was obtained when the amine was morpholine.

Work by Hoffmann[64] has shown that treatment of benzylidene-phenyl-amine-hydrobromide with diethylphenylphosphine in refluxing acetonitrile gave an α-aminobenzyl-phosphonium salt *(55)*, Scheme 27.

Scheme 27

$$PhCH{=}NPh.HBr + Et_2PPh \xrightarrow[reflux]{MeCN} \left[Et_2PPh-\underset{\displaystyle Ph}{\underset{|}{CH}}-NHPh \right]^{+} Br^{-} \quad (55)$$

This work was investigated further by Boehme and Haake[65,66] and by Knoll.[67] Salts of the type $[RR'N{=}CH_2]^{+}X^{-}$ were treated with triethyl and triphenylphosphine to yield salts analogous to *(55)*. In the case of triethylphosphine, where RR'N = morpholino, the product was isolated as a stable compound in quantitative yield. However, treatment of the compounds with bases did not give the corresponding free phosphines. The structures and properties of these compounds have been further studied by Kostyanovskii.[68]

1.6 The Reactivity of Aminomethylphosphines

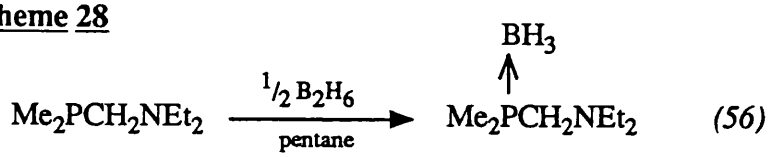
The reactions of aminomethylphosphines are generally centred around the phosphorus atom. It has been observed that P-C bond cleavage is far more likely to occur than N-C bond cleavage. This has been shown to proceed either by nucleophilic or electrophilic attack at phosphorus.

The treatment of aminomethylphosphines with secondary phosphines, e.g. $Ph_2PCH_2NEt_2$ with Ph_2PH, at elevated temperatures, has been studied by

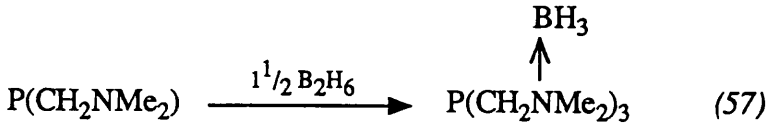
Maier.[69] The products of these reactions were wrongly assigned as $Ph_2P-CH_2-PPh_2$ type diphosphines, by assuming that the CH_2-N bond had cleaved. Further work by Kaska and Maier[70] has shown that the actual product from this reaction was tetraphenyldiphosphine, Ph_2P-PPh_2. The mechanism postulated suggested nucleophilic attack of phosphorus at phosphorus with concurrent cleavage of the P-C bond. Comparative experiments with phosphine-oxides showed no reaction.

Study of the basicity of phosphorus versus nitrogen in aminomethylphosphines has led to some interesting results. Work by Millar[56] on BH_3 adducts of $Me_2PCH_2NMe_2$ has shown ostensibly that P-B coordination occurs in preference to B-N coordination when the compounds were isolated as solids, *(56)*. Further investigation by Jugie *et al.*[71] addressed the problem in more detail. Adducts of $P(CH_2NMe_2)_3$ with BH_3 were studied in solution by ^{31}P, ^{11}B and ^{1}H n.m.r. In this case the reverse preference is observed with N-B coordination being preferred *(57)*. The proposed rationale of these investigations was that in the case of $P(CH_2NMe_2)_3$ the P-B adduct is less favoured on steric grounds. Following the order of basicity N > P, three N-BH_3 moieties are the kinetically favoured product and thus shielding phosphorus from coordination. It was proposed that P-B adducts are more stable than N-B adducts once formed, as in the case of Millar[56] where the stable thermodynamic P-B product was isolated *(56)*, Scheme 28.

Scheme 28



(56)

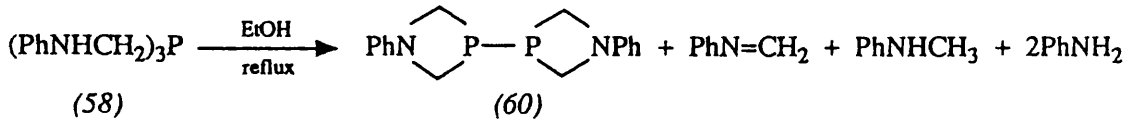


(57)

Trisanilinomethylphosphine *(58)* and tetrakis(anilinomethyl)phosphonium-

chloride *(59)* have been observed to disproportionate in boiling ethanol to give a novel bisphosphine *(60)*, which was identified by thorough interpretation of its ^1H n.m.r. spectrum.[72]

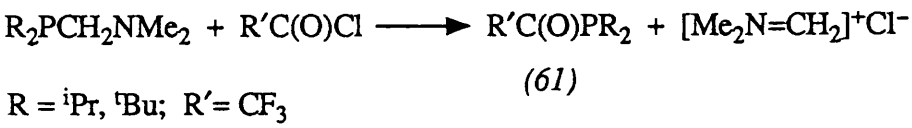
Scheme 29



(58) *(60)*

Reactions of aminomethylphosphines with acylating reagents have shown that electrophilic attack takes place at the phosphorus atom with cleavage of the P–C bond and the formation of an acylphosphine, *(61)*,[73] Scheme 30.

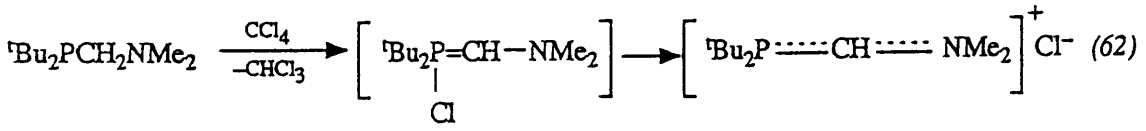
Scheme 30



Reactions of aminoalkylphosphines with alkylating reagents such as MeI and $PhCH_2Br$ have shown that the regioselectivity of the reaction depends on the basicity of the nitrogen atom, the steric constraints about phosphorus, and the type of alkylating reagent. For example, with the phosphine $R_2PCH_2NMe_2$, attack of MeI at phosphorus occurred to give a phosphonium salt, whereas $PhCH_2Br$ and HCl react at the nitrogen atom to form ammonium salts.

Dimethyl(aminomethyl)phosphines have been shown to react with carbon-tetrachloride at between -20° and 0°C to give aminophosphinocarbenium chloride salts.[74] It was suggested that the reaction proceeded *via* a P–chloroylide intermediate as shown in Scheme 31.

Scheme 31



1.7 Some Tertiary Phosphine Analogues to Aminomethylphosphines

Some interesting examples of phosphine ligands have been prepared that are analogues of $R_2PCH_2NR'R''$, where the nitrogen is replaced by either phosphorus or arsenic. A synthesis of methylene-bis-phosphanes has been reported by Appel.[75] These compounds were obtained by halosilane elimination from the reaction of (trimethylsilyl)methylphosphanes and chlorophosphanes as shown in Scheme 32.

Scheme 32

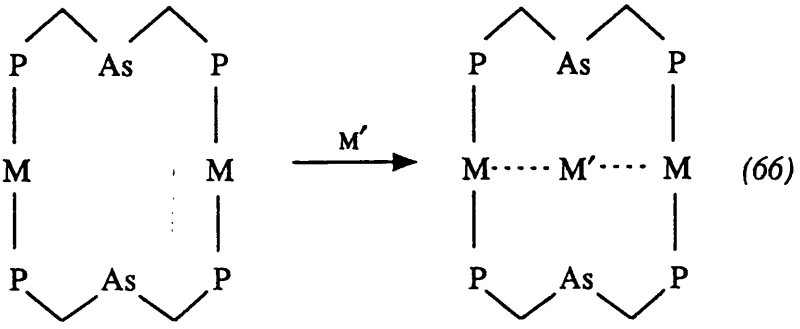
$$Ph_2PCH_2\text{-}TMS + Cl\text{-}XPh_2 \xrightarrow{-TMS\text{-}Cl} Ph_2PCH_2XPh_2 \quad (63) \quad X = P, As$$

$$2Ph_2PCH_2\text{-}TMS + PhPCl_2 \xrightarrow{-2\,TMSCl} \begin{matrix} Ph_2P \\ \diagdown \\ PPh \\ \diagup \\ Ph_2P \end{matrix} \quad (64)$$

The ligand bis(diphenylphosphinomethyl)phenylarsine *(65)* has been made by treating phenyldichloroarsine with diphenylphosphinomethyl lithium in tetrahydrofuran at -78°C.[76] This compound has been studied extensively by Balch,[77] as a tridentate ligand to give mixed metal metallomacrocycles *(66)* as illustrated in Scheme 33.

Scheme 33

$$PhAsCl_2 + Ph_2PCH_2Li \xrightarrow[-78^\circ C]{THF} \begin{matrix} Ph_2P \\ \diagdown \\ AsPh \\ \diagup \\ Ph_2P \end{matrix} \quad (65)$$



(66)

M = Rh; M'= Pd P As P = *(65)*

1.8 Aminoethylphosphines

The first example of an aminoethylphosphine was reported by Issleib[78,79] who treated monosodium phenylphosphide with β-chloroethylamine. The phosphorus atom could be further substituted by the addition of an alkylating reagent, R-X, as shown in Scheme 34.

Scheme 34

$$PhP(H)Na + ClCH_2CH_2NH_2 \longrightarrow \underset{(67)}{PhP(H)CH_2CH_2NH_2} + NaCl$$

$$(67) + Na + R-Cl \longrightarrow PhP(R)CH_2CH_2NH_2 + NaCl$$

$R = {}^{n}Bu, Cy$

Analogous reactions have been used to synthesise similar compounds. The compound $Ph_2PCH_2CH_2NMe_2$ *(68)* has been investigated as a ligand for transition metal complexes.[80-82] A similar compound $PhCH_2NHCH_2CH_2PPh_2$ *(69)* has been reported,[83] and its use as a P-N bridging ligand with various transition metal complexes was examined.

Scheme 35[80]

$$Ph_2PLi \xrightarrow[0^\circ,\ THF]{Cl\sim NMe_2} \xrightarrow[MeOH]{reflux} \underset{(68)}{Ph_2PCH_2CH_2NMe_2} + LiCl$$

A different synthetic route to aminoethylphosphines has appeared from Markl and Merkl,[84] who treated a secondary amine with diphenylvinylphosphine. The subsequent Michael-type addition gave an aminoethyldiphenylphosphine *(70)*, Scheme 36. Numerous variations were investigated including some examples of chiral amines and bis(aminoethyl)phosphines, although no metal complex chemistry was investigated.

Scheme 36

$$Ph_2P-CH=CH_2 + HNRR' \longrightarrow Ph_2PCH_2CH_2NRR' \quad (70)$$

$R = Me, Et, CH_2CH_2PPh_2$

$R' = CHMePh$, 3-pinanmethyl

These types of phosphines have not been examined in the present work but reviews on their chemistry are available.[85]

CHAPTER 2

Synthesis of Some Aminomethylphosphines via Hydroxymethylphosphonium Salts

2.1 Introduction

The development and variety of synthetic routes to aminomethylphosphines, as reviewed in Chapter 1, illustrates the diversity of substituted tertiary phosphines that are accessible by these routes. It is also clear that the modified Mannich reaction has been the most favoured route to a great many of the reported aminomethylphosphines. The most simple way of varying this synthesis is by using different amines. In this way alone the number of permutations is vast. Use of a variety of functional groups at phosphorus has also been of interest, including the use of compounds with phosphorus as a chiral centre.[9] An important step in this route to aminomethylphosphines is the preparation of hydroxymethylphosphines or phosphonium salts.

The first hydroxymethylphosphonium salt reported was THPC *(2)* by Hoffman[86] who reacted phosphine with formaldehyde and hydrogen chloride gas. This reaction had probably been carried out much earlier[87] but the products were not fully identified. No significant work was then reported for some 40 years. Shortly after the work on the reaction of *(2)* with amines by Coates and Hoye, work by Petrov[88,89,90] produced a number of hydroxymethylphosphorus compounds. The reaction of primary and secondary, alkyl and aryl phosphines with formaldehyde, acetaldehyde and benzaldehyde in the presence of hydrochloric acid yielded a range of hydroxyalkylphosphonium salts, illustrated in Scheme 1.

Scheme 1

$$RPH_2 \xrightarrow[HCl]{O \\ || \\ R'CH} [RP(CHR'OH)_3]^+Cl^- \qquad (71)$$

$$R_2PH \xrightarrow{O \\ || \\ R'CH} [R_2P(CHR'OH)_2]^+Cl^- \qquad (72)$$

R = Ph, Pr, Bu, Et; R′ = H, Me, Ph

Subsequent work by Petrov[91,17] investigated the reaction of these compounds with amines, as discussed in Chapter 1.

At the same time other workers investigated the reactions of phosphines with aldehydes and ketones in acidic media. Work by Buckler and Epstein[92,93] showed that hydroxyalkylphosphonium salts, under certain conditions, could undergo oxygen transfer to give hydroxyalkylphosphine oxides, Scheme 2. However, this was shown to be dependent upon refluxing the reaction mixture at 100°C in acid media, and on substituents on phosphorus. It was also shown that reactions of phosphines with formaldehyde gave only the corresponding phosphonium salts. The phosphonium salt $[Bu_2P(CH_2OH)_2]^+Cl^-$ was also reported, Scheme 2.

Scheme 2

$$(2) + PhCHO \xrightarrow[reflux]{HCl} (PhCHOH)_2P(O)CH_2Ph \quad (73)$$

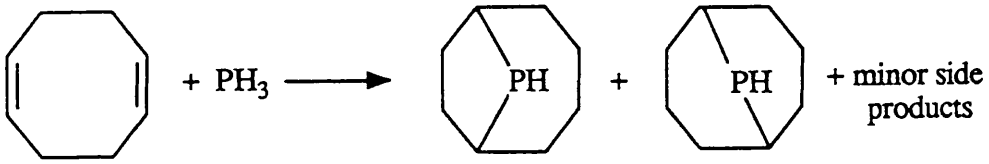
$$Ph_2PH + PhCHO \xrightarrow[reflux]{HCl} Ph_2P(O)CH_2Ph \quad (74)$$

$$Bu_2PH + HCHO \xrightarrow[reflux]{HCl} [Bu_2P(CH_2OH)_2]^+Cl^- \quad (75)$$

Trippett[94] also investigated these reactions. When hydroxymethyldiphenylphosphine was refluxed in toluene with acid only decomposition to diphenylphosphine and formaldehyde was observed. The synthesis of $[Ph_2P\{CH(Ph)OH\}_2]^+Cl^-$ under anhydrous conditions was also described. Tris-(hydroxymethyl)phosphine has been shown to react with alkyl halides to give alkyl(hydroxymethyl)phosphonium salts.[95] By dehydroxymethylation with a base and by further alkylation, an effective route to mono- and di-alkyl-(hydroxymethyl)phosphines has been developed.[96,97]

The range of hydroxymethylphosphines and phosphonium salts available has been shown to be substantial. Despite this only a limited range of these compounds have been significantly investigated in aminomethylphos-

phine synthesis, with diphenyl and phenyl(hydroxymethyl)phosphines predominating. In the present work hydroxymethyl phosphonium salts have been prepared from the phosphines; Ph_2PH *(77)*, Cy_2PH *(78)* and $(C_8H_{14})PH$ *(79)*, *(80)* phosphabicyclononane (symmetric (3,3,1) and asymmetric (4,2,1) isomers) Figure 1. The two isomers of $(C_8H_{14})PH$ have been separated to give the pure symmetric isomer in the form of a hydroxymethylphosphonium salt. Also in this Chapter, selected phosphonium salts have been used in the synthesis of a variety of aminomethylphosphines. In addition, some aminomethylphosphine-oxides have also been prepared.



(79) *(80)*

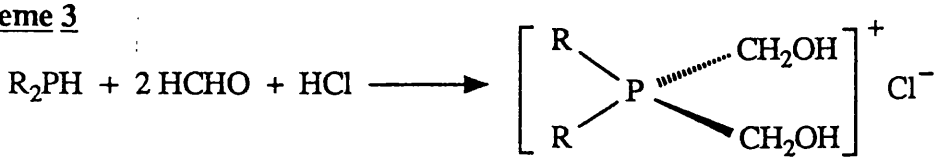
Ratio: 41.5 : 58.5

Figure 1

2.2 Preparation of $[R_2P(CH_2OH)_2]^+X^-$ phosphonium salts

Bis(hydroxymethyl)phosphonium chloride salts *(81)-(84)* were prepared in quantitative yield (95-99%) by the treatment of a secondary phosphine, R_2PH with aqueous formaldehyde and concentrated hydrochloric acid, Scheme 3. The compounds are highly crystalline white solids which are only soluble in polar solvents such as water or methanol. The phenyl derivative *(81)* has been reported previously.[89] The melting point obtained for *(81)* is in agreement with that previously quoted; 162°C (lit. 165°C).

Scheme 3



R = Ph,Cy *(81)(82)*; $R_2 = C_8H_{14}$ *(83)(84)*

Only one example of a quaternary salt of $C_8H_{14}PH$ *(79)*, *(80)* has previously been reported.[98] In this example a mixture of *(79)* and *(80)* were treated with hexyl bromide to give $[C_8H_{14}P(H)C_6H_{13}]^+Br^-$ *(85)*. The ^{31}P n.m.r. spectra of *(81)* and *(82)* show single peaks shifted upfield in relation to the parent phosphine, see Table 1. In a similar fashion the ^{31}P n.m.r. spectrum of *(83)* and *(84)* shows two peaks corresponding to the two isomers of the parent phosphine *(79)* and *(80)*. However, in the case of *(83)* and *(84)* the chemical shift change due to quarternisation is significantly different for each isomer, Table 1.

The bis[bis(hydroxymethyl)phosphonium] sulphate and [bis(hydroxymethyl)phosphonium] hydrogensulphate salt *(86)* and *(87)* was prepared by treating *(79)* and *(80)* with aqueous formaldehyde and concentrated sulphuric acid. Despite the presence of both mono and di anion salts in the compound, the ^{31}P n.m.r. spectrum shows only two signals corresponding to the (4.2.1) and (3.3.1) isomers.

$$[(C_8H_{14})P(CH_2OH)_2]^+HSO_4^- \text{ and } [(C_8H_{14})P(CH_2OH)_2]_2^+ SO_4^{2-}$$

In view of this it is not surprising that the chemical shifts of the two sulphate salt isomers *(86)* and *(87)* are practically identical to the corresponding chloride salt *(83)* and *(84)*.

2.3 Isolation of the symmetrical isomer *(86)* from *(86)* and *(87)*

The large ^{31}P n.m.r. chemical shift differences between the phosphonium salt isomers *(83)* and *(84)*, and *(86)* and *(87)* indicate some profound difference in the properties of the two isomeric species. Work by Hoye[99] has shown that sulphate/hydrogensulphate phosphonium salts can be decomposed to give methylphosphine-oxide compounds by refluxing in sulphuric acid and by removal of formaldehyde, e.g. Scheme 4.

Phosphine	^{31}P, δ	Phosphonium salt	^{31}P, δ	Phosphonium salt	^{31}P, δ
Cy_2PH *(78)*	-26.0	$Cy_2P^+(CH_2OH)_2Cl^-$ *(82)*	+28.3	$Cy_2P^+(CH_3CHOH)_2Cl^-$ *(90)*	+29.04
Ph_2PH *(77)*	-41.14	$Ph_2P^+(CH_2OH)_2Cl^-$ *(81)*	+16.73	$Ph_2P^+(CH_3CHOH)_2Cl^-$ *(91)*	+26.21
$(C_8H_{14})PH$ *(79)* *(80)*	-49.2 asym -54.6 sym	$(C_8H_{14})P^+(CH_2OH)_2Cl^-$ *(83)* *(84)*	+23.4 sym +55.66 asym		
		$[C_8H_{14})P(CH_2OH)_2]_2^+SO_4^{2-}$ *(86)* $/[(C_8H_{14})P(CH_2OH)_2]^+HSO_4^-$ *(87)*	+23.0 sym +55.66 asym		

Table 1

^{31}P n.m.r. data for phosphine starting materials and hydroxymethylphosphonium salts

Scheme 4

E.g. $[CyP(CH_2OH)_3]_2^+SO_4^{2-} \xrightarrow[13\,h\ -HCHO]{H_2SO_4,\ reflux} CyP(=O)(Me)(CH_2OH)$

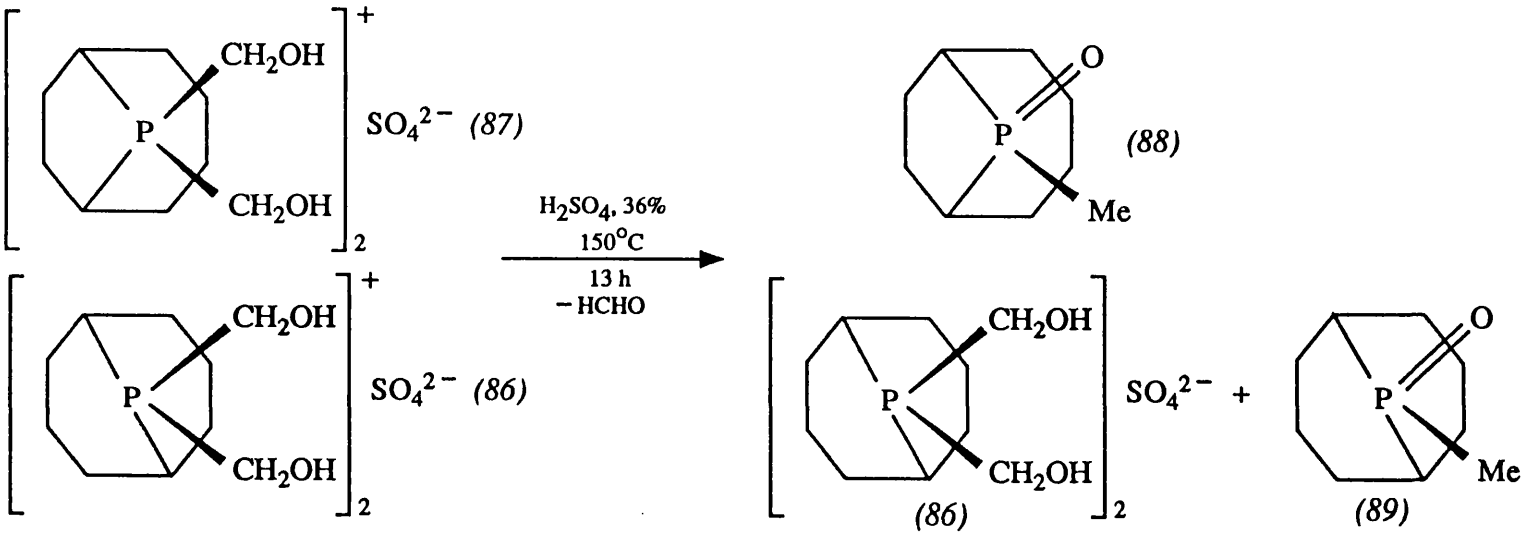
Using this method the phosphonium salts *(86)* and *(87)* were refluxed at 150°C in 36% sulphuric acid, Scheme 5. Formaldehyde solution was collected and removed with a Dean & Stark condenser thus moving any equilibrium away from the phosphonium salt. A sample of the reaction mixture was monitored by ^{31}P n.m.r. after 6.5h and showed that nearly 90% of the asymmetric isomer *(87)* had decomposed to give $(C_9H_{14})P(O)Me$ *(88)*, δ 88.0 p.p.m. However, only a small amount (<10%) of the symmetrical isomer *(86)* had decomposed. After a further 6.5h of refluxing, the ^{31}P n.m.r. spectrum of the mixture showed total conversion of *(87)* to the oxide *(88)* and only about 10% decomposition of *(86)* to the corresponding oxide *(89)*, δ 56.0 p.p.m.

The symmetrical phosphonium salt *(86)* was then isolated by recrystallisation from methanol in a 79.4% yield, based on the original isomer ratios of 58.5:41.5 (sym:asym). The formaldehyde solution collected from the reaction was titrated with sodium sulphite solution according to the equation:

$$HCHO + Na_2SO_3 + H_2O \longrightarrow NaOH + (NaSO_3)CH_2OH$$

Using thymolphthalein indicator to give a blue solution and by back titrating with acid to give a clear end point. The number of moles of formaldehyde collected was in agreement with the number of moles of oxides *(88)* and *(89)* produced. It was thought, from molecular models, that the unsymmetrical isomer *(87)* would be less stable than typical hydroxymethylphosphonium sulphate salts due to apparent bond strain about phosphorus. However, from the present results compound *(87)* shows a similar reactivity to other hydroxymethylphosphonium sulphate salts[99] under the given con-

Scheme 5



N.B. Hydrogensulphate salt, HSO_4^- omitted for clarity

ditions. Interestingly, the isomer *(86)* shows a much higher degree of stability than was predicted, probably due to the two six-membered heterocyclic rings forming the $C_8H_{14}P$ moiety, Figure 2.

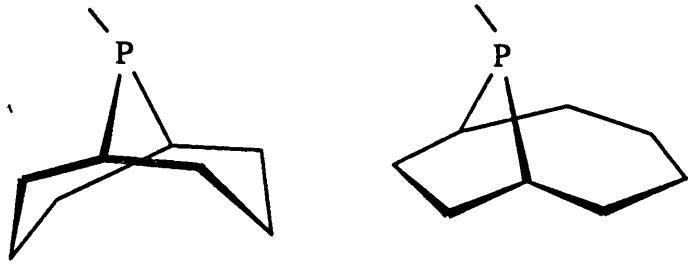


Figure 2 $C_8H_{14}P$ moieties, symmetric and asymmetric isomers

Various derivatives of phosphines *(79)* and *(80)* have been reported over the past 25 years[100-111] with applications in catalytic hydroformylation, as emulsifiers, flame retardants and polymer additives. In all these examples, the compounds are only reported as a mixture of isomers, therefore this is the first example of a derivative of *(79)* being isolated from its asymmetric isomer.

By treating a hot aqueous solution of the salt *(86)* with barium chloride, the symmetrical hydroxymethylphosphonium chloride salt *(83)* was precipitated.

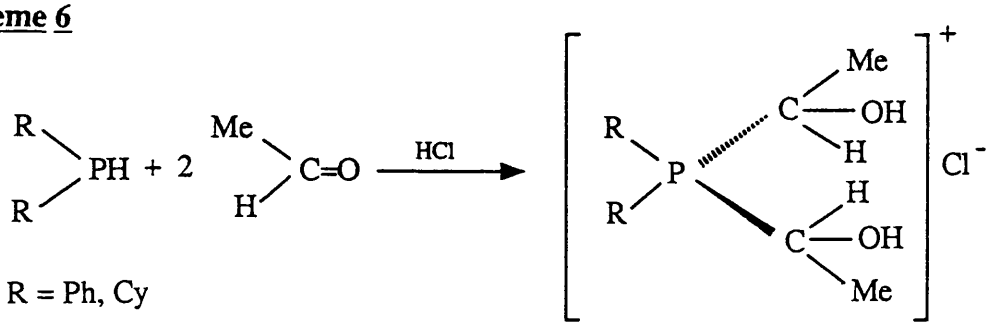
2.4 Preparation of $[R_2P(CH_3CHOH)_2]^+Cl^-$ phosphonium salts

The phosphonium salts *(90)* and *(91)* were prepared by treating the phosphines *(77)* or *(80)* with acetaldehyde and hydrochloric acid. They were isolated as highly crystalline white solids and were soluble in most polar solvents such as water and methanol. ^{31}P n.m.r. shifts are given for *(90)* and *(91)* in Table 1.

These compounds were considered as starting materials for the synthesis of chiral bisphosphines of the type $[R_2PCH(Me)]_2NR'$. However, with uncertain configuration of the hydroxyethyl moieties, of *(90)* and *(91)*, and

the possibility of having as many as three stereoisomers of the aminophosphine derivatives further work on these compounds was thought to be prohibitive. The compound *(91)* has been reported elsewhere,[90] prepared by a non-aqueous route using HCl gas, Ph_2PH *(77)* and acetaldehyde, in a solution of dry diethyl ether with a 78% yield.

Scheme 6



2.5 Structural features of $[Ph_2P(CH_2OH)_2]^+Cl^-$ *(81)*

The molecular structure of *(81)* is shown in Figure 3 and selected bond lengths and angles are given in Table 2. The compound consists of a quaternary phosphonium cation with a chloride anion. The packing diagram in Figure 4 shows short intermolecular contacts between the cation and anion. This is further supported by the short distances of the H(1)---Cl and H(2)---Cl non-bonded contacts, Table 2. The O---Cl distances are also typical for OH---Cl hydrogen bonds of 2.99-3.05 Å.[119] The geometry around phosphorus is essentially tetrahedral with C-P-C angles in the range of 107.1-111.2°. The P-C(1) and P-C(2) bond lengths of 1.822(5) and 1.838(6) Å are comparable to those reported for tertiary phosphonium alkyls of 1.800(15) Å.[161,162] The P-C(21) and P-C(31) bond distances of 1.786(3) and 1.781(3) Å also compare with those typical for tertiary phosphonium aryl compounds of 1.793(11) Å.[161,162] The C(1)-O(1) and C(2)-O(2) bond lengths of 1.400(7) and 1.409(7) Å appear slightly short when compared to typical CH_2-OH bond distances of 1.426(11) Å.[161,162] This however is in agreement with the presence of the positively charged phosphonium ion which would have the effect of shortening these C-O bonds.

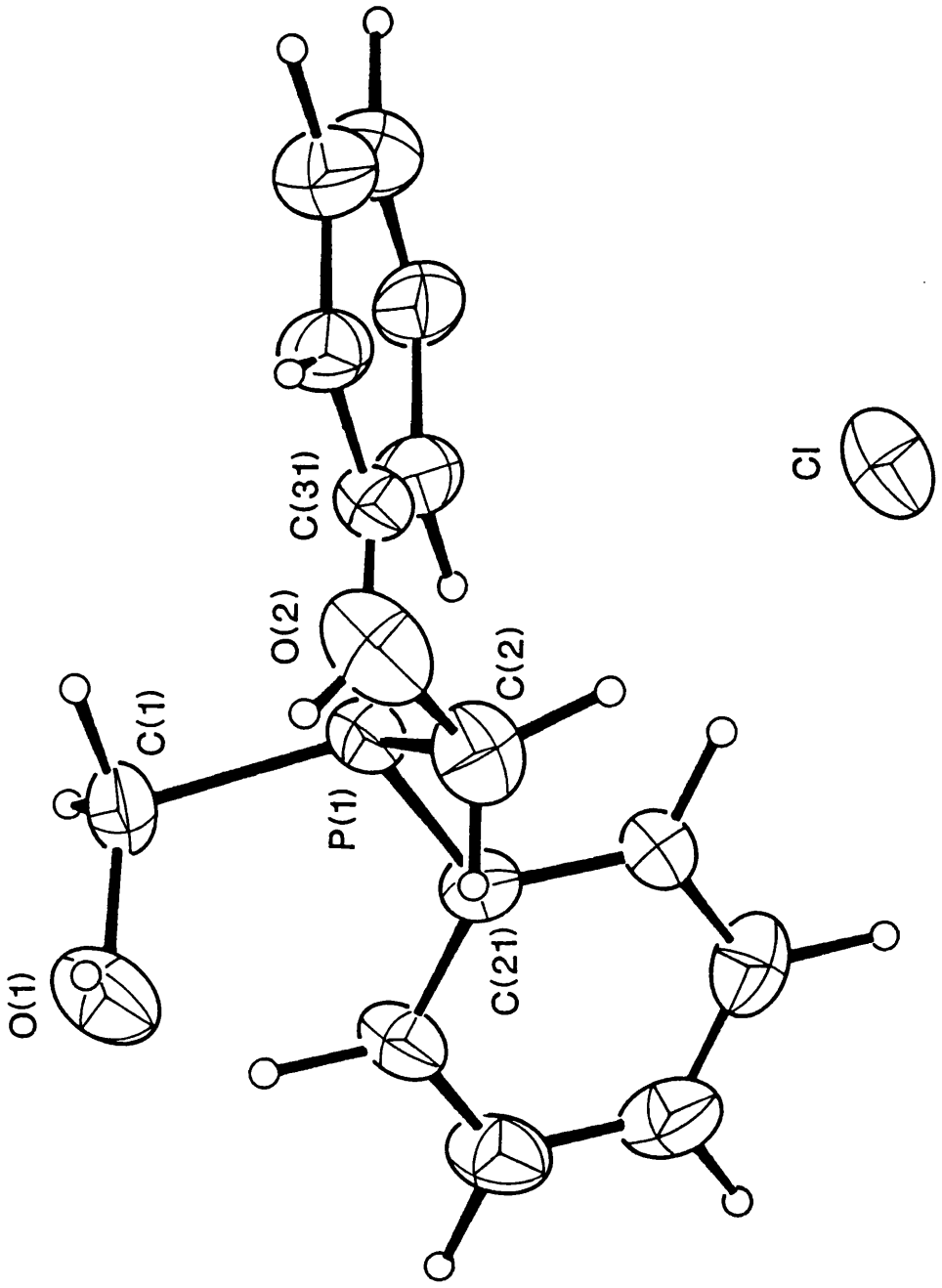


Figure 3
Molecular structure of $[Ph_2P(CH_2OH)_2]^+Cl^-$ *(81)*

Bond angle	(°)
C(2) — P(1) — C(1)	107.8 (3)
C(21) — P(1) — C(1)	108.8 (2)
C(31) — P(1) — C(1)	111.2 (2)
C(31) — P(1) — C(2)	107.1 (2)
C(21) — P(1) — C(2)	110.6 (2)
C(31) — P(1) — C(21)	111.3 (2)
O(1) — C(1) — P(1)	110.6 (4)
O(2) — C(2) — P(1)	112.1 (4)

Bond length	(Å)
C(1) — P(1)	1.822 (5)
C(2) — P(1)	1.838 (6)
C(21) — P(1)	1.786 (3)
C(31) — P(1)	1.781 (3)
C(1) — O(1)	1.400 (7)
C(2) — O(2)	1.409 (7)
H(1) — O(1)	0.79 (7)
H(2) — O(2)	0.68 (8)

Non-bonded contacts	(Å)
H(1) -------- Cl	2.227
H(2) -------- Cl	2.367
O(1) -------- Cl	3.020
O(2) -------- Cl	3.030

Table 2

Selected bond angles in (°) (with e.s.d. in parentheses) and bond lengths and non-bonded contacts (Å) (with e.s.d. in parentheses) for the phosphonium salt $[Ph_2P^+(CH_2OH)_2Cl^-]$ *(81)*

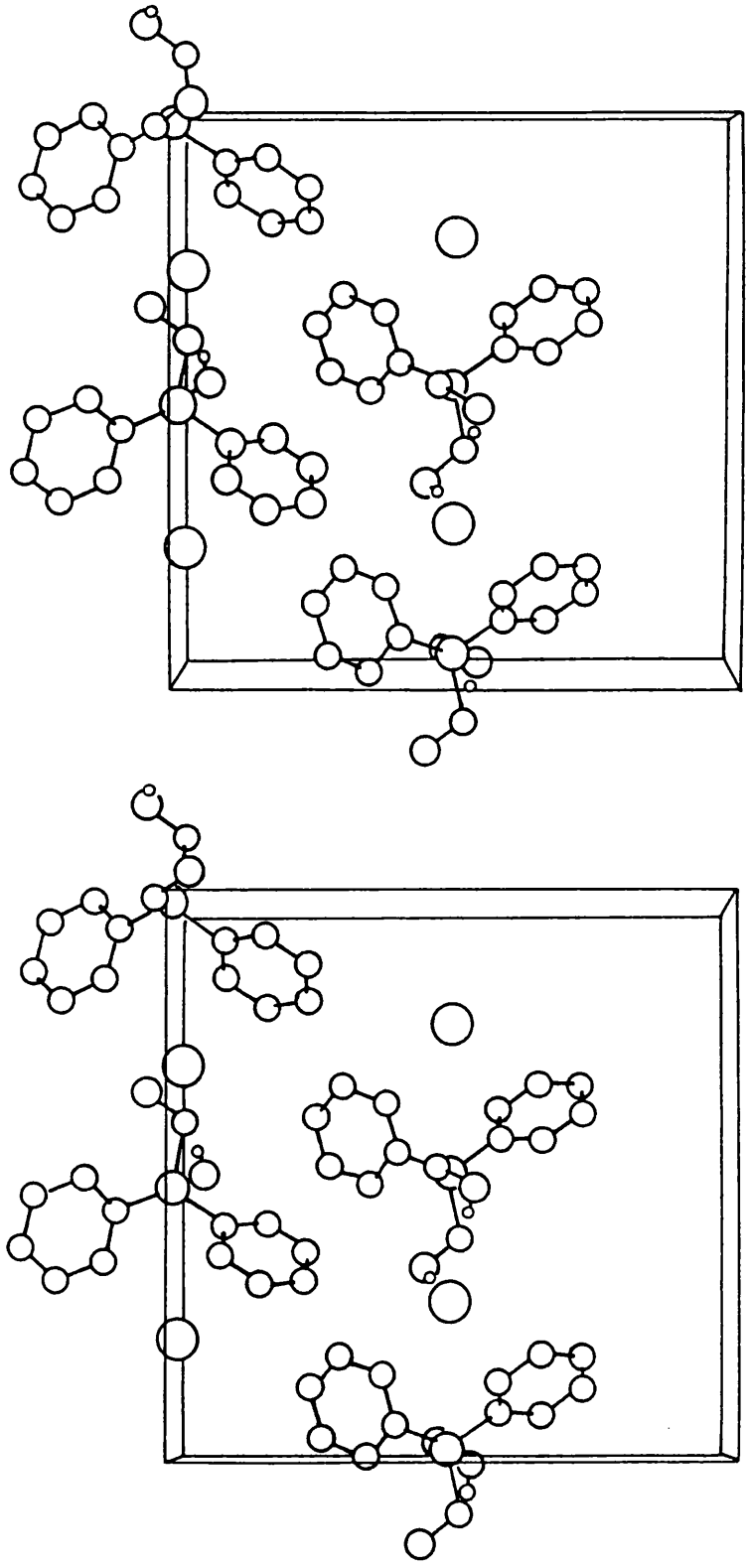


Figure 4
Packing diagram for $[Ph_2P(CH_2OH)_2]^+Cl^-$ *(81)*

2.6 Preparation of $P(CH_2N(Me)CH(Me)CH(OH)Ph)_3$, *(92)*

Treatment of an ethanolic solution of $[P(CH_2OH)_4]^+Cl^-$ *(2)* with triethylamine and (-) ephedrine, followed by addition of toluene gave *(92)* as a fine white powder in a 61% yield, Scheme 7.

Scheme 7

$$[P(CH_2OH)_4]^+Cl^- \xrightarrow{NEt_3} P(CH_2OH)_3 + [HNEt_3]^+Cl^-$$

$$P(CH_2OH)_3 + 3HN(Me)CH(Me)CH(OH)Ph \xrightarrow[EtOH]{reflux} (92)$$

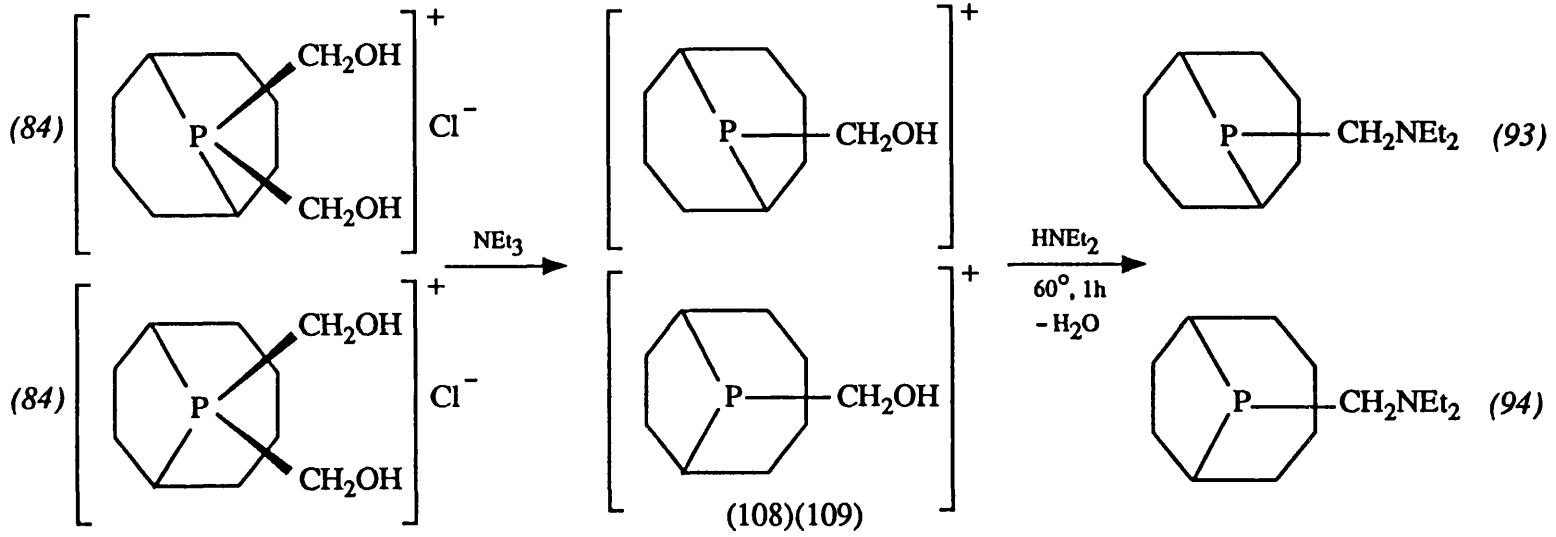
This new tertiary phosphine showed poor solubility in most common organic solvents except boiling methanol or methyl cyanide. The ^{31}P n.m.r. spectrum of *(92)* showed a single peak (Table 2) and elemental analysis was in agreement with the formulation. Attempts to make metal complexes of *(92)* by the addition of a methyl cyanide solution of the phosphine to $[PtCl_2(COD)]$, $[Mo(CO)_4(PiP)_2]$ or $[W(CO)_4(PiP)_2]$ gave products which were clearly complex mixtures from their ^{31}P n.m.r. The bulky and labile nature of the three ephedrine moieties about phosphorus in *(92)* may prohibit its chemistry as a monodentate phosphine ligand and was not investigated further.

2.7 Preparation of $R_2PCH_2NR^1R^2$ phosphines

The isomeric mixture of bis(hydroxymethyl)phosphonium salts *(83)* and *(84)* were treated with a base (NEt_3) and an amine ($HNEt_2$) to give $(C_8H_{14})PCH_2NEt_2$ *(93)* and *(94)* in an isomeric ratio of approximately 3:5 (asym:sym), Scheme 8.

The phosphines *(93)* and *(94)* were collected as a clear liquid in an 85% yield by fractional distillation, b.p. 124-126°C at 2.5 mmHg. In a similar manner to the phosphonium salts *(83)* and *(84)*, and *(86)* and *(87)*, the two phosphine isomers *(93)* and *(94)* exhibit a large difference in their ^{31}P n.m.r. chemical shifts (39.8 p.p.m.), Table 2. The hydroxymethylphosphine

Scheme 8


(84)
CH2OH
P
CH2OH
Cl-
+
NEt3
(84)
(108)(109)
HNEt2
60°, 1h
- H2O
CH2NEt2
(93)
(94)

intermediates *(108),(109)* (Scheme 8) were observed in the ^{31}P n.m.r. of the initial reaction mixture as single peaks at +1.0 and -36.0 p.p.m. respectively. The ^{1}H n.m.r. spectrum of *(93)* and *(94)* showed two sets of doublets for the $PC\underline{H}_2N$ protons at δ 2.4 and 2.8 p.p.m. corresponding to the two isomers. The shift differences were not as pronounced as the ^{31}P n.m.r. shifts for *(93)* and *(94)* but, not surprisingly, the $^{2}J(PH)$ coupling was also different in each case (2.2 and 1.5 Hz respectively, Table 3. The ^{13}C n.m.r. spectrum, however, only showed a single peak with second order splitting corresponding to the $P\underline{C}H_2N$ carbon.

Two more monodentate phosphine ligands have been prepared *(95)* and *(96)* using the chiral amines ephedrine and L-proline methyl ester. Phosphine *(95)* derived from (-) ephedrine was prepared by two different methods. By reaction of Ph_2PH *(77)* with formaldehyde and (-) ephedrine in diethyl ether a solution of the phosphine $Ph_2PCH_2N(Me)CH(Me)CH(OH)Ph$ *(95)* was obtained, Scheme 9. Attempts to isolate the pure phosphine by fractional distillation were unsuccessful since at high temperatures, >150°C the phosphine decomposes to give Ph_2PH *(77)* as the distillate.

The phosphine *(95)* was also prepared by treating the hydroxymethyl phosphonium salt *(81)* with triethylamine and (-) ephedrine, followed by gentle warming, Scheme 9.

Scheme 9

$$2\,Ph_2PH + 2\,HCHO \xrightarrow[Et_2O,\ reflux,\ 2h]{HN(Me)CH(Me)CH(OH)Ph} \textit{(95)}$$

$$\textit{(81)} + NEt_3 \xrightarrow[60^\circ,\ 1H,\ -H_2O,\ -HNEt_3Cl]{HN(Me)CH(Me)CH(OH)Ph} \textit{(95)}$$

The phosphine was then extracted from the reaction mixture and stored under nitrogen in a toluene solution. The second method proved to be the preferable method of preparation for these compounds mainly due to salts such as *(81)* being easier to handle than odorous, toxic, liquid phosphines like

Phosphine		^{31}P, δ	^{31}P, δ oxide
$P[CH_2N(Me)CH(Me)CH(OH)Ph]_3$	*(92)*	-54.04	+48.6
$Ph_2PCH_2N(Me)CH(Me)CH(OH)Ph$	*(95)*	-26.21	+29.04
$C_8H_{14}PCH_2NEt_2$	*(93)* *(94)*	-9.88 -48.8	—
$Ph_2PCH_2NCH_2CH_2CH_2CHCO_2Me$	*(96)*	-24.68	+35.5
$(Ph_2PCH_2)_2NCHMePh$	*(97)*	-27.83	+31.86
$(Ph_2PCH_2)_2NCHMeCO_2Et$	*(98)*	-26.38	+27.63
$(Ph_2PCH_2)_2NCHCH_2CHCH_2CH_2C(Me)C(Me)_2$	*(100)*	-28.63	—
$(Cy_2PCH_2)_2NCHMePh$	*(101)*	-18.35	+56.47
$(Cy_2PCH_2)_2NCHMeCO_2Et$	*(102)*	-18.15	+47.79
$(C_8H_{14}PCH_2)_2NCHMePh$	*(103)*	-46.6	—
$(Ph_2PCH_2)_2NCH_2CH_2OH$	*(104)*	-28.23	+32.06
$(Ph_2PCH_2)_2NCH_2CH=CH_2$	*(105)*	-28.84	+27.02
$(Ph_2PCH_2)_2NCH_2C\equiv CH$	*(106)*	-27.02	+26.20

Table 3

^{31}P n.m.r. shifts of phosphines and phosphine oxides

(77). The solvents toluene and dichloromethane proved to be good for storage of these compounds in solution as they have a lower solubility of oxygen than diethyl ether[112] and could probably be degassed more thoroughly. Solutions of most of the reported phosphines, when left standing in apparently degassed ether solutions for over seven days, showed signs of phosphine oxide in their ^{31}P n.m.r.

The phosphine $Ph_2PCH_2\overline{NCH_2CH_2CH_2CHCO_2Me}$ *(96)* was prepared from *(81)* in a similar method to *(95)* except a neutralised solution of L-proline methyl ester hydrochloride was used. Similarly, the phosphine was extracted and stored under nitrogen in a toluene solution. The phosphine oxides of *(95)* and *(96)* were prepared by stirring an acetone solution of the phosphine with a stoichiometric amount of hydrogen peroxide solution. ^{31}P n.m.r. data for *(95)*, *(96)* and their respective oxides are shown in Table 2.

Phosphine oxides of the reported phosphines in this Chapter were only characterised by ^{31}P n.m.r. so they could be used as useful markers in the further investigation of their chemistry.

2.8 Preparation of phosphines of the type $(R_2PCH_2)_2NR'$

Previous reports[33,36,38] of bis phosphines of this general formula have been fairly brief, as has been mentioned in Chapter 1. The ability to vary the nature of the phosphine by using a range of functional groups on P and N has been investigated by using the phosphonium salts *(81)*, *(82)* and *(83)* in conjunction with a variety of secondary amines. Chiral phosphines derived from optically pure amines have been considered as viable ligands for asymmetric catalysis.[38] In this work a range of optically active phosphines have been synthesised *(97)-(103)*, and also some non-chiral phosphines have been prepared *(104)-(106)*.

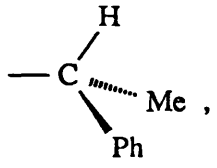
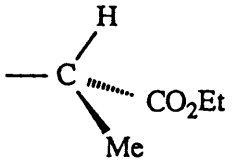
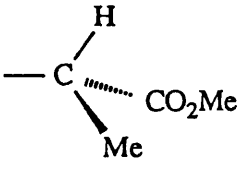
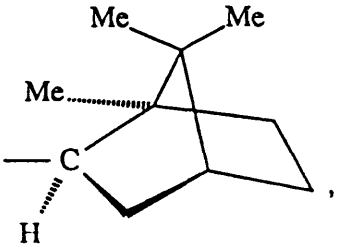
Phosphines *(97)-(100)* and *(104)-(106)* were prepared by treating the

phosphonium salt *(81)* with NEt_3 followed by addition of a secondary amine H_2NR and gentle reflux for 1h in a methanol/water solution, Scheme 10 (A). The amines used were R (+) phenylethylamine *(97)*, L-alanine ethyl ester *(98)*, L-alanine methyl ester *(99)* and R(+) norbornylamine *(100)*, for the chiral phosphines, and ethanolamine, allylamine and propargylamine for *(104)*, *(105)* and *(106)* respectively. The compounds were mainly isolated as highly viscous cloudy oils with yields in the range of 61.5-95%. Triethylamine and solvents evident in the ^1H n.m.r. of the crude oils required long periods (10-100h) under high vacuum, with occasional warming, to be removed. The phosphine *(98)*, however, was isolated as a white solid after several days under high vacuum. Attempts to recrystallise *(98)* or induce crystallisation in *(97)*, *(99)*, *(100)*, *(104)* and *(105)* in the solvents dichloromethane-light petroleum; toluene and methanol, and boiling isopropanol were unsuccessful.

^{31}P n.m.r. shifts for these phosphines and their oxides are shown in Table 3. Phosphine oxides were prepared and characterised for reference purposes as has been previously stated. The phosphine oxide of *(97)*, however, was isolated as a white crystalline solid *(97a)* and was characterised by ^{31}P and ^1H n.m.r., i.r. $\nu_{(P=O)}$ 1270 cm^{-1}, and by elemental analysis. This effectively confirmed the method of oxide preparation (see Experimental section).

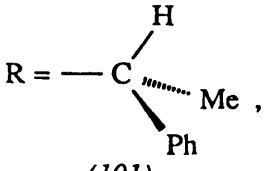
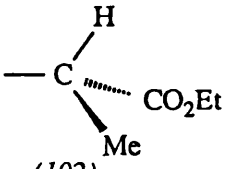
The phosphines *(101)* and *(102)* were prepared in a similar fashion to the phosphines derived from *(81)*, by treating the phosphonium salt *(82)* with NEt_3 followed by addition of a primary amine RNH_2, Scheme 10, (B). The phosphine *(101)* was isolated by addition of methanol to a solution of *(101)* in toluene at -15^oC to give large colourless crystals of *(101)* in a 56% yield. Attempts to induce crystallisation of *(102)* by similar methods were unsuccessful. ^{31}P n.m.r. shifts for *(101)* and *(102)* and their

[A] $2\,[Ph_2P(CH_2OH)_2]^+Cl^-$ (81) $\xrightarrow{NEt_3}$ $[2\,Ph_2PCH_2OH]$ (107) $\xrightarrow[H_2O/MeOH,\ 60°C,\ 1h]{H_2NR}$ $(Ph_2PCH_2)_2NR$

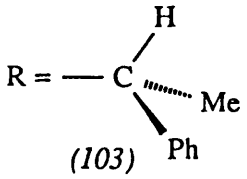
R =  (97),  (98),  (99),  (100),

$-CH_2CH_2OH$ (104), $-CH_2CH{=}CH_2$ (105), $-CH_2C{\equiv}CH$ (106)

[B] $2\,[Cy_2P(CH_2OH)_2]^+Cl^-$ (82) $\xrightarrow{NEt_3}$ $[2\,Cy_2PCH_2OH]$ (108) $\xrightarrow[H_2O/MeOH,\ 60°,\ 1\text{-}3h]{H_2NR}$ $(Cy_2PCH_2)_2NR$

R =  (101),  (102)

[C] $2\,[(C_8H_{14})P(CH_2OH)_2]^+Cl^-$ (83) $\xrightarrow{NEt_3}$ $[2(C_8H_{14})PCH_2OH]$ (109) $\xrightarrow[toluene,\ reflux,\ 3h]{H_2NR}$ $[(C_8H_{14})PCH_2)_2NR$

R =  (103)

Scheme 10

corresponding phosphine oxides are given in Table 2. The mass spectrum of *(101)* showed a peak at $^{m}/e$ 541 corresponding to the molecular ion and a 100% peak at $^{m}/e$ 211 assigned to the fragment $[Cy_2PCH_2]^+$.

The phosphine *(103)* was prepared by treating the pure symmetrical isomer of the phosphonium salt $[C_8H_{14}P(CH_2OH)_2]^+Cl^-$, *(83)*, with NEt_3 to form the hydroxymethylphosphine $(C_8H_{14})PCH_2OH$, *(109)*. This was extracted with toluene and refluxed at 110°C in the presence of R (+) phenylethylamine for 3h, Scheme 10, (C). Significantly more forcing conditions were required to prepare *(103)* in a good yield than the other isostructural aminomethylphosphines *(97)-(102)* and *(104)-(106)*. This may be due to some steric problems of the two rigid $C_8H_{14}P$- units being in close proximity in the product. This can be compared to the monodentate phosphines *(93)* and *(94)* containing the $C_8H_{14}P$- moiety which were prepared under much milder conditions, (60°, 1h). *(103)* was isolated as a sticky white, air-sensitive solid in a 48.5% yield and was stored and handled under nitrogen. The ^{31}P n.m.r. spectrum of *(103)* showed a single peak, Table 2, but attempts to prepare its phosphine oxide led to a variety of peaks in the region of +40 to +50 p.p.m., any of which could correspond to oxide $[C_8H_{14}P(O)CH_2]_2$-NCHMePh.

The hydroxymethylphosphine intermediates *(107)*, *(108)* and *(109)*, Scheme 10, were monitored in their respective reaction mixtures by ^{31}P n.m.r. as single peaks at δ, -12.0, -0.4 and +1.0 p.p.m. respectively, and confirmed the conversion of hydroxymethylphosphonium salts to hydroxymethylphosphines.

The phosphines *(97)-(99)* have been reported previously[10,33,36,37] although not in any detail. The phosphine *(97)* has only been reported in metal complexes with $Mo(CO)_4$ or $Ni(CO)_2$ and no n.m.r. or analysis data were given.[35] *(98)* has been reported by the same authors, both as a free phosphine and in a complex with $Mo(CO)_4$.[33] Only optical rotation and the ^{1}H

n.m.r. spectrum for *(98)* were quoted and the interpretation of the observed ^1H n.m.r. spectrum was oversimplified and is discussed in detail later in this Chapter. Compound *(99)* has been reported[37] in Rh(I) complexes of the type prepared in Chapter 3, but no data regarding the phosphine were quoted.

The ^1H and ^{13}C n.m.r. spectra of the reported bis-aminomethyl phosphines have been interpretated as fully as possible. Particular attention has been given to the n.m.r. properties of the P-C-N linkage and a summary of n.m.r. data for the PCH_2N moiety for phosphines with chiral N substituents are given in Table 4. It can be clearly seen that the proton n.m.r. shifts, J(PH) and J(PC) values differ between phosphines with phenyl groups on P and those with cyclohexyl or 1,5-cyclooctyl groups. This effect is most obvious for the J(PH) and J(PC) values which show an inversion of proportionality when the phosphorus substitents are changed from electron withdrawing (Ph) to electron donating (Cy, C_6H_{14}). The phenyl substituted phosphines show downfield shifts for the methylene protons of the PCH_2N linkage in their ^1H n.m.r. spectra, in relation to the alkyl substituted phosphines *(101)-(103)*. This can be attributed to the deshielding effect of the phenyl rings which has been observed in previous n.m.r. studies of organophosphines.[115] However, the most interesting feature of the PCH_2N link is the nature of the ABX pattern observed in the ^1H n.m.r. for all the phosphines *(97)-(103)*. Predictably the presence of a chiral centre β to the $-CH_2-$ moiety makes the two protons diastereotopic and they are observed as an AB pattern with a typical[113] $J(H^AH^B)$ geminal coupling of 13-14 Hz. The coupling to phosphorus, however, appears to be irregular as only one (H^A) of the protons (H^A and H^B) couples strongly to phosphorus. An example of this coupling is given in Figure 5, for the phosphine *(97)*. The nature of this coupling is discussed in Section 2.9.

Phosphine		^{31}P, δ	^{1}H, δ, $PC\underline{H}_2N$	^{13}C, δ, $P\underline{C}H_2N$	$^{2}J(PH^A)$, Hz	J(PC), Hz
(93) *(94)*	$C_8H_{14}PCH_2NEt_2$	-9.88 sym -48.8 asym	2.4 doublet, sym 2.8 doublet, asym	49.0 multiplet	2.2 sym 1.5 asym	—
(97)	$(Ph_2PCH_2)_2NCHMePh$	-27.83	3.8-4.05 ABX	56.2 doublet	6.0	5.0
(98)	$(Ph_2PCH_2)_2NCHMeCO_2Et$	-26.38	3.5-3.9 ABX	54.5 doublet	9.3	4.9
(99)	$(Ph_2PCH_2)_2NCHMeCO_2Me$	-26.62	3.5-3.85 ABX	54.95 doublet	9.0	4.7
(100)	$(Ph_2PCH_2)_2N$-norbornyl	-28.63	3.85 ABX	57.4 triplet	–	11.8
(101)	$(Cy_2PCH_2)_2NCHMePh$	-18.35	2.7-3.2 ABX	57.3 triplet	3.8	9.9
(102)	$(Cy_2PCH_2)_2NCHMeCO_2Et$	-18.15	2.7-3.2 ABX	56.7 triplet	6.8	10.2
(103)	$[(C_8H_{14})PCH_2]_2NCHMePh$	-46.6	3.0-3.25 ABX	48.0 doublet of doublets	2.9 $^{2}J(PH^B) = 2.2$	13.1 $^{3}J(PC) = 9.5$

Table 4
Correlated n.m.r. data for the PCH_2N linkage

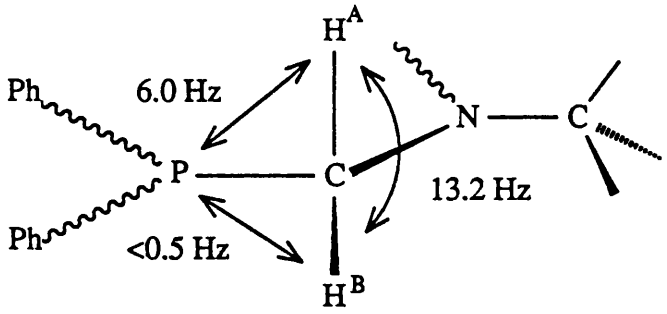


Figure 5 $J(H^AH^B)$, $J(PH^B)$ and $J(PH^A)$ coupling constants for *(97)*

2.9 N.m.r. studies of $(Cy_2PCH_2)_2NCHMePh$ *(101)* and $(Ph_2PCH_2)_2NCHMeCO_2Et$ *(98)*

By the use of $\{^{31}P-^{1}H\}$ heteronuclear shift correlation (HSC) n.m.r. experiments it has been possible to confirm the phosphorus-proton coupling observed in the upfield half of the ABX patterns. Selected regions of the HSC spectra of *(98)* and *(101)* are shown in comparison with corresponding regions from their ^1H n.m.r. spectra in Figures 6 and 7. The HSC spectrum of *(98)* shows a strong coupling, shown by contour density, to the half of the AB pattern at δ 3.45 p.p.m., but no coupling to the half at δ 3.85 p.p.m. The spectrum also reveals that phosphorus coupling is involved in the complex pattern assigned to the NCH proton of the chiral group. The HSC spectrum of *(101)* similarly shows P coupling to the half of the AB pattern at δ 2.6 p.p.m. and no coupling to the half at δ 2.8 p.p.m. Coupling of cyclohexyl protons on carbon atoms α and β to phosphorus can also be observed.

Asymmetric ABX spin systems have been previously observed in aminomethylphosphines[23,33,36] but full assignment of the data has not been reported for phosphines of the type $(R_2PCH_2)_2NR'$ (R' = chiral group). It has been suggested[23] that in six-membered aminomethylphosphine heterocycles that a phosphorus lone pair - proton dihedral angle of 180° gives a low value for J(PH), as discussed in Chapter 1, page 6. Many examples also

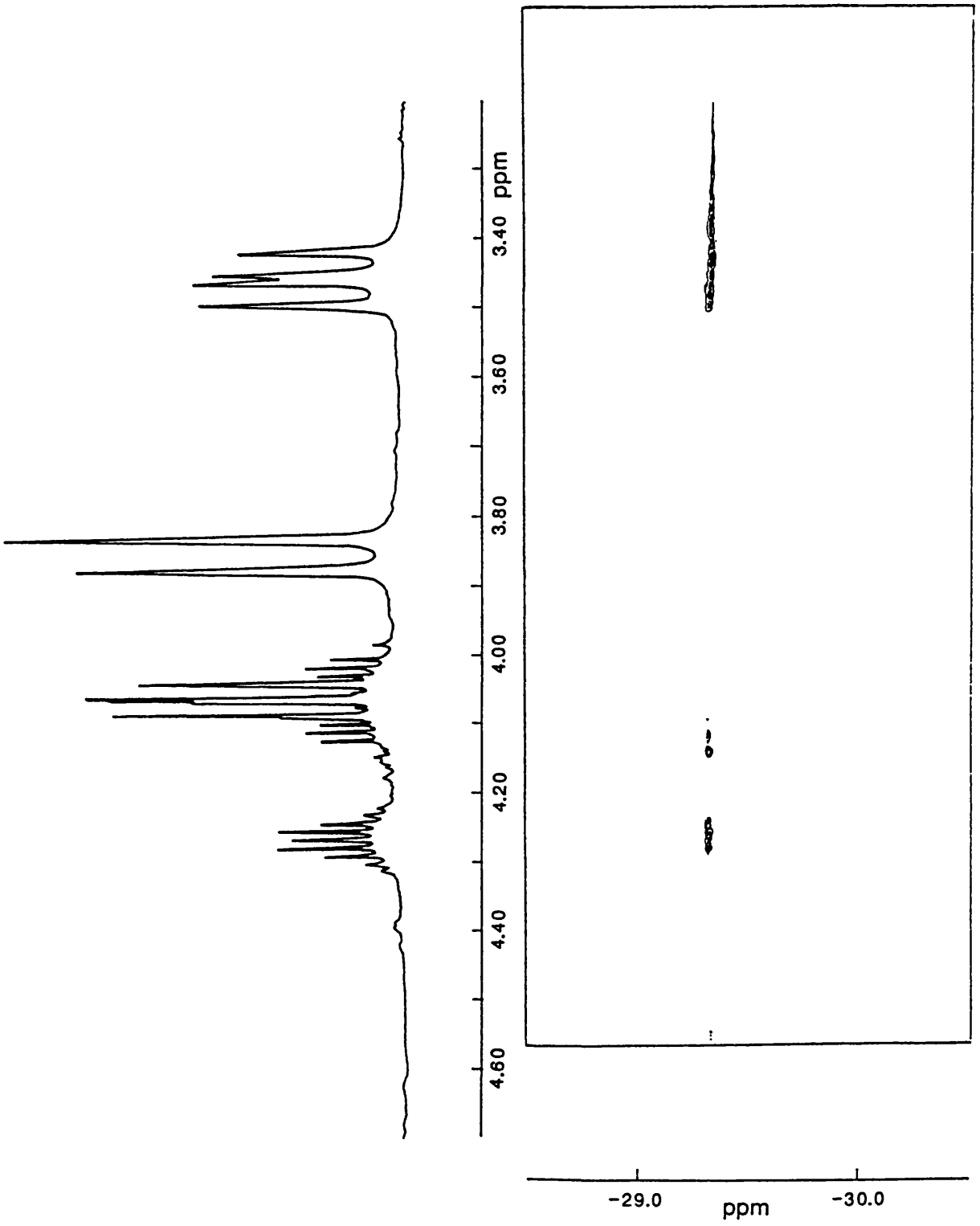


Figure 6
Selected regions of the $\{^{31}P\text{-}^{1}H\}$ (HSC) n.m.r. spectra of $[Ph_2PCH_2)_2NCHMeCO_2Et$ *(98)*

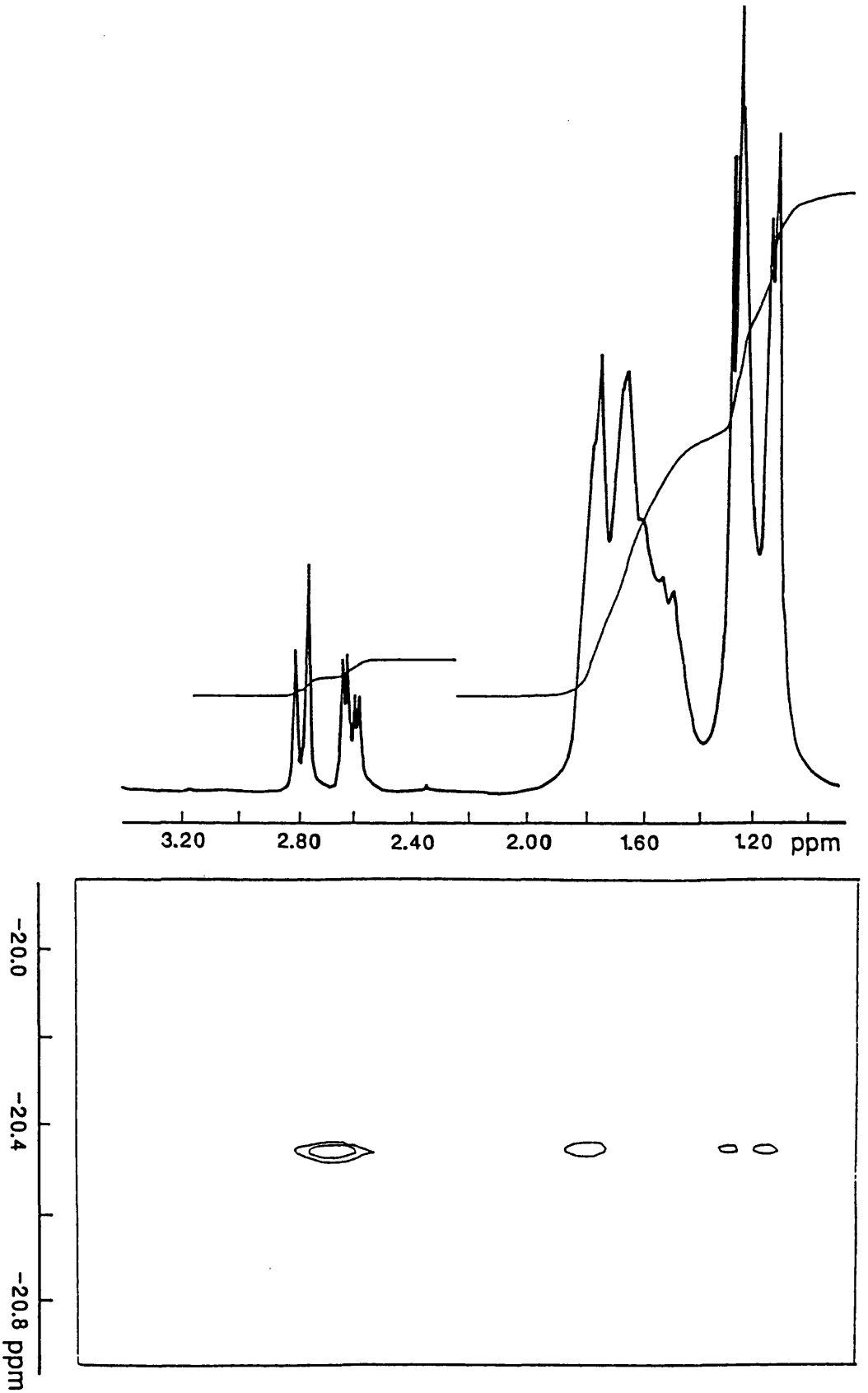
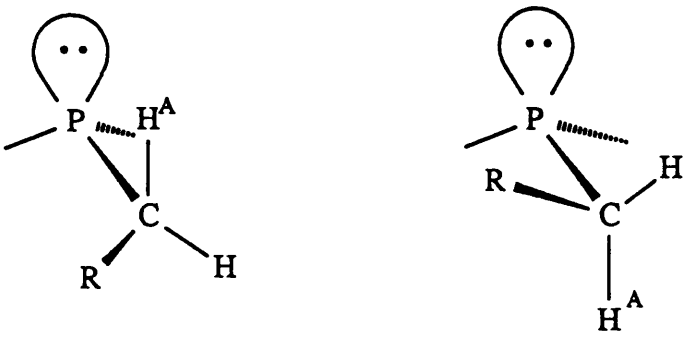


Figure 7
Selected regions of the $\{^{31}P\text{-}^{1}H\}$ (HSC) n.m.r. spectra of $(Cy_2PCH_2)_2NCHMePh$ *(101)*

exist[115] that show that the J(PH) coupling of methylene protons α to phosphorus depend on their proximity to the phosphorus lone pair. This behaves as a function of the dihedral angle between the phosphorus lone pair and the methylene protons as illustrated in Figure 8.



Angle = 0°
J(PH^A) High

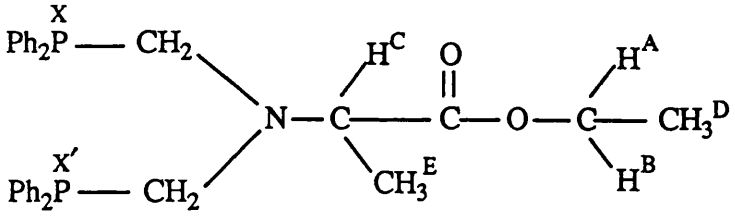
Angle = 180°
J(PH^A) Low

Figure 8 Phosphorus lone-pair to methylene proton H^A, dihedral angles and relative values expected for J(PH)

Crystallographic data for *(101)* shows that the dihedral angles of the methylene protons in relation to the phosphorus lone pair (161° and 87° for one arm of the phosphine and 145° and 107° for the other arm) although different, are not profound in relation to the extremes of 0° and 180°. This, however, would not necessarily be the case in solution when with solvent interactions a different conformation may be preferred. A variable temperature ^{1}H n.m.r. study of *(101)* was taken at 20 K intervals from 273 K to 373 K with no change in the PCH_2N signal. Therefore, the protons H^A and H^B remain significantly different in relation to phosphorus despite extensive warming. From molecular models it can be seen that *(101)* is a highly sterically hindered molecule and bond rotation of the bulky groups about nitrogen is limited to a specific pattern. An analogy to this form of rotation could be made to three meshing gears turning together around a nitrogen atom. It is interesting to note that the cis platinum dichloride complex of *(101)* shows the predicted symmetrical ABX with equal J(PH)

values for H^A and H^B. The limited degrees of freedom of these bulky phosphines must limit their conformations, even in heated solutions, such that there is always a differing relationship between the phosphorus lone pair, and the methylene protons, H^A and H^B, as seen in the ^1H n.m.r.

As has been mentioned, an earlier report of the phosphine *(98)* by Markl and Jin gave an oversimplified interpretation of its ^1H n.m.r. spectrum. They reported both the CH_2 of the ethyl ester group and the single proton of the chiral carbon, as quartets. As can be seen from the ^1H n.m.r. spectrum of *(98)* in Figure 6 the CH resonance at δ 4.3 p.p.m. and the OCH_2 resonance at δ 4.05 p.p.m. are far more complicated. By the use of selected homonuclear decoupling experiments the two patterns have been assigned to specific spin systems following the labelling of protons of *(98)* in Figure 9.



δ 4.05 p.p.m. (H^AH^B), $\underline{AB}CD_3$,	^2J (H^AH^B)	12.0 Hz
	^5J ($H^{AB}H^C$)	3.6 Hz
	^3J ($H^{AB}H^D$)	7.1 Hz
δ 4.3 p.p.m. (H^C), $AB\underline{C}E_3XX'$,	^3J (H^CH^E)	7.1 Hz
	^5J (H^CH^{AB})	3.6 Hz
	^4J ($H^CP^{XX'}$)	11.0 Hz

Figure 9

Irradiation of the methyl doublet assigned to H^E led to the second order pattern at δ 4.05 p.p.m. becoming an AB pattern with an additional coupling of 3.6 Hz. The AB pattern shows the diastereotopic nature of the protons H^A and H^B, even though they are on a carbon atom that is γ to the chiral centre. The irradiation of the methyl triplet assigned to H^E produced a change in the multiplet at δ 4.3 p.p.m. to a clearly defined

triplet of triplets, with the smaller coupling constant being 3.6 Hz. With the previous knowledge, from the HSC spectrum of *(98)*, that H^C coupled to the phosphorus atoms X and X′, then assignments for the spin systems for both H^C and H^{AB} can be made (Figure 9). However, it is surprising that the methylene resonance of the ester group was previously assigned[33] as a quartet, as even in the starting material; L-alanine ethyl ester, it appears as a multiplet in the ^1H n.m.r. spectrum.

2.10 Structural features of $(Cy_2PCH_2)_2NCHMePh$ *(101)*

The molecular structure of *(101)* is illustrated in Figure 10, and selected bond lengths and angles are shown in Table 5. Figure 10 gives a view of *(101)* looking directly down onto the lone pair of nitrogen. The diagram clearly shows the geometry of the bulky substituents, about the central atom, that is required to avoid steric interactions. The C-N-C bond angles; [110.8(4)° - 113.7(4)°], Table 5, reflect the presence of bulky substituents about nitrogen compared to NH_3 (106.8°),[116] but are far from the near planarity of the extremely bulky $N(SiMe_3)_3$, (119.6°).[117] The C-P-C angles between phosphorus cyclohexyl groups are large, [104.2(2)° - 106.8(2)°], typically comparable to those in P^tBu_3 of (105.7°).[118] The other C-P-C angles between cyclohexyl groups and PCH_2N carbon atoms C(3) and C(4) are more moderate; [97.8(2)° - 101.5(2)°], being only slightly larger on average than in PMe_3, (98.9°).[118] The phosphorus carbon bond distances of P(1)-C(3) and P(2)-C(4) appear within the typical range for P-C single bonds of 1.87(2)Å,[119] as are the phosphorus-cyclohexyl bond distances. The nitrogen-carbon bond distances for N(1)-C(3) and N(1)-C(4) also compare favourably with the N-C bond lengths in NMe_3, (1.47Å).[117,120] The approximate dihedral angles between the theoretical position of the phosphorus lone pair for P(1) and the methylene protons H(31) and H(32) are 145° and 107° respectively For the phosphorus atom P(2) and the methylene

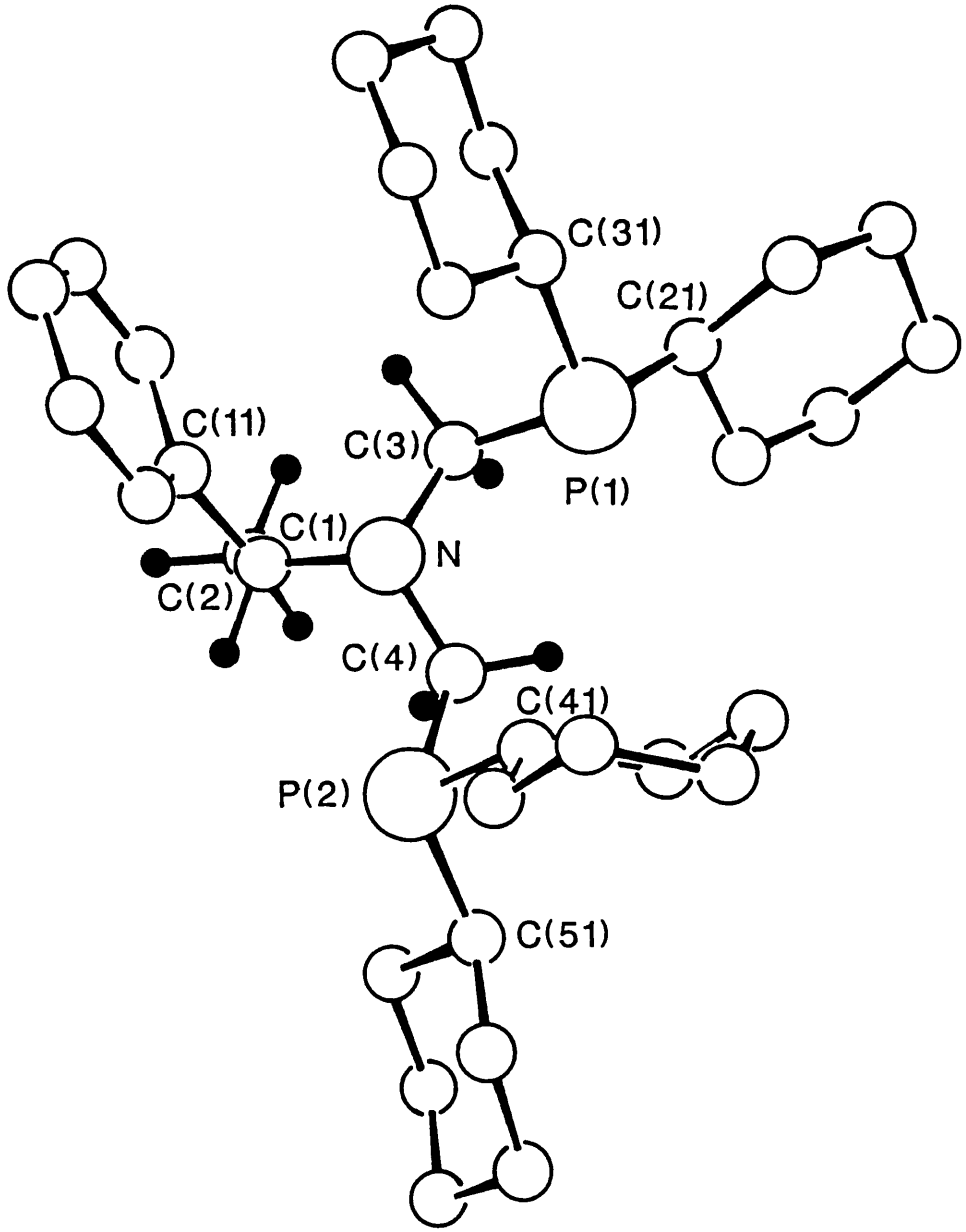


Figure 10 Molecular structure of $(Cy_2PCH_2)_2NCHMePh$ *(101)* with hydrogen atoms shown in black. All cyclohexyl H atoms have been omitted.

Bond angle	(°)
C(21) — P(1) — C(3)	100.1 (2)
C(31) — P(1) — C(3)	101.5 (2)
C(31) — P(1) — C(21)	104.2 (2)
C(51) — P(2) — C(4)	99.9 (2)
C(51) — P(2) — C(41)	106.8 (2)
C(41) — P(2) — C(4)	97.8 (2)
C(3) — N(1) — C(1)	113.7 (4)
C(4) — N(1) — C(1)	112.7 (4)
C(4) — N(1) — C(3)	110.8 (4)

Bond	(Å)
C(3) — P(1)	1.856 (5)
C(4) — P(2)	1.861 (4)
C(4) — N(1)	1.477 (6)
C(3) — N(1)	1.483 (5)
C(1) — N(1)	1.475 (6)
P(1) — C(21)	1.850 (5)
P(1) — C(31)	1.862 (6)
P(2) — C(41)	1.875 (5)
P(2) — C(51)	1.865 (5)

Table 5

Selected Bond Lengths in (Å) (with e.s.d. in parentheses) and bond angles in (°) (with e.s.d. in parentheses) for $(Cy_2PCH_2)_2NCH(Me)PH$ (101)

protons H(41) and H(42) the approximate dihedral angles are 161° and 87° respectively. This shows there is no apparent interaction between the phosphorus lone pairs and the methylene protons on C(3) and C(4).

2.11 Conclusion

A variety of bis hydroxymethyl phosphonium salts have been readily prepared from secondary phosphines. These highly crystalline compounds have been shown to be convenient precursors to a range of new aminomethyl-phosphines. The isolation of the 3-3-1 isomer of $[(C_8H_{14})P(CH_2OH)_2]^+HSO_4^-$ *(86)* allows new entry into non-isomeric mixtures of aminomethylphosphine derivatives of 3-3-1 phosphabicyclononane. In the synthesis of amino-methylphosphines of the type $(R_2PCH_2)_2NR'$ the ability to easily vary the substituents R and R′ using different phosphines and amines has been clearly demonstrated. Scope for synthesis of further new aminomethylphos-phines clearly exists with the investigation of different substituents at phosphorus, as well as on nitrogen, meriting consideration. In summary, the reaction of amines with hydroxymethylphosphonium salts to give amino-methylphosphines in good yield provides an easy synthetic route into a wide range of 'designer' tertiary phosphine ligands of potentially different properties.

2.12 Experimental

Microanalytical results, m.p., n.m.r. spectroscopic data and, in one case, mass spectra, are reported as far as possible for all reported phosphonium salts and aminomethylphosphines. Microanalyses were carried out by C.H.N. Analysis Ltd., Alpha House, Countesthorpe Road, South Wigston, Leicester, LE8 2PJ, and by Butterworth Laboratories Ltd., 54-56, Waldegrove Road, Teddington, Middlesex, TW11 8LG. M.p's were recorded on a

Gallenkamp melting point apparatus and are uncorrected. The ^{1}H n.m.r. spectra were recorded at room temperature on a Bruker AM300 spectrometer operating at 300.13 MHz, or on a Jeol EM 390 spectrometer operating at 90 MHz, with $SiMe_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field). Coupling constants J are in Hz. The $^{13}C-\{^{1}H\}$ n.m.r. spectra were recorded along with D.E.P.T. spectra in $[^{2}H_1]$-chloroform unless otherwise stated on a Bruker AM300 spectrometer operating at 75.47 MHz. The $^{31}P-\{^{1}H\}$ n.m.r. spectra were recorded in $[^{2}H_1]$-chloroform unless otherwise stated on either a Jeol JMM-FX60 spectrometer operating at 24.15 MHz with $[P(OH)_4]^{+}$ in $[^{2}H_2]$-water (0.0 p.p.m.) as external reference, with positive values to high frequency (low field). I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer as KBr discs unless otherwise stated.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere. The solvents, water, methanol, ethanol and isopropanol were distilled before use and the solvents dichloromethane, diethyl ether and toluene were dried and distilled under nitrogen prior to use, from the following drying agents: dichloromethane (calcium hydride); diethyl ether (sodium/benzophenone); toluene (sodium). The compounds diphenyl phosphine, calcium carbonate, triethylamine (-) ephedrine, diethylamine, L-proline methylester hydrochloride, D (+) α methylbenzylamine, L-alanine ethylester hydrochloride, ethanolamine, allylamine and propargylamine were used as supplied from Aldrich. The compounds L-alanine methyl ester hydrochloride and R (+) bornylamine was used as supplied from Fluka. The mixed isomers of phosphabicyclononane ($C_8H_{14}PH$) and dicyclohexylphosphine were used as supplied by Albright & Wilson Ltd. The compounds tetrahydrofuran, formaldehyde solution and hydrochloric acid solution were used as supplied from commercial sources.

2.12.1 Preparation of $[R_2P(CH_2OH)_2]^+X^-$ phosphonium salts.

(i)$[Ph_2P^+(CH_2OH)_2]Cl^-$(81)

A solution of HCHO (9cm^3,40% soln) and a solution of HCl (5cm^3,36% soln) were added to Ph_2PH (10g,54mmol) stirred under an atmosphere of nitrogen . The mixture became hot and homogeneous. On cooling a white solid crystallised out. This was filtered and recrystallised from boiling methanol,(15.0g,99% based on P).

(Found:C,59.47;H,5.79;P,10.64. $C_{14}H_{16}ClO_2P$ requires C,59.62; H,5.76; P,10.96%). M.p. 160-162^oC

N.m.r.(CD_3OD): $^{31}P-\{^1H\}$(24MHz),δ 16.73 p.p.m.

(ii)$[Cy_2P^+(CH_2OH)_2]Cl^-$(82)

A solution of HCHO (96cm^3,40% soln) and a solution of HCl (47.5cm^3, 36% soln) were added to Cy_2PH (100g,0.5mol) stirred under a nitrogen atmosphere. The mixture became hot and upon cooling a white solid crystallised out. This was filtered and recrystallised from boiling isopropanol,(144.3g,98% based on P).

(Found:C,57.2;H,9.52;P,10.16. $C_{14}H_{28}ClO_2P$ requires:C,57.0;H,9.6;P,10.5%).

M.p. 170-173^oC

N.m.r.(CD_3OD): ^1H(90MHz) δ 0.9-2.3[m,22H,Cy],4.3[d,4H,CH_2,^2J(PH)3.0], 4.5[s.b,2H,OH];

$^{31}P-\{^1H\}$(24MHz),δ 28.3 p.p.m.

(iii)$(C_8H_{14})P^+(CH_2OH)_2Cl^-$ (mixed isomers)(83)&(84)

A solution of HCHO (101cm^3,40%soln) and a solution of HCl (116cm^3, 36%soln) were added to $(C_8H_{14})PH$ (mixture of isomers) (249.8g,1.76mol) stirred under a nitrogen atmosphere. The temperature rose to 60^oC over 1h. On cooling two layers separated. The lower aqueous phase was decanted, washed with toluene and filtered through Dicalite. The solvent

was removed under reduced pressure yielding a white solid which was recrystallised from boiling methanol,(368.5g,95% based on P).

M.p. 242-246°C

N.m.r. (D_2O): $^{31}P-\{^1H\}$(24MHz),δ 23.39,55.66 p.p.m. (sym:asym)

(iv)$[(C_8H_{14})P^+(CH_2OH)_2]_2SO_4^{2-}$(86)&(87)

A solution of HCHO (405cm^3,40%soln) and a solution of H_2SO_4 (180cm^3, 98%soln) were added to $(C_8H_{14})PH$ (mixture of isomers) (365.3g, 2.51mol) stirred under a nitrogen atmosphere. The temperature rose to 70°C following addition and the reaction was mechanically stirred. Further HCHO solution (100cm^3,40%soln) was then added. On cooling two layers separated. The lower aqueous layer was filtered through Dicalite to produce a clear solution. The solvent was removed under reduced pressure yielding a white solid, which was recrystallised from methanol,(969g, 81.3% based on P).

M.p. 190-200°C

N.m.r.(D_2O):$^{31}P-\{^1H\}$(24MHz),δ 22.99,55.66 p.p.m.

(v)$[(C_8H_{14})P^+(CH_2OH)_2]_2SO_4^{2-}/[(C_8H_{14})P^+(CH_2OH)_2]HSO_4^-$ symmetrical isomer(86)

$[(C_8H_{14})P^+(CH_2OH)_2]_2SO_4^{2-}$ (mixed isomers)(125g,0.26mol) was dissolved in H_2SO_4 (70cm^3,36%) in a flask fitted with a dropping funnel, thermometer and a Dean & Stark condenser. The solution was heated to a constant 150°C. Distillate (about 10cm^3) was removed at regular intervals and replaced by distilled water (10cm^3). This procedure was continued for 13h, samples being monitored for decomposition of the asymmetric isomer at 6.5h intervals by ^{31}P n.m.r. The reaction mixture was then diluted with distilled water (60cm^3) and refluxed at 105-110°C. Further distillate was collected to remove any remaining HCHO. The solution was then filtered hot through carbon to remove any discolourations and

neutralised with solid $CaCO_3$ (100g,1.0mol). The solution was then filtered again and the volume reduced under reduced pressure. The resulting solid was recrystallised from boiling methanol,(58.1g,46.5% recovery,79.4% based on 3,3,1 isomer).

Analysis of distillate

The first distillate(136cm^3) was titrated with sodium sulphite solution, using a thymol phthalein indicator and was back titrated with HCl solution.

Yield: 3.6g HCHO in 136cm^3 of distillate.

Final distillate: 0.3g HCHO.

M.p. 208-210°C

N.m.r. (D_2O):$^{31}P-\{^1H\}$(24MHz),δ 21.78 p.p.m. (sym).

(Found:P,11.0. required: 10.3 to 12.3%, ratio 35:65, mono:di, cations.).

(vi)$[(C_8H_{14})P^+(CH_2OH)_2]Cl^-$(83)

The phosphonium salt $[(C_8H_{14})P^+(CH_2OH)_2)_2SO_4^{2-}$ (symmetrical isomer)(5g) was dissolved in hot distilled water(30cm^3) and $BaCl_2.2H_2O$ (2,5g,10mmol) in hot distilled water(30cm^3). The solution was allowed to cool and filtered through celite. The solvent was removed under reduced pressure and the resulting solid recrystallised from methanol,(3.56g,84% based on P).

(Found: C,50.5;H,8.3. $C_{10}H_{26}ClO_2P$ requires C,50.3;H,8.4%)

M.p. 248-250°C

N.m.r. (D_2O):$^{31}P-\{^1H\}$(24MHz),δ 23.39 p.p.m.

2.12.2 Preparation of $[R_2P(CH(Me)OH)_2]^+Cl^-$ phosphonium salts.

(vii)$[Ph_2P^+(CH(Me)OH)_2]Cl^-$(91)

CH_3CHO (7.5cm^3,0.13mol) and a solution of HCl (5cm^3,36%) were added to Ph_2PH (10g,54mmol) in tetrahydrofuran(100cm^3) stirred under an atmosphere of nitrogen. The mixture became hot and clear. The mixture was stirred

for 1h and solvent was then removed under reduced pressure to yield a white crystalline solid. The product was recrystallised from methanol/diethyl ether at -20°C, (6.9g,41% based on P).

(Found: C,61.9;H,6.4. $C_{16}H_{20}ClO_2P$ requires C,61.8;H,6.4%)

M.p. 128-130°C

N.m.r. (D_2O):^1H (90MHz),δ 1.25-1.8[m,6H,CH_3],5.60[m,2H,CH], 7.5-7.9[m,10H,Ph]; $^{31}P-\{^1H\}$(24MHz),δ 26.21 p.p.m.

(viii)$[Cy_2P^+(CH(Me)OH)_2]Cl^-$(90)

CH_3CHO (35cm^3,0.62mol) and a solution of HCl (26cm^3,36%) were added to Cy_2PH (55.8g,0.28mol) in diethyl ether(40cm^3), stirred under an atmosphere of nitrogen. The mixture became hot and clear. Upon cooling the solvents were removed under reduced pressure to yield a viscous mass. The mass was dissolved in boiling methanol and on addition of diethyl ether at -20°C, fine needles precipitated.(53.3g,59% based on P).

(Found: C,59.7;H,10.1. $C_{16}H_{32}ClO_2P$ requires C,59,5;H,9.9%)

M.p. 124-130°C

N.m.r. (CD_3OD):$^{31}P-\{^1H\}$(24MHz),δ 29.04 p.p.m.

2.12.3 Preparation of $R(CH_2NR'R")_3$ Phosphines

(i) $P(CH_2N(Me)CH(Me)CH(OH)Ph)_3$(92)

Triethylamine (4.9cm^3,35mmol) was added to a solution of $P^+(CH_2OH)_4Cl^-$ (10g,35mmol) in ethanol (50cm^3). Then ephedrine (17.5g, 0.1mol) was added and the solution refluxed under an atmosphere of nitrogen for 2h. On cooling the solution was washed with toluene and a white solid precipitated, which was filtered and stored under nitrogen,(11.23g,61% based on P).

(Found:C,69.8;H,8.8;N,7.5. $C_{33}H_{48}N_3O_3P$ requires C,70.0;H,8.5;N,7.4%)

M.p. 114-117°C

N.m.r.(CD_3OD)$^{31}P-\{^1H\}$(24MHz),δ -54.05 p.p.m.

2.12.4 Preparation of $R_2PCH_2NR'R''$ Phosphines.

(ii) $C_8H_{14}PCH_2NEt_2$(93)&(94)

$(C_8H_{14})P^+(CH_2OH)_2Cl^-$ (mixed isomers)(10g,45mmol) was dissolved in a 2:1 solution of water:methanol ($40cm^3$) and stirred under an atmosphere of nitrogen. A solution of Na_2SO_3 (11g,87mmol) in water ($25cm^3$) followed by diethylamine ($5cm^3$,97mmol) was then added. The mixture was heated to about 60^oc for 1h. On cooling the mixture separated into two layers. the upper organic layer was decanted and the product distilled under high vacuum and stored under nitrogen,(8.65g,84.7% based on P).

(Found:C,68.5;H,11.7;N,6.4. $C_{13}H_{26}NP$ requires C,68.7;H,11.5;N,6.2%).

B.p. 124-127°C at 2.5mm Hg

N.m.r. ($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -9.88,-48.8 p.p.m.

^1H (300MHz),δ 0.92[2t,3H,Me(asym+sym)^3J(HH)7.1],1.3-2.3[m,14H,C_8H_{14}],2.4 [d,2H,PCH_2(sym)^2J(PH)2.2],2.52[m,4H,NCH_2(asym+sym)^3J(HH)7.1,^4J(PH)0.85], 2.8[d,2H,PCH_2(asym)^2J(PH)1.5], $^{13}C-\{^1H\}$(75.47MHz),δ 12.7[s,Me],25.2 [d,PCH,J(PC)10.5],39.7[d,PCH,J(PC)11.8],49.0[m,PCH_2N], 50.5[d,NCH_2, ^3J(PC)15.1],51.9[d,NCH_2,^3J(PC)9.1] p.p.m.

(iii) $Ph_2PCH_2N(Me)CH(Me)CH(OH)Ph$(95)

A solution of HCHO ($2.5cm^3$,40%soln) was added to a solution of ephedrine (4.13g,25mmol) in diethyl ether ($25cm^3$). After 15 minutes Ph_2PH (4.65g,25mmol) was added to the mixture. The reaction was heated under gentle reflux on a water bath for 2h. The mixture was allowed to cool and degassed H_2O ($20cm^3$) and diethyl ether ($20cm^3$) were added. The mixture was shaken vigorously and the ether layer decanted and dried over magnesium sulphate. The solution was then filtered and stored under nitrogen.

N.m.r.($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -26.21 p.p.m.

(iv) $Ph_2PCH_2\overline{NCH_2CH_2CH_2CHCO_2Me}$(96)

Triethylamine (2.3cm^3,17mmol) was added to a stirred solution of $Ph_2P^+(CH_2OH)_2Cl^-$ (5g,17mmol) in water:methanol (2:1,30cm^3) under an atmosphere of nitrogen. Then L-proline methyl ester hydrochloride (2.69g, 16mmol) dissolved in water:methanol (2:1,30cm^3) with triethylamine (2.3cm^3,17mmol) was added. The solution was then heated to about 60^{o}C for 2h. On cooling two layers separated. Toluene (40cm^3) was added and the mixture was shaken. The upper organic layer was separated, dried over magnesium sulphate, filtered and stored under nitrogen,(4.3g,81% based on P).

(Found:C,68.5;H,6.8;N,4.1. $C_{19}H_{22}NO_2P$ requires C,69.1;H,6.7;N,4.2%)

N.m.r. ($CDCl_3$):$^{31}P-\{^1H\}$(24MHz),δ -24.68 p.p.m.

^1H (90MHz),δ 2.7[m,1H,CH],3.6[s,3H,Me],7.3[m,10H,Ph] p.p.m.

2.12.5 Preparation of $(R_2PCH_2)_2NR'$ Phosphines.

(v) $(Ph_2PCH_2)_2NCHMePh$(97)

NEt_3 (5.2cm^3,35mmol) was added to a stirred solution of $Ph_2P^+(CH_2OH)_2Cl^-$ (10g,35mmol) in water:methanol (2:1,60cm^3) under an atmosphere of nitrogen. D(+)α methylbenzylamine (2.3cm^3,18mmol) was added by a syringe. The mixture was heated to reflux on an oil bath for about 30 minutes. On cooling two layers separated. The product was extracted with toluene (40cm^3) and dried over magnesium sulphate, filtered and stored under nitrogen,(8.27g,91.4% based on P).

(Found:C,79.8;H,6.8;N,2.3. $C_{34}H_{33}NP_2$ requires C,79.4;H,6.2;N,2.6%)

N.m.r.($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -27.83 p.p.m.

^1H(300MHz),δ 1.55[d,3H,Me,^3J(HH)6.8],3.8-4.05[m,ABX,4H,PCH_2,^2J(PH)6.0, ^2J(HH)13.2],5.0[m,1H,CH],7.3[m,20H,Ph], $^{13}C-\{^1H\}$(75.47MHz),δ 15.9[s,Me], 56.2[d,PCH_2,J(PC)5.0],61.3[t,NCH,^3J(PC)9.0] p.p.m.

(vi) $(Ph_2PCH_2)_2NCHMeCO_2Et$(98)

Triethylamine (5.2cm^3,36mmol) was added to a stirred solution of $Ph_2P^+(CH_2OH)Cl^-$ (10g,35mmol) in water:methanol (2:1,60cm^3) under an atmosphere of nitrogen. Then L-alanine ethyl ester hydrochloride (4.44g,29mmol) dissolved in water:methanol (2:1,60cm^3) and triethylamine (5.2cm^3,35mmol) was added. The mixture was heated to reflux for 1h. On cooling two layers separated. The product was then extracted with dichloromethane (40cm^3) and dried over magnesium sulphate and filtered. The solvents were then removed under high vacuum for several days to yield a white solid,(5.58g,61.5% based on P).

(Found:C,71.5;H,6.5;N,2.9. $C_{31}H_{33}NO_2P_2$ requires C,72.5;H,6.5;N,2.9%)

M.p. 76-77^{o}C

N.m.r. ($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -26.38 p.p.m.

^1H (300MHz),δ 1.0[d,3H,Me,^3J(HH)7.1],1.15[t,3H,$CH_2\underline{Me}$,^3J(HH)7.13], 3.5-3.9 [m,ABX,4H,PCH_2,^2J(HH')13.2,^2J(PH')9.3,^2J(PH)<0.5],4.05[m,$\underline{ABCD}_3$,2H, $O\underline{CH}_2Me$,^2J(HH')12.0,^5J(HH)3.6,^3J(HH)7.1],4.3[m,$AB\underline{C}E_3XX'$,1H,NCH,^5J(HH)3.6, ^3J(HH)7.1,^4J(PH)11.0], 7.1-7.6[m,20H,Ph]. $^{13}C-\{^1H\}$(75.47MHz),δ 14[s,Me], 14.5[s,Me],54.95[d,PCH_2,J(PC)4.9],58.3[t,NCH,^3J(PC)9.4],59.9[s,OCH_2], 172.7[s,C=O] p.p.m.

(vii) $(Ph_2PCH_2)_2NCHMeCO_2Me$(99)

Triethylamine (2.5cm^3,34mmol) was added to a stirred solution of $Ph_2P^+(CH_2OH)_2Cl^-$ (5g,17.7mmol) in water:methanol (2:1,50cm^3) under an atmosphere of nitrogen. L-alanine methyl ester hydrochloride (1.24g, 8.9mmol) dissolved in water:methanol (2:1,50cm^3) was then added. The mixture was heated to 60^{o}C for 1h and then allowed to cool. The product was extracted with degassed dichloromethane (50cm^3) and dried over magnesium sulphate. The solvent was then removed under reduced pressure to yield a sticky white solid,(3.56g,80.5% based on P).

N.m.r. ($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -26.62 p.p.m.
^1H (300MHz),δ 1.0[d,3H,CHMe,^3J(HH)7.1],3.5[m,ABX,2H,PCH_2,^2J(HH')13.2,
^2J(PH')9.0],3.55[s,3H,OMe],3.85[d,ABX,2H,PCH_2,^2J(HH')13.2,^2J(PH)<0.5],
4.3[m,1H,CH],7.2-7.5[m,20H,Ph], $^{13}C-\{^1H\}$(75.47MHz),δ 14.7[s,Me],50.9
[s,OMe],54.95[d,PCH_2,J(PC)4.7],58.5[t,NCH,^{3}J(PC)9.2],173.0[s,$-CO_2Me$]
p.p.m.

(viii) $(Ph_2PCH_2)_2NCHCH_2CHCH_2CH_2C(Me)C(Me)_2$(100)

Triethylamine (1.8cm^3,13mmol) was added to a stirred solution of $Ph_2P^+(CH_2OH)_2Cl^-$ (3.7g,13mmol) in water:methanol (2:1,40cm^3) under an atmosphere of nitrogen. R(+) bornylamine (1.0g,6.5mmol) was then added. The mixture was heated to 50°C for 1h and then allowed to cool. The product was extracted with degassed dichloromethane (40cm^3) and dried over magnesium sulphate. The solvent was then removed under reduced pressure to yield a highly viscous oil,(3.39g,95% based on P).
N.m.r.($CDCl_3$):$^{31}P-\{^1H\}$(24MHz),δ -28.63 p.p.m.
^1H (300MHz),δ 0.55[s,3H,Me],0.67[s,3H,Me],0.81[s,3H,Me],0.9-1.05[m,3H,
-CHH'-],1.37[t,1H,CH,^{3}J(HH)4.2],1.4-1.55[m,3H,-CHH'-],3.0[m,1H,NCH],
3.85[m,ABX,4H, PCH_2,^{2}J(HH')13.5],7.2-7.5[m,20H,Ph]. $^{13}C-\{^1H\}$(75.47MHz),δ
16.1[s,Me],18.3 [s,Me],19.7[s,Me],27.0[s,CH_2],28.3[s,CH_2],44.2[s,CH],48.9
[s,C],49.5[s,C],57.4[t,PCH_2,J(PC)11.8],68.3[t,NCH,^{3}J(PC)7.2] p.p.m.

(ix) $(Cy_2PCH_2)_2NCHMePh$(101)

Triethylamine (8.5cm^3,84mmol) was added to a stirred solution of $Cy_2P^+(CH_2OH)_2Cl^-$ (24.3g,82.5mmol) in water:methanol (2:1,100cm^3) under an atmosphere of nitrogen and D(+)α methylbenzylamine (5.3cm^3,46mmol) was added. The mixture became highly viscous and toluene (50cm^3) was added. The reaction was heated to reflux on an oil bath for 45 minutes and then allowed to cool. The organic layer was decanted and dried over magnesium

sulphate and filtered. Methanol was then added to the toluene solution until it began to cloud. The solution was placed in a freezer at -15°C and large colourless crystals were collected,washed with methanol and dried under vacuum,(12.5g,56% based on P).

(Found:C,75.2;H,10.8;N,2.5. $C_{34}H_{57}NP_2$ requires C,75.3;H,10.5;N,2.6%)

M.p. 87-89°C

N.m.r. ($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -18.35 p.p.m.

^1H (300MHz),δ 1.4[d,3H,Me,^3J(HH)6.9],2.7-3.2[m,ABX,4H,CH_2,^2J(HH')12.9, ^2J(PH')3.8,^2J(PH)<0.5], 5.1[m,1H,CH,^3J(HH)6.9], 7.0-7.4[m,5H,Ph],

$^{13}C-\{^1H\}$(75.47MHz),δ 11.1[s,Me],47.9[m,PCH_2],57.3[t,CH,^3J(PC)9.9] p.p.m.

Mass spec:M/e: 541 (M^+,541),211(100%,Cy_2PCH_2),105(28%,CH(Me)Ph).

(x) $(Cy_2PCH_2)_2NCHMeCO_2Et$(102)

Triethylamine (1.5cm^3,20mmol) was added to a stirred solution of $Cy_2P^+(CH_2OH)_2Cl^-$ (3.15g,10.7mmol) in water:methanol (2:1,30cm^3) under an atmosphere of nitrogen. L-alanine ethyl ester hydrochloride (0.82g, 5.3mmol) dissolve in water:ethanol (2:1,30cm^3) with triethylamine (4.44cm^3,6mmol) was then added. The mixture was heated to 60°C for 3h and allowed to cool. The product was extracted with degassed dichloromethane (30cm^3) and dried over magnesium sulphate. The solvent was then removed under reduced pressure to yield a highly viscous oil,(2.53g,90% based on P).

(Found:C,70.1;H,10.4;N,2.9. $C_{31}H_{57}NO_2P_2$ requires C,70.9;H,10.9;N,2.7%).

N.m.r. ($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -18.15 p.p.m.

^1H (300MHz),δ 1.1-1.9[m,50H,Cy+2Me],2.7-3.2[m,ABX,4H,PCH_2,^2J(HH')14.0, ^2J(PH')6.8,^2J(PH)<0.5],4.3[q,2H,OCH_2,^3J(HH)7.13], 4.45[m,1H,CH],

$^{13}C-\{^1H\}$(75.47MHz),δ 13.5[s,Me],13.8[s,Me],29.5[d,PCH,J(PC)12.6],47.7 [sb,PCH_2],56.7[t,NCH,^3J(PC)10.2],59.2[s,OCH_2],172[s,$-CO_2Et$] p.p.m.

(xi) $(C_8H_{14}PCH_2)_2NCHMePh$(103)

Triethylamine (3.45cm^3,47mmol) was added to a stirred soloution of $[(C_8H_{14})P^+(CH_2OH)_2]_2SO_4^{2-}/(C_8H_{14})P^+(CH_2OH)_2.HSO_4^-$ (7g,25mmol) in water: methanol (2:1,40cm^3). $C_8H_{14}PCH_2OH$ was then extracted from the mixture with degassed toluene (100cm^3). D(+)α methylbenzylamine (1.5cm^3,13mmol) was added to the solution of $C_8H_{14}PCH_2OH$ and the mixture refluxed under nitrogen for 3h. The solvent was removed under reduced pressure. After three days at<1mmHg a white solid formed which was stored under nitrogen,(2.6g, 48.5% based on P).

N.m.r.($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ -46.6 p.p.m.

^1H (300MHz),δ 1.35[d,3H,Me,^3J(HH)6.8],1.5-2.2[m,28H,C_8H_{14}], 3.0-3.25 [m,ABX,4H, PCH_2,^2J(HH')13.8,^2J(PH')2.9,^2J(PH)2.0],4.35[m,1H,CH],7.15-7.4[m,5H,Ph], $^{13}C-\{^1H\}$(75.47MHz),δ 16.4[s,Me],48.0[dd,PCH_2,J(PC)13.1, ^3J(PC)9.5],60.3[t,CH,^3J(PC)9.7] p.p.m.

(xii) $(Ph_2PCH_2)_2NCH_2CH_2OH$(104)

Triethylamine (1.0cm^3,7.0mmol) was added to a stirred soution of $Ph_2P^+(CH_2OH)_2Cl^-$ (2.0g,7.0mmol) in water:methanol (2:1,40cm^3) under an atmosphere of nitrogen. Ethanolamine (0.21cm^3,3.5mmol) was then added. The mixture was heated to 50^{o}C for 1h and then allowed to cool. The product was extracted with degassed dichloromethane (40cm^3) and dried over magnesium sulphate. The solvent was then removed under reduced pressure to yield a viscous oil,(1.54g,96% based on P).

(Found:C,72.4;H,6.6;N,3.8. $C_{28}H_{29}NOP_2$ requires C,73.5;H,6.4;N,3.0%)

N.m.r.($CDCl_3$),$^{31}P-\{^1H\}$(24MHz),δ -28.23 p.p.m.

^1H (300MHz),δ 3.0[t,2H,CH_2N,^3J(HH)5.2],3.27[sb,exchange D_2O,1H,OH],3.45 [t, 2H,CH_2O,^3J(HH)5.2],3.85[d,4H,CH_2P,^2J(PH)3.3],7.2-8.0[m,20H,Ph] p.p.m.

$^{13}C-\{^1H\}$(75.47),δ 56.0[s,CH_2O],57.7-58.2[m,PCH_2,NCH_2] p.p.m.

(xiii) $(Ph_2PCH_2)_2NCH_2CH{=}CH_2$(105)

Triethylamine (1.0cm^3,7.0mmol) was added to a stirred solution of $Ph_2P^+(CH_2OH)_2Cl^-$ (2.0g,7.0mmol) in water:methanol (2:1,40cm^3) under an atmosphere of nitrogen. Allylamine (0.26cm^3,3.5mmol) was then added to the reaction. The mixture was heated to 50^{o}C for 1h and then allowed to cool. The product was extracted with degassed dichloromethane (40cm^3) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a viscous oil,(1.49g,94% based on P).

(Found:C,75.8;H,6.4;N,3.5. $C_{29}H_{29}NP_2$ requires C,76.8;H,6.4;N,3.1%)

N.m.r.($CDCl_3$),$^{31}P-\{^1H\}$(24MHz),δ -28.84 p.p.m.

^1H (300MHz),δ 3.45[m,6H,PCH_2,NCH_2,^2J(PH)2.9],5.04-5.22[m,2H,$=CH_2$],5.43-5.89[m,1H,CH=,^3J(HH)(cis)9.6,^3J(HH)(trans)17.6,^3J(HH)(vicinal)3.5], 7.2-7.4 [m,20H,Ph] p.p.m.

(xiv) $(Ph_2PCH_2)_2NCH_2C{\equiv}CH$(106)

Triethylamine (1.0cm^3,7.0mmol) was added to a stirred soution of $Ph_2P^+(CH_2OH)_2Cl^-$ (2.0g,7.0mmol) in water:methanol (2:1),40cm^3) under a nitrogen atmosphere. Propargylamine (0.25cm^3,3.5mmol) was then added to the reaction. The mixture was heated to 50^{o}C for 1h and then allowed to cool. The product was extracted with degassed dichloromethane (40cm^3) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a brown viscous oil, (1.0g,69% based on P).

N.m.r.($CDCl_3$),$^{31}P-\{^1H\}$(24MHz),δ -27.02 p.p.m.

The compound decomposed over 48h to compounds with ^{31}P n.m.r.,δ +25.0, +26.2 p.p.m. and therefore could not be obtained analytically pure.

2.12.6 Preparation of Phosphine-oxides

Phosphine oxides were prepared by teating an acetone solution of an aminomethyl phosphine with hydogen peroxide. Generally only the ^{31}P n.m.r. spectra of the products were taken, to be used as a reference.

However the oxide of $(Ph_2PCH_2)_2NCHMePh$ was isolated and characterised to confirm the method.

(i) $(Ph_2P(O)CH_2)_2NCHMePh$(97a)

Hydrogen peroxide solution ($1.0cm^3$,100vols) was added to a solution of $(Ph_2PCH_2)_2NCHMePh$ (4.7g,9.0mmols)in acetone ($50cm^3$). The mixture was stirred in air for 2-3h and then the solvent was removed under reduced pressure. The product was recrystallised from isopropanol and cooling at 0^oC in a fridge,(4.3g,87% based on P).

(Found:C,68.9;H,6.0;N,2.4. $C_{34}H_{33}NO_2P_2.2H_2O$ requires C,70.6;H,6.4;N,2.4%)

M.p. 128-131^oC

(N.m.r.)($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ 31.86 p.p.m.

^1H(300MHz),δ 1.31[d,3H,Me,J(HH)6.8],3.46-4.0[m,ABXX',4H,^{2}J(HH)15.2, $^2J(PH^A)$5.7,$^2J(PH^B)$7.5,$^4J(P'H^B)$1.2],4.88[q,1H,CH,^{3}J(HH)6.7],6.8-7.7[m,20H, Ph] p.p.m.

ir,υ_{max} 1270(P=O) cm^{-1},(KBr).

CHAPTER 3

Synthesis and Reactions of Some Transition Metal Complexes of Aminomethylphosphines

3.1 Introduction

Few metal complexes of aminomethylphosphines have been studied extensively and only two crystal structures have appeared to date.[13,41] Most of the literature containing metal complexes of aminomethylphosphines have been from workers primarily concerned with the phosphine synthesis and investigations of the complexes have been brief. The first report of an aminomethylphosphine metal complex was from Grim *et al.*[13] with the crystal structure of $[Mo(CO)_4\{Ph_2PCH_2N(Me)CH_2CH_2N(Me)CH_2PPh_2\}]$ *(127)*. This compound exhibited a rare nine-membered chelate ring of cis geometry and thus supported the observed infrared data. Further work by Grim,[7] and his co-workers, investigated numerous metal-carbonyl complexes of some multidentate aminomethylphosphine *(16)*, *(17)*, *(18)*, *(19)* (Figure 1, Scheme 1), as mentioned in Chapter 1.

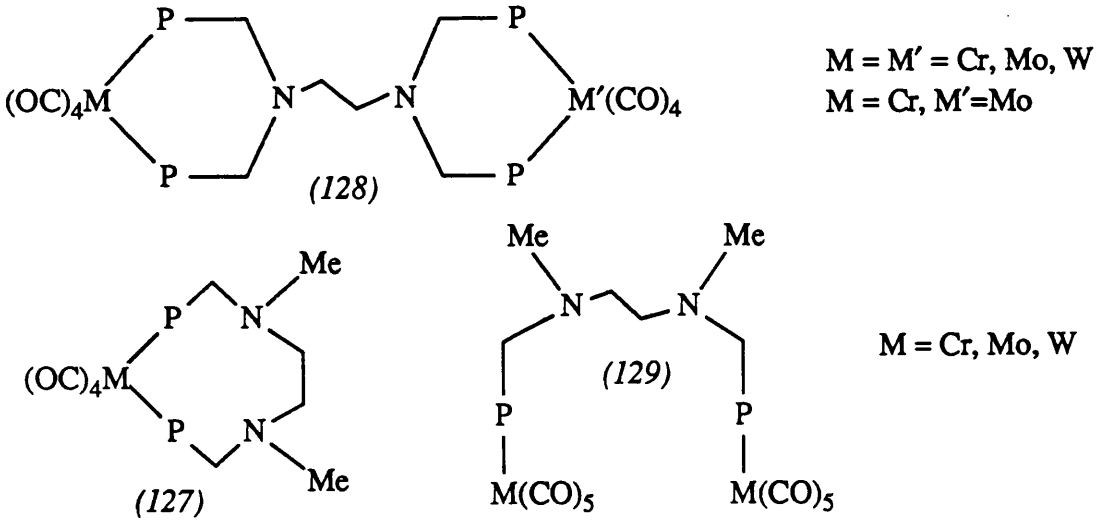
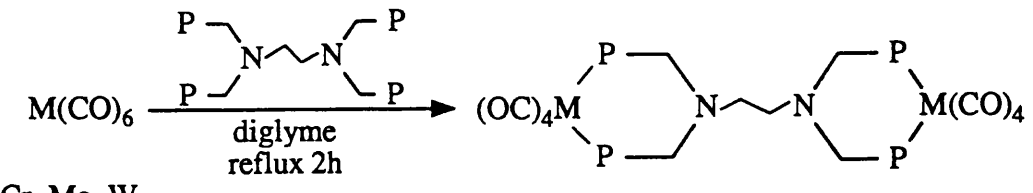


Figure 1

Scheme 1

E.g.



M = Cr, Mo, W

It was proposed that heteronuclear coordination would be possible with these ligands but none of the compounds reported contained a coordinated nitrogen.

A large number of the reported metal complexes come from Markl and Yu Jin in their extensive work on aminomethylphosphines,[11,32-35] Scheme 2. Nearly all these compounds are carbonyl complexes of molybdenum, prepared from $Mo(CO)_6$, although a few nickel complexes were also reported. Complex *(131)* appears, with a structurally related ligand, as a trans isomer of the related cis complex *(127)*. In most cases only mass spectroscopy and infrared spectroscopy were used to characterise these compounds. Unlike their phosphine precursors no characterisation by n.m.r. was used.

The chemistry of $Ph_2PCH_2NEt_2$ as a heteronuclear bridging ligand has been investigated in both homodinuclear and heterodinuclear metal complexes.[121-123] Complexes of the type $[MCl_2(Ph_2PCH_2NEt_2)]$ (M = Pd, Pt) were assigned as being dimeric from molecular weight determination. By the comparison of the ^1H and ^{31}P spectra of these complexes with those of the free ligand both P and N coordination were assigned. These complexes are expected to exist as two structural isomers,[122] Figure 2.

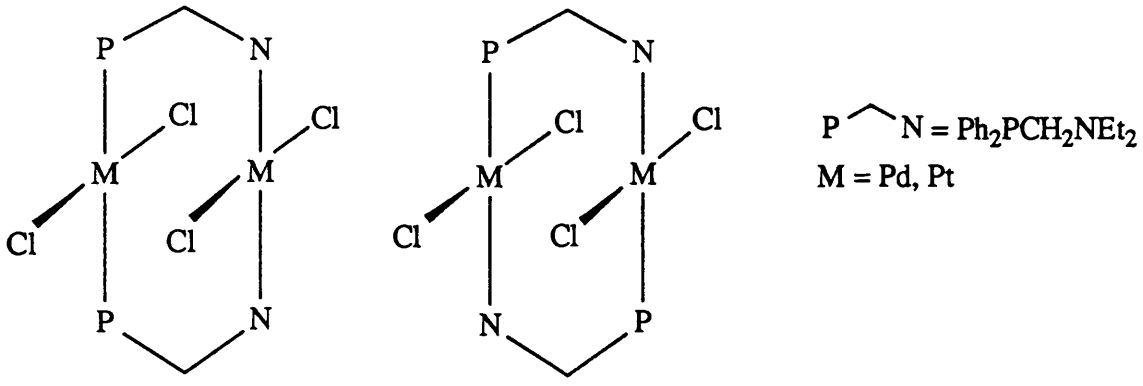
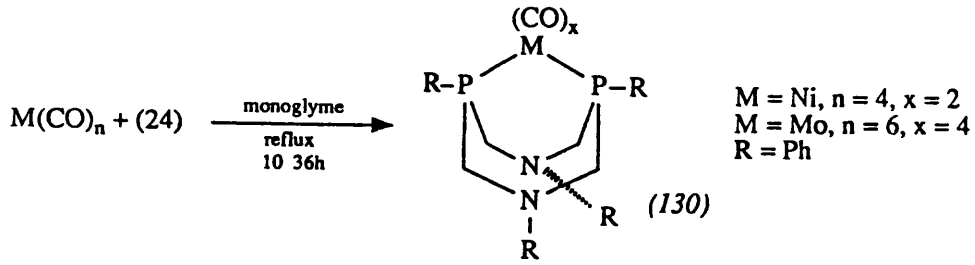
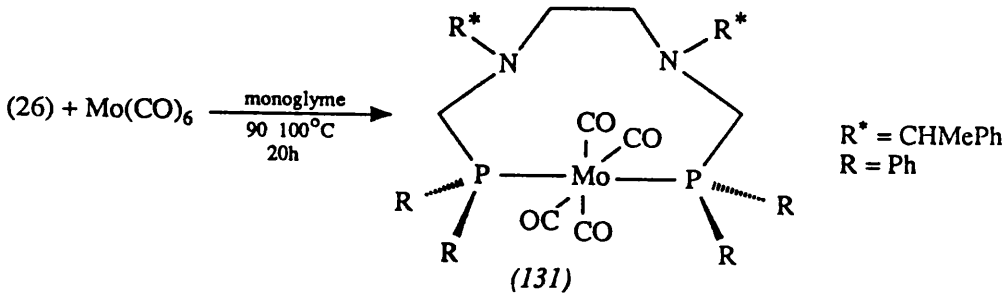
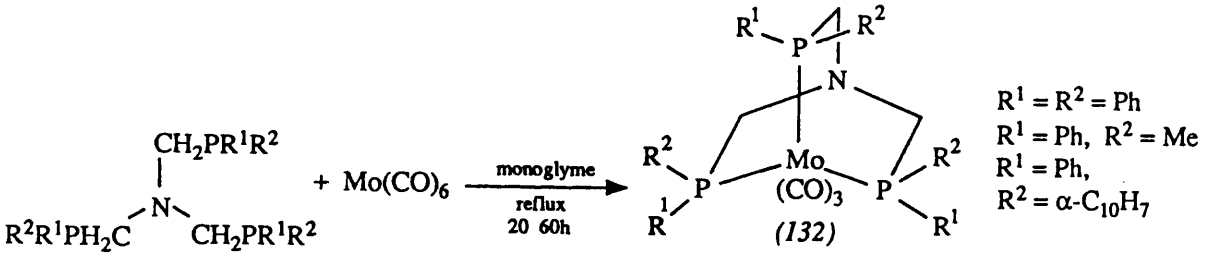


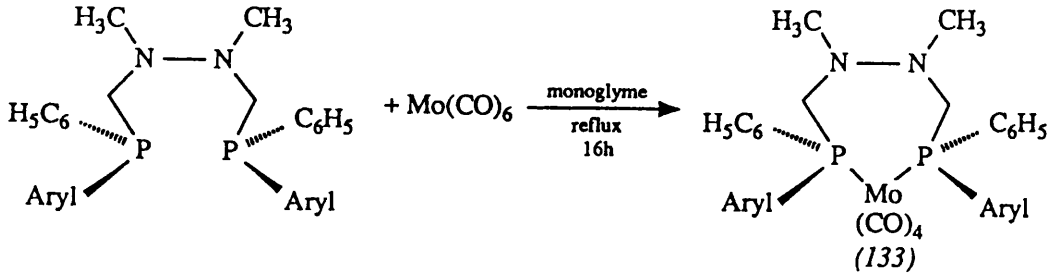
Figure 2

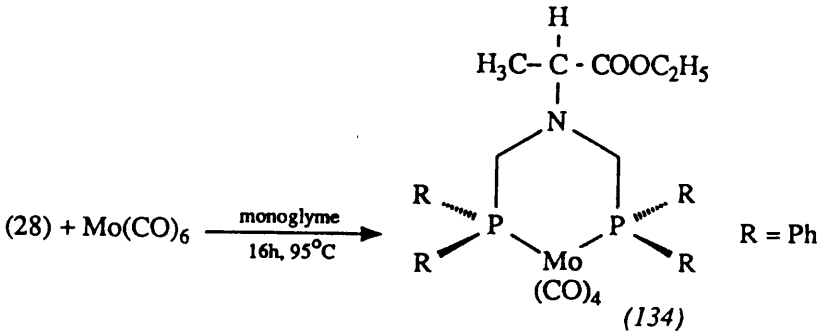
Rhodium complexes of $Ph_2PCH_2NEt_2$ have also been reported.[123] Treatment of the monomeric unit $[RhCl(CO)(Ph_2PCH_2NEt_2)_2]$ with $[RhCl(CO)_2]_2$ gave the isomeric compounds *(135)* and *(136)*, Figure 3. In a similar way treatment


M(CO)n + (24)
monoglyme
reflux
10 36h
(CO)x
M
R-P
P-R
N
N
R
R
M = Ni, n = 4, x = 2
M = Mo, n = 6, x = 4
R = Ph
(130)


(26) + Mo(CO)6
monoglyme
90 100°C
20h
R*
N
N
R*
CO
CO
P
Mo
P
R
R
OC
CO
R
R
R* = CHMePh
R = Ph
(131)

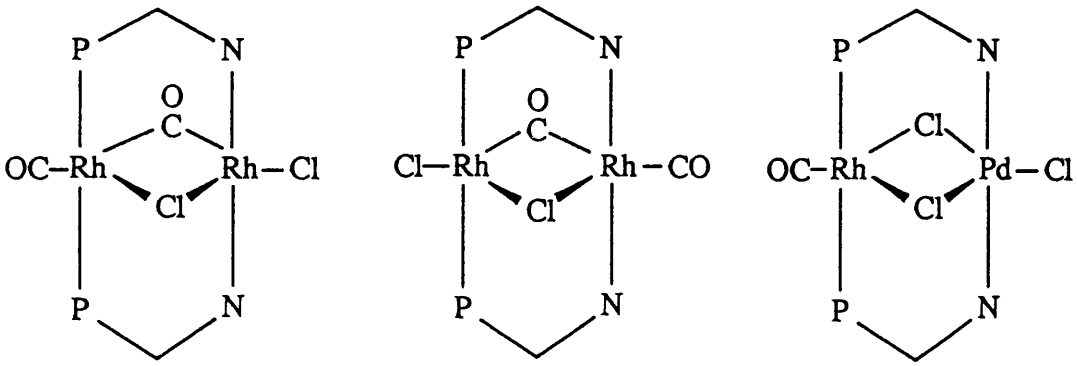

CH2PR1R2
N
R2R1PH2C
CH2PR1R2
+ Mo(CO)6
monoglyme
reflux
20 60h
R1
P
R2
N
R2
Mo
(CO)3
P
R2
R1
R1
R1 = R2 = Ph
R1 = Ph, R2 = Me
R1 = Ph,
R2 = α-C10H7
(132)


H3C
CH3
N
N
H5C6
C6H5
P
P
Aryl
Aryl
+ Mo(CO)6
monoglyme
reflux
16h
H3C
CH3
N
N
H5C6
C6H5
P
P
Aryl
Mo
(CO)4
Aryl
(133)


H
H3C- C - COOC2H5
N
(28) + Mo(CO)6
monoglyme
16h, 95°C
R
R
P
P
R
R
Mo
(CO)4
R
R
R = Ph
(134)

Scheme 2

of $[RhCl(CO)(Ph_2PCH_2NEt_2)_2]$ with $[PdCl_2(COD)]$ gave a compound with its structure tentatively assigned as *(137)*, but various other bridging arrangements of the chlorine and carbonyl ligands were also considered.



(135) (136) *(137)*

Figure 3

By using a monomeric, phosphorus coordinated complex as the starting material the bridging ligand isomerism in Figure 2 was avoided.

Tzshach *et al.*,[36] extending their investigations of optically active bis aminomethylphosphine derivatives, have synthesized a series of rhodium hydrogenation catalysts, Scheme 3.

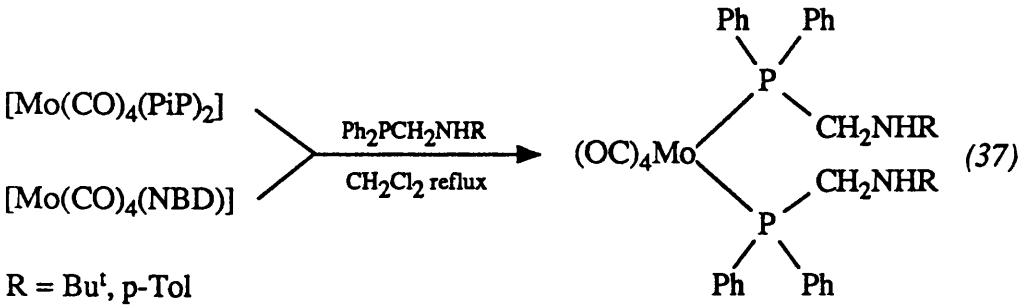
Scheme 3

$$[RhCl(diene)]_2 + (Ph_2PCH_2)_2NR^* \xrightarrow[-AgCl]{AgBF_4} [Rh(diene)(Ph_2PCH_2)_2NR^*]^+ BF_4^-$$

diene = 1,5 cyclooctadiene, norbornadiene
$R^* = CH(Me)CO_2Me$, $CH(Me)CO_2Na$

These compounds were isolated as red/brown solids and were characterised by ^{31}P n.m.r. and elemental analysis. Their use in homogeneous asymmetric hydrogenation is discussed in Chapter 4.

Recently molybdenum complexes of the phosphine Ph_2PCH_2NHR (R = Bu^t, p-Tol) have been reported and a crystal structure of *(37)* has appeared,[40] Scheme 4. Under certain conditions the two coordinated phosphines can condense to give a six-membered chelating ring, Chapter 1, Scheme 18.



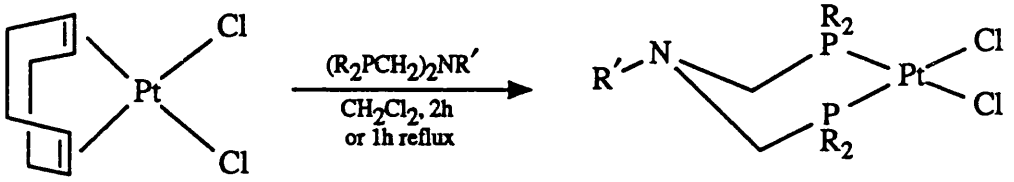
Scheme 4

Extending the study of aminomethylphosphine synthesis in Chapter 2, this Chapter investigates the synthesis of a variety of transition metal complexes. Thus Ni(II), Pd(II), Pt(II), Co(II), Mo(0), W(0), Rh(I) and Ir(I) complexes of $[(R_2PCH_2)_2NR']$ bidentate phosphines have been prepared and characterised. Pt(II)-Sn(IV) complexes were also prepared but some problems were encountered with their low solubility in common solvents. Attempts to prepare Pt(0) complexes were unsuccessful as were attempts to prepare metallacyclobutanone complexes of Pt(II).

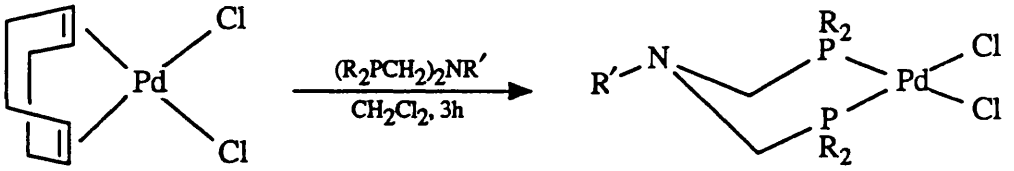
3.2 Preparation of cis $[MCl_2(R_2PCH_2)_2NR']$ complexes M = Pt, Pd, Ni

A vast number of transition metal phosphine complexes have been reported over the years. These complexes have not only served as excellent characterisation adducts for the phosphine ligands but more importantly have been used as effective catalyst precursors.

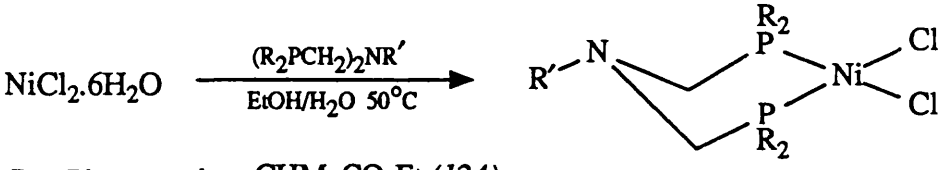
The complexes *(110)-(115)* of the type $[PtCl_2(R_2PCH_2)_2NR']$ were prepared in the present study by treating a dichloromethane solution of $[PtCl_2(COD)]$ with a stoichiometric amount of the relevant phosphine, Scheme 5. The compounds were isolated as white or very pale yellow crystalline solids in yields of 67-80%, and were highly soluble in dichloromethane. The palladium complexes *(116)-(123)*, $[PdCl_2(R_2PCH_2)_2NR']$ were prepared by treating a dichloromethane solution of $[PdCl_2(COD)]$ with a stoichiometric amount of the relevant phosphine, Scheme 5. The complexes were isolated as

[1] 

R = Ph R′ = CHMePh *(110)*, $CHMeCO_2Et$ *(111)*,
$\underline{CHCH_2CHCH_2CH_2C}(Me)\overline{C(Me)_2}$ *(112)*
R = Cy R′ = CHMePh *(113)*, $CHMeCO_2Et$ *(114)*
$R_2 = C_8H_{14}$ R′ = CHMePh *(115)*

[2] 

R = Ph R′ = CHMePh *(116)*, $CHMeCO_2Et$ *(117)*, CH_2CH_2OH *(121)*,
$CH_2CH{=}CH_2$ *(122)*, $CH_2C{\equiv}CH$ *(123)*
R = Cy R′ = CHMePh *(118)*, $CHMeCO_2Et$ *(119)*
$R_2 = C_8H_{14}$ R′ = CHMePh *(120)*

[3] 

R = Ph R′ = $CHMeCO_2Et$ *(124)*
R = Cy R′ = CHMePh *(125)*, $CHMeCO_2Et$ *(126)*

Scheme 5

yellow crystalline solids in yields of 64-94% and were soluble in dichloromethane, chloroform and benzene. However, the complex *(123)*, $[PdCl_2(Ph_2PCH_2)_2NCH_2C{\equiv}CH]$ could not be isolated from the reaction mixture and was only observed in solution as a single peak in the ^{31}P n.m.r. spectrum at δ 9.47 p.p.m. The nickel complexes *(124)-(126)*, $[NiCl_2(R_2PCH_2)_2NR']$ were prepared by treating a warm ethanolic solution of a phosphine with a solution of $NiCl_2.6H_2O$ in water, Scheme 5. The compounds were recrystallised as golden brown crystalline flakes in 57-64% yields similar to the reported $NiCl_2$ complexes of dppp[124] and dCypp.[125] The phenyl derivative *(124)* showed a significantly lower melting point, ~110° less, than the similar cyclohexyl derivatives *(125)* and *(126)*. Most of the reported complexes crystallise with their solvent of crystallisation, either dichloromethane or chloroform in one mole or half mole equivalents. However, some complexes crystallized either with, or without solvent present in the product. This was thought to be dependent on the speed of crystallisation and also on the extent of drying time, with heating, in vacuo.

Previous studies[126] of platinum dichloride complexes of six-membered ring chelating phosphines have suggested that these compounds are dimeric with the phosphines bridging two metals instead of chelating, Figure 4. Molecular weight determinations for the reported platinum-dichloride com-

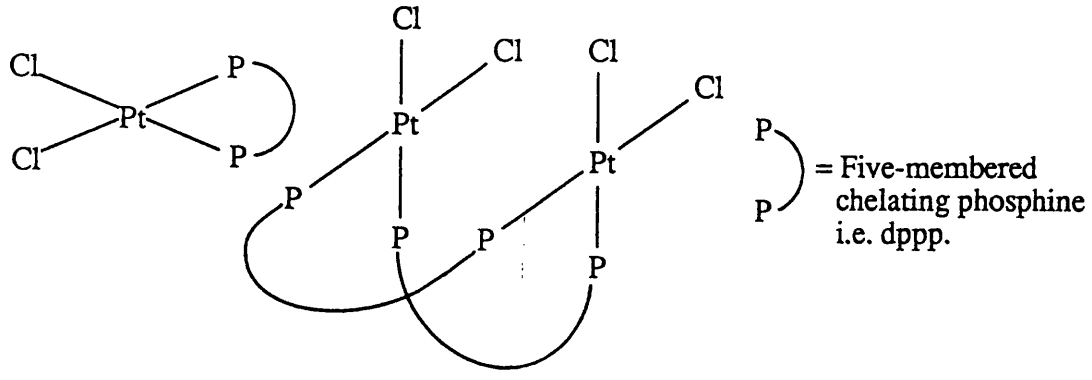


Figure 4
Monomeric and dimeric isomers of platinum dichloride complexes of six-membered ring chelating phosphines.

plexes have given seemingly meaningless results as weights found were consistently lower than expected for a monomer. Therefore it is doubtful, even given significant errors, that the complexes are dimeric. A report of the crystal structure of $[PtCl_2(dppp)]$[127] shows that the compound is monomeric, thus supporting our belief that the reported compounds are monomers.

The ^{31}P n.m.r. spectra of the platinum, palladium and nickel complexes are given along with the free ligand shift and the coordination shift Δ, defined by $\Delta = \delta(\text{complex}) - \delta(\text{free ligand})$, in Table 1. The J(PtP) coupling constant for the platinum complexes are shown in Table 2. The coordination shift Δ has been correlated for many metal phosphine complexes[128,129] and has been used to show trends within a series of analogous compounds. The values for Δ for the platinum complexes are generally of the same order (18-23 p.p.m.) except for *(115)* which has the novel C_8H_{14} substituted phosphine ligand *(103)*. The Δ values for the nickel complexes *(124)-(126)* also show a consistent trend of the same order (32.5-36.5 p.p.m.). However, only the phenyl substituted ligands of the palladium complexes show a uniform correlation of Δ shift (34-37 p.p.m.). The cyclohexyl substituted ligands (45-47.6 p.p.m.) and the C_8H_{14} substituted ligand (51.2 p.p.m.) gave much larger values. Previous work[128] has shown that Δ shifts for palladium complexes are larger than in platinum complexes given the same ligand which is in agreement with the observed data. The high Δ shifts for the C_8H_{14} substituted ligands of both platinum and palladium can be attributed to bond strain about phosphorus, as the conformational rigidity of the $C_8H_{14}P$- moieties in the chelating phosphine *(103)* will undoubtedly be placed under strain when both phosphorus atoms are coordinated to a metal. As the C-P-C bond angle/bond strain in tertiary phosphines is the most important factor affecting chemical shift,[130]

Complex		$\delta^{31}P$	$\delta^{31}P$ ligand	$\Delta^{31}P$
$[PtCl_2(Ph_2PCH_2)_2NCHMePh]$	*(110)*	-7.26	-27.83	20.57
$[PtCl_2(Ph_2PCH_2)_2NCHMeCO_2Et]$	*(111)*	-8.67	-26.38	17.71
$[PtCl_2(Ph_2PCH_2)_2NCHCH_2CHCH_2CH_2C(Me)C(Me)_2]$	*(112)*	-7.68	-28.63	20.95
$[PtCl_2(Cy_2PCH_2)_2NCHMePh]$	*(113)*	5.04	-18.35	23.39
$[PtCl_2(Cy_2PCH_2)_2NCHMeCO_2Et]$	*(114)*	3.63	-18.15	21.78
$[PtCl_2(C_8H_{14}PCH_2)_2NCHMePh]$	*(115)*	-15.52	-46.6	31.08
$[PdCl_2(Ph_2PCH_2)_2NCHMePh]$	*(116)*	9.66	-27.83	37.49
$[PdCl_2(Ph_2PCH_2)_2NCHMeCO_2Et]$	*(117)*	7.66	-26.38	34.04
$[PdCl_2(Cy_2PCH_2)_2NCHMePh]$	*(118)*	29.24	-18.35	47.59
$[PdCl_2(Cy_2PCH_2)_2NCHMeCO_2Et]$	*(119)*	27.22	-18.15	45.37
$[PdCl_2(C_8H_{14}PCH_2)_2NCHMePh]$	*(120)*	4.63	-46.6	51.23
$[PdCl_2(Ph_2PCH_2)_2NCH_2CH_2OH$	*(121)*	7.46	-28.23	35.69
$[PdCl_2(Ph_2PCH_2)_2NCH_2CH=CH_2]$	*(122)*	8.29	-28.84	37.13
$[NiCl_2(Ph_2PCH_2)_2NCHMeCO_2Et]$	*(124)*	10.24	-26.38	36.62
$[NiCl_2(Cy_2PCH_2)_2NCHMePh]$	*(125)*	16.33	-18.35	34.68
$[NiCl_2(Cy_2PCH_2)_2NCHMeCO_2Et]$	*(126)*	14.32	-18.15	32.47

Table 1

^{31}P chemical shifts and phosphine coordination shifts (in p.p.m.) for metal complexes of the type $MCl_2(R_2PCH_2)_2NR'$, M = Pt, Pd, Ni.

it seems quite reasonable that it is the cause of the large Δ shifts in complexes *(115)* and *(120)*.

The coupling constants J(PtP), Table 2, for the platinum complexes *(110)-(115)* are of the predicted order for six-membered chelates of phosphines trans to chlorine (~3420 Hz)[128,130,131] except for the C_8H_{14} substituted phosphine which shows a lower value of (3242.0 Hz). This may be related to the nature of the coordinated $C_8H_{14}P$- moiety as is observed with the effect on coordination shift Δ.

As with the phosphines the ^1H n.m.r. spectra of the PCH_2N linkage of the metal complexes have also been of interest. Selected ^1H and ^{13}C n.m.r. data for the PCH_2N linkage of platinum complexes are given in Table 2 and for palladium and nickel complexes are given in Table 3. Platinum complexes *(110)-(112)*, with phenyl substituents on phosphorus show second order multiplets in the ^1H n.m.r. for the PCH_2N linkage with a resolvable J(PtH) coupling of 31-36 Hz. The complexes *(113)* and *(114)* with cyclohexyl substituents on phosphorus however show ABX patterns with equal J(PH) values of 2.4-2.9 Hz for both methylene protons H^A and H^B. The palladium complexes of the cyclohexyl substituted phosphines, *(118)* and *(119)* show ABX and AB patterns respectively, with the ABX pattern showing a J(PH) coupling of 2.1 Hz. The nickel complex *(125)* also shows an AB pattern for the PCH_2N protons. The remaining palladium and nickel complexes with phenyl substituted ligands show second order multiplets for the PCH_2N protons, with unresolvable coupling, however, the signals do appear to be symmetrical unlike the ABX patterns of the free phosphines. Therefore it is evident that the asymmetric J(PH) coupling observed in the free phosphines is cancelled on coordination/chelation to a metal, which is to be predicted. In a six-membered chelating ring the phosphorus lone pairs are involved in bonding to the metal and the protons are effectively pointing

Complex	J(PtP)	^{1}H δ PC$\underline{H}_2$N	^{13}C δ P$\underline{C}$H$_2$N	J(PH)	J(PtH)	J(PC)
(110)	3405.2	3.5 m	54.5 d	—	36.0	50.1
(111)	3427.7	3.7 m	54.1 d	—	36.0	59.9
(112)	3413.0	3.5 m	56.2 d	—	31.1	55.5
(113)	3460.0	2.7 ABX	45.4	2.9	—	51.9
(114)	3461.9	2.9 ABX	46.0	2.4	—	48.5
(115)	3242.0	2.7 m	—	—	—	—

Table 2

Selected ^{31}P, ^{1}H and ^{13}C n.m.r. data for $PtCl_2(R_2PCH_2)_2NR'$ complexes.
[All J coupling constants are in Hz; ^{1}H and ^{13}C chemical shifts are in p.p.m.]

Complex	^{1}H δ PC$\underline{H}_2$N	^{13}C δ P$\underline{C}$H$_2$N	J(HH)	J(PH)	J(PC)
(116)	3.42 m	53.6 d	—	—	49.4
(117)	3.67 m	54.5 d	—	—	44.8
(118)	2.68 ABX	45.0 d	14.0	2.1	42.4
(119)	3.0 AB	46.5 d	14.6	—	42.5
(121)	3.5 AXX′	—	—	4.4 3.1	—
(124)	3.8 m	53.6 d	—	—	46.3
(125)	2.4 AB	46.4 m	13.7	—	—
(126)	2.65 m	46.7 m	—	—	—

Table 3

Selected ^{1}H and ^{13}C n.m.r. data for the PCH_2N linkage in $MCl_2(R_2PCH_2)_2NR'$ complexes (M = Pd, Ni).
[All J values are in Hz; ^{1}H and ^{13}C chemical shifts are in p.p.m.]

away from them, Figure 5, so the coupling J(PH) will be low or non-existent.

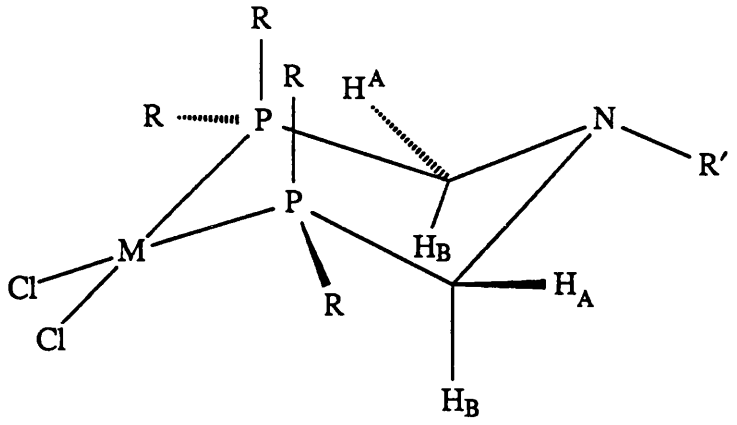


Figure 5

Geometrical relationship between phosphorus lone pair and methylene protons H^A and H^B in six-membered chelate ring of a bis(amino methyl phosphine) metal dichloride complex.

The nitrogen substituent R′ is shown in an equatorial conformation in Figure 5. However, with nitrogen inversion, and the possibility of ring flip, this conformation will be in equilibrium with an invertomer where R′ is in an axial position. This invertomer would be less favoured in an equilibrium as there would be strong 1-3 diaxial interactions between R′ and the R groups on both phosphorus atoms. When R = Cy, the increase in steric bulk will make this invertomer very unfavourable and it is expected that the complexes with cyclohexyl substituted phosphines will greatly prefer the conformation shown in Figure 5. This reasoning may explain why complexes with cyclohexyl substituted ligands *(113)*, *(114)*, *(118)*, *(119)* and *(125)* show resolved AB and ABX patterns for the PCH_2N protons in the ^1H n.m.r., and the complexes with phenyl or cyclooctyl substituted ligands show complex patterns, where equilibrium with the other invertomer is less restricted.

As observed in the free phosphines the presence of phenyl groups on phosphorus in the metal complexes deshields the methylene protons and

carbon atom of the PCH_2N link.[115] This can be seen by their downfield shifts in the ^1H and ^{13}C n.m.r. spectra, Tables 2 and 3, compared to the cyclohexyl and C_8H_{14} derivatives. Despite the differing nature of many of the n.m.r. features of the PCH_2N moiety in these complexes, the J(PC) values are of a similar order, (50-60 Hz) for the platinum complexes and (42-49 Hz) for the palladium complexes.

Different substituents R′ on nitrogen have little or no observable effect on the ^1H and ^{13}C n.m.r. parameters of the PCH_2N link.

3.3 Structural properties of $[PdCl_2(Ph_2PCH_2)NCH_2CH_2OH]$ *(121)*

The molecular structure of complex *(121)* is illustrated in Figure 6 which also gives the crystallographic numbering system, and a summary of selected bond lengths and angles is given in Table 4. Bond lengths and angles for the similar $[PdCl_2(dppp)]$ complex *(138)*[132] are also given, for comparison, in Table 4.

The view of *(121)* in Figure 6, clearly shows that the geometry about the palladium atom is essentially square planar, although the P(1)-Pd- P(2) angle is slightly less than 90^o (87.9^o). The phosphine ligand coordinates to palladium in a six-membered cis chelate with the phosphorus atoms trans to the chlorine ligands. The chelate ring adopts a chair conformation, Figure 6a, which contrasts to the twisted boat conformation observed for *(138)*.[131] This is probably due to the $-CH_2CH_2OH$ substituent which adopts an equatorial position in the chair structure. There are no interactions between the palladium atom and either the nitrogen or oxygen atoms. The Pd-Cl bond distances are typical[132] for complexes of this type, although the two bond lengths are slightly unequal [2.355(2) and 2.368(2)Å]. The P(2)-C(1) and P(1)-C(2) bond lengths of the PCH_2N link of the coordinated aminomethylphosphine are similar to the $P-CH_2$ bond distances of dppp in

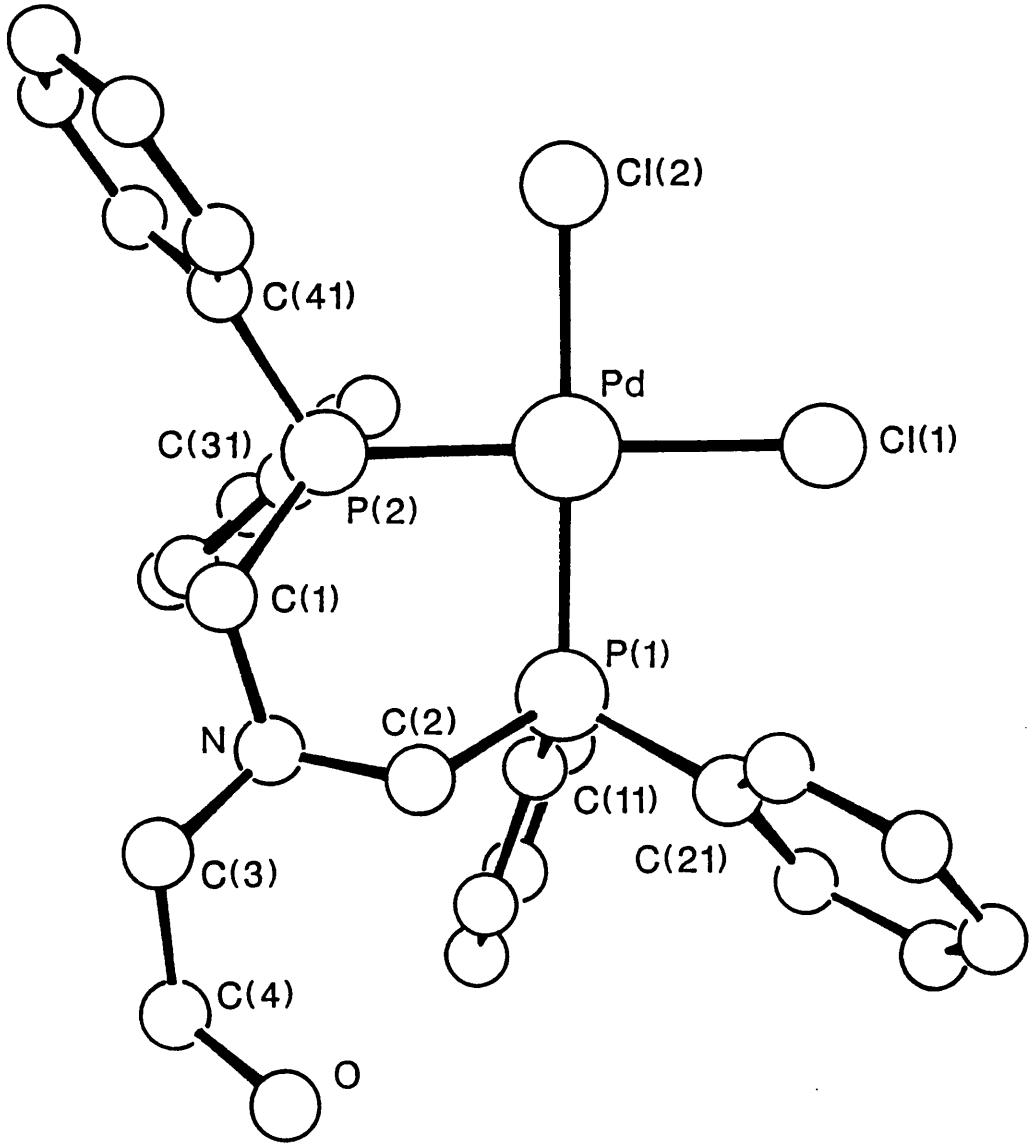


Figure 6 Molecular structure of $[PdCl_2(Ph_2PCH_2)_2NCH_2CH_2OH]$ *(121)* with all hydrogen atoms omitted.

Bond	*(121)* (Å)	$[PdCl_2(dppp)]$ (Å)
Pd – Cl(1)	2.335(2)	2.351(1)
Pd – Cl(2)	2.368(2)	2.358(2)
Pd – P(1)	2.256(2)	2.244(1)
Pd – P(2)	2.236(2)	2.249(2)
P(1) – C(2)	1.822(7)	1.820(5)
P(2) – C(1)	1.839(8)	1.840(4)
P(1)(2) – C(Ph)	av. 1.802(5)	av. 1.817(5)
C(1) – N	1.463(9)	—
C(2) – N	1.470(9)	—
Bond Angle	*(121)* (°)	$[PdCl_2(dppp)]$ (°)
Cl(1) – Pd – Cl(2)	90.2(1)	90.78(5)
Cl(1) – Pd – P(1)	174.5(1)	171.88(5)
Cl(1) – Pd – P(2)	91.1(1)	91.10(5)
Cl(2) – Pd – P(1)	90.7(1)	87.74(5)
Cl(2) – Pd – P(2)	178.1(1)	177.68(5)
P(1) – Pd – P(2)	87.9	90.58(5)
C(2) – N – C(1)	111.9(6)	—
C(3) – N – C(2)	117.6(6)	—
C(3) – N – C(1)	107.5(5)	—
P(1) – C(2) – N	112.8(5)	—
P(2) – C(1) – N	115.7(5)	—

Table 4

Selected bond lengths and angles for the complex $[PdCl_2(Ph_2PCH_2)_2NCH_2CH_2OH]$ *(121)* compared to similar data for $[PdCl_2(dppp)]$ *(138)*.[132]

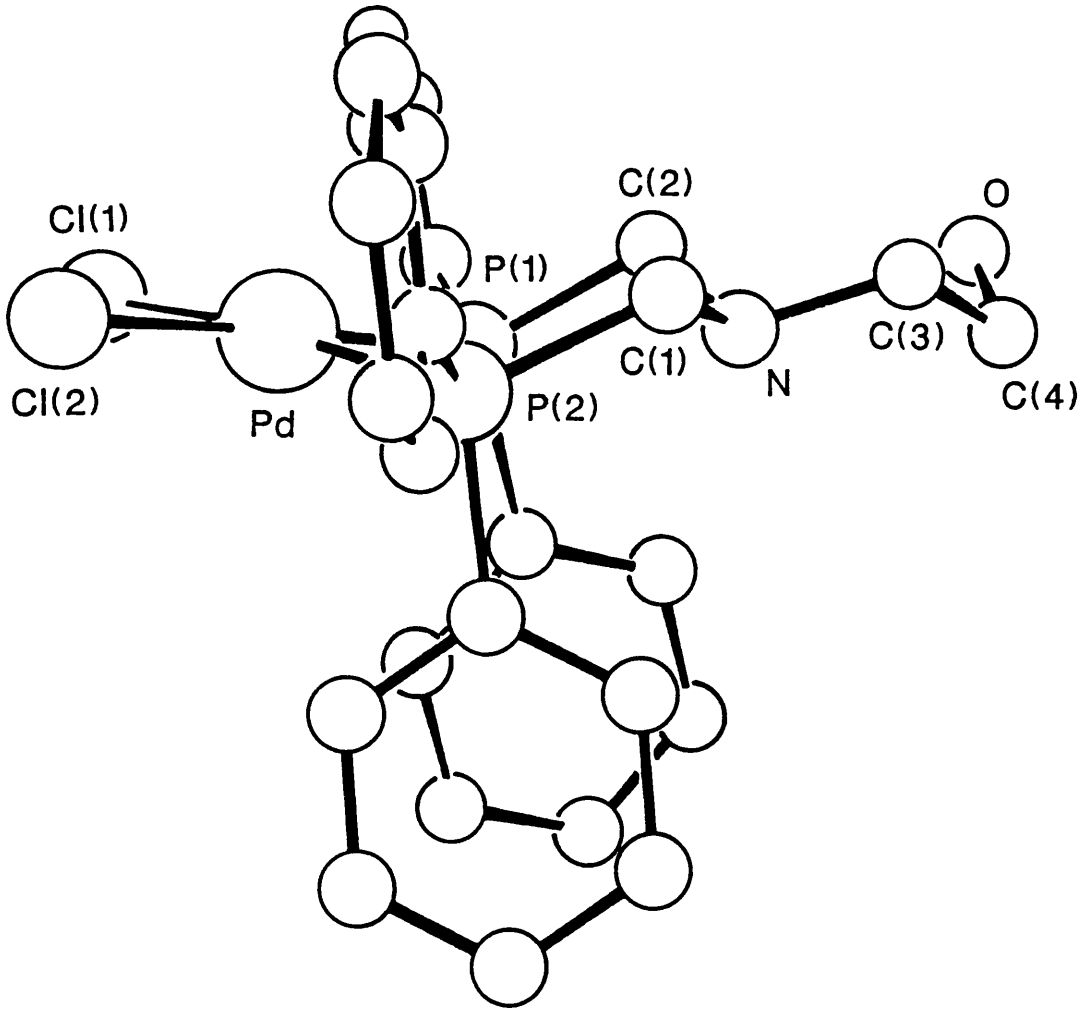


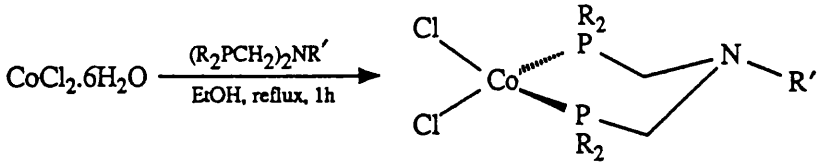
Figure 6a Another view of the molecular structure of $[PdCl_2(Ph_2PCH_2)_2NCH_2CH_2OH]$ *(121)* showing the chair conformation of the chelating phosphine.

(138). The C(1)-N and C(2)-N bond lengths are comparable to the C-N bond distances in the PCH_2N link for the previously reported aminomethylphosphine complexes.[13,40] The C-N-C bond angles for carbon atoms (1), (2) and (3) are unequal reflecting the 'lopsided' conformation of the CH_2CH_2OH group. This conformation may also account for the slight twist of the phenyl ring of carbon atom C(11). The bond angles of P(1)-C(2)-N and P(2)-C(1)-N are 112.8° and 115.7° respectively showing the slight distortion from tetrahedral for the carbon atoms (1) and (2).

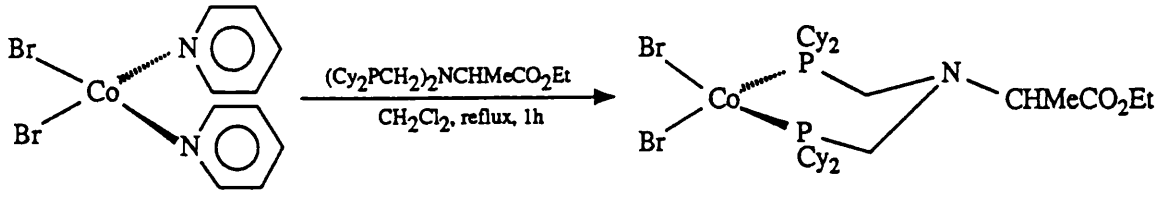
3.4 Preparation of $[CoX_2(R_2PCH_2)_2NR']$ complexes (X = Cl, Br

The cobalt dichloride complexes *(139)*, *(140)* and *(141)* were prepared by refluxing an ethanolic solution of $CoCl_2.6H_2O$ with the relevant phosphine, Scheme 6. The compounds were isolated as fine green powders with yields of 71-91%. Attempts to recrystallise the compounds led to the formation of dark oils which could be converted back to powders when stirred with dry diethyl ether. The cobalt dibromide complex *(142)* was prepared by refluxing a dichloromethane solution of $[CoBr_2Py_2]$ with the phosphine *(102)*, Scheme 6.

Scheme 6



R = Ph R' = CHMePh, $CHMeCO_2Et$ *(139),(140)*
R = Cy R' = CHMePh *(141)*



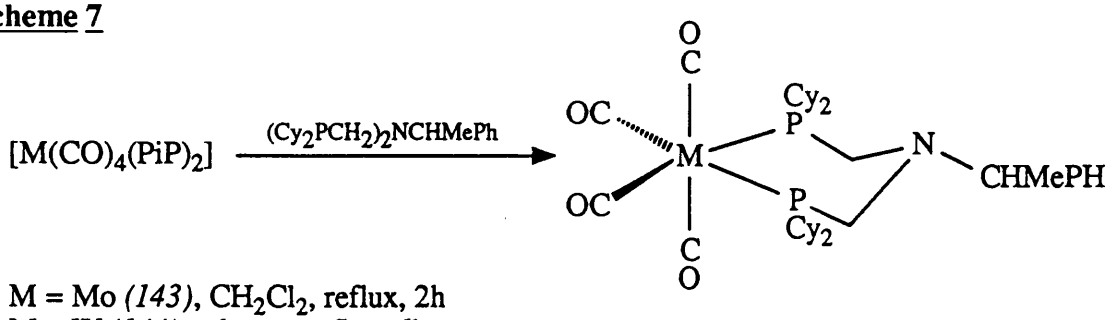
(142)

Compound *(142)* was isolated as a bright bluish/green microcrystalline powder in an 87% yield which is in accord with previously reported cobalt dibromide phosphine complexes.[133] The elemental analysis of *(142)* was found to be 1.1% high for nitrogen indicating the presence of unreacted $[CoBr_2Py_2]$, which could not be separated by successive recrystallisations. A better method of preparation would be to start from $CoBr_2.6H_2O$ by the same route as the $CoCl_2$ complexes but this was not investigated. The complexes are all paramagnetic, high spin $\underline{d}^7$, consequently the ^{31}P and ^1H n.m.r. spectra were severely broadened. The i.r. spectra of the complexes, *(140)* and *(142)*, show maximum absorptions at 1725 and 1730 cm^{-1} respectively which are assigned to ν(C=O) for the ester carbonyl group of the ligand. Absorptions assigned to ν(Co-Cl) at about 310 cm^{-1} were observed for the cobalt dichloride complexes *(139)*, *(140)* and *(141)*.

3.5 Preparation of cis-$M(CO)_4(Cy_2PCH_2)_2NCHMePh$ complexes (M = Mo, W)

The complexes *(143)* and *(144)* were prepared by treating the corresponding molybdenum or tungsten-tetracarbonyl bis-piperidine complexes with the phosphine *(101)*. The reaction proceeds with facile replacement of the piperidine ligands by the chelating aminomethylphosphine with the tungsten complex requiring more forcing conditions, Scheme 7.

Scheme 7



M = Mo *(143)*, CH_2Cl_2, reflux, 2h
M = W *(144)*, toluene, reflux, 6h

The complexes were isolated as yellow-brown crystalline solids in 48-57% yields and had a high solubility in dichloromethane. The ^{31}P n.m.r.

spectra of the complexes *(143)* and *(144)* show single peaks at δ 22.6 p.p.m. and δ 3.4 p.p.m. respectively. These compare to the ^{31}P n.m.r. shifts for $[Mo(CO)_4(dppp)]$ and $[W(CO)_4(dppp)]$ of δ 21.0 p.p.m. and δ 0.0 p.p.m.[128] The coordination shifts Δ for *(143)* and *(144)*, +40.7 and +21.5, are also of a similar order to the dppp complexes[128] thus supporting the assignment of a six-membered chelate. The i.r. spectra of the complexes show absorptions in the ν(CO) region indicative of approximately (ignoring chiral group on N) C_{2v} symmetry and cis geometry about the metal atom supporting chelate formation.[134,135] Selected i.r. data for *(143)* and *(144)* is shown in comparison to equivalent data for $[Mo(CO)_4(PCy_2Ph)_2]$ *(145)*[136] in Table 5.

Table 5

Infrared spectra in the ν(CO) stretching region of complexes *(143)*, *(144)* and *(145)*

Complex	ν(CO) cm^{-1}		
	A_1	B_1	B_2
(143)	2004	1892	1868
(144)	2000	1875	1865
(145)	2012	1890	1877

The infrared spectra of *(143)* and *(144)* are in agreement with trends in ν(CO) frequencies that show a dependence on electronic properties and steric bulk of the phosphine ligands. The second band predicted for the symmetry element A_1,[134,136] at ≈1910 cm^{-1} were only identified as unresolved shoulders and are not reported.

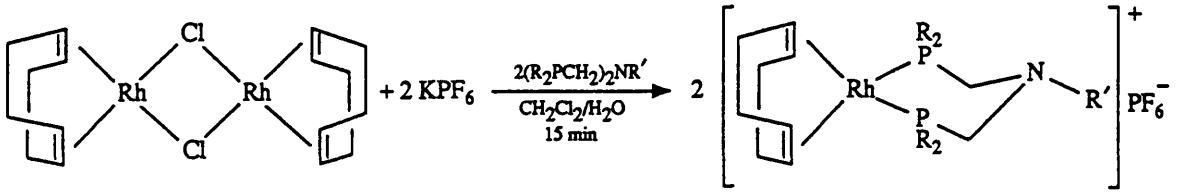
3.6 Preparation of $[Rh(COD)(R_2PCH_2)_2NR']^+PF_6^-$ complexes

Complexes of the type $[Rh(diene)L_2]^+X^-$, where X^- is a non-coordinating counter ion and L is a monodentate tertiary phosphine or L_2 is a chelating

diphosphine, have been shown to be versatile and easily prepared catalyst precursors.[137] The use of the reported complexes *(146)-(150)* in catalytic homogeneous hydrogenation is investigated in Chapter 4.

The complexes *(146)-(150)* were prepared by treating a two-phase system of $[RhCl(COD)]_2$ and KPF_6 in dichloromethane and water with the relevant phosphine; Scheme 8.

Scheme 8



R = Ph, R' = CHMePh *(146)*, $CHMeCO_2Et$ *(147)*, $CHCH_2CHCH_2CH_2C(Me)C(Me)_2$ *(148)*
R = Cy, R' = CHMePh *(149)*, $CHMeCO_2Et$ *(150)*

The products were precipitated as fine orange-brown powders in yields of 57-87%. The compounds are air-stable as solids but show slight discolouration to a sandy-brown colour after 12 months or longer. The ^{31}P n.m.r. spectra of *(146)-(150)* show sharp doublets with an identical J(RhP) coupling of 141.6 Hz for all the complexes. The PF_6^- counter ions were observed at about δ -143.5 p.p.m. with J(PF) coupling of about 711 Hz. The signals were observed as septets with the outer lines not being observed. ^{31}P n.m.r. data regarding the phosphine moiety of complexes *(146)-(150)* are given in Table 6 along with coordination shifts Δ.

A similar complex, $[Rh(NBD)(Ph_2PCH_2)_2NCHMeCO_2Me]^+BF_4^-$ *(151)* has been reported previously[36] with its ^{31}P n.m.r. spectrum exhibiting a doublet at δ 11.9 p.p.m. and J(RhP) coupling of 145 Hz. Further comparison can be found with the complex $[Rh(NBD)dppp]^+BF_4^-$ *(152)* which exhibits a doublet at δ 14.1 p.p.m. and J(RhP) 148 Hz in its ^{31}P n.m.r. spectrum.[138] The coordination shifts, Δ, of the complexes *(146)-(150)*, ~27-36 p.p.m., also compare favourably with similar $[Rh(diene)dppp]^+X^-$ complexes,[138] $\Delta \approx 31$

Table 6

^{31}P n.m.r. data for $[Rh(COD)(R_2PCH_2)_2NR']PF_6^-$ complexes and coordination shift Δ. Chemical shifts in p.p.m. relative to H_3PO_4 at δ 0.0 p.p.m.

Complex	δ ^{31}P complex	δ ^{31}P ligand	J(RhP)	Δ (p.p.m.)
(146)	8.56	-27.83	141.6	36.39
(147)	7.9	-26.38	141.6	34.28
(148)	8.16	-28.63	141.6	36.79
(149)	9.97	-18.35	141.6	28.32
(150)	8.93	-18.15	141.6	27.08

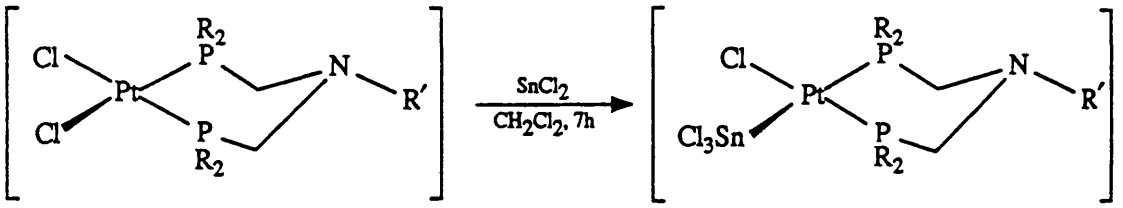
p.p.m. However, the cyclohexyl substituted complexes *(149)* and *(150)* show smaller coordination shifts than phenyl complexes in contrast to the trend in coordination shift observed for the Ni, Pd, Pt complexes discussed in Section 3.2.

3.7 Preparation of $[PtCl(SnCl_3)(R_2PCH_2)_2NR']$ complexes

Complexes of the type $[PtCl(SnCl_3)P_2]$, where P = monodentate phosphine or P_2 = chelating bisphosphine, have been known for some time as effective hydroformylation catalysts.[139] The use of complexes of this type, using chelating aminomethylphosphine ligands, in homogeneous catalytic hydroformylation is investigated in Chapter 4.

The complexes *(153)-(156)* were simply prepared by treating a dichloromethane solution of the corresponding platinum-dichloride complex *(110)*, *(111)*, *(113)* or *(114)* with anhydrous tin-dichloride at room temperature, Scheme 9. The complexes were isolated as pale yellow/orange powders or as white crystals in low yields, 27-35%. The complexes *(153)*, *(155)* and *(156)* displayed poor solubility in most common organic solvents, the best being acetone and/or dichloromethane, though an initial warming was usually

Scheme 9



R = Ph, R′ = CHMePh *(153)*, $CHMeCO_2Et$ *(154)*
R = Cy, R′ = CHMePh *(155)*, $CHMeCO_2Et$ *(156)*

required. The complex *(154)* was totally insoluble in all common organic solvents. It was however soluble in dimethylsulphoxide, in which it decomposed to give the starting material *(111)*, observed from its ^{31}P n.m.r. spectrum. Although *(154)* could not be characterised by n.m.r. its elemental analysis (C, H, N), melting point and infrared spectrum were consistent with its structure and as compared with the other complexes. Previous ^{31}P n.m.r. studies of complexes of this type have noted that room temperature n.m.r. spectra are often broad or featureless.[140] This appears to be the case in some respects for *(156)* which only appears as a single peak at δ 14.7 p.p.m. with platinum satellites, J(PPt) 3480.7 Hz, in its ^{31}P n.m.r. spectrum. The room temperature ^{31}P n.m.r. of complexes *(153)* and *(155)* fortuitously appear as ABX patterns indicative of cis complexes of this type.[140] The room temperature ^{31}P n.m.r. spectra of *(153)*, *(155)* and *(156)* are summarised in Table 7.

Table 7

^{31}P n.m.r. data for $[PtCl(SnCl_3)(R_2PCH_2)_2NR']$ complexes with the chemical shift of the $[PtCl_2(R_2PCH_2)_2NR']$ starting materials given for comparison. Shifts are in p.p.m. relative to H_3PO_4 at δ 0.0 p.p.m.

Complex	δ Complex	J(PPt) Hz	$J(P^AP^B)$ Hz	δ Starting material
(153)	-2.41 -8.87	2866.2 3202.7	19.5	-7.26 *(110)*
(155)	13.3	2917.0 3298.0	14.7	5.03 *(113)*
(156)	14.7	3480.7	—	3.63 *(114)*

The ^{31}P n.m.r. spectrum of *(155)* consists of a large central feature and AB pattern, platinum satellites; Figure 7 (A). The different J(PPt) values observed are indicative[140] of one phosphorus trans to chlorine, (the larger value), and the other opposite a ligand of stronger trans influence such as $-SnCl_3$. From the appearance of the central peak it appears that both arms of the expected central AB pattern overlap and thus create a single peak.

The ^{31}P n.m.r. spectrum of *(153)* is typical for complexes of this type,[130,140] consisting of a central AB pattern and corresponding Pt-coupled satellites, Figure 7 (B). The different J(PPt) values are again typical for complexes of this type.[130,140] The J(PPt) values along with the J(PP) values for *(153)* and *(155)*, Table 7, can be compared, roughly, to those from the ^{31}P n.m.r. spectrum of $[PtCl(SnCl_3)DIOP]$,[130,140] J(PPt) 3510 Hz, trans to Cl; J(PPt) 2852 Hz, trans to $SnCl_3$, $^2J(PP)$ 17.9 Hz.

The i.r. spectra of the complexes *(153)-(156)* show a number of overlapping bands in the region of 300-350 cm^{-1} where M-Cl stretches for ν(Pt-Cl) and ν(Sn-Cl) occur.[141] The maxima in these regions are given in the experimental section. The i.r. spectra of *(154)* and *(156)* confirm the presence of the ester group in the phosphine ligands by ν(C=O) absorptions at 1730 and 1715 cm^{-1} respectively.

3.8 Reactions of $(Cy_2PCH_2)_2NCHMePh$ *(101)* with Various Metal Complexes

The reactions of chelating diphosphines with complexes of the type $[IrCl(CO)_2NH_2R]$ have been shown[126,142,143] to give complexes of the type A, Figure 8.

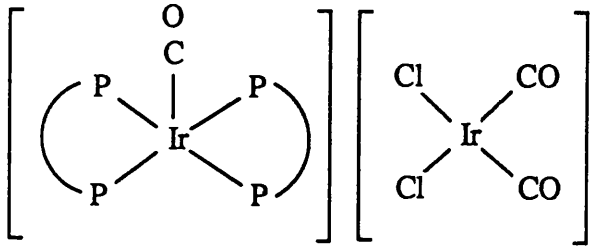


Figure 8 Complex A

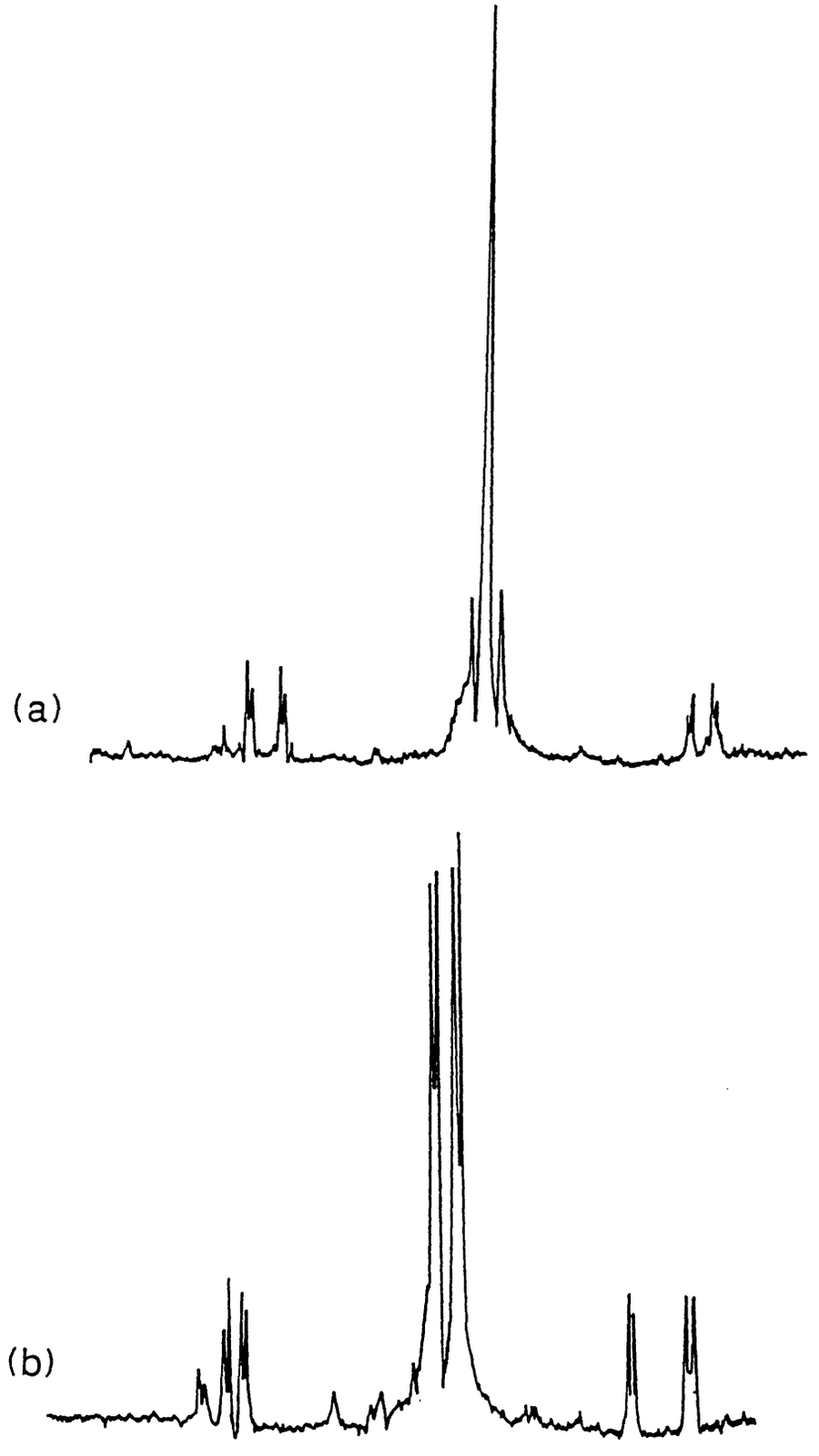


Figure 7 The room temperature ^{31}P n.m.r. spectra of complexes *(155)* (A) and *(153)* (B).

Stoichiometric quantities of *(101)* and $[IrCl(CO)_2P\text{-}(NH_2C_6H_4Me)]$ were refluxed in THF for 12 hours to give a deep orange/red crystalline product *(157)* in a low yield. The product shows a sharp melting point at 268-270°C and was readily soluble in dichloromethane and chloroform. The ^{31}P n.m.r. spectrum of *(157)* showed a single broadened peak at δ 16.73 p.p.m. and the ^{1}H n.m.r. spectrum showed a typical spectrum for *(101)* in a metal complex, by comparison to previously reported compounds in this Chapter. Interestingly, the i.r. spectrum showed no $\nu(CO)$ absorptions, 1700-2000 cm^{-1}, showing that the starting material had lost both carbonyl ligands. When left standing in air for several days the crystals of *(157)* began to show signs of orange/brown discolouration on the crystal surface. Further evidence of this was found when attempts to obtain an X-ray crystal structure of *(157)* showed increasingly poor data with time, indicating a gradual change in the nature of the crystal. This was initially attributed to loss of the solvent of crystallisation. However, the character of *(157)* is remarkably similar to previously reported[144-147] complexes of the type $[Ir(P\text{-}P)_2]Cl$, P-P = chelating diphosphine. The complex colours are similar as are the melting point ranges, 225-270°C and also the complexes irreversibly react with O_2 on standing in air.[148] One example is reported[149] that has a similar method of preparation to *(157)*, by refluxing a $[IrCl(CO)_2NH_2R]$ complex with excess phosphine dppe in benzene. On this basis we can propose the structure of *(157)*, Figure 9, and show from its elemental analysis that it crystallises with one-and-a-half moles of chloroform, in comparison to the above example[149] which gives the dppe complex with two moles of benzene. The addition of oxygen to the complex may explain the problems with the X-ray crystallography and the ^{31}P n.m.r. as even small amounts of paramagnetic oxygen may tend to broaden the spectrum. The bulky phosphines having a labile nature would also explain the broad ^{31}P n.m.r.

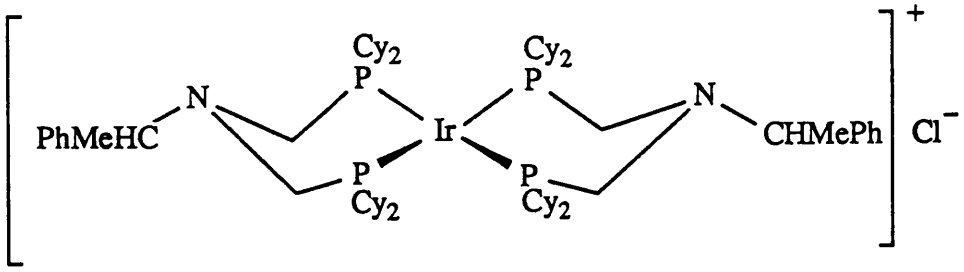
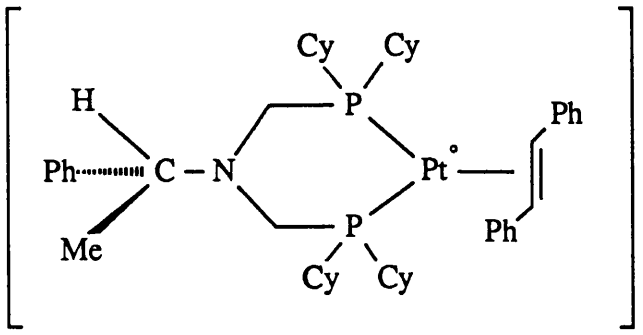


Figure 9 The assigned structure of *(157)*

Complexes of the type $[Pt(PR_3)_2(olefin)]$ have been shown to undergo substitution reactions of (PR_3) when reacted with moderately bulky phosphines.[150] The reaction of $[Pt(PPh_3)_2$trans-stilbene$]$ with *(101)* in THF yielded, after work-up, a pale brown solid *(158)* in low yield with a melting point of 210-216°C. The ^{31}P n.m.r. spectrum of *(158)* showed a single platinum-phosphine compound δ 17.35 p.p.m., J(PPt) 3251 Hz, that did not correspond to the starting material. Signals corresponding to the trans-stilbene protons,  , could not be resolved in the ^1H n.m.r. spectrum of *(158)*, however, integration of the spectrum revealed a ratio of 3 phenyl groups to one equivalent of the phosphine *(101)*. Complex *(158)* is tentatively assigned as $[Pt\{(Cy_2PCH_2)_2NCHMePh\}$trans-stilbene$]$ but further characterisation would be required to confirm this suggestion.



(158)

Substitution by *(101)* of PPh_3 in $[PtCl_2(PPh_3)_2]$ has also been investigated but no conclusive results were obtained. The ^{31}P n.m.r. spectrum of the reaction mixture showed both 'free' *(101)*, δ -18.3 p.p.m. and 'free' PPh_3, δ -5.04 p.p.m. but no platinum complexes could be isolated.

$[Pd_2(DBA)_3].CHCl_3$ is known as a good starting material for Pd^o complexes[151] as the DBA ligand is easily displaced by stronger coordinating ligands such as phosphines. Treatment of $[Pd_2(DBA)].CHCl_3$ with *(101)* in refluxing toluene yielded a complex mixture of products, from the ^{31}P n.m.r. spectrum, and no single compounds could be isolated or identified.

3.9 Reactions of $[PtCl_2(R_2PCH_2)_2NCR']$ complexes

$[Pt^o(P-P)_2]$ and $[Pd^o(P-P)_2]$ complexes, (P-P) = chelating diphosphine are known to be useful catalysts for a variety of synthetic reactions,[152,153] including asymmetric syntheses. Preparations of complexes of this type, by the reduction of $[PtCl_2(P-P)]$ complexes by sodium-borohydride[154] or hydrazine[155] in the presence of excess (P-P) have been known for some time. In a similar way it is possible to prepare similar complexes with different 'second' substituents by using an excess of a different phosphine (P-P) or an olefin or acetylene.

Attempts to prepare Pt^o complexes such as these by reduction of $[PtCl_2(Cy_2PCH_2)_2NCHMePh]$ *(113)* using hydrazine hydrate in the presence of either excess *(101)* or excess diphenyl acetylene gave only unreacted starting material. However, reaction of *(113)* with $NaBH_4$ in the presence of excess trans-stilbene gave a complex mixture, from its ^{31}P n.m.r. spectrum, from which no compounds could be isolated.

The reaction of Ag_2O with $[PtCl_2P_2]$ complexes, P = monodentate tertiary phosphine or P_2 = chelating diphosphine, in the presence of $RCO_2CHCOCHCO_2R$ (R = Me, Et, Ph) to give metallocyclobutanone complexes of the type $[P_2PtCH(RO_2C)COCHCO_2R]$ has been studied in some detail.[214,215] Reactions were carried out on the complexes *(110)* and *(113)* by refluxing in a dichloromethane solution with excess Ag_2O and an excess of diethyl 1-3 acetone dicarboxylate, Scheme 10.

Scheme 10

$$[PtCl_2(R_2PCH_2)NR'] \xrightarrow[Ag_2O,\ CH_2Cl_2,\ \text{reflux, 4h}]{EtO_2CCH_2COCH_2CO_2Et} \text{complex mixture}$$

R′ = CHMePh, R = Cy *(113)*, Ph *(110)*

In both cases a complex mixture was observed in the ^{31}P n.m.r. spectra of the reaction mixtures in which no platinum-phosphine compounds could be identified.

3.10 Conclusion

A range of new transition metal complexes of aminomethylphosphines have been readily prepared and characterised. All reported complexes except $[Ir\{(Cy_2PCH_2)_2NCHMePh\}_2]^+Cl^-$ *(157)* are air stable and the complexes of Pt(II), Pd(II) and Ni(II) were also obtained in good yields. The complexes of the type $[PtCl(SnCl_3)(R_2PCH_2)_2NR']$ and $[Rh(COD)(R_2PCH_2)_2NR']^+PF_6^-$ have served as useful catalyst precursors for catalytic hydroformylation and hydrogenation. Further reactions of complexes of the type $[PtCl_2(R_2PCH_2)_2NR']$ with various reagents either show no reaction or have led to complex mixtures. A useful addition to the present work would be to pursue the preparation of palladium and platinum (0) complexes of chelating aminomethylphosphines.

3.11 Experimental

The general experimental and spectroscopic techniques were as described in Chapter 2. Experiments were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. The solvents hexane, light petroleum (40-60°) and tetrahydrofuran (THF) were dried and distilled under nitrogen prior to use, from the following drying agents, hexane (sodium), light petroleum (sodium), THF (sodium/ benzophenone). The solvents acetone and dimethylsulphoxide were used as supplied from commercial sources. The compounds $NiCl_2.6H_2O$ (BDH), $CoCl_2.6H_2O$ (BDH), KPF_6 (Ventron), $SnCl_2$ (Hopkin & Williams), diethyl 1-3 acetonedicarboxylate (Aldrich), silver(I) oxide (BDH), trans-stilbene (Aldrich), diphenylacetylene (Aldrich), sodium borohydride (BDH) and hydrazine hydrate (Aldrich) were used as supplied from commercial sources. The compounds $[PtCl_2(COD)]$,[156] $[PdCl_2(COD)]$,[157] $[Mo(CO)_4(PiP)_2]$ and $[W(CO)_4(PiP)_2]$,[136] $[Rh(COD)Cl]_2$,[158] $[IrCl(CO)_2NH_2C_6H_4Me]$,[157] $[Pt(PPh_3)_2$(trans-stilbene)][159] and $[Pd_2(DBA)_3].CHCl_3$,[160] were prepared as described in the literature. Precious metal salts were obtained on loan from Johnson Matthey plc.

3.11.1 Preparation of cis-$[MCl_2(R_2PCH_2)_2NR']$ complexes, M = Pt,Pd,Ni.

(i) $[PtCl_2(Ph_2PCH_2)_2NCHMePh]$(110)

A solution of $(Ph_2PCH_2)_2NCHMePh$ (0.14g,0.27mmol) in toluene ($1cm^3$) was added to a stirred solution of $[PtCl_2(COD)]$ (0.1g,0.27mmol) in dichloromethane ($40cm^3$). The mixture was brought to reflux under a nitrogen atmosphere for 1h. Addition of light petroleum to the cooled solution yielded white crystals which were filtered and dried in vacuo.(0.14g,67% based on Pt).

(Found:C,47.8;H,4.5;N,1.6.$C_{34}H_{35}Cl_2NP_2Pt.CH_2Cl_2$ requires C,48.4;H,4.3; N,1.6%). M.p. 239-240°C.

N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ -7.26 [s,J(PPt)3408.2] p.p.m. ^1H(300MHz),δ 1.25[d,3H,Me,^{3}J(HH)7.4],3.5[m,4H,PCH_2,J(HPt)36.0],3.8[q,1H, CH,^{3}J(HH)7.4],6.9-7.8[m,20H,Ph] p.p.m.$^{13}C-\{^1H\}$(75.47MHz),δ 12.2[s,Me], 54.5[d,PCH_2,J(CP)50.1],67.3[t,NCH,^{3}J(CP)5.3],127-136[m,Ph] p.p.m.

(ii) $[PtCl_2(Ph_2PCH_2)_2NCHMeCO_2Et]$(111)

A solution of $(Ph_2PCH_2)_2NCHMeCO_2Et$ (0.55g,1.1mmol) in dichloromethane ($2cm^3$) was added to a solution of $[PtCl_2(COD)]$ (0.4g,1.1mmol) in dichloromethane ($40cm^3$). The mixture was stirred for 2h under a nitrogen atmosphere. Addition of light petroleum to the solution yielded a white precipitate. This was filtered and recrystallised from dichloromethane-light petroleum, (0.656g,79% based on Pt).

(Found; C,52.6;H,4.9;N,2.0. $C_{31}H_{33}Cl_2NO_2P_2Pt$ requires C,47.7;H,4.2; N,1.9%). M.p. 270-272°C decomp.

N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ -8.67 [d,J(PPt)3427.7] p.p.m. ^1H (300MHz),δ 0.85[d,3H,Me,^{3}J(HH)7.2],1.15[t,3H,Me,^{3}J(HH)7.0],3.36 [q,1H,CH,^{3}J(HH)7.1],3.7[m,4H,PCH_2,^{3}J(HPt)36.05],4.0[m,2H,OCH_2],7.4-7.9[m, 20H,Ph], $^{13}C-\{^1H\}$(75.47MHz),δ 14.1[s,Me],14.9[s,Me],54.1[d,PCH_2,J(CP) 59.9],60.9[s,OCH_2],65.4[t,NCH,^{3}J(CP)10.2],127-134[m,Ph],171.4[s,C=O]p.p.m.

ir, ν_{max} 1725(C=O);Pt-Cl,323,295 cm^{-1},(KBr).

(iii) [$PtCl_2((Ph_2PCH_2)_2NCHCH_2CHCH_2CH_2C(Me)C(Me)_2)$](112)

A solution of $((Ph_2PCH_2)_2NCHCH_2CHCH_2CH_2C(Me)C(Me)_2)$ (0.3g,0.55mmol) in dichloromethane ($2cm^3$) was added to a stirred solution of [$PtCl_2$(COD)] (0.2g,0.53mmol) in dichloromethane ($40cm^3$). The mixture was stirred for 2h under a nitrogen atmosphere. Addition of light petroleum to the solution yielded a white crystalline precipitate which was filtered and dried in vacuo,(0.34g,76% based on Pt).

(Found; C,52.7;H,5.1;N,1.8. $C_{36}H_{41}Cl_2NP_2Pt$ requires C,53.0;H,5.0;N,1.7%).

M.p. >320°C.

N.m.r.(CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ -7.68[d,J(PPt)3413.0] p.p.m.

^1H (300MHz),δ 0.68[s,3H,Me],0.71[s,3H,Me],0.79[s,3H,Me],1.1-1.8[m,7H], 2.6[m,1H,NCH],3.54[m,4H,PCH_2,^3J(HPt)31.1],7.1-7.9[m,20H,Ph] p.p.m.

$^{13}C-\{^1H\}$(75.47MHz),δ 17.8[s,Me],18.7[s,Me],20.1[s,Me],26.9-28.7[s,CH_2], 43.8[s,CH],49.3-50.5[s,C],56.2[d,PCH_2,J(CP)55.5],74.6[t,NCH,^{3}J(CP)10.0], 128-134[m,Ph] p.p.m.

(iv) [$PtCl_2(Cy_2PCH_2)_2NCHMePh$](113)

$(Cy_2PCH_2)_2NCHMePh$ (0.145g,0.27mmol) was added to a stirred solution of [$PtCl_2$(COD)] (0.1g,0.27mmol) in dichloromethane ($40cm^3$). The mixture was brought to reflux for 1h under a nitrogen atmosphere. Addition of light petroleum to the cooled solution yielded white crystals which were filtered and dried in vacuo,(0.17g,78% based on Pt).

(Found:C,48.4;H,6.8;N,1.6.$C_{34}H_{57}Cl_2NP_2Pt.CH_2Cl_2$ requires C,47.1;H,6.6; N,1.7%). M.p.240-250°C decomp.

N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ 5.04[d,J(PPt)3460.0] p.p.m.

^1H (300MHz),δ 1.35[d,3H,Me,^{3}J(HH)6.8],1-2.3[m,44H,Cy],2.7[m,ABX,4H,PCH_2, J(HH)14.0,^{2}J(HP)2.9],3.85[q,1H,CH,^{3}J(HH)6.7],7.3[m,5H,Ph] p.p.m.

$^{13}C-\{^{1}H\}$(75.47MHz),δ 13.0[s,Me],26-36[m,Cy],45.4[d,PCH_2,J(CP)51.9],68.0[t, NCH,^{3}J(CP)9.5],128-129[m,Ph] p.p.m.

(v) [$PtCl_2(Cy_2PCH_2)_2NCHMeCO_2Et$](114)

A solution of $(Cy_2PCH_2)_2NCHMeCO_2Et$ (0.715g,1.36mmol) in toluene ($0.5cm^3$) was added to a stirred solution of [$PtCl_2$(COD)] (0.5g,1.33mmol) in dichloromethane ($40cm^3$). The mixture was stirred for 2h under a nitrogen atmosphere. Addition of light petroleum to the solution yielded white crystals which were filtered and dried in vacuo,(0.79g,75% based on Pt). (Found:C,47.0;H,6.7;N,1.7.$C_{31}H_{57}Cl_2NO_2P_2Pt$ requires C,46.3;H,7.1;N,1.7%). M.p. 314-315°C.

N.m.r.(CD_2Cl_2),$^{31}P-\{^{1}H\}$(24MHz),δ +3.63 [d,J(PPt)3461.9] p.p.m.

^{1}H (300MHz),δ 1.0-2.8[m,50H,4Cy+2Me],2.9-3.0[m,ABX,4H,PCH_2,^{2}J(HH)14.5, ^{2}J(HP)2.4], 3.46[q,1H,CH,^{3}J(HH)7.1],4.2[q,2H,OCH_2,^{3}J(HH)7.0] p.p.m.

$^{13}C-\{^{1}H\}$(75.47MHz),δ 14.5[s,Me],15.0[s,Me],29.9[d,PCH^2,J(CP)10.5],61.1[s, OCH_2],66.0[s,NCH],171.1[s,C=O] p.p.m.

ir,ν_{max} 1725(C=O) cm^{-1},(KBr).

(vi) [$PtCl_2(C_8H_{14}PCH_2)_2NCHMePh$](115)

$(C_8H_{14}PCH_2)_2NCHMePh$ (0.23g,0.54mmol) was added to a stirred solution of [$PtCl_2$(COD)] (0.2g,0.54mmol) in dichloromethane ($80cm^3$). The mixture was stirred under a nitrogen atmosphere for 2h. Addition of light petroleum to the solution yielded a white precipitate which was filtered, washed with diethyl ether and dried in vacuo.(0.3g,80% based on Pt). (Found :C,41.8;H,5.7;N,1.8. $C_{26}H_{41}Cl_2NP_2Pt.0.5CH_2Cl_2$ requires C,42.3; H,5.4;N,1.8%). M.p. 264-266°C.

N.m.r. (CD_2Cl_2),$^{31}P-\{^{1}H\}$(24MHz),δ -15.52[d,J(PPt)3242.0] p.p.m.

^{1}H(300MHz),δ 1.48[d,3H,Me,^{3}J(HH)6.8],1.6-2.4[m,28H,C_8H_{14}],2.6-2.7 [m,4H,PCH_2],4.0[q,1H,NCH,^{3}J(HH)6.8],7.2-7.5[m,5H,Ph] p.p.m.

(vii) [$PdCl_2(Ph_2PCH_2)_2NCHMePh$](116)

$(Ph_2PCH_2)_2NCHMePh$ (0.36g,0.7mmol) in dichloromethane (2.6cm^3) was added to a solution of [$PdCl_2(COD)$] (0.2g,0.68mmol) in dichloromethane (40cm^3). The mixture was stirred for 3h under a nitrogen atmosphere. The solvent was then removed under reduced pressure and the resulting solid recrystallised from dichloromethane–diethyl ether. The resulting yellow crystals were filtered and dried in vacuo,(0.37g,70% based on Pd). (Found: C,57.4;H,4.8;N,2.0 $C_{34}H_{33}Cl_2NP_2Pd$ requires C,57.9;H,4.7;N,2.0%). M.p. 252–254°C.

N.m.r. (CD_2Cl_2), $^{31}P-\{^1H\}$(24MHz),δ 9.66 p.p.m.

^1H (300MHz),δ 1.3[d,3H,Me,^3J(HH)6.9],3.42[m,4H,PCH_2],3.82[q,1H,CH,^3J(HH) 6.9], 6.9–7.8[m,25H,Ph] p.p.m. $^{13}C-\{^1H\}$(75.47MHz),δ 12.5[s,Me],53.6[d, PCH_2,J(CP)49.4],66.9[t,NCH,^3J(CP)9.7],127–139[m,Ph] p.p.m.

(viii) [$PdCl_2(Ph_2PCH_2)_2NCHMeCO_2Et$](117)

$(Ph_2PCH_2)_2NCHMeCO_2Et$ (0.36g,0.7mmol) in dichloromethane (2cm^3) was added to a solution of[$PdCl_2(COD)$] (0.2g,0.68mmol) in dichloromethane (40cm^3). The mixture was stirred for 3h under a nitrogen atmosphere. The solvent was the removed under reduced pressure and the resulting solid recrystallised from dichloromethane–diethyl ether. The resulting yellow crystals were filtered and dried in vacuo,(0.45g,94% based on Pd). (Found: C,51.7;H,4.8;N,2.0 $C_{31}H_{33}Cl_2NO_2P_2Pd.0.5CH_2Cl_2$ requires C,51.6; H,4.6;N,1.9%). M.p. 152–154°C sublimes.

N.m.r.(CD_2Cl_2), $^{31}P-\{^1H\}$(24MHz),δ 7.66 p.p.m.

^1H (300MHz),δ 0.9[d,3H,Me,^3J(HH)7.2],1.15[t,3H,$CH_2\underline{CH}_3$,^3J(HH)6.9],3.4 [q,1H,CH,^3J(HH)7.2],3.67[m,4H,PCH_2],4.0[m,2H,OCH_2],7.4–7.9[m,20H,Ph] p.p.m.$^{13}C-\{^1H\}$(75.47MHz),δ 14.5[s,Me],15.2[s,Me],54.5[d,PCH_2,J(CP)44.8] ,61.4[s, OCH_2],65.4[t,NCH,^3J(CP)8.9],128–134[m,Ph],171.9[s,C=O] p.p.m.

ir,ν_{max} 1722(C=O) cm^{-1},(KBr).

(ix) $[PdCl_2(Cy_2PCH_2)_2NCHMePh]$(118)

$(Cy_2PCH_2)_2NCHMePh$ (0.56g,1.0mmol) was added to a solution of $[PdCl_2(COD)]$ (0.3g,1.0mmol) in dichloromethane ($40cm^3$). The mixture was stirred for 3h under a nitrogen atmosphere. Addition of petroleum ether to the solution yielded a yellow precipitate which was filtered and recrystallised from chloroform and diethyl ether. The resulting crystals were filtered and dried in vacuo,(0.605g,84% based on Pd). (Found:C,50.4;H,7.1;N,1.5.$C_{34}H_{57}Cl_2NP_2Pd.CHCl_3$ requires C,50.7;H,7.0; N,1.7%). M.p. 306-308°C.

N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ 29.24 p.p.m.

^1H (300MHz),δ 1.0-2.4[m,44H,Cy],1.44[d,3H,Me,^3J(HH)6.8],2.68[m,ABX,4H, PCH_2, ^2J(HH)14.0,^2J(HP)2.1],3.9[q,1H,CH,^3J(HH)6.8],7.33[m,5H,Ph] p.p.m.

$^{13}C-\{^1H\}$(75.47MHz),δ 12.1[s,Me],45.0[d,PCH_2,J(CP)42.4],66.9[t,NCH,^3J(CP) 9.2],127-128[m,Ph] p.p.m.

(x) $[PdCl_2(Cy_2PCH_2)_2NCHMeCO_2Et]$(119)

$(Cy_2PCH_2)_2NCHMeCO_2Et$ (0.7g,1.2mmol) in dichloromethane ($4cm^3$) was added to a solution of $[PdCl_2(COD)]$ (0.33g,1.1mmol) in dichloromethane ($40cm^3$). The mixture was stirred for 3h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the resulting yellow solid was recrystallised from chloroform-diethyl ether. The resulting yellow crystals were filtered and dried in vacuo,(0.52g,64% based on Pd). (Found:C,47.1;H,7.5;N,1.7 $C_{31}H_{57}Cl_2NO_2P_2Pd.CHCl_3$ requires C,46.7;H,7.1; N,1.7%). M.p.320-322°C.

N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ 27.22 p.p.m.

^1H (300MHz),δ 1.2-2.5[m,50H,4Cy+2Me],3.0[m,AB,4H,PCH_2,^2J(HH)14.6],3.6 [q,1H,NCH,^3J(HH)7.0],4.22[q,2H,OCH_2,^3J(HH)7.1], $^{13}C-\{^1H\}$(75.47MHz),δ 14.4 [s,Me],15.0[s,Me],25.9-30.2[m,CH_2,Cy],36.8[m,CH,Cy],46.5[d,PCH_2,J(CP)42.5, 61.0[s,OCH_2],65.4[t,NCH,^3J(CP)9.0],171.6[s,C=O] p.p.m.

(xi) [$PdCl_2(C_8H_{14}PCH_2)_2NCHMePh$](120)

$(C_8H_{14}PCH_2)_2NCHMePh$ (0.38g,0.7mmol) was added to a solution of [$PdCl_2(COD)$] (0.2g,0.68mmol) in dichloromethane ($50cm^3$). The mixture was stirred for 3h under a nitrogen atmosphere. The solvent was then removed under reduced pressure and the resulting solid recrystallised from chlorofom-diethyl ether. The yellow crystalline product was filtered and dried in vacuo.(0.3g,73% based on Pd).

(Found:C,45.5;H,5.9;N,2.1. $C_{26}H_{41}Cl_2NP_2Pd.CHCl_3$ requires C,44.6;H,5.8; N,1.9%). M.p. 175-179°C

N.m.r.(CD_2Cl_2), $^{31}P-\{^1H\}$(24MHz),δ 4.63 p.p.m.

^1H (90MHz),δ 1.54[d,3H,Me,$^3J(HH)$6.8],1.6-2.4[m,28H,C_8H_{14}]3.4-3.6[m, PCH_2],4.1[q,1H,CH,$^3J(HH)$6.8],7.3[m,5H,Ph] p.p.m.

(xii) [$PdCl_2(Ph_2PCH_2)_2NCH_2CH_2OH$](121)

$(Ph_2PCH_2)_2NCH_2CH_2OH$ (0.5g,1.1mmol) in solution of dichloromethane ($4cm^3$) was added to a solution of [$PdCl_2(COD)$] (0.3g,1.0 mmol) in dichloromethane ($40cm^3$). The mixture was stirred for 3h under a nitrogen atmosphere. The solvent was then removed under reduced pressure, and the resulting yellow solid was recrystallised from chloroform and diethyl ether. The crystalline product was filtered and dried in vacuo,(0.54g,85% based on Pd).

(Found: C,52.8;H,4.7;N,2.2. $C_{28}H_{29}Cl_2NOP_2Pd$ requires C,53.0;H,4.6;N,2.2%). M.p. 152-154°C decomp.

N.m.r. ($CDCl_3$), $^{31}P-\{^1H\}$(24MHz),δ 7.46 p.p.m.

^1H(300MHz),δ 1.5[sb,1H,OH],2.75[t,2H,$^3J(HH)$4.8],3.48[t,2H,CH_2O,$^3J(HH)$4.7], 3.52[m,AXX',4H,PCH_2,$^2J(PH)$4.4,$^4J(PH)$3.1],7.2-7.9[m,20H,Ph] p.p.m.

ir,ν_{max} 3460(OH),1660(Phenyl) cm^{-1},(KBr).

(xiii) [$PdCl_2(Ph_2PCH_2)_2NCH_2CH{=}CH_2$](122)

$(Ph_2PCH_2)_2NCH_2CH{=}CH_2$ (0.68g,1.5mmol) in a solution of dichloromethane

($5cm^3$) was added to a solution of $[PdCl_2(COD)]$ (0.4g,1.36mmol) in dichloromethane ($40cm^3$). The mixture was then stirred for 3h under a nitrogen atmosphere. The solvent was then removed under reduced pressure and the resulting yellow residue was recrystallised from chloroform and diethyl ether. The crystalline product was the filtered and dried in vacuo,(0.79g,92% based on Pd).

(Found; C,54.3;H,4.7;N,2.0. $C_{29}H_{29}Cl_2NP_2Pd$ requires C,55.2;H,4.6;N,2.2%).

M.p. 148-149°C decomp.

N.m.r. ($CDCl_3$) $^{31}P-\{^1H\}$(24MHz),δ 8.29 p.p.m.

^1H (90MHz),δ 3.02-3.46[m,6H,PCH_2/NCH_2],4.94-5.8[m,3H,olefinic],7.1-7.98 [m,20H,Ph] p.p.m.

(xiv) $[PdCl_2(Ph_2PCH_2)_2NCH_2C{\equiv}CH]$(123)

The compound was prepared by the same methods as previous palladium-dichloride-diphosphine complexes and the ^{31}P n.m.r. spectrum of the reaction mixture showed a single prodouct at, δ 9.47 p.p.m. Attempts to isolate the product resulted in decomposition and loss of the single ^{31}P n.m.r. signal.

(xv) $[NiCl_2(Ph_2PCH_2)_2NCHMeCO_2Et]$(124)

$(Ph_2PCH_2)_2NCHMeCO_2Et$ (0.43g,0.8mmol) was dissolved in ethanol (50cm3) and warmed to 50°C under a nitrogen atmosphere. A solution of $NiCl_2.6H_2O$ (0.2g,1.5mmol) in water ($20cm^3$) was then added and the mixture stirred for 1h. On cooling a pale brown precipitate formed which was filtered off and reprecipitated from dichloromethane-light petroleum. The product was filtered and dried in vacuo,(0.33g,64% based on P).

(Found: C,51.9;H,5.1;N,2.2. $C_{31}H_{33}Cl_2NNiO_2P_2$ requires C,57.8;H,5.1; N,2.2%). M.p. 110-115°C decomp.

N.m.r.(CD_2Cl_2), $^{31}P-\{^1H\}$(24MHz),δ 10.24 p.p.m.

^1H (300MHz),δ 0.9[d,3H,Me,^3J(HH)7.2],1.14[t,3H,$CH_2\underline{CH}_3$,^3J(HH)7.1],3.3

[q,1H,CH,^{3}J(HH)7.2],3.8[m,4H,PCH_2],4.0[m,2H,OCH_2],7.5-8.03[m,20H,Ph]p.p.m.
$^{13}C-\{^{1}H\}$(75.47MHz),δ 14.3[s,Me],14.9[s,Me],53.6[d,PCH_2,J(CP)46.3],61.1[s,
OCH_2],64.9[s,NCH],128-136[m,Ph],171.6[s,C=O] p.p.m.
ir,ν_{max} 1725(C=O);ν(Ni-Cl) 325,352 cm^{-1},(KBr).

(xvi) [$NiCl_2(Cy_2PCH_2)_2NCHMePh$](125)

$(Cy_2PCH_2)_2NCHMePh$ (0.3g,0.55mmol) was dissolved in ethanol (50cm^3) and warmed to 50°C under a nitrogen atmosphere. To this was added a solution of $NiCl_2.6H_2O$ (0.13g,0.55mmol) in water (20cm^3). The mixture was stirred for 1h and allowed to cool. The precipitate was filtered and recrystallised from dichloromethane-light petroleum. The resulting golden flakes were filtered and dried in vacuo.(0.21g,57% based on P).
(Found:C,58.7;H,8.5;N,2.0. $C_{34}H_{57}Cl_2NNiP_2.0.5CH_2Cl_2$ requires C,58.8;H,8.1; N,2.0%). M.p. 258-260°C.
N.m.r.(CD_2Cl_2),$^{31}P-$(24MHz),δ 16.33 p.p.m.
^{1}H (300MHz),δ 1.1-2.16[m,50H,4Cy+2Me],2.4[m,AB,PCH_2,^{2}J(HH)13.7],3.8[q,1H, NCH,^{3}J(HH)6.7],7.-7.4[m,5H,Ph] p.p.m. $^{13}C-\{^{1}H\}$(75.47MHz),δ 13.5[s,Me], 26.7-31.5 [m,CH_2,Cy],37.5[m,PCH,Cy],46.4[m,PCH_2],67.8[m,NCH],128.8-129.5 [m,Ph] p.p.m.

(xvii) [$NiCl_2(Cy_2PCH_2)_2NCHMeCO_2Et$](126)

$(Cy_2PCH_2)_2NCHMeCO_2Et$ (0.3g,0.6mmol) was dissolved in ethanol (50cm^3) and warmed to 50°C under a nitrogen atmosphere. To this was added a solution of $NiCl_2.6H_2O$ (0.13g,0.55mmol) in water (20cm^3). The mixture was stirred for 1h and allowed to cool. The resulting brown solid was filtered and recrystallised from dichloromethane-light petroleum to yield golden brown flakes. These were filtered and dried in vacuo.(0.22g,61% based on P).
(Found:C,54.0;H,8.6;N,2.0. $C_{31}H_{57}Cl_2NNiP_2.0.5CH_2Cl_2$ requires C,53.3;H,8.2; N,2.0%). M.p. 226-228°C
N.m.r.(CD_2Cl_2),$^{31}P-\{^{1}H\}$(24MHz),δ 14.32 p.p.m.

^1H (300MHz),δ 1.24-2.26[m,50H,4Cy+2Me],2.6-2.7[m,4H,PCH_2],3.43[q,1H,CH], 4.18[q,2H, OCH_2], $^{13}C-\{^1H\}$(75.47MHz),δ 14.5[s,Me],15.0[s,Me],26.6-30.8[m, CH_2,Cy],36.9[d,PCH,Cy,J(CP)30.2],46.7[m,PCH_2],61.0[s,OCH_2],65.4[s,NCH], 171.7[s,C=O] p.p.m.

ir,ν_{max} 1730(C=O);Ni-Cl,325,340 cm^{-1},(KBr).

3.11.2 Preparation of $[CoX_2(R_2PCH_2)_2NR']$ complexes.

(i) $[CoCl_2(Ph_2PCH_2)_2NCHMePh]$(139)

A solution of $(Ph_2PCH_2)_2NCHMePh$ (0.45g,0.9mmol) in dichloromethane ($2cm^3$) was added to a stirred solution of $CoCl_2.6H_2O$ (0.2g,0.84mmol) in ethanol ($40cm^3$). The mixture was brought to reflux under a nitrogen atmosphere for 1h. On cooling the volume was reduced to about $5cm^3$ under reduced pressure. Addition of light petroleum yielded a green powder which was filtered and dried in vacuo.(0.39g,71% based on Co).

(Found:C,58.1;H,5.4;N,1.9.$C_{34}H_{33}Cl_2CoNP_2.CH_2Cl_2$ requires C,57.4;H,4.8; N,1.9%).

M.p. 130-131°C decomp.

ir,ν(Co-Cl) 310 cm^{-1},(KBr).

(ii) $[CoCl_2(Ph_2PCH_2)_2NCHMeCO_2Et]$(140)

A solution of $(Ph_2PCH_2)_2NCHMeCO_2Et$ (0.5g,1.0mmol) in dichloromethane ($2cm^3$) was added to a stirred solution of $CoCl_2.6H_2O$ (0.2g,0.84mmol) in ethanol ($40cm^3$). The mixture was brought to reflux under a nitrogen atmosphere for 1h. On cooling the volume was reduced to about $5cm^3$ under reduced pressure. Addition of light petroleum yielded a fine green powder which was filtered and dried in vacuo.(0.49g,91% based on Co).

(Found:C,52.2;H,4.7;N,2.0.$C_{31}H_{33}Cl_2CoNO_2P_2.CH_2Cl_2$ requires C,52.7;H,4.8; N,1.9%).

M.p. 116-118°C sublimation.

ir,ν_{max} 1725(C=O)cm^{-1},ν(Co-Cl),307 cm^{-1},(KBr).

(iii) [$CoCl_2(Cy_2PCH_2)_2NCHMePh$](141)

$(Cy_2PCH_2)_2NCHMePh$ (0.45g,0.83mmol) was added to a stirred solution of $CoCl_2.6H_2O$ (0.2g,0.84mmol) in ethanol(40cm^3). The mixture was brought to reflux for 1h under a nitrogen atmosphere. On cooling the volume was reduced to about 5cm^3 under reduced pressure. Addition of light petroleum yielded a fine green powder. This was filtered and dried in vacuo.(0.51g, 90% based on Co).

(Found:C,58.0;H,8.1;N,2.3. $C_{34}H_{57}Cl_2CoNP_2.0.5CH_2Cl_2$ requires C,58.0;H,8.3; N,2.0%).

M.p. 220-222°C sublimation.

ir,ν(Co-Cl) 310,340 cm^{-1},(KBr).

(iv) [$CoBr_2(CyPCH_2)_2NCHMeCO_2Et$](142)

A solution of $(Cy_2PCH_2)_2NCHMeCO_2Et$ (0.56g,1.0mmol) in dichloromethane (2.5cm^3) was added to a stirred solution of [$CoBr_2Py_2$] (0.4g,1.0mmol) in dichloromethane(40cm^3). The mixture was brought to reflux under a nitrogen atmosphere for 1h. On cooling the volume was reduced to about 5cm^3 under reduced pressure. Addition of light petroleum yielded a fine bright green powder. This was filtered and dried in vacuo.(0.66g,87% based on Co).

(Found:C,44.6;H,6.8;N,2.8. $C_{31}H_{57}NBr_2CoO_2P_2.CH_2Cl_2$ requires C,45.6;H,7.0; N,1.7%, High N indicates pyridine impurity).

M.p. 140-146°C sublimation.

ir,ν_{max} 1730(C=O) cm^{-1},(KBr).

3.11.3 Preparation of cis-[$M(CO)_4(Cy_2PCH_2)_2NCHMePh$] complexes, M = Mo,W.

(i) [$Mo(CO)(Cy_2PCH_2)_2NCHMe$](143)

$(Cy_2PCH_2)_2NCHMePh$ (0.3g,0.55mmol) was added to a solution of [$Mo(CO)pip_2$] (0.2g,0.55mmol) in dichloromethane (40cm^3). The mixture was brought to reflux under a nitrogen atmosphere for 2h. The solvents were then removed under reduced pressure and the resulting solid washed in

methanol. The resulting yellow precipitate was filtered and recrystallised from dichloromethane and methanol,(0.2g,48% based on Mo).

M.p. 238-246°C

N.m.r.(CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ 22.6 p.p.m.

ir,ν_{max} 2004,1892,1868(C≡O) cm^{-1},(KBr).

(ii) [W(CO)$_4$(Cy$_2$PCH$_2$)$_2$NCHMePh](144)

$(Cy_2PCH_2)_2NCHMePh$ (0.4g.0.74mmol) was added to a solution of $[W(CO)_4pip_2]$ (0.34g,0.73mmol) in toluene ($50cm^3$). The mixture was brought to reflux under a nitrogen atmosphere for 6h. The solvents were then removed under reduced pressure and the residue was washed with methanol. The resulting yellow precipitate was filtered and dried in vacuo, (0.35g, 57% based on W).

M.p. 152-154°C decomp.

N.m.r.(CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ 3.4[s] p.p.m.

ir,ν_{max} 2000,1875,1865(C≡O) cm^{-1},(KBr).

3.11.4 Preparation of [Rh(COD)(R$_2$PCH$_2$)$_2$NR']$^+$PF$_6^-$ complexes.

(i) [Rh(COD)(Ph$_2$PCH$_2$)$_2$NCHMePh]$^+$PF$_6^-$(146)

A solution of $(Ph_2PCH_2)_2NCHMePh$ (0.21g,0.4mmol) in dichloromethane ($1.5cm^3$) was added to a mixture of $[Rh(COD)Cl]_2$ (0.1g,0.2mmol) and KPF_6 (0.1g,0.5mmol) in dichloromethane ($20cm^3$) and water ($10cm^3$). The mixture was stirred vigorously at room temperature for 15 minutes under a nitrogen atmosphere. The dichloromethane layer was then removed and washed with water. The volume was reduced to about $5cm^3$ under reduced pressure and ethanol ($5cm^3$) was added. Addition of diethyl ether to the solution precipitated a fine orange-brown powder which was filtered and dried in vacuo,(0.3g,86% based on Rh).

(Found:C,55.3;H,5.1;N,1.9. $C_{42}H_{47}F_6NP_3Rh.0.5CH_2Cl_2$ requires C,55.7;H,5.0; N,1.5%). M.p. 140-142°C.

N.m.r.(CD_2Cl_2), $^{31}P-\{^1H\}$(24MHz), δ 8.56[d,J(PRh) 141.6],-143.6 [septet, J(PF)711.2] p.p.m.

(ii) [Rh(COD)(Ph_2PCH_2)$_2$NCHMeCO$_2$Et]$^+PF_6^-$(147)

A solution of (Ph_2PCH_2)$_2$NCHMeCO$_2$Et (0.43g,0.82mmol) in dichloromethane (1.5cm^3) was added to a mixture of [Rh(COD)Cl]$_2$ (0.2g,0.4mmol) and KPF_6 (0.2g,0.4mmol) in dichloromethane (30cm^3) and water (20cm^3). The mixture was stirred vigorously at room temperature for 15 minutes under a nitrogen atmosphere. The dichloromethane layer was removed and washed with water. The volume was then reduced to about 5cm^3 under reduced pressure and ethanol (5cm^3) was added. Addition of diethyl ether to the solution precipitated a fine orange-brown powder. This was filtered and dried in vacuo,(0.56g,79% based on Rh).

(Found: C,52.9;H,5.1;N,1.8. $C_{42}H_{47}F_6NO_2P_3Rh.0.5CH_2Cl_2$ requires C,52.4; H,5.0;N,1.8%). M.p. 176°C.

N.m.r.(CD_2Cl_2), $^{31}P-\{^1H\}$(24MHz), δ 7.9[d,J(PRh) 141.6], -143.8 [septet, J(PF)712.8] p.p.m.

(iii) [Rh(COD)(Ph_2PCH_2)$_2$NCHCH$_2$CHCH$_2$CH$_2$C(Me)C(Me)$_2$]$^+PF_6^-$(148)

A solution of (Ph_2PCH_2)$_2$NCHCH$_2$CHCH$_2$CH$_2$C(Me)C(Me)$_2$ (0.44g,0.8mmol) in dichloromethane(2cm^3) was added to a mixture of [Rh(COD)Cl]$_2$ (0.2g, 0.4mmol) and KPF_6 (0.2g,1.0mmol) in dichloromethane (30cm^3) and water (20cm^3). The mixture was stirred vigorously at room temperature for 15 minutes under an atmosphere of nitrogen. The dichloromethane layer was then removed and washed with water. The volume was reduced to about 5cm^3 under reduced pressure and ethanol (5cm^3) was added. Addition of diethyl ether to the solution precipitated a fine orange-brown powder which was filtered and dried in vacuo,(0.42g,57% based on Rh).

(Found: C,56.9;H,6.0;,N,1.9. $C_{44}H_{53}F_6NP_3Rh.0.5CH_2Cl_2$ requires C,56.4;

H,5.7; N,1.5%). M.p. 184-188°C decomp.
N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ 8.16[d,J(PRh)141.6],-144.2[septet, J(PF)713.0] p.p.m.

(iv) [Rh(COD)(Cy_2PCH_2)$_2$NCHMePh]$^+PF_6^-$ (149)

(Cy_2PCH_2)$_2$NCHMePh (0.43g,0.8mmol) was added to a mixture of [Rh(COD)Cl]$_2$ (0.2g,0.4mmol) and KPF_6 (0.2g,0.4mmol) in dichloromethane (30cm^3) and water (20cm^3). The mixture was stirred vigorously at room temperature for 15 minutes under a nitrogen atmosphere. The dichloromethane layer was then removed and washed with water. The volume was reduced to 5cm^3 under a reduced atmosphere and ethanol (5cm^3) was added. Addition of diethyl ether to the solution precipitated a fine orange-brown powder which was filtered and dried in vacuo,(0.58g,81% based on Rh).
(Found: C,54.0;H,7.7;N,1.5 $C_{42}H_{66}NF_6P_3Rh.0.5CH_2Cl_2$ requires C,54.6;H,7.4; N,1.5%). M.p. 180-184°C.
N.m.r.(CD_2Cl_2),$^{31}P-\{^1H\}$(24MHz),δ 9.97[d,J(PRh) 141.6],-144.2[septet,J(PF) 707.5] p.p.m.

(v) [Rh(COD)(Cy_2PCH_2)$_2$NCHMeCO_2Et]$^+PF_6^-$ (150)

A solution of (Cy_2PCH_2)$_2$NCHMeCO_2Et (0.41g,0.8mmol) in dichloromethane (1.5cm^3) was added to a mixture of [Rh(COD)Cl]$_2$ (0.2g,0.4mmol) and KPF_6 (0.2g,1.0mmol) in dichloromethane (30cm^3) and water (20cm^3). The mixture was stirred vigourously at room temperature under a nitrogen atmosphere for 15 minutes. The dichloromethane layer was then removed and washed with water. The volume was then reduced to about 5cm^3 under reduced pressure and ethanol (5cm^3) was added. Addition of diethyl ether to the solution precipitated a fine orange-brown powder. This was filtered and dried in vacuo,(0.614g,87% based on Rh).
(Found; C,49.5;H,7.7;N,1.6. $C_{39}H_{69}F_6NO_2P_3Rh.0.5CH_2Cl_2$ requires C,50.7;

H,7.5;N,1.5%). M.p. 165-166°C.

N.m.r.(CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ 8.93[d,J(PRh)141.6],-144.0[septet,J(PF) 710.0] p.p.m.

3.11.5 Preparation of [PtCl($SnCl_3$)(R_2PCH_2)$_2$NR'] complexes

(i) [PtCl($SnCl_3$)(Ph_2PCH_2)$_2$NCHMePh](153)

Anhydrous stannous chloride (0.08g,0.35mmol) was added to a solution of [$PtCl_2$(Ph_2PCH_2)$_2$NCHMePh] (0.15g,0.18mmol) in dichloromethane (50cm^3). The mixture was stirred for 7h under a nitrogen atmosphere. The solution was then filtered and the solvent removed under reduced pressure. The resulting solid was recrystallised from a dichloromethane-acetone solution by addition of hexane. The white crystalline product was filtered and dried in vacuo,(0.06g, 35% based on Pt).

(Found; C,40.3;H,3.4;N,1.22. $C_{34}H_{35}Cl_4NP_2PtSn.0.5CH_2Cl_2$ requires C,40.3; H,3.4;N,1.36%). M.p. 250-252° decomp.

N.m.r. (CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ -5.84[m,ABX,$^2J(P^AP^B)$19.5,$J(P^APt)$2866.2, $J(P^BPt)$3202.7] p.p.m.

ir,ν(M-Cl) 320,336 cm^{-1},(polythene).

(ii) [PtCl($SnCl_3$)(Ph_2PCH_2)$_2$NCHMeCO$_2$Et)](154)

Anhydrous stannous chloride (0.1g,0.53mmol) was added to a stirred solution of [$PtCl_2$(Ph_2PCH_2)$_2$NCHMeCO$_2$Et)] (0.2g,0.28mmol) in dichloromethane (50cm^3) under a nitrogen atmosphere. After 7h the solution was filtered and the solvent removed under reduced pressure. The resulting solid was insoluble in all common organic solvents and decomposed to give the starting material when dissolved in dimethyl sulphoxide. The pale yellow product was washed with diethyl ether then filtered and dried in vacuo,(0.09g,35% based on Pt).

(Found: C,37.2;H,4.0;N,1.4. $C_{31}H_{33}Cl_4NO_2P_2PtSn.0.5CH_2Cl_2$ requires C,37.5;

H,3.4;N,1.4%). M.p. >320°C.

ir,ν 1730 (C=O) ;(M-Cl),300,323 cm^{-1},(KBr).

(iii) [PtCl($SnCl_3$)(Cy_2PCH_2)$_2$NCHMePh)](155)

Anhydrous stannous chloride (0.1g,0.53mmol) was added to a solution of [$PtCl_2$(Cy_2PCH_2)$_2$NCHMePh)] (0.2g,0.28mmol) in dichloromethane (50cm^3). The mixture was stirred for 7h under a nitrogen atmosphere. The solution was then filtered and the solvent was removed under reduced pressure. The resulting residue was recrystallised from dichloromethane-acetone by addition of hexane to give white crystals which were filtered and then dried in vacuo,(0.07g,27% based on Pt).

(Found; C,38.7;H,5.6;N,1.5. $C_{34}H_{57}Cl_4NP_2PtSn.CH_2Cl_2$ requires C,38.8;H,5.5; N,1.3%). M.p.320-322°C decomp.

N.m.r. (CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ 13.3[m,ABX,J(P^AP^B)14.7.J(P^APt)2917, J(P^BPt)3298] p.p.m.

ir,ν(M-Cl) 278,305 cm^{-1},(polythene).

(iv) [PtCl($SnCl_3$)(Cy_2PCH_2)$_2$NCHMeCO$_2$Et)](156)

Anhydrous stannous chloride (0.08g,0.35mmol) was added to a stirred solution of [$PtCl_2$(Cy_2PCH_2)$_2$NCHMeCO$_2$Et)] (0.15g,0.16mmol) in dichloromethane (50cm^3) under a nitrogen atmosphere. After 7h the solution was filtered and the solvent was removed under reduced pressure. The resulting solid was recrystallised from dichoromethane-acetone by addition of hexane. The orange product was filtered and dried in vacuo,(0.05g,32% based on Pt).

(Found;C,35.9;H,5.7;N,1.5.$C_{31}H_{57}Cl_4NO_2P_2PtSn.0.5CH_2Cl_2$ requires C,36.5; H,5.6;N,1.4%). M.p. Slowly turns black 220-280°C, decomp.

N.m.r.(CD_2Cl_2) $^{31}P-\{^1H\}$(24MHz),δ 14.7 [d,J(PPt)3480.7] p.p.m.

ir,ν_{max}1715(C=O);ν(M-Cl) 295(sh),335 cm^{-1},(KBr).

3.11.6 Reaction of $(Cy_2PCH_2)_2NCHMePh$ with $[IrCl(CO)_2\ p\text{-}(NH_2C_6H_4Me)]$.

$(Cy_2PCH_2)_2NCHMePh$ (0.27g,0.5mmol) was added to a stirred solution of $[IrCl(CO)_2\ p\text{-}(NH_2C_6H_4Me)]$ (0.2g,0.5mmol) in tetrahydrofuran ($100cm^3$). The mixture was then refluxed under an atmosphere of nitrogen for 12h. The solvent was removed under reduced pressure and the resultant residue recrystallised from chloroform and diethyl ether to yield deep red crystals of (157),(0.09g,27% based on Ir).

(Found: C,55.9;H,7.4;H,1.9. $C_{68}H_{114}ClIrN_2P_4.1.5CHCl_3$ requires C,55.9; H,7.8; N,1.9%). M.p. 268-270°C

N.m.r. ($CDCl_3$) $^{31}P\text{-}\{^1H\}$(24MHz),δ 16.73 p.p.m.

^1H (90MHz),δ 0.7-2.3[m,94H,8Cy+2Me],2.4-2.9[m,8H,PCH_2],3.7 [m,2H,CH], 7.1-7.3[m,10H,Ph] p.p.m.

ir, No absorptions in the region 1700-2000cm^{-1},(Nujol)

3.11.7 Reaction of $(Cy_2PCH_2)_2NCHMePh$ with $[Pt(trans\text{-}stilbene)(PPh_3)_2]$.

$(Cy_2PCH_2)_2NCHMePh$ (0.26g,0.48mmol) was added to a solution of $[Pt(trans\text{-}stilbene)(PPh_3)_2]$ (0.2g,0.22mmol) in tetrahydrofuran ($50cm^3$). The mixture was stirred for 2h at room temperature under an atmosphere of nitrogen. The ^{31}P n.m.r. spectrum of the mixture showed a variety of compounds but no starting material. The solvent was then removed under reduced pressure and the resulting residue was washed in diethyl ether for 48h. The pale brown precipiate,(158) that formed was then filtered and dried in vacuo.

(Found; C,46.9;H,6.2;N,1.7%). M.p. 210-216°C decomp.

N.m.r.(CD_2Cl_2) $^{31}P\text{-}\{^1H\}$(24MHz),δ 17.35 [d,J(PPt)3251.0] p.p.m.

^1H(90MHz),δ 1.0-3.1[m,51H,Cy,Me,PCH_2],3.9[m,1H,NCH],7.1-7.8[m,15H,Ph] p.p.m.

3.11.8 Reaction of $(Cy_2PCH_2)_2NCHMePh$(101) with $[PtCl_2(PPh_3)_2]$.

$(Cy_2PCH_2)_2NCHMePh$ (0.07g,0.13mmol) was added to a stirred solution of

$[PtCl_2(PPh_3)]$ (0.1g,0.13mmol) in dichloromethane ($10cm^3$) under a nitrogen atmosphere. After 1h a ^{31}P n.m.r. spectrum showed free PPh_3 and free $(Cy_2PCH_2)_2NCHMePh$,(-5.04 and -18.3 p.p.m. respectively), but no phosphorus-platinum compounds could be identified or isolated.

3.11.9 Reaction of $(Cy_2PCH_2)_2NCHMePh$(101) with $[Pd_2(DBA)_3].CHCl_3$.

$(Cy_2PCH_2)_2NCHMePh$ (0.25g,46mmol) was added to a stirred solution of $[Pd_2(DBA)_3].CHCl_3$ (2.4g,23mmol) in toluene ($50cm^3$). The mixture was then refluxed under nitrogen for 3h and allowed to cool. The solvent was removed under reduced pressure. The ^{31}P n.m.r. spectrum of the resulting residue showed a multitude of peaks and no phosphorus containing solids could be isolated.

3.11.10 Reaction of $[PtCl_2((Cy_2PCH_2)_2NCHMePh)]$(113) with Ag_2O and diethyl 1,3-acetonedicarboxylate.

(1) Diethyl 1,3-acetonedicarboxylate (0.05g,0.25mmol) was added to a solution of $[PtCl_2((Cy_2PCH_2)_2NCHMePh)]$ (0.1g,0.12mmol) in dichloromethane ($30cm^3$) with Ag_2O (0.12g,0.52mmol). The mixture was brought to reflux for 4h under a nitrogen atmosphere. The ^{31}P n.m.r. spectrum of the mixture showed a variety of peaks none of which corresponded to the starting material or exibited platinum coupling. No phosphorus containing solids could be isolated from the mixture.

(2) A similar reaction was carried out using $[PtCl_2((Ph_2PCH_2)_2NCHMePh)]$(110) with identical results.

3.11.11 Reaction of $[PtCl_2((Ph_2PCH_2)_2NCHMePh)]$(110) with Hydrazine Hydrate and trans-stilbene.

(1) Hyrazine hydrate (0.1g,1.7mmol) was added to a stirred solution of $[PtCl_2((Cy_2PCH_2)_2NCHMePh)]$ (0.1g,0.12mmol) in ethanol ($20cm^3$). After 10 minutes the solution was filtered and trans-stilbene (0.06g,0.33mmol) was

added. The solution was then heated to 60°C for 1h and allowed to cool. The ^{31}P n.m.r. spectrum of the solution showed only unreacted starting material.

(2) Similar reactions were attempted in the presence of diphenylacetylene or $(Cy_2PCH_2)_2NCHMePh$(101) with identical results to (1).

3.11.12 Reaction of $[PtCl_2((Cy_2PCH_2)_2NCHMePh)]$(113) with $NaBH_4$ and trans-stilbene.

$NaBH_4$ (0.05g,1.3mmol) was added to a stirred solution of $[PtCl_2((Cy_2PCH_2)_2NCHMePh$ (0.1g,0.12mmol) in ethanol (20cm^3). After 10 minutes the solution was filtered and trans-stilbene (0.06g,0.33mmol) was added. The mixture was heated to 60°C for 1h and turned dark brown in colour. The ^{31}P n.m.r. spectrum of the solution showed a multitude of unidentifiable peaks. Attempts to isolate any solid resulted in a insoluble black precipitate.

CHAPTER 4

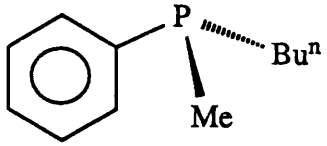
Catalytic Hydrogenation and Hydroformylation using Chiral Aminomethylphosphine Complexes of Rh(I) and Pt(II)

4.1 Introduction

4.1.1 Asymmetric hydrogenation with Rh(I) complexes

Selective homogeneous hydrogenation with organometallic catalysts has been shown to be an important part of organic synthesis. The area of research and development in this field has been vast and reviews have appeared covering applications[163] and important developments.[164] The extension of homogeneous organometallic catalysts to asymmetric synthesis has proved to be of great importance. The biological activity of many pharmaceuticals relies on absolute configuration and hence one enantiomer; e.g. (S)-Dopa in the treatment of Parkinsons disease.[165] Thus the ability of a catalyst with chiral ligands to produce optically pure compounds (often referred to as asymmetric induction) from asymmetric hydrogenation is highly desirable. There have been a number of reviews covering key developments in this area[165-167] and also texts covering stereochemistry, selectivity and mechanisms are available.[168] Developments led from the discovery by Wilkinson[169] of chlorotris (triphenylphosphine)rhodium, $[RhCl(PPh_3)_3]$ *(159)* which was found to be a highly efficient homogeneous hydrogenation catalyst. Further modifications of this catalyst by Schrock and Osborn[137,170,171] produced improved reactivity by using cationic complexes of the type $[Rh(diene)P_2]^+X^-$, P_2 = 2 monodentate or 1 bidentate phosphine; X = ClO_4, BF_4 or PF_6.

The first attempts to obtain asymmetric induction in hydrogenation using chiral monodentate phosphines gave only very modest results.[172] The first major development was by Kagan and Dang who showed that much higher asymmetric induction was possible using the chiral chelating phosphine DIOP *(163)*.[173,174] A variety of other chiral bisphosphines have since been applied to this system and very high (~99%) enantiomeric excesses in hydrogenation have been reported, Figure 1 and Table 1.[172,174-180,185]



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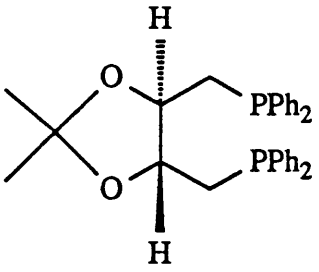

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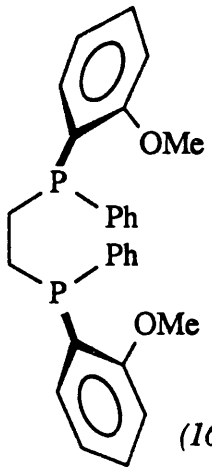
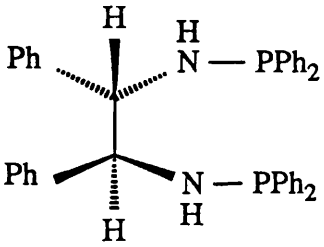
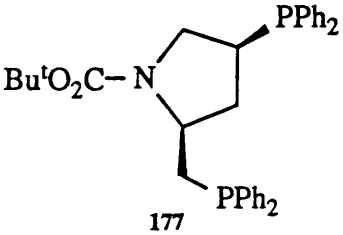


(164)[175,185]



(165)[176]



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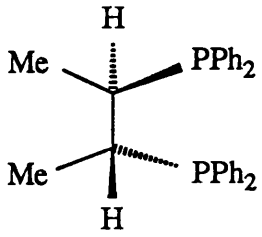
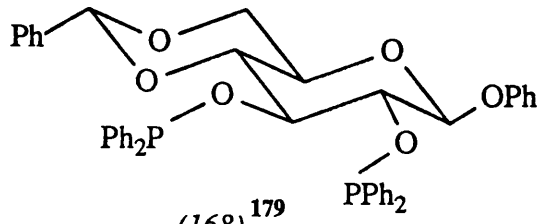
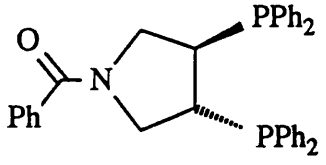


(167)[178]

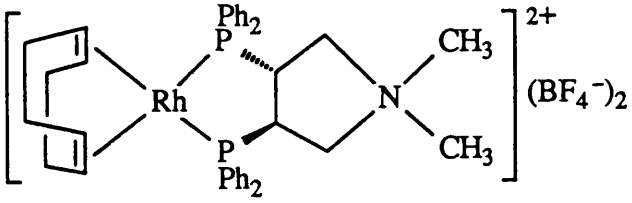


(168)[179]



(169)[180]

Figure 1
Chiral bisphosphines used in asymmetric hydrogenation with Rh(I) catalysts



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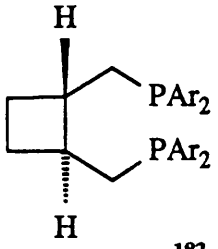

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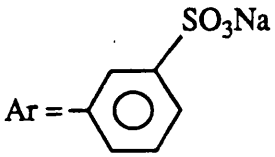


Figure 2

Table 1
Results of asymmetric hydrogenation of Z-α-acetamidocinnamic acid

Phosphine	Chemical yield	Enantiomeric excess
(162)	—	15%
(163)	66%	72%
(164)	—	93-94%
(165)	90-100%	92-95%
(166)	90-100%	87%
(167) (a)	>90%	74-89%
(168)	99%	99%
(169)	99%	99%

(a) 99-100% ee obtained for hydrogenation of other substrates

Some of these compounds have also been extended to polymer supported[181] and water soluble catalysts[182,183] which overcome the problem of catalyst recovery, Figure 2.

The effectiveness of these catalysts in asymmetric hydrogenation probably relies on a chiral array of the phenyl groups bonded to phosphorus[168,178] which provide half of a 'lock and key' system for the prochiral substrate. This chiral array is maintained by the chiral puckered conformation of the phosphine chelate. In an example where phosphorus phenyl substituents were replaced with ethyl groups a sharp decrease in asymmetric induction was observed.[176] Because of the 'lock and key' system, created by the chiral phosphine-metal and a prochiral substrate, only a limited range of substrates can be hydrogenated with high enantioselectivity. Two examples of this are (i) that only Z-enamides and acrylic acids can be hydrogenated with high selectivity,[175] compared to their E isomers; (ii) that polar groups on the double bond are necessary

for the 'lock and key' coordination to work successfully.[167,168]

Only two examples of chiral aminomethylphosphines in asymmetric hydrogenation have been reported[10,38] using phosphines of the type $(Ph_2PCH_2)_2NCH(Me)CO_2R$, R = H, Na, Me. Only modest results have been obtained for the hydrogenation of (Z) α-acetamidocinnamic acid, i.e. 30-35% enantiomer excess. The phosphine chelates used were thought to have an achiral chair conformation so asymmetric induction was low. Other work has compared chiral chelating six-membered ring diphosphines that have either chair (chair-phos) or skew (skew-phos) conformations.[185] In the hydrogenation of (Z) α-acetamidocinnamic acid, skew-phos gave 90% enantiomeric excess while chair-phos gave only a 20% enantiomeric excess. In the present work chiral phosphines of the type $(R_2PCH_2)_2NR^*$ have been investigated in the hydrogenation of (Z) α-acetamidocinnamic acid.

4.1.2 Asymmetric hydroformylation with platinum-tin-phosphine complexes

The insertion of $SnCl_2$ into a platinum-chlorine bond to form Pt-$SnCl_3$ moieties has been known for some time.[186,187] However, the potential of these compounds as catalysts was not immediately realised. Early work showed that tertiary phosphine[188] and arsine[189] complexes of $PtCl_2$ could be used as effective hydroformylation catalysts. The first reported use of a platinum-tin catalyst in hydroformylation was by Schwager and Knifton.[139] Using $[PtCl_2(PPh_3)_2]$ *(170)* + $SnCl_2$, in a ratio of 1:5, under 70 atmospheres of CO/H_2 at 65°C, 1-heptene was converted to 1-octanal in a 90% yield, Scheme 1.

Scheme 1

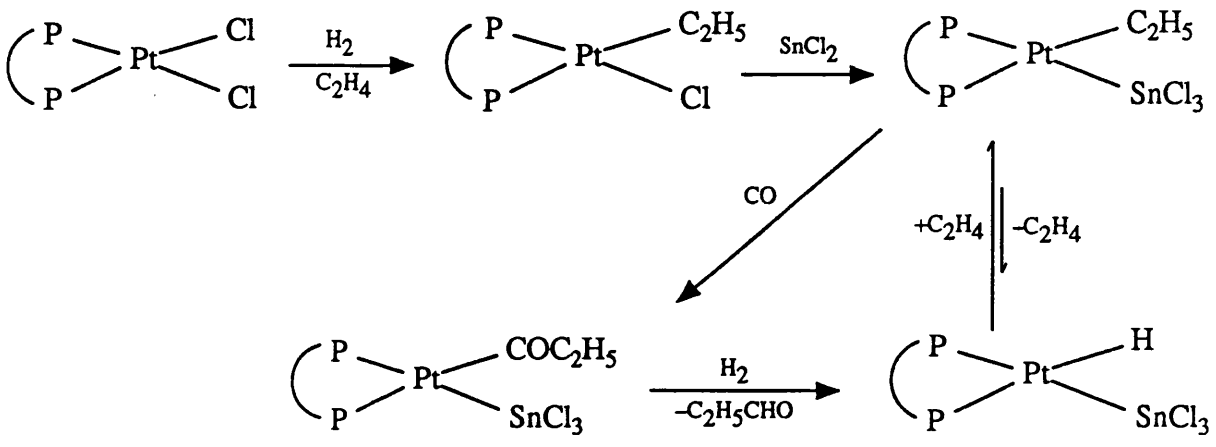
$$C_5H_{11}CH{=}CH_2 \xrightarrow[CO/H_2\ 70\ atm,\ 66^\circ C]{(170)\ +\ SnCl_2} \underset{\substack{90\% \\ linear}}{C_7H_{15}CHO} + \underset{\substack{10\% \\ branched}}{C_5H_{11}CH(CHO)CH_3}$$

Further work using tertiary phosphines, phosphites or arsines as ligands

followed and good selectivity for linear products was observed,[190,191] Scheme 1. Work by Hsu and Orchin[192] has also shown that the complex $[PtH(SnCl_3)(CO)(PPh_3)_2]$ *(171)* to be a highly efficient hydroformylation catalyst. Reaction rates five times that produced by $[Co_2(CO)_8]$ *(172)* and a 95% selectivity for linear aldehydes was reported.

A detailed investigation into the optimisation of hydroformylation results has shown that bidentate phosphines forming seven-membered chelate rings give the highest reactivity.[193,194] With phosphines such as DIOP and dppb up to 99% yield of linear aldehyde products were obtained. The reactivity and mechanisms of these systems have been studied extensively[195] but the mechanisms particularly regarding the role of the $SnCl_3^-$ ligand do not appear to be fully understood. In depth investigations into the behaviour of the $SnCl_3^-$ ligand in $[PtCl_2(CO)(PPh_3)] + SnCl_2$ systems, using spectroscopic, solvent and catalytic studies have been reported.[196-198] Complexes such as *(171)* and of the type $[PtCl(COR)(PPh_3)_2]$ have been isolated from catalytic hydroformylation mixtures.[199] These compounds are thought to be important catalytic intermediates.[200,201] The study of these complexes and related compounds of the type $[Pt(SnCl_3)R(P_2)]$ and $[PtH(SnCl_3)(P_2)]$, P = PPh_3 or P_2 = chelating phosphine, have led to mechanisms being proposed for monodentate[202] and bidentate[203] phosphine ligands, Scheme 2.[203]

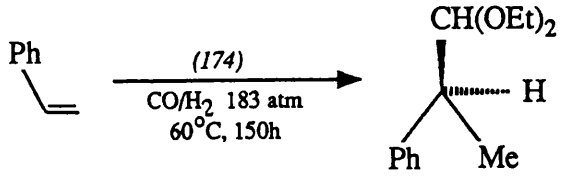
Scheme 2[203]



Although very little work has been published on the application of these catalysts to asymmetric synthesis,[167,204] some good results have been achieved. Early work[205] showed that the deuterioformylation of (Z) or (E)-2-butene, catalysed by [PtCl($SnCl_3$)DIOP] *(172)*, gave predominantly erythro- or threo- 1,3(D_2)-2-butanal, in 66 and 84% enantiomeric excess respectively. Other work reported that the hydroformylation of styrene with [(-)DBP-DIOP-$PtCl_2$] *(173)* + $SnCl_2$ gave a 94% enantiomeric excess of (S)-2-phenyl propanal.[206] The same workers later found that their optical rotation measurements were in error and an 80% enantiomeric excess was reported.[207] In the second case[207] the optical yields were determined by integration of the ^1H n.m.r. spectra, using chiral shift reagents to separate the (R) and (S) enantiomers. This method has proven to be far more reliable than optical rotation measurements for enantiomeric excess determination.

The best results in asymmetric hydroformylation to date have come from Stille.[208] The hydroformylation of styrene with [PtCl($SnCl_3$)BPPM] *(174)* in the presence of triethylorthoformate gave the corresponding chiral acetal in greater than 96% enantiomer excess and quantitative yield, Scheme 3.

Scheme 3



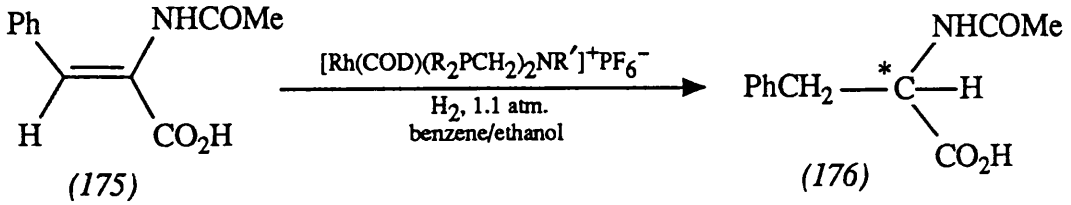
Hydrolysis of the acetal was reported to give (S)-2-phenyl propanal without loss of configuration. However, much longer catalytic reaction times were required, 150h compared to 6h, without triethylorthoformate. Other work by Stille[209,210] has investigated the use of these catalysts on polymer supports but only a 65% enantiomeric excess for hydroformylation has so far been reported.

There have been no previous reports of the application of aminomethylphosphines in catalytic hydroformylation or asymmetric hydroformylation. However, the use of optically active amines as building blocks for chiral phosphine ligands has been of interest.[211] In the present work, the hydroformylation of styrene is investigated using complexes of the type $[PtCl(SnCl_3)(R_2PCH_2)_2NR^*]$ that have previously been discussed in Chapter 3. The chirality of the products were also studied as the presence of a chiral group R^* on the phosphine may give asymmetric induction.

4.2 Catalytic hydrogenation of α-acetamidocinnamic acid using catalyst precursors of the type $[Rh(COD)(R_2PCH_2)_2NR']^+PF_6^-$

The hydrogenation of α-acetamidocinnamic acid *(175)* has become the 'classic' test for asymmetric induction in homogeneous catalysis using rhodium(I)-chiral phosphine catalysts. Hydrogenation reactions were carried out under standard conditions for all reactions, using the preformed catalyst precursors *(146)-(150)* reported in Chapter 3. The details of the reaction method are given in the Experimental Section 4.6. The reaction is outlined in Scheme 4 and the substrate and conditions were selected to give direct comparison with previous works.[10,37,168]

Scheme 4



(175) *(176)*

The reaction times, overall and optical yields, or enantiomer excess (e.e), are given in Table 2. Results for the catalytic hydrogenation of α-acetamidocinnamic acid *(175)* using $[Rh(NBD)Cl]_2$ *(177)* + 4 PPh_3, to give racemic products is given as a general comparison. The reaction times were

Table 2

Catalytic hydrogenation of α-acetamidocinnamic acid *(175)*

Catalyst precursor	Reaction time (h)	Chemical yield (%)	Optical yield (%)
(146)	6.15	79	0
(147)	5.15	72	1.0
(148)	5.00	85	2.0
(149)	6.00	71	1.9
(150)	6.00	80.5	2.4
$[Rh(NBD)Cl]_2 + 4\ PPh_3$	5.00	95%	–

Solvent: Benzene/Ethanol (1:1), Rh : substrate ratio 1:220
Optical yield ≡ enantiomeric excess [defined by R + S/|R - S| x 100]

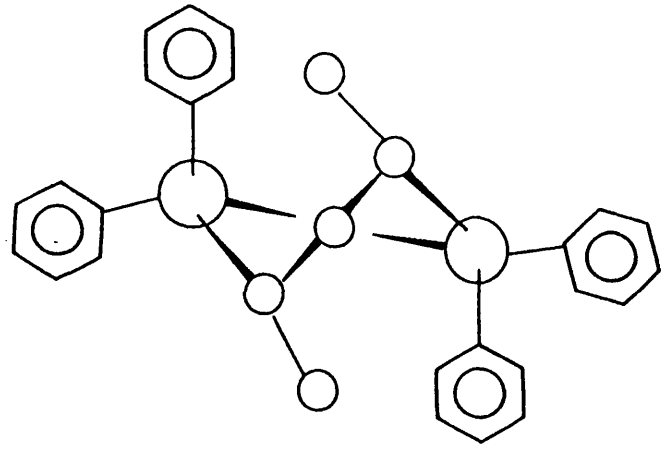
reasonably consistent at 5 to 6 hours and were comparable to previous studies.[37] The uptake of hydrogen was usually rapid at the beginning of a reaction but after 10/15 minutes settled down to a steady rate, until the reaction was complete. The solvent ratio of benzene to ethanol of 1:1 has been reported to give optimum rates of reaction[37] and used in all experiments. The yields in all the hydrogenations were observed to be quantitative by ^1H n.m.r. spectra of the crude reaction mixtures. The presence of multiplets at δ 4.75 p.p.m. (CH) and δ 3.1 p.p.m. ($-CH_2$) are indicative of N-acetylphenyl alanine *(176)* and integrated to exactly 1H and 2H respectively in relation to other signals. Also observed was the change of the phenyl region signals from overlapping multiplets at δ 7.2-7.7 p.p.m. to a clearly defined single peak at δ 7.2 p.p.m. The enantiomeric excess of the products was measured by optical rotation against pure N-acetyl L-phenyl alanine, $[\alpha]_D^{22}$ + 47.4° (EtOH) and were calculated from the following equations.[168,213]

$$\frac{[\alpha]_D \text{ observed}}{[\alpha]_D \text{ pure}} \times 100 = \text{enantiomeric excess, \%}$$

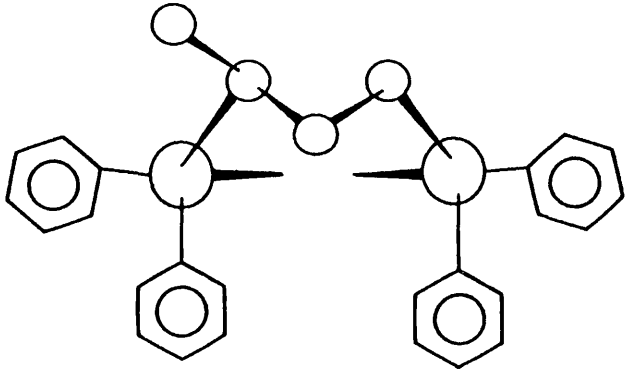
$$[\alpha]_D^t = \frac{\alpha}{lc}$$

α = observed rotation at temperature t°C
l = length of polarimeter cell
c = concentration in g/cm^3

Optical yields reported for previous studies of structurally similar rhodium-aminomethyl phosphine catalysts[10,37] (27-35% e.e) could not be repeated. From Table 2 it can be seen that the products from all the hydrogenations were essentially racemic with all results being similar. It is clear that change in chiral substituents at nitrogen had no effect on reaction times, yields or optical yields. It was also observed that the presence of bulky cyclohexyl groups on the phosphine ligands also had no noticeable effect on the reaction. The lack of asymmetric induction observed using these types of chiral ligand can be explained by their conformation in six-membered metal chelates. The bulky chiral substituents at nitrogen will prefer to adopt an equatorial position, in a chair conformation, to avoid 1,3 diaxial interactions with the phosphorus substituents. This conformation would give an achiral array of the phenyl or cyclohexyl substituents on phosphorus which would not act as a specific 'lock' in the binding of a prochiral substrate to the metal centre. The analogy of these ligands to chair-phos *(178)* gives a good explanation of the conformational requirements of six-membered ring chelating phosphine ligands in asymmetric synthesis.[185] The chair and skew conformations of metal coordinated chair-phos *(178)* and skewphos *(179)* are shown in Figure 3.[185] The asymmetric skew conformation of *(179)* gives good optical yields in the hydrogenation of *(175)*, but the achiral chair conformation of *(178)* gives only low asymmetric induction as seen with chelating chiral aminomethylphosphines.



Skewphos *(179)*



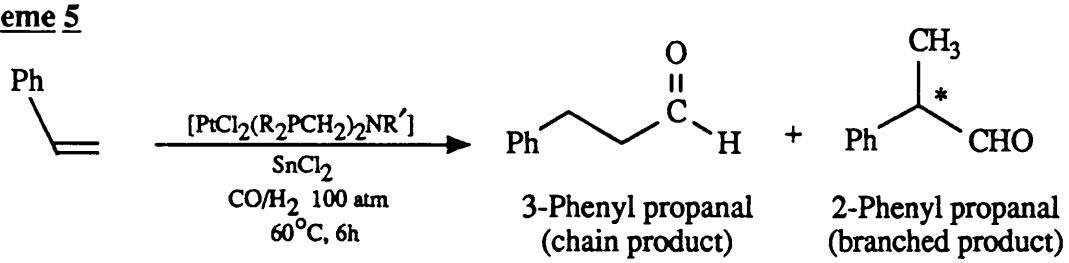
Chairphos *(178)*

Figure 3 Preferred conformations of skewphos and chairphos[185]

4.3 Asymmetric Catalytic Hydroformylation of Styrene using the Catalyst System $[PtCl_2(R_2PCH_2)_2NR']$ + $SnCl_2$

Hydroformylation experiments were carried out under standard conditions for all the catalyst precursors, enabling the merits of each catalyst to be directly compared. The substrate styrene was selected as it has been a well-studied prochiral substrate in asymmetric catalytic hydroformylation with platinum-tin catalysts.[206,207,210] Previous studies[206,207,210] of this system have employed synthesis gas pressures of up to 180 atm. The results given in present work were limited to the autoclave's maximum working pressure of 100 atm but as reaction rate is proportional to the overall pressure in these reactions[194] the results are relative. Initial studies showed that the % conversion and optical yields were identical for either preformed or *in situ* prepared catalysts. The catalysts that were used were prepared *in situ* by dissolving the relevant platinum complexes *(110)-(115)* in benzene and stirring with a three-fold excess of $SnCl_2$ for 20 minutes prior to adding the solution to the autoclave. The catalytic hydroformylation of styrene is outlined in Scheme 5.

Scheme 5



A summary of the results for the catalytic hydroformylation of styrene is given in Table 3 with a resumé of the reaction conditions.

Reactions involving cyclohexyl substituted phosphines and/or ethyl ester substituted phosphines *(111)*, *(113)*, *(114)* showed no reaction. Involvement of the ethyl ester group in the course of the reaction is unknown. Previous work[203] with chelating cyclohexyl phosphines in similar hydroformylation catalysis have shown poor reactivity which has been

Table 3
Catalytic hydroformylation of styrene

Catalyst precursor + $SnCl_2$	Chemical yield (%)	Product isomer ratio branch/chain	Optical yield (%)
(110)	9	36 : 1	31
(111)	No reaction	—	—
(112)	15	7 : 1	23
(113)	No reaction	—	—
(114)	No reaction	—	—
(115)	47	1 : 2.2	0

Solvent: Benzene, Reaction time: 6h, Temperature: 60°C, Pressure $CO:H_2$; 100 atm (1470 p.s.i.), Pt:Sn ratio 1:3, Pt:substrate ratio, 1:5000 approx.

attributed to electronic effects. However, the steric bulk of the cyclohexyl groups may also play a part in limiting the catalyst's activity particularly in intermediates involved in the rate limiting step. The catalyst system *(110)* + $SnCl_2$ shows a large preference for the chiral branched product and gives the best results for asymmetric induction (31% e.e). The catalyst system *(112)* + $SnCl_2$ gives a slightly higher yield than *(110)* but a lower branch to chain product ratio and a lower optical yield (23% e.e). The catalyst *(115)* + $SnCl_2$ shows remarkably high yields, in comparison to *(110)* and *(112)*, and the branch to chain product ratio is significantly different, being slightly in preference to the non-chiral chain product. Most of the previous reports[207,210] of asymmetric hydroformylation of styrene using platinum-tin catalysts have shown typical branch to linear chain product ratios of around 1:3 and 1:4. This shows a very good selectivity for the chiral branched product by the *(110)* + $SnCl_2$ system. These patterns for reactivity may be linked to the rate limiting step in hydroformylation which is generally thought[194,203,212] to be the

oxidative addition of hydrogen to a platinum acyl intermediate which, in this case, would give the intermediates A and B, Figure 4.

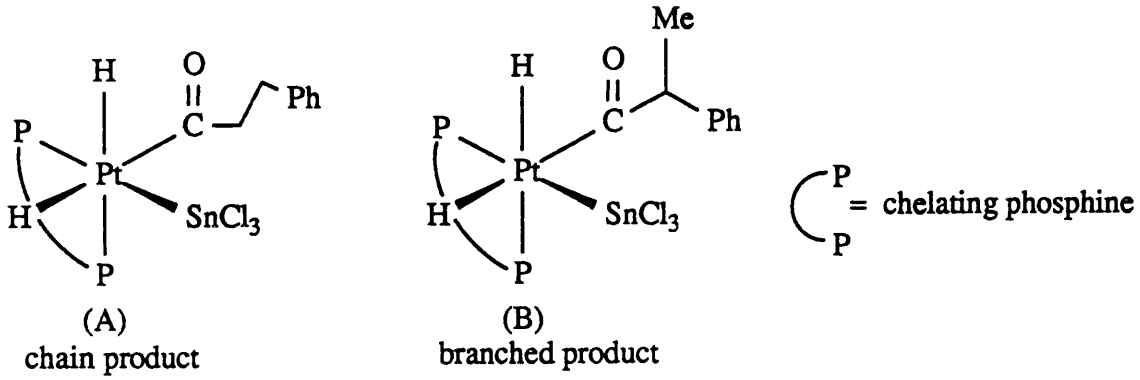


Figure 4

The intermediate (A) is less sterically hindered than (B) and it would be reasonable to expect bulky phosphines to favour chain products in hydroformylation. The results for *(115)* are almost certainly attributable to the nature of the C_8H_{14} moiety on phosphorus. These groups have a highly limited flexibility and would not be expected to form a chiral 'lock' and the lack of asymmetric induction in hydroformylation is predictable. The same rigidity of these ligands' substituents may have some steric effects which favour the chain products and show a higher reaction rate than the equivalent phenyl substituted catalyst *(110)* + $SnCl_2$.

The hydroformylation of styrene using *(110)* + $SnCl_2$ in the presence of triethylorthoformate by the reported method of Stille[208] showed no reaction after 150h at 100 atm.

4.4 Determination of optical yields of hydroformylation reactions by ^1H n.m.r. spectroscopy

As mentioned in Section 4.1 the determination of optical yields from the hydroformylation of styrene by ^1H n.m.r. spectroscopy and chiral shift reagents[207] has proven to be a far more reliable method than by optical rotation measurements. The formyl proton of the chiral product 2-phenyl

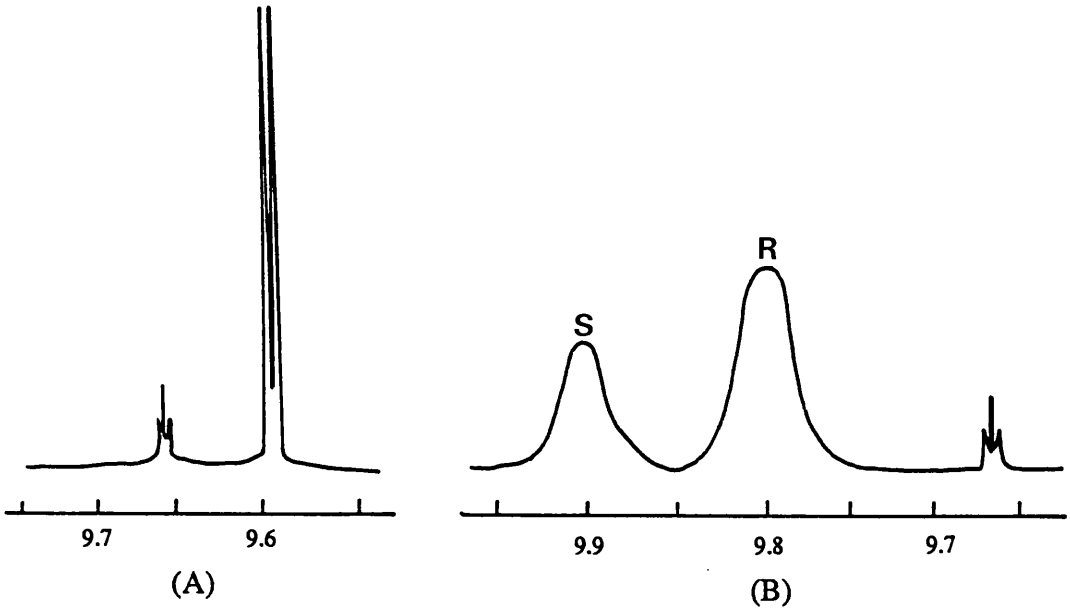


Figure 5 The ^1H n.m.r. spectrum of the products in the formyl region from the hydroformylation of styrene in the presence of *(110)* + $SnCl_2$.

(A) The distilled reaction mixture, showing a doublet for 2-phenyl propanal and a triplet for 3-phenyl propanal.

(B) The same mixture in the presence of $[Eu(hfc)_3]$, showing the formyl doublet of 2-phenyl propanal split into R and S components.

The formyl proton for 3-phenyl propanal remains unchanged.

propanal appears as a doublet at δ 9.6 p.p.m., coupled to the proton attached to the chiral carbon. The methyl signal appears as a doublet at δ 1.35 p.p.m., also coupled to the proton of the chiral carbon. Addition of the chiral shift reagent tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorato], europium(III) [$Eu(hfc)_3$] to the sample splits these two signals into their enantiomeric components, Figure 5. From integration of the signals the yields of R and S components can be easily determined and hence the enantiomeric excess can be calculated from

$$\frac{|R-S|}{R+S} \times 100 = \text{enantiomeric excess \%}$$

R and S are the amount of R and S isomers present in the mixture.

4.5 Conclusion

Hydrogenation of α-acetamidocinnamic acid *(175)* with chiral aminomethylphosphine complexes of rhodium showed no asymmetric induction in disagreement to previous reports. Reaction rates and yields obtained from these catalysts show no advantage over existing complexes. The hydroformylation of styrene using chiral aminomethylphosphine complexes of platinum in the presence of $SnCl_2$ has shown asymmetric induction with up to 31% enantiomeric excess of 2-phenylpropanal being observed. The ability of chiral aminomethylphosphines, with the chiral centre on nitrogen, to give asymmetric induction in hydroformylation but not in hydrogenation is not understood. This may depend on many factors, not the least of which would be the chelating phosphine's preferred conformation in the catalytic intermediates which is unknown. The high reactivity observed for the 1-5 cyclooctyl substituted phosphine catalyst is not fully understood and is worthy of further investigation.

4.6 Experimental

General experimental and spectroscopic techniques were as described in Chapters 2 and 3. Hydrogenations were carried out in a Schlenk flask fitted with a septum cap, connected to a standard hydrogenation apparatus. This consisted of a burette and bulb for monitoring gas uptake, a barometer, hydrogen gas inlet and vacuum pump outlet. Hydroformylations were carried out in a 100 cm^3, glass-lined Roth autoclave, fitted with a thermostatted heating jacket and pressure head connected to a cylinder of synthesis gas ($CO:H_2$, 1:1). Optical rotations were measured with a Perkin-Elmer 141 polarimeter at a concentration of $5 \times 10^{-3} g/cm^3$ in 95% ethanol. The compounds triethylorthoformate and styrene were obtained from commercial sources and distilled prior to use. The solvents ethanol and benzene were dried and distilled from sodium under a nitrogen atmosphere prior to use.

(Z) α-Acetamidocinnamic acid and $Eu(hfc)_3$ were used as supplied from Aldrich. The catalyst precursors *(110)-(115)* and *(146)-(150)* were used as prepared in Chapter 3. Dihydrogen and synthesis gas ($CO:H_2$, 1:1) were used as supplied from commercial sources (BOC).

[1] Hydrogenation of α-acetamidocinnamic acid using $[Rh(COD)(R_2PCH_2)_2NR']^+ PF_6^-$ catalyst precursors

Hydrogenation reactions were carried out by identical methods for the catalyst precursors *(146)-(150)*, the general procedure being as follows. The catalyst precursor *(146)-(150)* (0.01g) was dissolved in a benzene-ethanol solution (1:1, 10 cm^3) and placed in a Schlenk flask fitted with a septum cap, under a nitrogen atmosphere. The substrate α-acetamidocinnamic acid (0.5g, 2.4 mmol) was also dissolved in a benzene-ethanol solution (1:1, 40 cm^3) under a nitrogen atmosphere. The Schlenk flask containing the catalyst solution was then connected to the hydrogenation apparatus and

evacuated and purged with hydrogen and the process repeated. After allowing the catalyst solution to stir under an atmosphere of hydrogen for 20 mins the substrate solution was added *via* a syringe through the septum cap. The bulb of the hydrogenation apparatus was then adjusted to bring the internal pressure to 1.1 atm. This pressure was kept constant throughout the reaction time. The reaction was stopped when no further uptake of hydrogen was monitored on the burette by evacuating the gas from the system. The reaction mixture was reduced to a residue under reduced pressure and the crude products were analysed by ^1H n.m.r. in solution of deuterochloroform. The residue was then dissolved in hot acetone and filtered through celite. The product, N-acetyl phenylalanine was crystallised out at -30° in a freezer. The product was then filtered and washed with cold dichloromethane to remove any remaining traces of catalyst. Optical rotation measurements were carried out on the products in ethanol solution using a pure sample of N-acetyl (L) phenyl alanine $[\alpha]_D^{22}$ + 47.4° (EtOH) as the reference.

[2] Hydroformylation of Styrene using the catalyst system $[PtCl_2(R_2PCH_2)_2NR']$ + $SnCl_2$

Hydroformylations were carried out by a standard procedure for the catalyst precursors *(110)-(115)*, using a standard time, temperature and pressure for all reactions (6h, 60°C, 100 atm). The general procedure was as follows. The catalyst precursor *(110)-(115)* (0.02g, 0.25 mmol) and anhydrous stannous chloride (0.02g, 0.1 mmol) was dissolved in benzene (5 cm^3). The autoclave was purged with nitrogen and the catalyst solution and styrene (10 cm^3, 86.6 mmol) were then added. The autoclave was then flushed twice with synthesis gas (50 atm) and the pressure released. The vessel was then filled with synthesis gas (100 atm) and brought to a constant 60°C for 6h. After allowing to cool the pressure was slowly

released and the reaction mixture was distilled to separate from the catalyst. The percentage conversion and the ratio of branch and chain products was determined by integration using ^1H n.m.r.

[3] Hydroformylation of Styrene in the presence of triethylorthoformate using the catalyst system $[PtCl_2(Ph_2PCH_2)_2NCHMePh] + SnCl_2$

The method used was identical to that described in [2] except triethylorthoformate (20 cm^3) was added and the reaction conditions were 150h, 60°C, 100 atm. The ^1H n.m.r. spectrum of the mixture after distillation showed only styrene and triethylorthoformate and no reaction products.

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