THE SYNTHESIS OF AMINOALKYLPHOSPHINES AND THEIR METAL COMPLEXES

Thesis submitted for the Degree of

Doctor of Philosophy

by

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To Mum and Dad

TITLE: **THE SYNTHESIS OF AMINOALKYLPHOSPHINES AND THEIR METAL COMPLEXES**

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ABSTRACT

Chapter 1 reviews the literature concerning the synthesis and reactivity of late transition metal amide complexes, particular mention being given to their synthesis *via* functionalised phosphine ligands. The preparation and characterisation of the new bidentate ligands $Ph_2PCH_2CH_2NHR$ [R = ^tBu, CH_2Ph, CH(Me)Ph] and $Ph_2PCH_2CH_2N(CH_2Ph)_2$ and their corresponding hydrochloride salts are reported in Chapter 2. Chapter 3 discusses the synthesis of some platinum and palladium complexes of the ligands $Ph_2PCH_2NH^tBu$ (R = ^tBu, p-tol) and Ph_2PCH_2OH. The structure of *cis*-$[Pt(Ph_2PCH_2OH)_2Cl_2]$ was confirmed by X-ray diffraction. The reactivity of some of these complexes towards the formation of bimetallic complexes and deprotonations is discussed. The reactions of ligands $Ph_2PCH_2CH_2NHR$ and their hydrochloride salts, forming a variety of both platinum and palladium complexes, are reported in Chapter 4. The structures of both *cis*-$[Pt(Ph_2PCH_2CH_2NH^tBu)(Ph_2PCH_2CH_2NH^tBu)Cl]Cl$ and $[Pd(Ph_2PCH_2CH_2NH^tBu)Cl_2]$ were determined by X-ray diffraction. Attempts to deprotonate some of the platinum complexes to form platinum amide complexes are also discussed. Chapter 5 describes the syntheses of several new iron(II) and ruthenium(II) complexes of the ligands $Ph_2PCH_2CH_2NHR$, their chirality and the reactivity of these complexes towards deprotonation.

STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy entitled "The Synthesis of Aminoalkylphosphines and their Metal Complexes" is based on work in Department of Chemistry of the University of Leicester between the period October 1986 and November 1989.

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

Signed: Julie Neild Date: 26/11/91

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ABBREVIATIONS AND SYMBOLS

General and Physical:

Å	-	Angström unit
br	-	Broad
°C	-	Centigrade
cm^{-1}	-	Wavenumber
cm^3	-	Cubic centimetres
d	-	Doublet
δ	-	Chemical shift
(°)	-	Degrees
g	-	Gramme
h	-	Hour
Hz	-	Hertz
Ir	-	Infrared
K	-	Kelvin
m	-	Multiplet
MHz	-	Megahertz
min	-	Minute
mmol	-	Millimole
mp	-	Melting point
n.m.r.	-	Nuclear magnetic resonance
p.p.m.	-	Parts per million
$\{^1H\}$	-	Proton decoupled
q	-	Quartet
s	-	Singlet
t	-	Triplet

ABBREVIATIONS AND SYMBOLS ***(Continued)*** **.....**

Chemical:

Ac	-	Acetyl
acac	-	Anion of pentane-2,4-dione
Ar	-	Aryl
bipy	-	2,2′-Bipyridine
^{t}Bu	-	t-Butyl
bzac	-	Anion of 1-benzyl pentane-2,4-dione
COD	-	cis, cis-Cyclo-octa-1,5-diene
Cp	-	Cyclopentadienyl anion
Cp^{*}	-	Pentamethylcyclopentadienyl anion
Cy	-	Cyclohexane
dba	-	Dibenzylideneacetone
DIOP	-	2,3-O-Isopropylidene-2,3-dihydroxy-1,4 bis(diphenylphosphino)-butane
diox	-	Dioxane
DMF	-	N,N-Dimethylformamide
dmpe	-	1,2-Bis(dimethylphosphino)ethane
dppm	-	Bis(diphenylphosphino)methane
dppe	-	1,2-Bis(diphenylphosphino)ethane
Et	-	Ethyl
hfac	-	Anion of 1,1,1,5,5,5-hexafluoropentane-2,4-dione
Me	-	Methyl
Ph	-	Phenyl
Pr	-	n-Propyl
^{i}Pr	-	i-Propyl
Py	-	Pyridine
SHOP	-	Shell higher olefin process
tfac	-	Anion of 1,1,1-trifluoropentane-2,4-dione
THF	-	Tetrahydrofuran
p-tol	-	4-Methylphenyl

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CHAPTER 1

The Importance, Preparation and Reactions of Late Transition Metal Amide Complexes

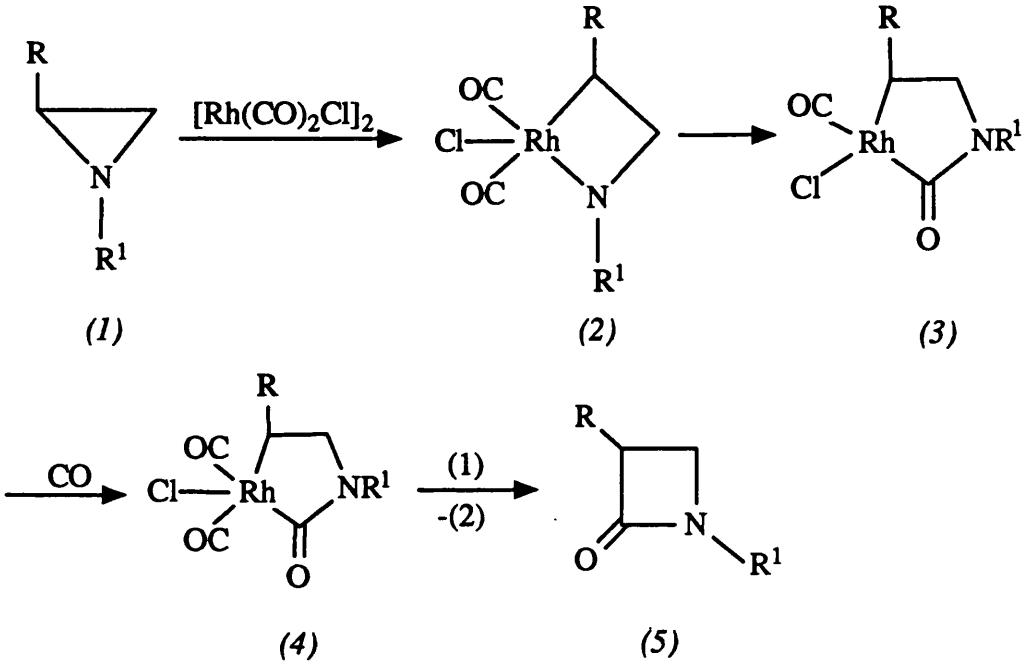
1.1 INTRODUCTION

For many years, complexes of the platinum group metals containing metal to carbon bonds have been studied intensely because of their success as active homogeneous catalysts.[1-3] Conversely, complexes containing metal to nitrogen bonds have been relatively unexplored, and little is known of the chemistry of this type of bond.

Recently, late transition-metal amides have started to receive greater attention due to their possible implication as intermediates in certain catalytic reactions. However, the rôles played by M-N bonds in many of these reactions are far from clear.

The synthesis of β-lactams, an important class of antibiotics, is a subject which has attracted much interest over many years. Some have concentrated on conventional organic synthesis whilst others have focussed on routes involving transition metal complexes. Most of the latter have involved stoichiometric quantities of the transition-metal complex.[4-6] However, Alper *et al.*[7] have developed the palladium-induced carbonylation of aziridines using a catalytic amount of the palladium complex, $Pd(PPh_3)_4$, to form bicyclic β-lactams. They later developed this to form monocyclic β-lactams *via* the enantiospecific and stereospecific rhodium(I) catalysed carbonylation and ring expansion of aziridines,[8,9] and postulated that the mechanism for this reaction involves the formation of a rhodium amide bond, Scheme 1. Oxidative addition to rhodium(I) of the most substituted carbon-nitrogen bond of the aziridine gives the rhodium(III) species *(2)*. Carbonyl insertion into the M-C bond, rather than the M-N bond, followed by carbonylation gives complex *(4)*. The β-lactam could then be formed by reductive elimination of *(5)* with or without the assistance of another molecule of aziridine. Alper has also exploited this type of reaction to synthesise α-methylene β-lactams from methylene aziridine[10] and azetidine-2,4-diones from α-lactams.[11]

Late transition-metal amide complexes have also been postulated as intermediates in the synthesis of carbamates from amines, carbon monoxide, alcohols and oxygen. Carbamates are an important class of compounds, not only as agricultural chemicals or pesticides,[12] but also as precursors of isocyanates. Carbamates are thermally dissociated to give isocyanates and alcohols in good yields. The usual method of preparation of carbamates is from isocyanates and alcohols, and isocyanates are synthesised through the phosgenation of amines. It is



Possible mechanisms for the carbonylation and ring expansion of aziridines to β-lactams.

Scheme 1

therefore highly attractive to develop an effective catalyst system to produce carbamates as this would preclude the use of dangerous phosgene.

Fukuoka *et al.* have designed a catalyst system,[13,14] comprising a platinum group metal and an alkali metal halide or onium halide, which seems to be effective in preparing carbamates directly from amines, carbon monoxide, oxygen and alcohols, Scheme 2. Experiments with

$$R^1NH_2 + CO + R^2OH + \tfrac{1}{2}O_2 \xrightarrow[\substack{86\ kg/cm^2\\160\text{-}170^\circ C\\2\ hrs}]{Pd/NaI} R^1NHCO_2R^2 + H_2O$$

R^1 = Ph; R^2 = Et

Scheme 2

different combinations of metals and halides showed the most effective halide species was iodide and that palladium and rhodium were the most active metal species. In each case, the major product was the carbamate with a small amount of the N,N′-disubstituted urea being formed. The proposed catalytic cycle for this reaction involves a metal amide species.

Similar work has been published by Alper *et al.*[15] They found that treatment of p-toluidine

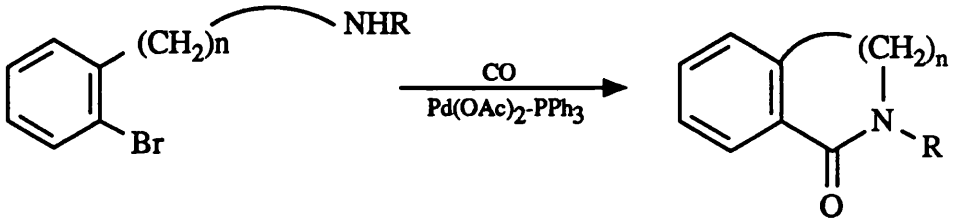
with carbon monoxide, oxygen, methanol and hydrochloric acid; using palladium(II) chloride as a catalyst and copper(II) chloride as a reoxidant; at room temperature and atmospheric pressure; gave methyl N-tolyl carbamate in 68% yield. This reaction occurs under very mild conditions and was found to be applicable to a series of aromatic amines. It is therefore superior to the Fukuoka method[13,14] which requires harsher conditions. It was found however that the reaction was too slow to be commercially viable, and the use of elevated pressures led to explosive mixtures of carbon monoxide and oxygen. Also, the use of oxygen at atmospheric pressures led to an undesirable side reaction, associated with the co-production of water, that is the conversion of carbon monoxide to carbon dioxide. To overcome these problems, Alper[16] utilized di-tert-butyl peroxide as a substitute for oxygen. This was shown to be effective in the conversion of both aliphatic and aromatic primary amines to carbamate esters at room temperature and atmospheric pressure. The use of elevated pressures resulted in the major product, from aromatic amines, being ureas rather than carbamates. Extension of the carbonylation reaction to secondary amines afforded both a carbamate ester and an oxamate ester which is the result of a double carbonylation reaction. The mechanisms described in this paper, which involve metal amide complexes, are similar to those proposed for the double carboxylation of halides to α-ketoamides.[17-22] Work published by Giannoccara[23] using a similar catalyst system (palladium dichloride or a palladium(II) complex and copper(II) chloride) indicates that under mild conditions the major products are N,N′-disubstituted ureas, whilst carbamate esters are only formed under more drastic conditions. This is obviously different to the Alper system[15] and Giannoccara concludes that a different mechanism must be operating in this system.

A system reported by Heck *et al.*[24] for the palladium-catalysed carbo-alkoxylation and amidation of aryl halides, Scheme 3, has been developed by Ban[25] to synthesise benzolactams. Ban reports that this synthesis is superior to existing processes for benzolactams, which are

$$ArX + R^1NH_2 + R^2_3N \xrightarrow[Pd(OAc)_2/PPh_3]{CO} ArCONHR^1 + R^2_3NH^+X^-$$

Scheme 3

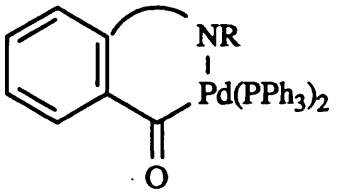
lengthy and have serious practical limitations. o-Bromo aminoalkyl benzenes were reacted with carbon monoxide in the presence of palladium(II) acetate and triphenylphosphine, Scheme 4.



R=CH_2Ph; n=1, 2,3 *(6), (7), (8)* *(11), (12), (13),*
R=H; n=2, 3 *(9), (10)* *(14), (15)*

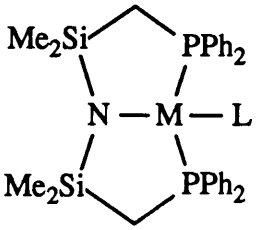
Scheme 4

The palladium amide complex *(16)* is proposed as an intermediate in the reaction mechanism for this process.



(16)

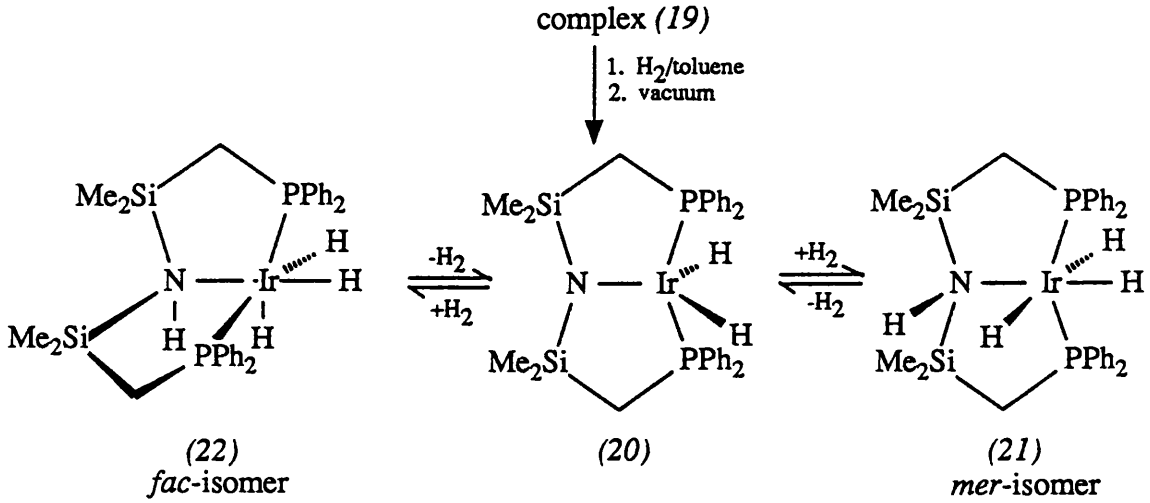
Late transition-metal amide complexes have also been known to activate dihydrogen and act as hydrogenation catalysts.[26,27] Complexes *(17)* and *(18)* both hydrogenate 1-hexene to hexane under one atmosphere of hydrogen at 22°C. These rhodium amidophosphines show surprisingly high alkene isomerisation activity, which is unusual since most rhodium phosphine dihydride species show very little tendency to isomerise alkenes. The unusual activity and mechanistic details of these systems are not fully understood. A ligand-assisted heterolytic splitting of dihydrogen has also been shown to occur when complex *(19)* is reacted



(17) L=cyclooctene, M=Rh
(18) L=PPh_3, M=Rh
(19) L=cyclooctene, M=Ir

with hydrogen, Scheme 5. The co-ordinatively unsaturated complex *(20)* was isolated on

removal of solvent and hydrogen. However, in hydrogen-saturated solutions complex *(20)* is not observed by ^1H nmr, the signals being consistent with the presence of complex *(21)*. Complex *(22)* was observed when complex *(19)* was stirred in a concentrated pentane solution under hydrogen. Under nitrogen, complex *(22)* decomposes to give a mixture of *(20)* and *(21)*. The formation of *(22)* and *(21)* from complex *(20)* is formally an intramolecular, ligand-assisted, heterolytic splitting of dihydrogen. It has yet to be determined how important these reactions are to the mechanism of hydrogenation.



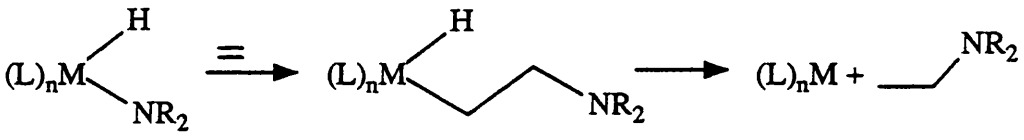
Scheme 5

Late transition-metal amides may be of importance in the development of a catalytic cycle for the amination of alkenes to alkylamines. The hydration of alkenes to alcohols occurs with as simple a catalyst as sulphuric acid.[28] However, the corresponding catalytic amination under mild conditions is not yet known and has long been a challenge to chemists. The reaction of ammonia with simple alkenes is known to be thermodynamically feasible.[29] Alkylamines are produced commercially by reaction of ammonia and the corresponding alcohol, in the presence of hydrogen, over a acidic oxide supported metal catalyst.[30] Since simple alcohols are mainly derived from alkenes it is clear that there would be raw material and other economic advantages in the efficient direct synthesis of alkylamines from ammonia and alkenes.

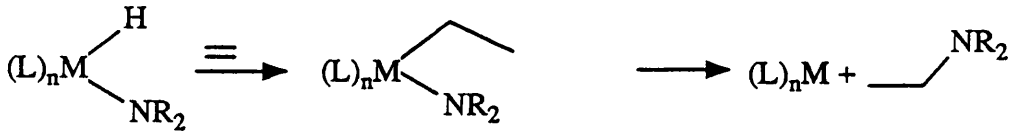
There is no general procedure for alkene amination but a possible mechanism might involve a Wacker-type process where ammonia could attack a coordinated alkene. Unfortunately, the primary amine product would be more reactive than ammonia and would react to give a

secondary amine, which would in turn produce a tertiary amine. Therefore, isolation of the primary amine product might prove to be difficult.

An alternative catalytic cycle might involve oxidative addition of an amine to a late transition-metal complex, forming an hydridoamido complex, followed by insertion of the alkene and subsequent reductive elimination of the amine product. The alkene could insert into the M-N bond, Scheme 6, or the M-H bond, Scheme 7. If one considers that tetrafluoro-ethylene will insert into a Pt-O bond[31] and that Pt-N bonds have been shown to be thermo-dynamically less stable than Pt-C bonds,[32] then insertion of alkenes into a Pt-N bond may be thermodynamically feasible. Trogler and Cowan[33] have provided evidence for some initial steps in such a sequence and Milstein[50,51] has reported a full catalytic cycle for the addition of aniline to norbornylene using an iridium amide (see Scheme 35, p.22).



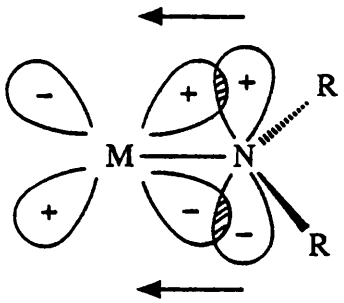
Scheme 6



Scheme 7

It can be seen from the previous examples how late transition-metal amide complexes may be important in homogeneous catalysis. Interest in these amides is now increasing as their utilization for such catalytic purposes is being realised.

The scarcity of platinum group amide complexes is often associated with the unfavourable hard base - soft metal interaction. Many different theories have been suggested to explain the preference of 'hard' acids for 'hard' bases and 'soft' acids for 'soft' bases.[34-37] However there seems to be no one simple theory and many phenomena can influence the strength of a chemical bond. In contrast to late transition-metals, early transition metal amide complexes are relatively common. This difference can be accounted for in terms of the π-donor properties of the amide ligand, and the d-orbitals on the metal centre; π donation (Fig. 1) to the metal from a lone pair of electrons on the nitrogen obviously requires vacant d-orbitals, which are



"π-bonding in a metal amide"

Figure 1

generally too high in energy for the complexes of the later transition-metals. The vacant d-orbitals of the earlier transition-metals allows these metals to act as more efficient electron acceptors; therefore they form stronger bonds with amide ligands. In addition, the earlier transition-metals are hard acids and are commonly in higher oxidation states than the later metals. A comparable group of ligands to the amides are the alkoxide ligands, OR^-, which are also hard bases and which behave in a similar manner to amides when coordinated to late transition metals.

Late transition-metal amide complexes are generally difficult to isolate and many are kinetically unstable with respect to β-hydride elimination. For this reason early attempts to isolate rhodium amides were unsuccessful,[38] resulting in decomposition generating metal hydrides, Scheme 8. Use of bis(trimethylsilyl)amide, thereby excluding β-hydride elimination, allowed the first examples of late transition-metal amides to be synthesised,[39] Scheme 9.

$$RhCl(PPh_3)_3 \xrightarrow{LiNMe_2} RhH(PPh_3)_3 + CH_2 = NMe \quad (23)$$

Scheme 8

$$RhCl(PPh_3)_3 \xrightarrow{LiN(SiMe_3)_2} Rh(PPh_3)_3N(SiMe_3)_2 \quad (24)$$

Scheme 9

A common assumption is that weak M-N bonds lower the intrinsic barrier to β-hydride elimination by raising the ground state free energies of metal amides compared to those of alkyl and aryl derivatives. However, Bryndza *et al.* have shown that Pt-O bond energies are

similar to Pt-C bond energies, and that the observed instability of platinum and ruthenium alkoxide complexes is kinetic in origin.[32,40,41] They have reported L_nM-X bond strengths, calculated from measurements of equilibrium constants of a series of reactions of the complexes $Cp^*(PMe_3)_2RuX$ and (DPPE)PtMeX (where X = OMe or NPh_2). This type of σ-bond metathesis reaction, Scheme 10, is thermoneutral in character; thus the difference in H-X and H-Y bond dissociation energies is the same as the difference in L_nM-X and L_nM-Y bond dissociation energies.

$$L_nM\text{–}X + H\text{–}Y \overset{R_{eq}}{\rightleftharpoons} L_nM\text{–}Y + H\text{–}X$$

L_nM = (DPPE)PtMe; $Cp^*(PMe_3)_2Ru$

Scheme 10

Using these reactions, Bryndza calculated that L_nM-O bonds were not inherently weak, but had bond dissociation energies comparable to L_nM-C, where C is sp^3 hybridised. He also showed that L_nM-N bonds were consistently weaker than L_nM-O or L_nM-C bonds. It now remains to be proven whether the instability of M-N bonds can be accounted for thermodynamically by this difference in bond strengths, or as with M-O bonds, the instability is of kinetic origin.

1.2 PREPARATION OF LATE TRANSITION METAL AMIDE COMPLEXES

There have been a number of reviews[41] of late transition metal amides which have reported several methods of preparation for these complexes. One of the most common is through metal-exchange or metathesis reactions. Bryndza *et al.* have prepared air-sensitive chelating bisphosphine platinum amides by treating the corresponding platinum chlorides with substituted lithium amides in tetrahydrofuran,[42] Scheme 11.

$$L_2PtRCl + LiNR'R'' \longrightarrow \underset{(25)\text{-}(37)}{L_2PtR[NR'R'']}$$

L_2 = dppe/dmpe; R = Me/Ph/CH_2Ph; R′ = Me; R″ = Ph
R′ = H; R″ = CH_2Ph

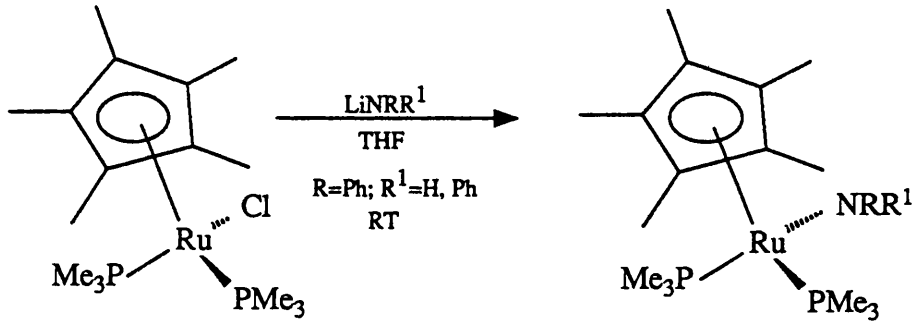
Scheme 11

Trogler *et al.*[33] were successful in the preparation of the extremely air-sensitive trans-$PtH(NHPh)(PEt_3)_2$ from a platinum nitrate and sodium phenylamide, Scheme 12.

$$\underset{(38)}{\text{trans–PtH}(NO_3)(PEt_3)_2} + \text{NaNHPh} \longrightarrow \underset{(39)}{\text{trans–PtH}(NHPh)(PEt_3)_2}$$

Scheme 12

Ruthenium amides have also been prepared by Bryndza *et al.*[32] using a metathesis-type reaction with lithium amides, Scheme 13, from ruthenium chlorides.



(40) *(41)*

Scheme 13

The parent amide ($-NH_2$) complexes, having both hydride and alkyl substituents on the platinum metal, have been prepared by deprotonation of the corresponding ammine complexes,[43] Scheme 14. The product is found to undergo dimerisation to give *syn* and *anti* isomers of $[PtR(\mu\text{-}NH_2)L]_2$, except when L = PCy_3.

$$\underset{(42)\text{-}(48)}{\text{trans–}[Pt(L)_2(R)NH_3]ClO_4} + \text{base} \longrightarrow \underset{(49)\text{-}(55)}{\text{trans–}Pt(L)_2(R)(NH_2)}$$

R = H; L = PPh_3, PEt_3 or PCy_3
R = Me; L = PPh_3, PEt_3, $PMePh_2$ or PCy_3

Scheme 14

An alternative method of preparation is *via* oxidative addition reactions. Stone and Green[44] reported the first synthetic route of this type to hydrido, alkoxo, and amido derivatives, Scheme 15, when they published their observations on the reaction of $Pt(PCy_3)_2$ with alcohols and amines. There have been many subsequent examples of oxidative addition of O-H bonds

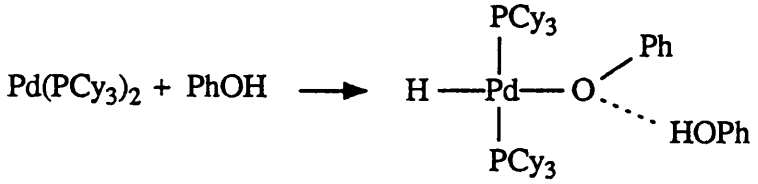
$$Pt(PCy_3)_2 + H\text{–}X \longrightarrow \underline{trans}\text{–}Pt(PCy_3)_2(X)(H)$$

(56)-(59)

H–X = HOPh; HOC_6H_4–p–R, pyrrole, pentafluoroaniline

Scheme 15

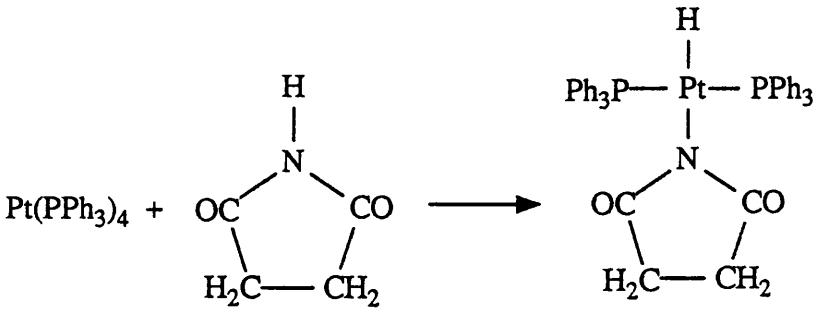
to L_nM centres. Otsuka[45] reported isolating <u>trans</u>-$[P(^iPr)_3]_2PtH(OH)$ from the reaction of $Pt[P(^iPr)_3]_3$ and water. The oxidative addition of phenol to a bulky palladium(0) bisphosphine complex has also been reported,[46] Scheme 16.



····· indicates hydrogen bond *(60)*

Scheme 16

However, oxidative addition reactions of N-H bonds to a zerovalent metal species have mainly been observed for activated amines and amides, C(O)NHR, where pKa's approach those of alcohols. Roundhill[47] reported the reaction of various imides with zerovalent platinum and palladium complexes. The imides used included succinimide, phthalimide, saccharin, and parabanic acid, having pKa's ranging from 6.1 to 11.7. The reaction of platinum with succinimide is shown in Scheme 17. Similar reactions of succinimide and



(61)

Scheme 17

$Pd(PCy_3)_2$ were reported by Yamamoto *et al.*[48] Tetrazoles which behave as weak acids have

also been shown to react in this manner.[49] More recently, Milstein[50,51] has demonstrated the oxidative addition of ammonia, Scheme 18, and aniline, Scheme 19, to some electron-rich iridium(I) complexes. The latter is of importance in the amination of alkenes (Scheme 35, p.23).

$$IrCl(PEt_3)_2(C_2H_4)_2 + NH_3(l) \longrightarrow [Ir(PEt_3)_2(H)(NH_3)(\mu\text{-}NH_2)]_2Cl_2 + C_2H_4$$

(62)

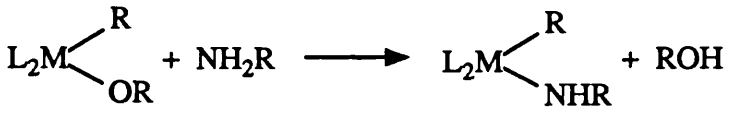
Scheme 18

$$IrCl(PMe_3)_3(C_8H_{14}) + NH_2Ph \longrightarrow Ir(PMe_3)_3(NHPh)(H)Cl$$

(63)

Scheme 19

An alternative approach to the preparation of late transition metal amides is *via* the reaction of amines with metal alkoxides, Scheme 20. Bryndza *et al.* have proved this method successful in the synthesis of PtMe(NMePh)dppe,[42] Scheme 21.



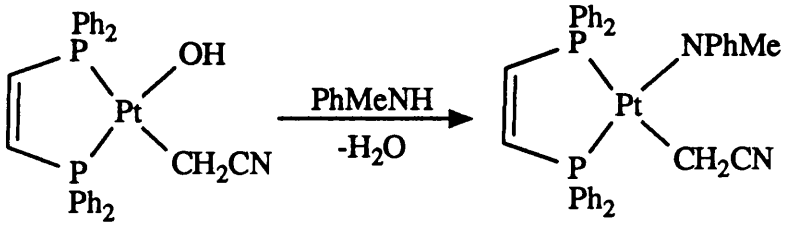
Scheme 20

$$(DPPE)MePt(OMe) + HNMePh \rightleftharpoons (DPPE)MePt(NMePh) + HOMe$$

(64) *(65)*

Scheme 21

They also used this method to make some ruthenium complexes. Ros[52] also used n-methylaniline in the preparation of a platinum amide complex *(67)* from the corresponding hydroxo complex, *(66)* Scheme 22.



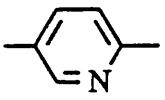
(66) *(67)*

Scheme 22

A few non-general amide syntheses proceed through reactions of organic azides. The

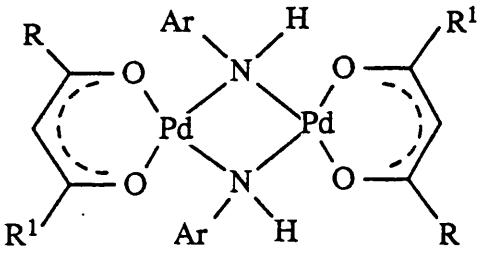
mechanisms are not fully understood and the methods not widely employed. Beck and Bauder[53,54] have prepared a number of unique amides through this procedure, Scheme 23.

$$\underline{\text{trans}}\text{-}(R_3P)_2Pt(H)(X) + R^1N_3 \longrightarrow \underline{\text{trans}}\text{-}(R_3P)_2Pt(NHR^1)(X)$$
(68)-(82)

where R = Et, Ph; X = Cl, NCO, N_3, CN
R^1 = Ph, PhCO, $PhSO_2$, p-$NO_2C_6H_4$, CO_2Et, O_2N 

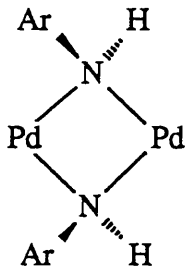
Scheme 23

Binuclear complexes of palladium have also been prepared, from the reaction of bis(β-diketonate) complexes of palladium with substituted aniline derivatives.[55] Refluxing in benzene leads to the formation of dimers of the type $Pd_2(\beta\text{-dik})_2(\mu\text{-NHAr})_2$ *(84)*. The central

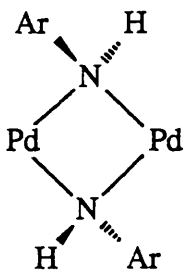


$R=R^1=CH_3$,acac *(84a)*
$R=CH_3$, $R^1=CF_3$,tfac *(84b)*
$R=CH_3$, R^1=Ph, bzac *(84c)*
$R=R^1=CF_3$, hfac *(84d)*

bis(aryl amido) section of the complexes can exist in two isomeric forms: *syn* and *anti*. The two isomers can be identified in solution but not isolated. There are thought to be a number of possible intermediates for this reaction, in which the β-diketonate ligands abstract a proton from the aniline.



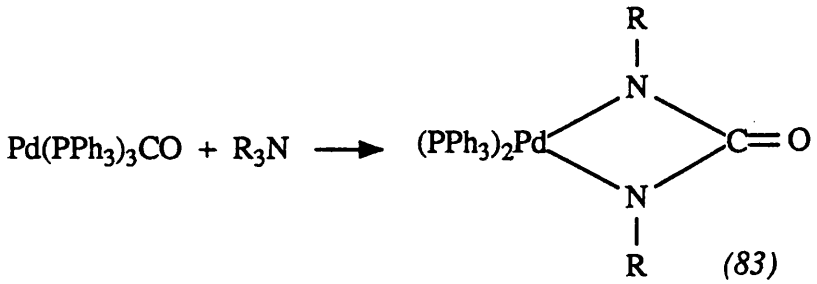
syn



anti

A whole series of urylene complexes have been prepared by the reaction of metal carbonyls with organic azides. Both dimeric and monomeric, Scheme 24, derivatives have been

isolated.[55,56] However, the stability of such complexes can be attributed to the electron withdrawing effect of the carbonyl group and the ρ-sulphonyl toluene substituents on the nitrogen.



(83)

R = ρ-$CH_3C_3H_4SO_2$

Scheme 24

1.3 THE PREPARATION OF LATE TRANSITION METAL AMIDES FROM FUNCTIONALISED PHOSPHINE LIGANDS

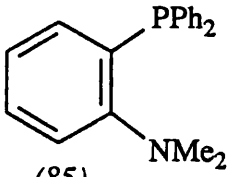
Other approaches to the study of late transition metal amides have concentrated on stabilising M-N bonds by inclusion in chelate rings. Apart from the urylene complexes described above, these chelating ligands usually take the form of amino-functionalised phosphines, and are often described as 'hybrid' ligands (i.e. containing both hard and soft donor groups). Usually this means a combination of phosphorous or arsenic with either oxygen or nitrogen. The number of donor groups incorporated into a ligand dictates whether the ligand is bi- or tri-dentate. They can be conveniently divided into two groups: those with aryl groups acting as a backbone to connect the hard and soft donor groups; and those with alkyl backbones connecting the different donor groups.

Examples of aryl-functionalised phosphines containing various 'hard' donor groups include the hydroxophosphine complexes of the type:

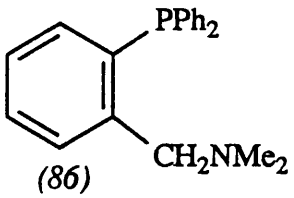
$[M(CO)\{P^tBu_2(C_6H_4O)\}\{P^tBu_2(C_6H_4OMe\text{–}2)\}]$
where M = Rh, Ir

synthesised by Shaw *et al.*[57,58] whilst Storhoff[59] used (o-cyanophenyl)diphenylphosphine as a bridging ligand in rhenium(I) complexes. The first aryl-functionalised phosphines which incorporated tertiary amines were synthesised by Rauchfuss and Roundhill.[60-64] They

synthesised platinum, palladium, rhodium and iridium chelate complexes of the ligands *(85)*

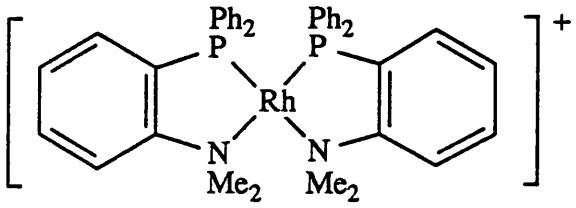


(85)



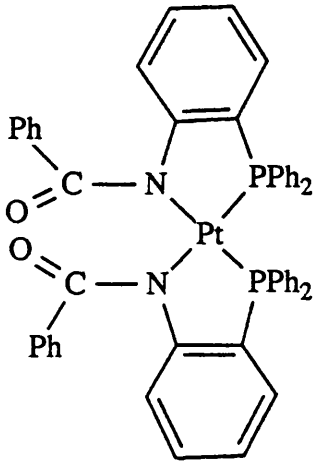
(86)

and *(86)*. It was found that reaction of carbon monoxide with the rhodium chelate complex *(87)* reversibly displaced the amine functionality.

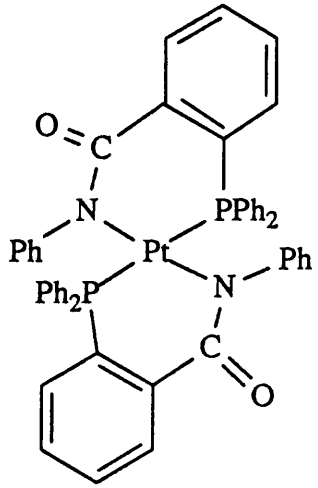


(87)

This work was later developed by Roundhill[65-70] to form functionalised phosphines which contained secondary amines. These ligands are of particular interest because deprotonation of the amine functionality leads to the formation of metal amide bonds. Roundhill reported the synthesis of various metal amide complexes by this method. Most of the earlier examples were prepared from ligands which incorporated a carbonyl group. However, later examples, where the carbonyl group is not present, indicate that the stability of these complexes does not depend on the carbonyl, but the presence of the chelate ring. Two examples, complexes *(88)* and *(89)*, are shown. These ligands were also used to facilitate oxidative addition of an N-H

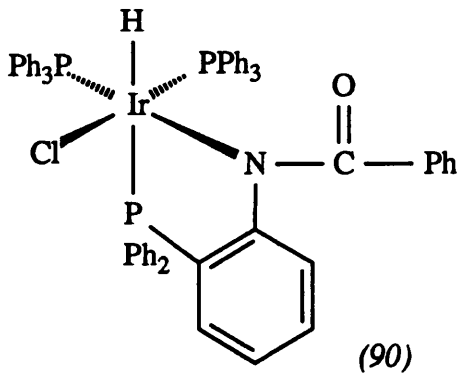


(88)



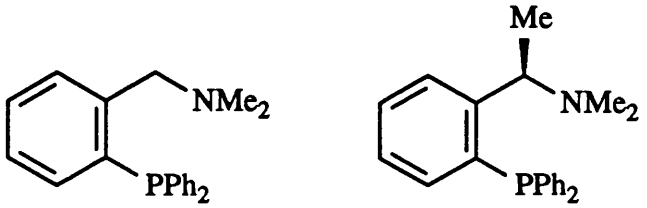
(89)

bond to iridium(I), generating an iridium amide complex *(90)*.



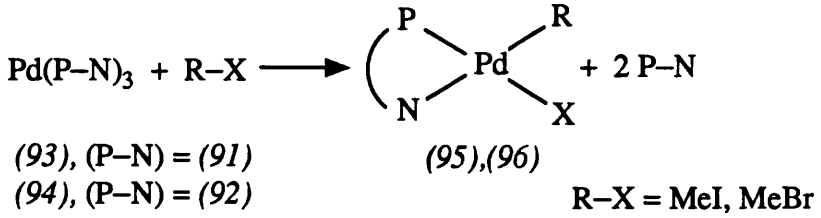
(90)

Cooper *et al.*[71-74] have also synthesised chelated amide complexes using the similar ligand, (o-diphenylphosphino)aniline. Recently, they reported the use of this ligand in the formation of amide-bridged rhodium(II) dimers.



(91) *(92)*

The bidentate phosphorus- and nitrogen-containing ligands, *(91)* and *(92)*, were used by Boersma *et al.*[75] to form air-sensitive palladium(0) complexes, $Pd(P\text{-}N)_3$, *(93)* and *(94)*. Oxidative addition of organic halides, R-X, such as methyl iodide and methyl bromide afforded the palladium(II) chelate complexes *(95)-(96)* illustrated in Scheme 25.



(93), (P–N) = *(91)*
(94), (P–N) = *(92)*

(95),*(96)*

R–X = MeI, MeBr

Scheme 25

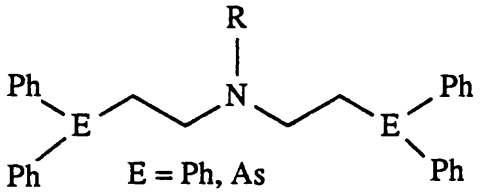
Similarly, there are many examples of 'hybrid' functionalised phosphines containing an alkyl backbone linking the various functional groups. Storhoff *et al.*[76] incorporated a cyano group, while Shaw[77-78] concentrated on carboxylic esters, carboxylic acids and β-ketophosphines. Examples of functionalised phosphines containing sulphur donor groups have been

synthesised by Sanger,[79-80] Sacconi[81] and Rigo.[82]

Amines have also been incorporated into hybrid functionalised phosphines which contain an alkyl backbone. Fryzuk *et al.*[26,27,81-85] used a tridentate ligand, which co-ordinates with one nitrogen, and two phosphorus donor atoms, to form rhodium, iridium, platinum, palladium and nickel amide complexes.

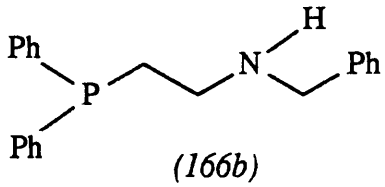
Knebel *et al.*[88] used the ligand $Ph_2PCH_2CH_2NMe_2$ to form molybdenum chelate complexes and found that the amine functionality was displaced by carbon monoxide. Kumar[89] later used the same ligand, as well as $Ph_2PCH_2CH_2CH_2NMe_2$ and other ligands containing oxygen and sulphur functionalities, to form platinum(II) complexes. The amino function was found to be a sufficiently good nucleophile to displace chloride when a five-membered chelate ring was formed, but not when the product would contain a six-membered chelate ring. In the case of $Ph_2PCH_2CH_2CH_2NMe_2$ chelation occurred only on the addition of silver tetrafluoroborate.

Furthermore, Taqui Khan *et al.*[90-94] have reported the synthesis of a number of bi- and tridentate ligands with phosphorus, arsenic, nitrogen and oxygen functional groups. The hybrid ligand *(97)*, containing a tertiary amine, was used to form ruthenium(II),(III), cobalt(III), rhodium(I),(III), iridium(I),(III), nickel(II), palladium(II) and platinum(II) chelated complexes, where all three donor atoms are co-ordinated to the metal. The corresponding secondary amine ligand, *(98)* was also used to synthesise a variety of metal complexes.



R = Benzyl *(97)*
R = H *(98)*

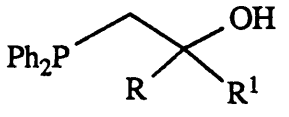
Of greater interest in the formation of late transition metal amide complexes is the bidentate ligand[90] *(166b)*, which contains a secondary amine functionality. The method by which Khan



(166b)

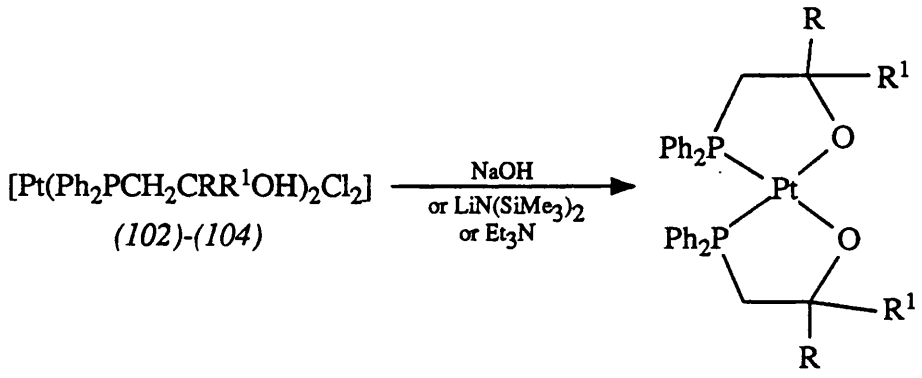
claims to have prepared this ligand is discussed in detail in Chapter 2. Khan reports the synthesis of a wide variety of chelate complexes of this ligand, but makes no mention of any deprotonation reactions, which have been reported previously for amide and alkoxide complexes by Roundhill,[65-70] Cooper,[71-74] Pringle[95-99] and Payne.[100-102]

One of the most interesting and recent examples of the utilization of hybrid functionalised phosphines has been the use of some alcohol-containing phosphine ligands *(99)-(101)* by



R=H; R^1=H *(99)*
R=H; R^1=Me *(100)*
R=Me; R^1=Me *(101)*

Pringle *et al.*[95-99] The complexes *(102)-(104)* formed with these ligands were deprotonated to afford chelate-stabilised alkoxo platinum *(105)-(107)*, Scheme 26, and palladium complexes.

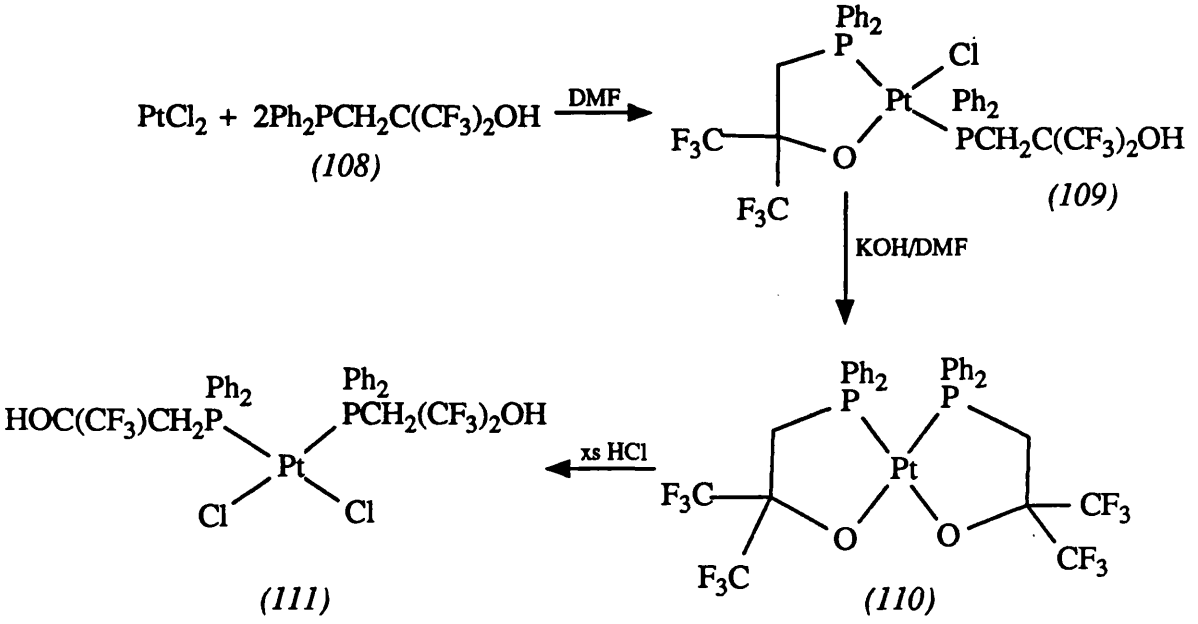


Scheme 26

The air-stable complexes *(105)-(107)* were recrystallised from aqueous methanol, and could be refluxed in alcoholic potassium hydroxide for 16 hours without showing any signs of decomposition. Pringle reports that these complexes are kinetically stabilised by the conformation of the chelate ring orientating the β-hydrogens away from the metal. A similar explanation has been used for the stability of cyclic metal alkyls. This result indicates that Pt-O bonds are not inherently weak, and that the previously observed instability is probably due to kinetic factors (facile β-hydride elimination) rather than thermodynamic ones. Due to the exceptional stability of these complexes, Pringle was able to look at some reactions of the

Pt-OR bond. He has studied the insertion of SO_2, CO, and 3,5-$Me_2C_6H_3NC$ into the Pt-O bond of these chelate complexes. This type of reaction is of interest because of its implication in catalytic processes.

A similar type of ligand, which contains a fluorinated alkoxy function together with an aryl phosphino group, has been reported by Payne and Willis[100-102] to form alkoxide complexes with a variety of metals. The reaction of this ligand, $Ph_2PCH_2C(CF_3)_2OH$ *(108)*, with platinum dichloride is shown in Scheme 27. However, this ligand can form a range of complexes with platinum, acting as a unidentate neutral ligand, coordinating through phosphorus only, or as a bidentate, uninegative ligand chelating to the metal through both phosphine and alkoxide groups. Payne and Willis have also shown how interconversion between these different types of coordination can be brought about by reaction with either acid or base, Scheme 27.



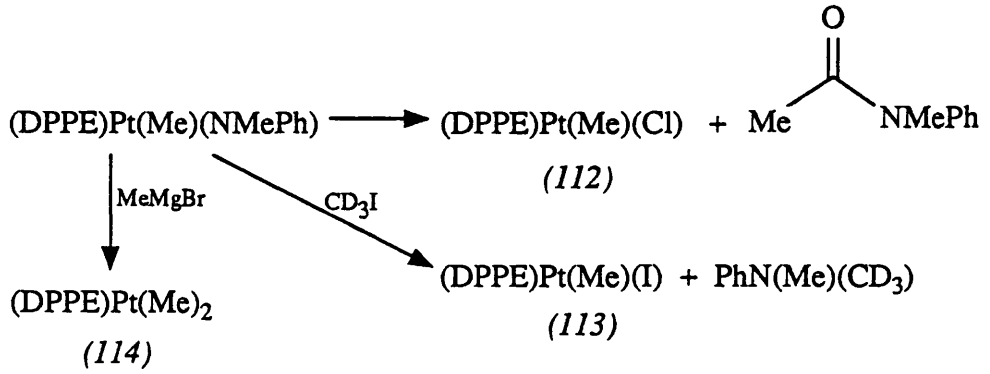
Scheme 27

1.4 REACTIONS OF LATE TRANSITION METAL AMIDE BONDS

One of the principal aims of preparing late transition metal amide complexes is to study the reactivity of the metal nitrogen bond. The reactivity of the complexes has been attributed to weak M-N bonds, but as described previously, these complexes are now thought to possess at

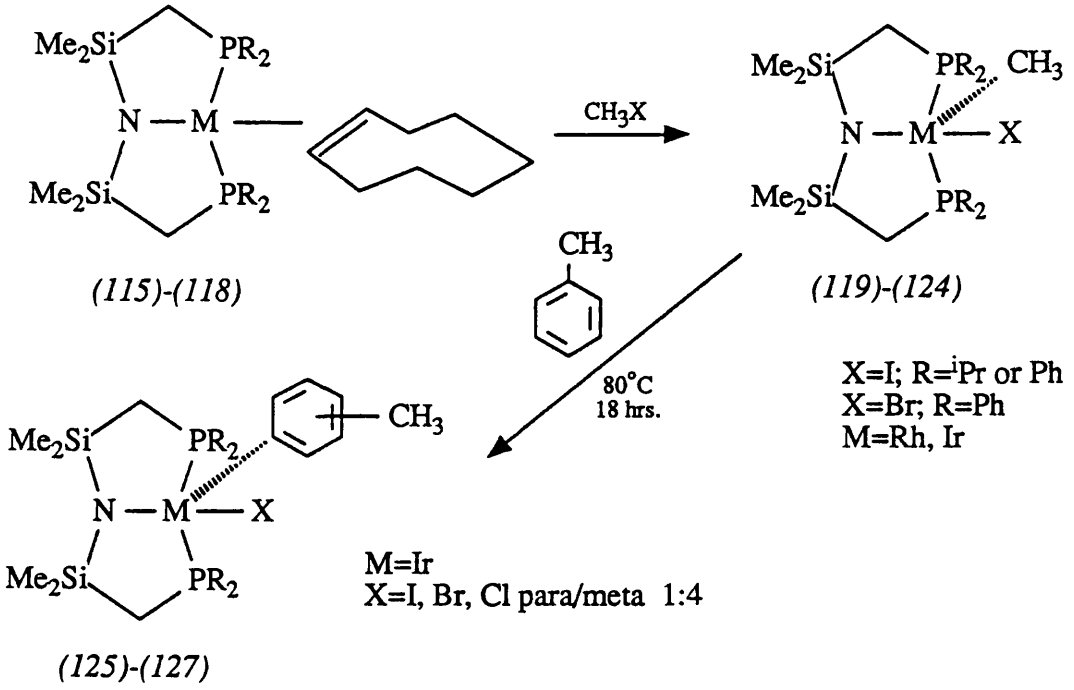
least moderate stability.

Bryndza *et al.* have shown that late transition metal amides can act as strong nucleophiles, but do not need dissociation of free amide to react with electrophiles. They have been shown to react with acetyl chloride and methyliodide, and to act as good leaving groups when reacted with methyl magnesium bromide, Scheme 28.



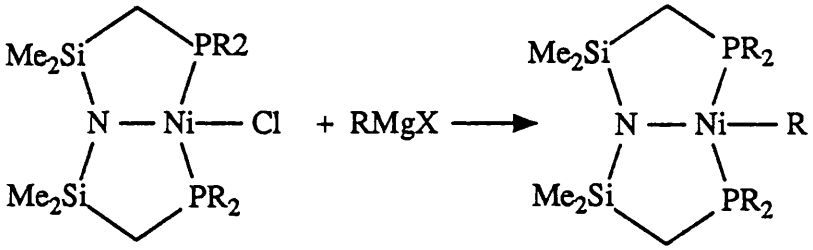
Scheme 28

The chelating amides prepared by Fryzuk[83-87] show interesting reactivity towards nucleophiles and electrophiles. The rhodium(I) and iridium(I) chelating amides *(115)-(118)* react, through oxidative addition reactions with methyl iodide, to form rhodium(III) and iridium(III) methyl iodo derivatives *(119)-(124)*, Scheme 29.



Scheme 29

The iridium amide also reacts with toluene[85] to give an amido tolyl derivative *(125)-(127)*, Scheme 29. In both cases the metal amide bond does not react since it is incorporated into two five-membered chelate rings, and there is another activated bond with which the methyl halides or toluene may react. Nickel chelating amido chlorides,[86,87] can be treated with strong nucleophiles such as alkyl, alkenyl, and aryl Grignard reagents to generate new alkyl, alkenyl and aryl amides, Scheme 30. The chelation of these amide ligands may prevent their displacement as a leaving group in the manner noted for the non-chelated amides in Scheme 28.



(128)-(130) *(131)-(133)*

R=Me, CH_2CHCH_2, $CHCH_2Ph$

Scheme 30

Insertion reactions are another important group of reactions of the late transition metal amides. When carbon monoxide is reacted with the nickel alkyl, alkenyl or aryl complexes *(128)-(130)*, Scheme 30, the carbon monoxide does not insert into the amide bond, but into the Ni-R bond to generate acyl derivatives. These reactions are not surprising since insertion into the Ni-N bond would convert two five-membered rings into two six-membered rings.

The first example of carbon monoxide insertion into an amide bond was discovered by Bryndza,[42] Schemes 31 and 32. The carbon monoxide insertion product from the complex

$$\underset{(134)}{(DPPE)Pt(Me)[N(CH_2C_6H_5)(H)]} \xrightarrow{CO} \underset{(135)}{(DPPE)Pt(Me)[C(O)N(CH_2C_6H_5)(H)]}$$

Scheme 31

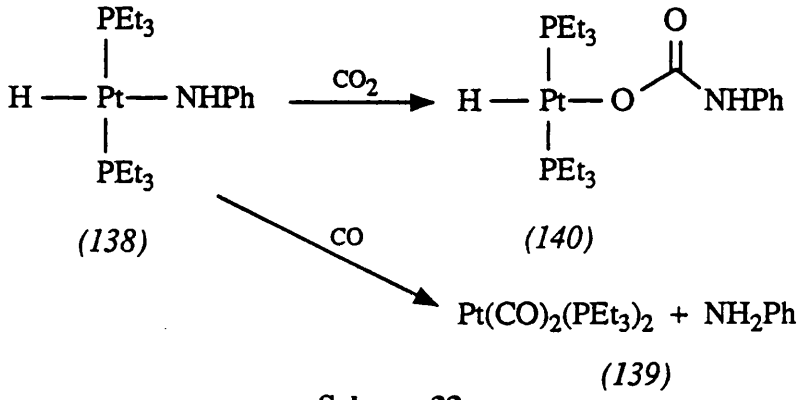
$$\underset{(136)}{(DPPE)Pt(Me)[NMe_2]} \xrightarrow{CO} \underset{(137)}{(DPPE)Pt(Me)[C(O)NMe_2]}$$

Scheme 32

(dppe)Pt(NMePh)(Me) was not isolated since de-insertion seems to be facile. These reactions

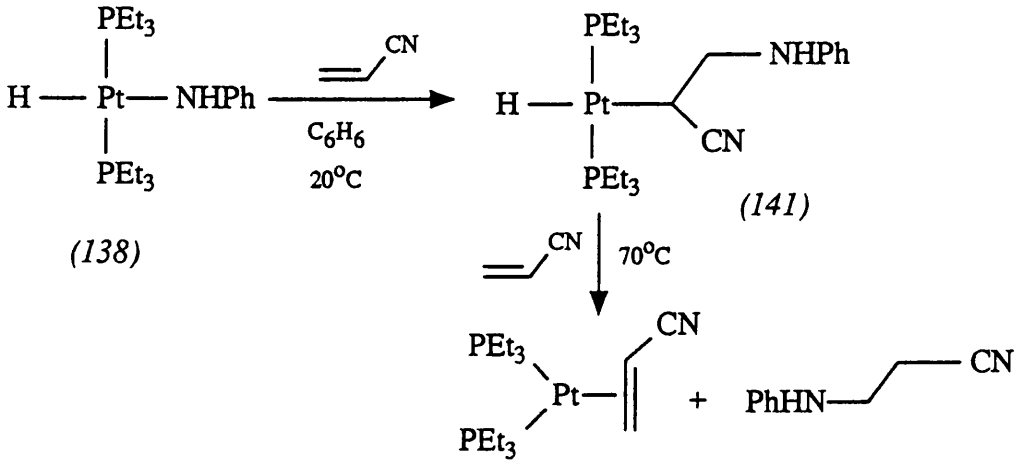
are similar to the insertion of carbon monoxide into Pt-O bonds for the analogous platinum alkoxides.[52,103-106]

Trogler and Cowan[33] have found that reaction of the platinum amide complex *(138)*, Scheme 33, with carbon monoxide leads to the elimination of aniline, whereas carbon dioxide inserts to generate a new platinum urethane complex *(140)*.



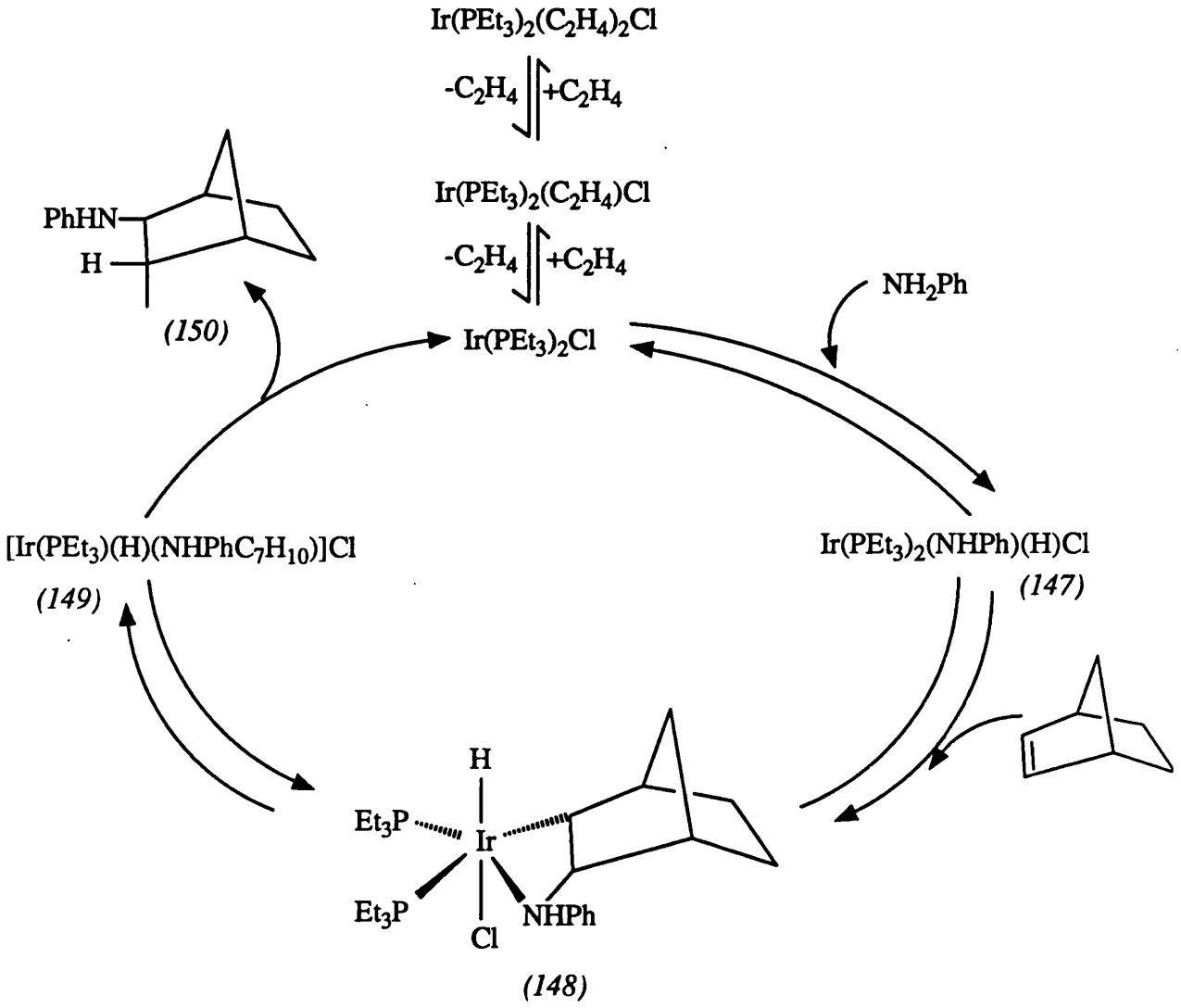
Scheme 33

Trogler has also studied the insertion of acrylonitrile into complex *(138)*, Scheme 34. This reaction is a regioselective 1,2 insertion into the Pt-N bond of complex *(138)* forming a new hydrido alkyl species, complex *(141)*. When the sample is heated to 70°C for 48 hours, reductive elimination occurs producing 3-anilinopropionitrile. These results are particularly interesting since they show that a hydridoamido complex can be used to model an insertion-reductive elimination sequence. This may be involved in the addition of an N-H bond to an alkene (see p.6).



Scheme 34

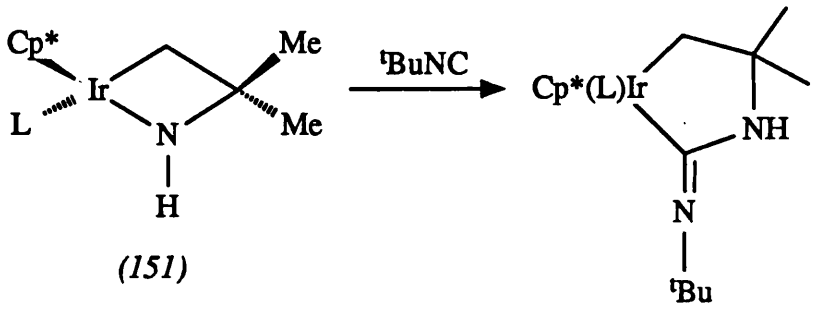
The first example of a complete catalytic cycle for the amination of alkenes has been reported by Milstein *et al.*[50,51] They demonstrated the individual steps for the stoichiometric addition of aniline to norbornylene with the iridium complex, $Ir(PEt_3)_2(C_2H_4)_2Cl$ *(144)*, then examined the whole catalytic process, Scheme 35. The major steps involved are N-H oxidative addition, reaction of the resulting amido hydride complex *(147)* with the alkene to form the azometallacycle, and C-H reductive elimination resulting in the *cis* addition of aniline to the *exo* face of norbornylene.



Scheme 35

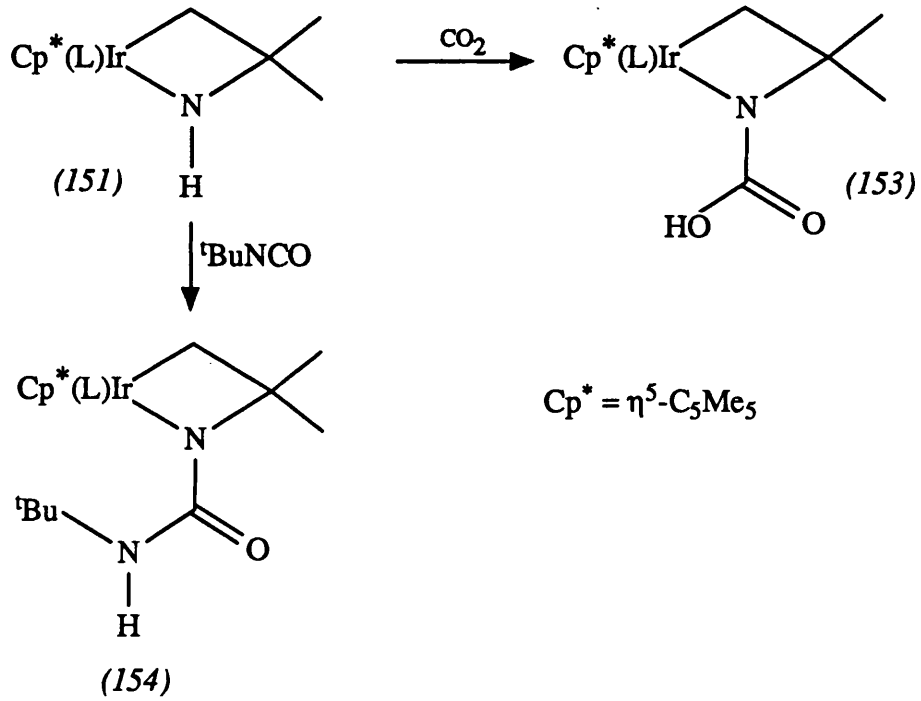
Bergman[107] has reported the insertion of ^tBuNC into an iridium amide, Scheme 36. However reaction with carbon dioxide and tert-butyl isocyanate, Scheme 37, does not involve

insertion into the Ir-N bond. On this occasion the iridium amide complex behaves in a similar manner to organic amides.



(151) *(152)*

Scheme 36

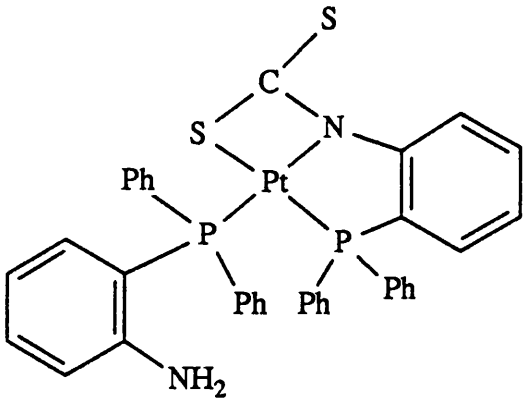


(151) *(153)* *(154)*

Scheme 37

Cooper and Downes have reported the synthesis of a platinum amide complex, $[Pt(PNH^-)_2]$, where PNH_2 is (o-diphenylphosphino)aniline. Reaction of carbon disulphide with this complex results in the formation of an addition compound, $[Pt(PN{\cdot}CS_2)(PNH_2]$, complex *(155)*,[107] containing a P, S, and N bonded tridentate ligand with four- and five-membered rings fused to platinum.

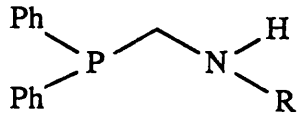
The reactions that late transition metal amides are known to undergo, demonstrate that there



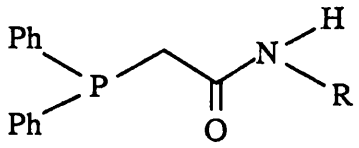
(155)

are no standard reaction pathways. Much remains to be discovered to understand the rôles that electronic, steric, isomeric, or other factors play in influencing their reactivity.

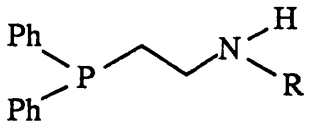
The following chapters will describe the preparation and utilization of the amino functionalised phosphines below in the formation of late transition metal amide complexes in a similar manner to that employed by both Pringle[95-99] and Payne.[100-102]

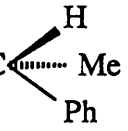


R=^{t}Bu; p-tol *(156), (157)*



R=^{t}Bu *(158)*



R=^{t}Bu, CH_2Ph,  *(166 a-c)*

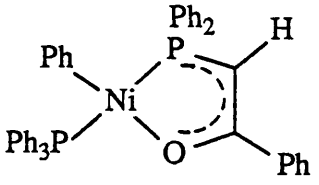
CHAPTER 2

Synthesis of some Aminoalkylphosphines, $Ph_2P(CH_2)_nNHR$ (n = 1, 2)

2.1 INTRODUCTION

One of the most effective ways to change the behaviour of a metal ion is to make changes to its ligands. If changes are made in the first co-ordination sphere of the metal, then the effects on the properties of the entire complex can be dramatic. However, if modifications are made to the ligand superstructure and its substituents, then the changes on the properties of the complex are more subtle and predictable. Ligand modifications have been applied to the co-ordination chemistry of tertiary phosphines and are becoming increasingly popular due to their applicability to catalysis. The idea of preparing low-valent transition metal complexes containing bidentate ligands which have both a hard and soft donor group has also progressed in recent years. Such ligands can be utilized in homogeneous catalysis since a hard donor atom co-ordinated to a soft metal is susceptible to displacement by a substrate molecule, whereas the chelate effect confers additional stability on the catalyst precursor, in the absence of the substrate. Other types of functionalised phosphines, each designed for a specific catalytic purpose, include di- and polyphosphines, chiral phosphines, polymer bound phosphines, ether phosphines, aminophosphines and carbonylphosphines.

An example of a functionalised phosphine complex catalyst is the SHOP catalyst, complex *(159)*, which catalyses the formation of linear α-olefins from ethylene.[108-109] The chelating β-ketophosphine ligand is responsible for the remarkably high selectivity of this process.

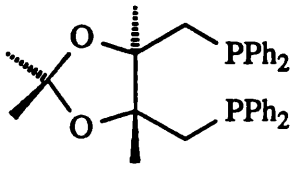


(159)

Functionalised phosphines can also be utilized in the formation of binuclear bridged complexes, which are of interest because of the increased versatility they allow in catalyst design. Complexes with two or more metal centres can have several advantages over a catalyst containing a single metal, and a number of binuclear phosphine - ligand bridged complexes have been shown to function as catalysts or catalytic precursors.[110-115]

The stereochemistry of catalytic reactions can be controlled by the chelate ring in chiral

chelating ligands, such as the now-famous DIOP ligand *(160)*,[116] which gives good yields in the asymmetric hydrogenation of dehydroamino acid derivatives. In this type of ligand, the chiral centre which controls asymmetric induction is three bonds removed from the metal and spatially remote from it. The chelate ring in some way controls the orientation of the P-Ph rings, which in turn determine the stereochemical outcome of the rate determining stage in the catalysis.



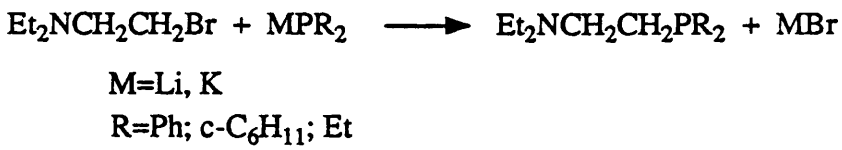
DIOP

(160)

Recently, chelating aminoalkylphosphine ligands of the type $R_2P(CH_2)_nNR'R''$ have also become common. Ligands containing primary or secondary amines are particularly interesting since they allow for further functionalisation and also deprotonation, useful in the formation of metal amide bonds. Roundhill[65-70] and Cooper[71-74] have both used amino aryl functionalised phosphines to form chelate-stabilised metal amide bonds, however the analogous aminoalkyl functionalised phosphines have yet to be used in such a manner.

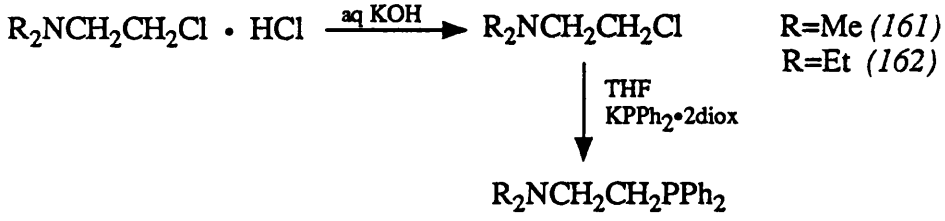
The secondary aminoalkyl functionalised phosphines, Ph_2PCH_2NHR are easily prepared from Ph_2PCH_2OH and primary amines, RNH_2.[134-137] However, the phosphines of the type $Ph_2PCH_2CH_2NHR$ are much more difficult to prepare. Only one synthesis of a primary aminoalkyl functionalised phosphine of this type has been described (Khan *et al.*[90]). However, many syntheses of tertiary amine containing $Ph_2PCH_2CH_2NR_2$ ligands have been reported, the first being in 1965 by Issleib *et al.*[117] They used various metal phosphides to produce the ligands $R_2PCH_2CH_2NEt_2$, Scheme 38. Also, it was found that when lithium diphenyl-phosphide was used, a metal-halogen exchange reaction occurred and the side products $R_2P–PR_2$ (R = c-C_6H_{11}; Et) and $Et_2N(CH_2)_4NEt_2$ were formed. Separation of these side products proved difficult.

Knebel *et al.*[118] prepared $Ph_2PCH_2CH_2NR_2$ (R = Me; Et) using a similar method, Scheme 39. The unprotected amine intermediates, *(161)* and *(162)*, are unstable at room temperature



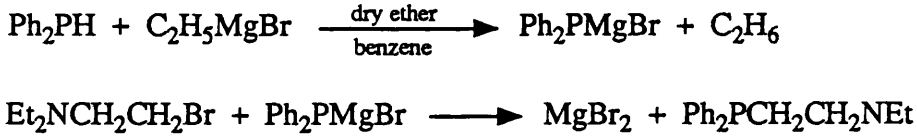
Scheme 38

and were stored at -80°C. Both Anderson[89] and Meek[119] used lithium diphenylphosphide to produce $Ph_2PCH_2CH_2NMe_2$ in the same manner as Knebel. Taylor *et al.*[120] employed a



Scheme 39

slightly different method by using a Grignard-type reagent in place of an alkali-metal phosphide, Scheme 40. The ligand $Ph_2PCH_2CH_2NH_2$, 2-(diphenylphosphino)ethylamine has also been prepared from lithium diphenylphosphide and aziridine.[121]



Scheme 40

As mentioned previously, the only reported preparation of a ligand of the type $Ph_2PCH_2CH_2NHR$ has been by Khan *et al.*,[90] who reported the preparation of $Ph_2PCH_2CH_2NHCH_2Ph$. Their method, Scheme 41, is an extension of those reported by Issleib,[117] Knebel,[118] Anderson[89] and Meek.[119] The synthesis involves reaction of ethanol amine with benzyl chloride to give the monosubstituted amine product, $PhCH_2N(H)CH_2CH_2OH$. This is then chlorinated with thionyl chloride affording the quaternary ammonium salt, which on treatment with 10% aqueous sodium hydroxide solution forms the free amine, $PhCH_2N(H)CH_2CH_2Cl$. Reaction of this with potassium diphenylphosphide gives $PhCH_2N(H)CH_2CH_2PPh_2$ as a yellow oil. This can then be converted into the

hydrochloride salt by treatment with aqueous HCl. Further discussion of this synthesis is presented in Section 2.2.

$$PhCH_2Cl + H_2NCH_2CH_2OH \xrightarrow[\text{ethanol}]{K_2CO_3} PhCH_2NHCH_2CH_2OH$$

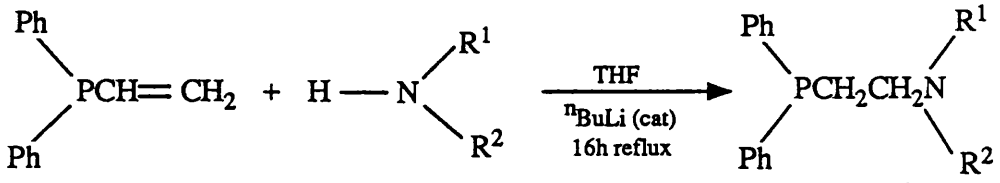
$$PhCH_2N(H)CH_2CH_2OH \xrightarrow[\text{ii) 10\% NaOH}]{\text{i) } SOCl_2} PhCH_2N(H)CH_2CH_2Cl$$

$$PhCH_2N(H)CH_2CH_2Cl + KPPh_2 \cdot 2diox \longrightarrow PhCH_2N(H)CH_2CH_2PPh_2$$

$$PhCH_2N(H)CH_2CH_2PPh_2 + HCl \xrightarrow{MeOH} PhCH_2N(H)CH_2CH_2PPh_2 \cdot HCl$$

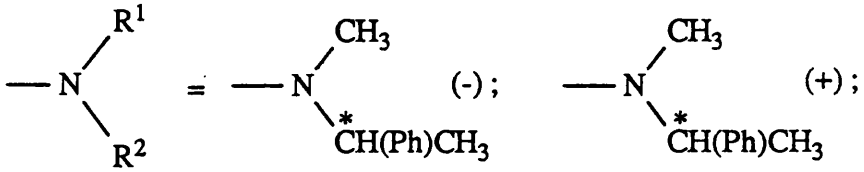
Scheme 41

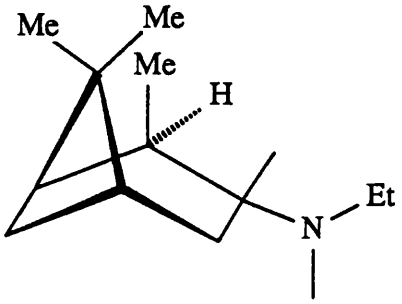
An alternative method of preparation of ligands of the type $Ph_2PCH_2CH_2NR_2$ was reported by Märkl *et al.*[122] This involves the reaction of vinyl diphenylphosphine with both primary and secondary chiral amines. This Michael-type addition utilizes n-butyllithium as a base catalyst. The secondary amines, Scheme 42, react with vinyldiphenylphosphine to give the



(163)-(165)

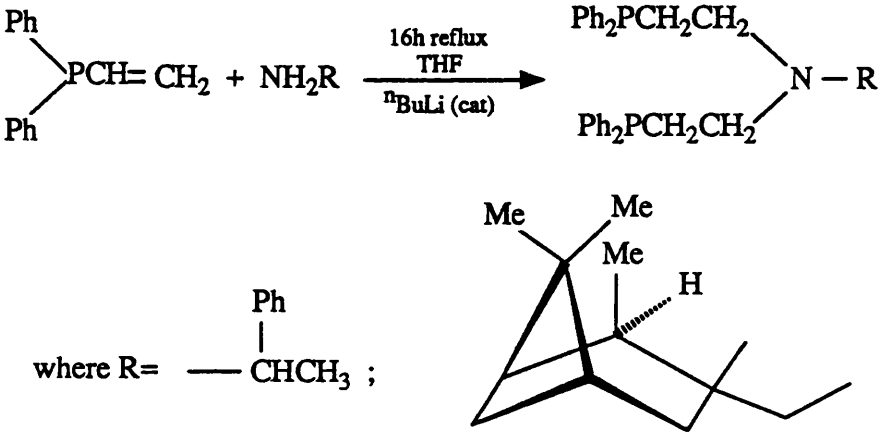
where





Scheme 42

aminoalkylphosphines $Ph_2PCH_2CH_2NR_2$ *(163)-(165).* However, primary amines react with 2 moles of phosphine to produce disubstituted amine products, Scheme 43. This Chapter describes an extension of Märkl's reaction,[122] in which ligands of the type $Ph_2PCH_2CH_2NHR$ [where R = ^{t}Bu, CH_2Ph, CH(Me)Ph] and $Ph_2PCH_2CH_2N(CH_2Ph)_2$ are formed.



Scheme 43

The aminoalkylphosphines of the type Ph_2PCH_2NHR (where R = ^{t}Bu, p-tol), which are used in Chapter 3, have been prepared by Healey.[123] The general synthesis of these reactions is described in Scheme 44. The method used is an extension of the methods of Märkl[124] and

$$Ph_2PCH_2OH + NH_2R \longrightarrow Ph_2PCH_2NHR + H_2O$$

(156)-(157)

R=^{t}Bu; p-tol

Scheme 44

Hoye,[125] using solid Ph_2PCH_2OH, which had previously only been isolated as an oil. This condensation reaction occurs rapidly at room temperature. In addition, the ligands $Ph_2PCH_2N(R)CH_2PPh_2$ (R = ^{t}Bu, p-tol), which are also used in Chapter 3, have been prepared by a similar method, Scheme 45. The ligand $Ph_2PCH_2C(O)NH^tBu$ *(158)*, used in Chapters 4

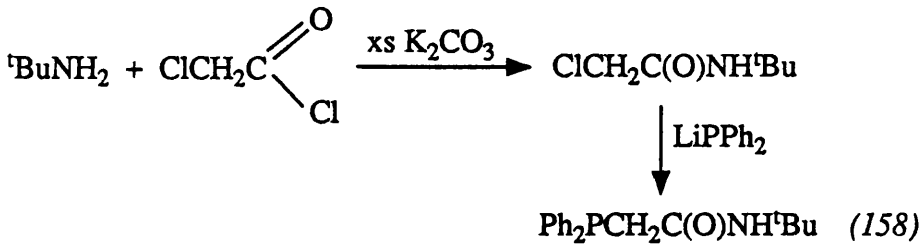
$$Ph_2PCH_2OH + Ph_2PCH_2NHR \longrightarrow Ph_2PCH_2N(R)CH_2PPh_2$$

R=^{t}Bu; p-tol

Scheme 45

and 5 was also prepared by Healey[123] using conventional organic reactions, Scheme 46.

^{31}P-{^{1}H} nmr data for these ligands which were prepared by Healey,[123] but utilized in this work are reported in Table 4.



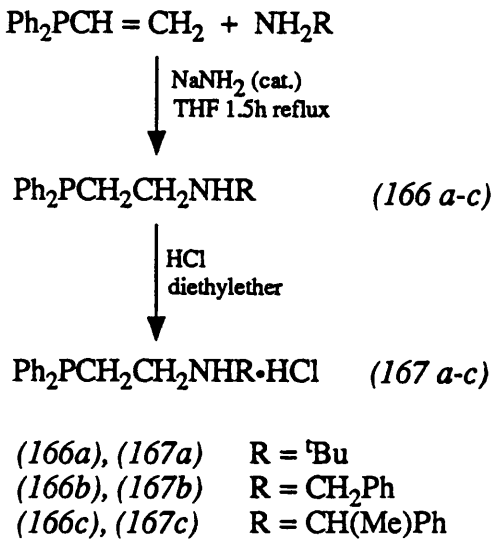
Scheme 46

2.2 RESULTS AND DISCUSSION

2.2.1 Preparation of Diphenylphosphinoethylamine Ligands

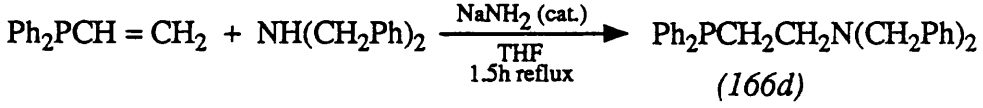
The base-catalysed addition of primary and secondary amines to vinyldiphenylphosphine using n-butyllithium as the base catalyst[122] was described in Section 2.1. Attempts to repeat this reaction with catalytic amounts of n-butyllithium and tert-butylamine failed, the ^{31}P-{^{1}H} nmr spectrum indicating only the presence of unreacted vinyldiphenylphosphine. When a stoichiometric amount of n-butyllithium was used, a reaction occurred producing unwanted butyldiphenylphosphine, presumably the other product is vinyllithium. Due to the difficulties in maintaining a catalytic amount of n-butyllithium, since too little resulted in no reaction and too much in the unwanted reaction above, it was decided to experiment with alternative bases. It was found that sodium amide is a convenient catalyst for this reaction, its low solubility in the THF solvent means that it is present in solution in small amounts. Refluxing vinyldiphenylphosphine with an excess of amine in THF, with sodium amide as a catalyst, gave the diphenylphosphinoethylamines, $Ph_2PCH_2CH_2NHR$ (R = ^{t}Bu, CH_2Ph, CH(Me)Ph) *(166a-c)* in good yields, Scheme 47.[126] This contrasts with the reported reaction with primary amines, using n-butyllithium as the base catalyst,[122] which gave only ligands of the type $Ph_2PCH_2CH_2NRCH_2CH_2PPh_2$, Scheme 43. However, it is probable that these reactions go through a $Ph_2PCH_2CH_2NHR$ intermediate, since a 2:1 stoichiometric ratio of vinyldiphenylphosphine and amine were used.

The ligand *(166a)* was isolated as a pale yellow crystalline solid, however *(166b)* and



Scheme 47

(166c) were isolated as oils. An excess of amine was used in each case to minimise the formation of bis(diphenylphosphinoethyl)amines. Removal of excess amine under vacuum was more difficult for *(166b)* and *(166c)* since benzylamine and α-phenylmethylamine have higher boiling points than t-butylamine. The presence of small amounts of amine impurity may prevent the crystallisation of *(166b)* and *(166c)*. When the secondary amine dibenzylamine was used instead of the primary amines, the product was found to be $Ph_2PCH_2CH_2N(CH_2Ph)_2$ *(166d)*, which was isolated as a pale yellow oil, Scheme 48.



Scheme 48

2.2.2 ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} Nmr Spectra of the Ligands *(166a-d)*

The ligands have been characterised by their ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} nmr spectra (see Tables 1 and 2). All the ligands show a single resonance in the ^{31}P-{^1H} nmr spectrum at around δ -20 ppm. Changing the substituent on nitrogen seems to have little effect on the chemical shift of this signal. The ^{13}C-{^1H} nmr spectra each show two doublets which have chemical shifts in the regions of δ 29 and δ 46 ppm due to the C_2H_4 backbone. In addition, signals are observed due to the R substituent on nitrogen and the phenyl groups. Previous

assignments of these doublets in similar types of ligands have been based on the relative magnitudes of $^1J(P-C)$ and $^2J(P-C)$, and are somewhat confused. Since, in the course of this research a series of ligands have been prepared, which vary only in the nature of the R substituents on nitrogen, it has been possible to base our arguments on chemical shift data as well as the magnitude of the coupling constants. The signals appearing further downfield show a greater range of δ, consistent with being bonded to nitrogen, when the substituent groups are varied. Therefore, we assign the downfield signal at approximately δ 46 ppm to the CH_2 group adjacent to the nitrogen and the signal at approximately δ 29 ppm to the CH_2 group adjacent to the phosphorus. From these assignments it was found that $^2J(P-C)$ is greater than $^1J(P-C)$ for all the ligands *(166a-d)*. This relationship in the magnitudes of $^2J(P-C)$ and $^1J(P-C)$ was also suggested for $Ph_2PCH_2CH_2NMe_2$,[89] however a previous study of tertiary phosphines concluded that $^1J(P-C)$ and $^2J(P-C)$ for alkyl side chains were approximately equal in magnitude.[127] All these examples contrast with the assignment made recently for the ligand $Ph_2PCH_2CH_2NHR{\cdot}HCl$ (R=CH_2Ph),[90] where assignments were made on the basis that $^1J(P-C)$ was greater than $^2J(P-C)$.

The ^1H nmr spectra of the ligands *(166a-d)* show two multiplets in the region δ 2-3 ppm due to the $-CH_2CH_2-$ backbone as well as signals due to the phenyl groups and the R substituent on nitrogen. The multiplet at lower field has been assumed to result from the CH_2 next to the nitrogen and the higher field multiplet to the CH_2 adjacent to the phosphorus, as was suggested by the $^{13}C-\{^1H\}$ nmr spectra. These two multiplets in ligand *(166a)* are shown in Figure 2. Signals A and B are second order, derived from a triplet of doublets (A) and a triplet (B). Two separate proton decoupling experiments were carried out on these multiplets. Irradiation of the higher field multiplet, A, caused B to collapse into a single resonance. However, irradiation of B caused A to collapse into a doublet (J_{PH} = 8.5 Hz), indicating that only multiplet A is coupled to phosphorus. This is not inconsistent with the assignment of B as the CH_2 group adjacent to phosphorus, since the magnitude of J_{PH} is not necessarily dependent on the proximity of the CH_2 group to the phosphorus atom.

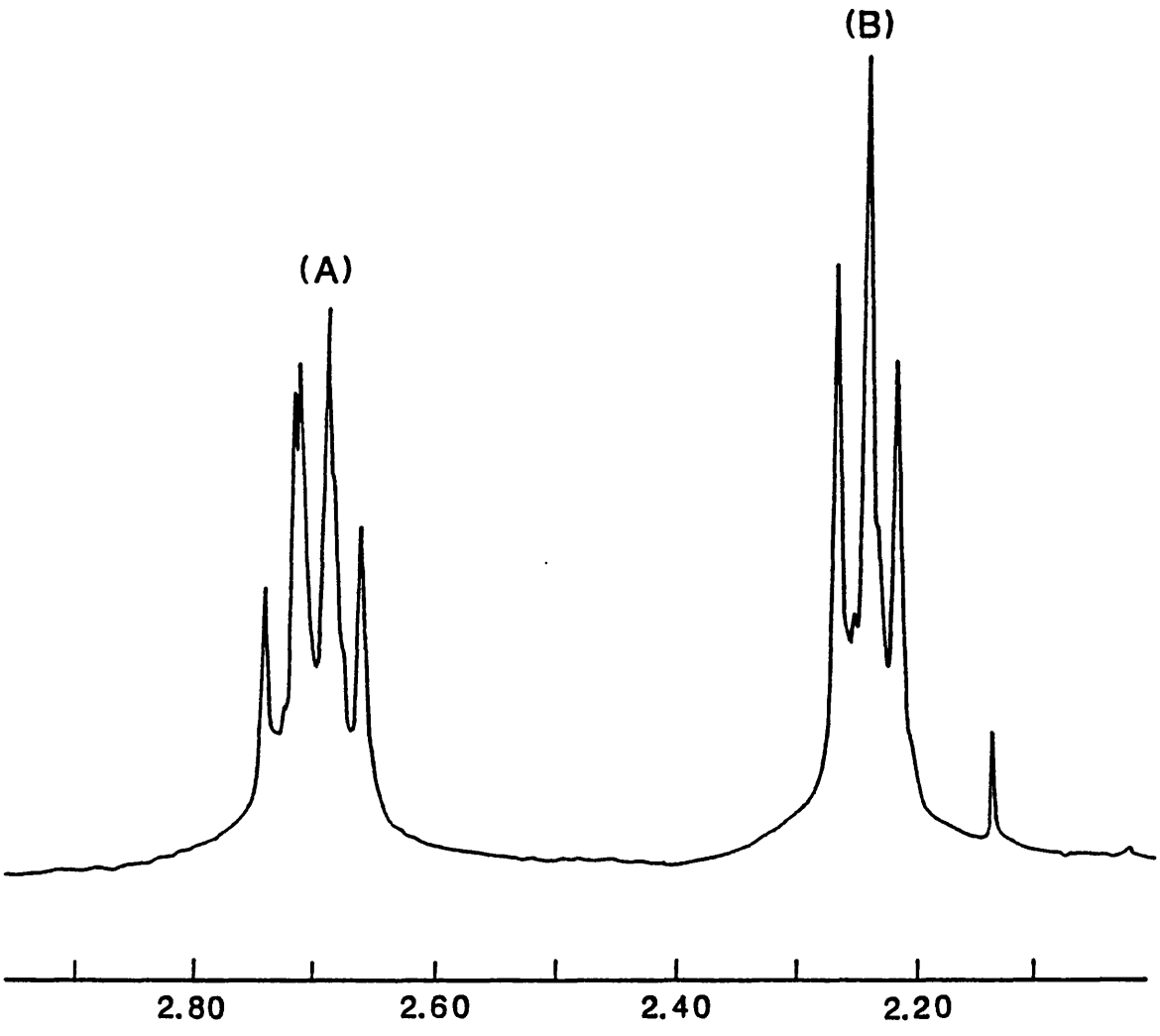


Figure 2
^{1}H Nmr Spectrum for Methylene Protons of Ligand $Ph_2PCH_2CH_2NH^tBu$ *(166a).*

2.2.3 Preparation of Diphenylphosphinoethylamine hydrochloride salts, $Ph_2PCH_2CH_2NHR{\cdot}HCl$

The ligands *(166a-d)* were reacted, as solutions in diethyl ether with HCl gas, yielding the hydrochloride salts $Ph_2PCH_2CH_2NHR{\cdot}HCl$ (R = ^{t}Bu, CH_2Ph, CH(Me)Ph) *(167a-c)* (Scheme 47) and $Ph_2PCH_2CH_2N(CH_2Ph)_2{\cdot}HCl{\cdot}MeOH$ *(167d)*. The salts *(167a-d)* were recrystallised from methanol to give white, crystalline, hygroscopic solids which were stored under a dry atmosphere. After standing in air for one week the signals in the ^1H nmr spectra, due to the N-H protons broadened, presumably due to exchange with the water protons. On standing for longer periods of time the white solids turned into pale yellow oils. The hygroscopic nature of these salts has resulted in difficulty in obtaining accurate elemental analyses. The analyses of the hydrochloride salts *(167a-c)* are consistent with the presence of approximately 0.5 moles of water (see Table 3). The water may have become associated with the salts during the period of time between dispatch and the recording of the analyses or it may have been present from the start, perhaps due to insufficient drying of the HCl gas.

2.2.4 ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} Nmr Spectra of the Hydrochloride Salts *(167a-d)*

The salts *(167a-d)* have been characterised on the basis of their ^{31}P-{^1H}, ^{13}C-{^1H} and ^1H nmr spectra (Tables 1 and 2). All the salts show a single resonance in the ^{31}P-{^1H} nmr spectrum at approximately δ -20 ppm. The ^{13}C-{^1H} nmr spectra show two doublets around δ 43 and δ 24 ppm, due to the C_2H_4 backbone, as well as signals due to the phenyl groups and the R substituents on nitrogen. The ^1H nmr spectra of *(167a-b)* have signals similar to those in *(166a-b)* with the addition of a broad signal corresponding to the N-H proton in the region δ 9.5-10.5 ppm. The ligand *(167c)* has a slightly different ^1H nmr spectrum to that of *(166c)* due to the chiral R substituent on the nitrogen. The N-H protons are diastereotopic and the presence of the chiral R group leads to the appearance of two signals, one for each of the N-H protons, at δ 10.4 and δ 10.0 ppm. The signal at δ 4.15 ppm, assigned to the C-H proton of the CHMePh group, is a multiplet rather than a quartet as observed for *(166c)*. When a D_2O shake was carried out the N-H signals disappeared and the multiplet at δ 4.15 ppm collapsed into a quartet, indicating the presence of coupling between the N-H protons and the C-H proton of

the R substituent. The signals due to the CH_2 protons of the C_2H_4 backbone are overlapping and since these two signals are coupled to each other, the observed multiplet is second order in nature. As expected, this multiplet does not collapse on addition of D_2O.

The ^1H nmr spectrum of the salt *(167b)* (Table 1) shows two multiplets at δ 2.60 and δ 2.85 ppm assigned to the $-CH_2CH_2-$ backbone, as well as a singlet at δ 3.95 due to the CH_2 group of the benzyl substituent. This data contrasts to that reported by Khan and Reddy[90] for $Ph_2PCH_2CH_2NHBz{\cdot}HCl$, which gives shifts of multiplets at δ 4.2 and δ 2.7 ppm, assigned to the $-CH_2CH_2-$ backbone. A singlet at δ 3.5 ppm due to the CH_2 of the benzyl group is also reported. The salt $Ph_2PCH_2CH_2N(CH_2Ph)_2{\cdot}HCl{\cdot}MeOH$ *(167d)* has been prepared independently from vinyldiphenylphosphine and dibenzylamine, followed by treatment with HCl, as described in Section 2.3. The ^1H nmr spectrum for *(167d)* is identical to that described for '$Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl$' by Khan and Reddy.[90] *(167d)* has been found to co-crystallise with one mole of methanol. It is probably this molecule of crystallisation which has confused Khan and Reddy in their reported isolation of '$Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl$'. The ligand that they more probably isolated is $Ph_2PCH_2CH_2N(CH_2Ph)_2{\cdot}HCl{\cdot}MeOH$, *(167d)* formed as a result of dibenzylation of the aminoethanol used in their preparation. The 300 MHz ^1H nmr spectrum of *(167d)* (Table 1) reveals that the signal at δ 2.7 ppm consists of two separate multiplets at δ 2.65 and δ 2.95 ppm which have been assigned to the CH_2 groups in the $-CH_2CH_2-$ backbone. Also, the multiplet at δ 4.2 ppm consists of two doublets of doublets at δ 4.3 and δ 4.5 ppm, which have been assigned to the CH_2 protons of the benzyl groups. Each CH_2 group consists of two diastereotopic protons which couple to each other and to the proton on the nitrogen, Figure 3.

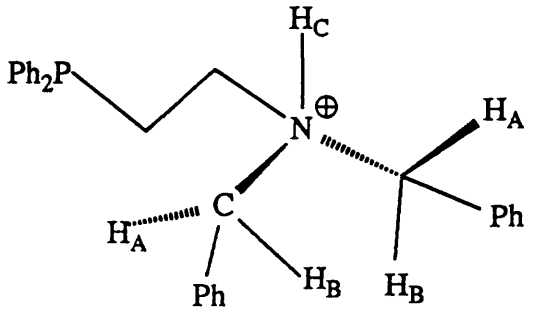
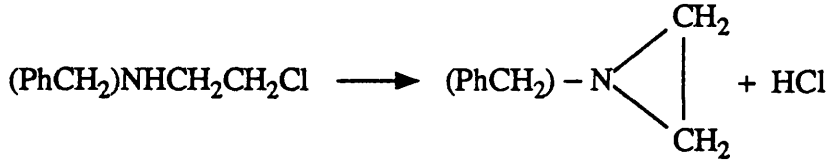


Figure 3

There are three different coupling constants, J_{HA-HB}, J_{HA-HC} and J_{HB-HC}. The singlet at δ 3.5 ppm has been assigned to the methanol of crystallisation which is also observed in the $^{13}C-\{^1H\}$ nmr spectrum at δ 50 ppm.

2.2.5 Attempted Preparation of $Ph_2PCH_2CH_2NHCH_2Ph$ by the method of Khan and Reddy [Ref. 90]

To further verify these results it was attempted to repeat the synthesis of $Ph_2PCH_2CH_2NHCH_2Ph$ as reported by Khan and Reddy,[90] starting from 2-aminoethanol and benzyl chloride. However, it was found that the only benzylated product from this initial step was dibenzylaminoethanol, even when only one equivalent of benzyl chloride was used. The dibenzylaminoethanol was separated from unreacted 2-aminoethanol by flash column chromatography. The production of dibenzylaminoethanol, rather than monobenzylamino-ethanol is a predictable result, since the monobenzylaminoethanol will be more reactive towards benzyl chloride than the starting material, 2-aminoethanol. This result could explain Khan and Reddy's[90] isolation of $Ph_2PCH_2CH_2N(CH_2Ph)_2 \cdot HCl \cdot MeOH$. Even if Khan and Reddy had succeeded in preparing the monobenzylaminoethanol, $(PhCH_2)NHCH_2CH_2OH$, it is unlikely that they would have succeeded in preparing $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)*. Our attempts at preparing *(166b)* via Khan's method, using commercially available $(PhCH_2)NHCH_2CH_2OH$ all failed. This is probably due to nucleophilic attack of the amine on the carbon adjacent to chlorine, Scheme 49, eliminating HCl. The dibenzyl derivative does not undergo this reaction since it cannot eliminate HCl.



Scheme 49

2.3 EXPERIMENTAL

Reactions and general manipulations were performed under an inert atmosphere of nitrogen, using degassed solvents, dried by distillation over an appropriate drying agent, as follows:

(i) n-alkanes, petroleum ether (40°-60°C fraction) benzene and toluene from sodium;

(ii) tetrahydrofuran and diethylether from sodium/benzophenone;

(iii) dichloromethane, acetonitrile and amines from calcium hydride;

(iv) methanol from magnesium turnings and iodine.

Microanalyses were performed by Butterworth Laboratories Ltd., 54-56, Waldegrave Road, Teddington, Middlesex. Mass spectra were recorded on a V. G. Micromass 16B instrument operating at 70 eV. Output was tabulated and calibrated by a linked computer. $^{31}P-\{^{1}H\}$ nmr spectra were recorded in dichloromethane, unless otherwise stated, using Jeol JNM-FX60 (operating at 24.15 MHz) and FX90Q (operating at 36.21 MHz) with $[P(OH)_4]^+$ in $[^2H_2]$-water (0.0 ppm) as an external reference, with positive values to high frequency (low field). ^{1}H and $^{13}C-\{^{1}H]$ nmr spectra were recorded at room temperature in $[^2H_1]$-chloroform, unless otherwise stated. ^{1}H nmr were recorded using a Varian EM390 (operating at 90 MHz) or Bruker AM300 (operating at 300.13 MHz) spectrometers. $^{13}C-\{^{1}H]$ nmr spectra were recorded on a Bruker AM300 spectrometer, operating at 75.47 MHz. Chemical shifts for ^{1}H and $^{13}C-\{^{1}H\}$ nmr spectra were recorded in ppm on the d scale with tetramethylsilane (0.0 ppm) as an internal reference. Jeol FX60, FX90Q and Bruker AM300 spectrometers were operated in the Fourier transform mode. Coupling constants J are in Hz.

Vinyl magnesium bromide, t-butylamine, benzylamine, dibenzylamine and 2-aminoethanol were obtained from Aldrich Chemical Co. Ltd. Chlorodiphenylphosphine and L-(-)-α-phenylethylamine were obtained from Lancaster Synthesis Ltd.

2.3.1 Preparation of vinyldiphenylphosphine

To a 1.0M solution of vinyl magnesium bromide (100 cm^3, 100 mmol) in THF was added dropwise with cooling, chlorodiphenylphosphine (13.8 cm^3, 76.8 mmol). The mixture was stirred for 1.5h and allowed to warm to room temperature. A 10% solution of aqueous ammonium chloride (15 cm^3) was added slowly to the cooled mixture. When the exothermic reaction was complete, dichloromethane (3 x 30 cm^3) was used to extract the product, which was then dried with anhydrous magnesium sulphate. Removal of the dichloromethane under vacuum afforded a yellow oil, which was purified by vacuum distillation yielding vinyldiphenylphosphine as a colourless, air-sensitive oil (12.6g, 77%).

2.3.2 Preparation of $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of vinyldiphenylphosphine (2.4g, 11.53 mmol) in THF (50 cm^3) was added tert-butylamine (4.56 cm^3, 46.12 mmol) and sodium amide (2 spatulas full, approximately 0.4g, from a suspension in toluene). The mixture was refluxed under a nitrogen atmosphere for 1.5h. The sodium amide was destroyed by addition of aqueous ammonium chloride solution (15 cm^3 of a 10% solution). The phosphine was extracted from the aqueous layer with dichloromethane (3 x 15 cm^3) and dried with anhydrous magnesium sulphate. The dichloromethane was removed under vacuum and the product dissolved in petroleum ether and filtered to remove any insoluble impurities. Recrystallisation from petroleum ether gave $Ph_2PCH_2CH_2NH^tBu$ *(166a)* as a cream solid (2.80g, 85%). The phosphine was identified on the basis of its $^{31}P-\{^1H\}$, $^{13}C-\{^1H\}$ and ^1H nmr spectra (see Tables 1 and 2) and its microanalysis (see Table 3).

Mass spectrum m/e (relative intensity): 285 (15), 270 (7), 200 (100), 185 (28), 108 (20), 100 (14), 86 (52), 57 (26), 28 (99).

2.3.3 Preparation of $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)*

This was prepared in a similar manner to $Ph_2PCH_2CH_2NH^tBu$ *(166a)* above, from vinyldiphenylphosphine (5.34g, 25.2 mmol) and benzylamine (6.61 cm^3, 62.9 mmol). After refluxing for 1.5h the solution became deep purple in colour. This colour disappeared during the aqueous work-up. Excess benzylamine was removed from the product by heating at 60°C under vacuum. The product, $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)* (5.84g, 73%) was isolated as a yellow oil and identified on the basis of its $^{31}P-\{^1H\}$, $^{13}C-\{^1H\}$ and ^1H nmr spectra (see Tables 1 and 2).

2.3.4 Preparation of $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*

This was prepared as for $Ph_2PCH_2CH_2NHCH_2Ph$ from vinyldiphenylphosphine (2.32g, 10.93 mmol) and L-(-)-α-phenylethylamine (3.05 cm^3, 38.29 mmol). The product $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*, was isolated as a colourless oil (3.07g, 84%) and was identified on the basis of its $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ nmr spectra (see Tables 1 and 2).

2.3.5 Preparation of $Ph_2PCH_2CH_2N(CH_2Ph)_2$ *(166d)*

This was prepared in a similar way to $Ph_2PCH_2CH_2NHCH_2Ph$, using vinyldiphenylphosphine (1.91g, 9.0 mmol) and a slight excess (1.1 equivalent) of dibenzylamine (1.77 cm^3, 9.2 mmol). Excess amine was removed by heating at 150°C under vacuum. $Ph_2PCH_2CH_2N(CH_2Ph)_2$ *(166d)* was isolated as a pale yellow oil (2.89g, 79%) and was identified on the basis of its ^{31}P-{^1H}, ^{13}C-{^1H} and ^1H nmr spectra (see Tables 1 and 2).

2.3.6 Preparation of $Ph_2PCH_2CH_2NH^tBu{\cdot}HCl$ *(167a)*

Hydrogen chloride gas was bubbled through a solution of $Ph_2PCH_2CH_2NH^tBu$ (3.0g, 10.51 mmol) in diethyl ether (50 cm^3). After a few seconds a white solid precipitated, the diethyl ether was removed *in vacuo* and the product was recrystallised from methanol giving $Ph_2PCH_2CH_2NH^tBu{\cdot}HCl$ *(167a)* (2.78g, 82%) as white crystals. The product was identified on the basis of its ^{31}P-{^1H}, ^{13}C-{^1H} and ^1H nmr spectra (see Tables 1 and 2) and its microanalysis (see Table 3).

2.3.7 Preparation of $Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl$ *(167b)*

This was prepared in the same way as $Ph_2PCH_2CH_2NH^tBu{\cdot}HCl$, using $Ph_2PCH_2CH_2NHCH_2Ph$ (2.2g, 7.00 mmol). Recrystallisation of the white solid from methanol afforded $Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl$ *(167b)* as white crystals (1.98g, 80%). The product was identified on the basis of its ^{31}P-{^1H}, ^{13}C-{^1H} and ^1H nmr spectra (see Tables 1 and 2) and its microanalysis (see Table 3).

2.3.8 Preparation of $Ph_2PCH_2CH_2NHCH(Me)Ph{\cdot}HCl$ *(167c)*

This was prepared as for $Ph_2PCH_2CH_2NH^tBu$, using $Ph_2PCH_2CH_2NHCH(Me)Ph$ (1.4g, 4.30 mmol) affording white crystals of $Ph_2PCH_2CH_2NHCH(Me)Ph{\cdot}HCl$ *(167c)* (1.18g, 75%). The product was identified on the basis of its ^{31}P-{^1H}, ^{13}C-{^1H} and ^1H nmr spectra (see Tables 1 and 2) and its microanalysis (see Table 3).

2.3.9 Preparation of $Ph_2PCH_2CH_2N(CH_2Ph)_2{\cdot}HCl{\cdot}(MeOH)$ *(167d)*

This was prepared as for $Ph_2PCH_2CH_2NH^tBu{\cdot}HCl$, using $Ph_2PCH_2CH_2N(CH_2Ph)_2$ (1.8g, 4.40 mmol), yielding white crystals of $Ph_2PCH_2CH_2N(CH_2Ph)_2{\cdot}HCl{\cdot}(MeOH)$ *(167d)* (1.35g,

64%). The product was identified on the basis of its $^{31}P-\{^1H\}$, $^{13}C-\{^1H\}$ and ^1H nmr spectra (see Tables 1 and 2) and its microanalysis (see Table 3).

2.3.10 Reaction of $NH_2CH_2CH_2CH$ with $PhCH_2Cl$

To a solution of 2-aminoethanol (6.04 cm^3, 0.1 mol) in ethanol (50 cm^3) was added a solution of benzylchloride (11.5 cm^3, 0.1 mol) in ethanol (60 cm^3) and potassium carbonate (20g, 0.15 mol). The mixture was stirred for 1h, after which time the solution was filtered and the ethanol removed under vacuum. Thin layer chromatography and ^1H nmr showed the presence of two compounds which were separated by flash column chromatography. The product $(PhCH_2)_2NCH_2CH_2OH$ and unreacted $H_2NCH_2CH_2OH$ were identified on the basis of their ^1H nmr spectra.

$(PhCH_2)_2NCH_2CH_2OH$, ^1H nmr, $CDCl_3$: δ (H) 7.8-6.7 (m, 10H), 3.5 (t, 2H), 2.6 (t, 2H) and 2.4 (br, 1H).

$H_2NCH_2CH_2OH$, ^1H nmr, $CDCl_3$: δ (H) 3.7 (t, 2H), 2.9 (t, 2H) and 2.4 (s, 1H).

TABLE 1

^{31}P-{^{1}H} and ^{1}H nmr Spectra of Aminoalkylphosphine Ligands *(166), (167)*

Compound	δ (^{31}P)[a] (p.p.m.)	δ (^{1}H)[b] (p.p.m.)
(166a)	-20.6	1.25 (s, 9H, ^{t}Bu), 2.24 [t, 2H, CH_2, $J_{(HH)}$ 7.5] 2.70 [dt, 2H, CH_2, $J_{(HH)}$ 7.5, $J_{(PH)}$ 8.5], 7.35 (m, 10H, Ph)
(167a)	-19.9	1.25 (s, 9H, ^{t}Bu), 2.84 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 7.55 (m, 10H, Ph), 9.40 (br, 2H, NH_2)
(166b)	-20.6	1.60 (s, br, NH), 2.29 [t, 2H, CH_2, $J_{(HH)}$ 7.5], 2.78 [td, 2H, CH_2, $J_{(HH)}$ 7.5, $J_{(PH)}$ 8.5], 3.70 (s, 2H, $\underline{CH_2}$Ph), 7.5 (m, 15H, Ph)
(167b)	-20.4	2.62 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 3.95 (s, 2H, $\underline{CH_2}$Ph), 7.35 (m, 15H, Ph), 10.10 (s, br, 2H, NH_2)
(166c)	-20.8	1.28 [d, 3H, Me, $J_{(HH)}$ 6.5], 2.22 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 3.70 [q, 1H, $J_{(HH)}$ 6.5], 7.30 (m, 15H, Ph)
(167c)	-20.8	1.69 [d, 3H, Me, $J_{(HH)}$ 6.6], 2.75 (m, 4H, CH_2), 4.13 (m, 1H, CH), 7.30 (m, 15H, Ph), 9.99 (s, br, 1H, NH), 10.38 (br, 1H, NH)
(166d)	-20.4	2.25 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 3.55 (s, 4H, $\underline{CH_2}$Ph), 7.29 (m, 20H, Ph)
(167d)	-19.8	1.70 (br, 1H, MeO$\underline{H}$), 2.65 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 3.46 (s, 3H, $\underline{Me}$OH), 4.05 [dd, 2H, CH, $J_{(HH)}$ 5, 13], 4.30 [dd, 2H, CH, $J_{(HH)}$ 2, 13], 7.4 (m, 20H, Ph), 12.5 (s, br, 1H, NH)

[a] In dichloromethane at room temperature;
[b] In $CDCl_3$ at room temperature, at 300 MHz.

TABLE 2

^{13}C-{^{1}H} nmr Spectra[a] of aminoalkylphosphine ligands *(166), (167)*

Compound	δ (^{13}C)[b] (p.p.m.)
(166a)	28.9 ($C\underline{Me}_3$), 29.9 [d, C_1, $^1J_{(PC)}$ 12], 39.4 [d, C_2, $^2J_{(PC)}$ 21], 50.4 ($\underline{C}Me_3$), 128-139 (Ph)
(167a)	24.9 [d, C_1, $^1J_{(PC)}$ 14], 26.0 ($C\underline{Me}_3$), 39.4 [d, C_2, $^2J_{(PC)}$ 28], 57.0 ($\underline{C}Me_3$), 128-136 (Ph)
(166b)	29.0 [d, C_1, $^1J_{(PC)}$ 12], 46.0 [d, C_2 $^2J_{(PC)}$ 20], 53.6 ($\underline{C}H_2Ph$), 125-140 (Ph)
(167b)	24.1 [d, C_1, $^1J_{(PC)}$ 16], 43.2 [d, C_2, $^2J_{(PC)}$ 26], 50.1 ($\underline{C}H_2Ph$), 128-136 (Ph)
(166c)	24.2 (Me), 29.1 [d, C_1, $^1J_{(PC)}$ 12], 44.1 [d, C_2, $^2J_{(PC)}$ 19.6], 57.8 (CH), 126-145 (Ph)
(167c)	20.7 (Me), 24.2 (s, br, C_1), 43.0 [d, br, C_2, $^2J_{(PC)}$ 22], 58.5 (CH), 127-136 (Ph)
(166d)	25.6 [d, C_1, $^1J_{(PC)}$ 13], 49.7 [d, C_2, $^2J_{(PC)}$ 22], 57.8 [$\underline{C}H_2Ph$], 126-140 (Ph)
(167d)	22.5 [d, C_1, $^1J_{(PC)}$ 17], 47.4 [d, C_2, $^2J_{(PC)}$ 29], 50.6 (MeOH), 56.7 ($\underline{C}H_2Ph$), 128-136 (Ph)

[a] At 75.47 MHz in dichloromethane at room temperature;

[b] The carbon atoms of the ethyl backbone are numbered as follows: $Ph_2PC_1C_2NRR^1$.

TABLE 3

Elemental Analyses of Aminoalkylphosphine Ligands

Compound	Empirical Formulae	Found (%)			Required (%)		
		C	H	N	C	H	N
(166a)	$C_{18}H_{24}NP$	75.17	8.28	4.27	75.76	8.48	4.91
**(167a)*	$C_{18}H_{25}NClP$	65.98	7.45	4/44	67.18	7.83	4.35
**(167b)*	$C_{21}H_{23}NClP$	69.57	6.62	3.86	70.88	6.52	3.94
**(167c)*	$C_{22}H_{25}NClP$	69.92	6.96	3.94	71.44	6.81	3.79
(167d)	$C_{29}H_{33}NClOP$	72.57	6.87	3.14	72.87	6.96	2.92

* Compounds *(167a, b and c)* are consistent with up to 0.5 mole of water

TABLE 4

^{31}P-{^{1}H} Nmr Data for Ligands prepared by Healey [Ref. 123]

Ligand	δ (P)/ppm [a]
Ph_2PCH_2OH	-10.5
$Ph_2PCH_2NH^tBu$	-16.3
Ph_2PCH_2NHp-tol	-19.0
$(Ph_2PCH_2)_2N^tBu$	-25.3
$(Ph_2PCH_2)_2N$p-tol	-27.2
$Ph_2PCH_2C(O)NH^tBu$	-15.1

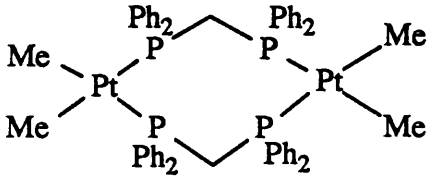
[a] All spectra measured in $CDCl_3$ at room temperature

CHAPTER 3

Synthesis and Reaction of some Aminomethylfunctionalised Phosphine, Ph_2PCH_2NHR, Complexes of Pt and Pd

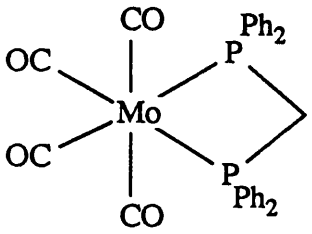
3.1 INTRODUCTION

The ligands Ph_2PCH_2NHR are analogous to the diphosphine $Ph_2PCH_2PPh_2$,[129] dppm, which is most commonly found as a bridging ligand, as in complex *(170)*, rather than a chelating ligand. This is probably due to an unfavourable chelate ring size. Examples of



(170)

dppm behaving as a chelating ligand have been reported,[130] but the four-membered ring formed is strained and the number of such complexes is far less than the number of known bridged complexes. Examples of some chelate complexes[130-137] include *(171)* and *(172)*. Modifications of the dppm ligand can affect its reactivity. For example, electronic



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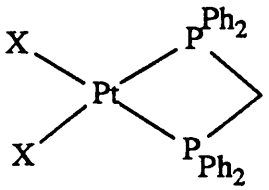


(172)

where X=
Cl, Br, I, Me, Ph,
p-tolyl

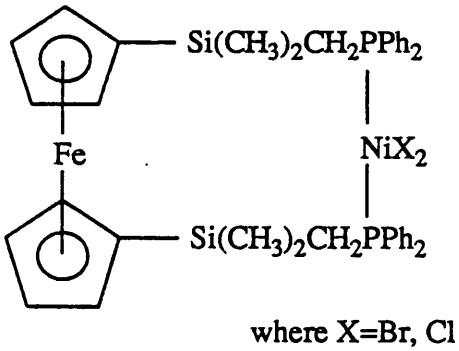
properties can be modified by changing the substituents on the phosphorus, but substitution at the methylene group will have less of an effect. Changing phosphorus for another Group V element such as arsenic will increase the M-L bond length and therefore alter the strain on the chelate ring.

The ligands Ph_2PCH_2NHR, R = ^tBu, p-tol can be compared to dppm and this Chapter describes the reactivity of these ligands with platinum and palladium complexes. The study focuses on the ability of the ligands to co-ordinate through phosphorus and nitrogen. Also, an investigation is made into the reactivity of the unco-ordinated end of the co-ordinated functionalised phosphines, in particular with a view to making bimetallic complexes.

Binuclear phosphine-bridged complexes have been attracting interest because of their potential as catalysts[110-114] and also because of their interesting structural and reactivity

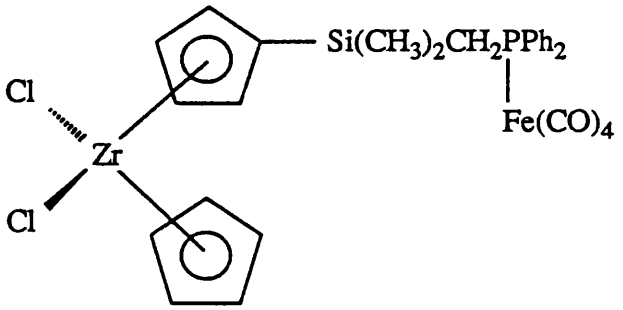
features. Complexes containing two or more metal atoms can have several advantages over mononuclear complexes. The presence of two metals can allow multi-electron redox reactions to take place which could not be handled by a single metal.[3] They have also been shown to reduce small molecules such as dinitrogen and nitriles,[1] which can be more easily activated by attachment to several metal centres.

Recently, binuclear complexes containing bifunctional ligands with two very different binding sites, each capable of bonding to a different type of metal have received some attention. These ligands can be used to link dissimilar transition metals e.g. early and late transition metals, within the same complex, increasing the catalytic potential of the complex. Schore[149] has used the ligand [dimethyl(diphenylphosphinomethyl)silyl]cyclopentadienyl lithium to form some heterobimetallic iron-nickel and zirconium-iron complexes *(173)* and *(174)*.



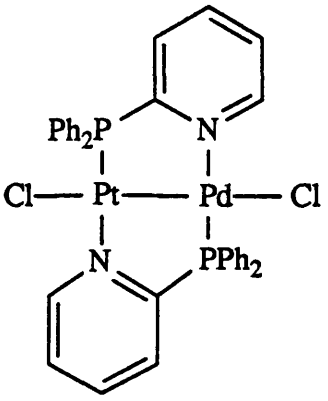
where X=Br, Cl

(173)



(174)

Balch *et al.*[144] have reported the use of 2-(diphenylphosphino)pyridine to form binuclear bridging metal complexes. The ligand reacts with Group VIII metals *via* co-ordination of the phosphorus atom. These complexes can then co-ordinate to a second metal through the pyridine nitrogen. The most thermodynamically stable complexes formed have ligands in a 'head-to-tail' arrangement, with one phosphorus and one nitrogen bound to each metal centre, as in complex *(175)*. However, complexes where both phosphorus atoms are co-ordinated to one metal and both nitrogens to the other, in a 'head-to-head' arrangement, can also be formed, as in complex *(176)*. In this 'head-to-head' arrangement the reactivity of the metals is likely to be altered to a greater extent.



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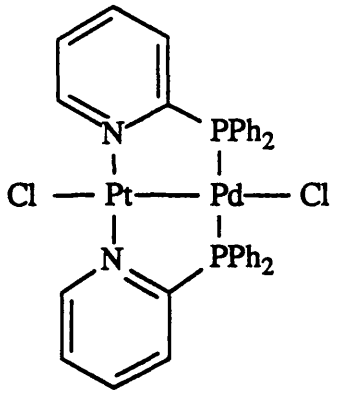
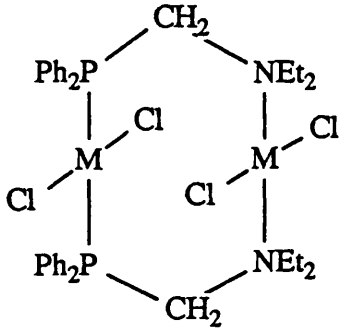


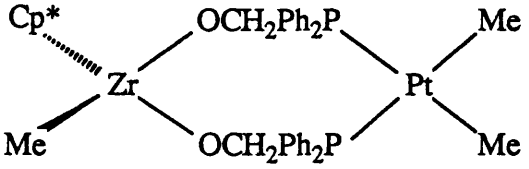
(176)

Dagnac *et al.*[138,139] used the ligand diethyl(diphenylphosphinomethyl)amine, $Ph_2PCH_2NEt_2$, to form binuclear complexes *(177)*. These complexes react with carbon monoxide to form carbonyl bridged complexes. In this case the ligands are arranged in a 'head-to-head' manner.



(177a), M=Pt
(177b), M=Pd

Wolczanski[140] has used the bridging ligand Ph_2PCH_2OH to synthesise a variety of early-late heterobimetallic complexes. These include zirconium-platinum *(178)* and zirconium-rhodium complexes.



(178)

An alternative approach to the synthesis of bimetallic complexes may involve the preparation of two mononuclear complexes which are then linked together by the reaction of functional groups on the phosphine ligands. This approach was suggested by the phosphine synthesis[123-125] in Scheme 50. In the case where R = ^{t}Bu this reaction occurs rapidly at room

temperature.

$$Ph_2PCH_2OH + Ph_2PCH_2NHR \longrightarrow Ph_2PCH_2N(R)CH_2PPh_2 + H_2O$$

Scheme 50

This Chapter will partly look at the possibility of this type of condensation reaction with ligands which are co-ordinated to metal centres. Such reactions could have wide ranging applicability forming linkages between an enormous variety of complexes. Another area of reactivity which will be considered is the ability of the ligand $Ph_2PCH_2NH^tBu$ to form four-membered chelate rings (comparable to those formed by dppm[137]) by means of deprotonation of the amine.

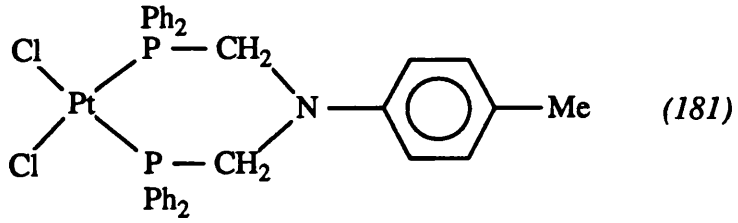
3.2 RESULTS AND DISCUSSION

3.2.1 Reaction of Pt with $Ph_2PCH_2NH^tBu$ and Ph_2PCH_2NHp-tol

The reaction of the aminoalkylphosphine, $Ph_2PCH_2NH^tBu$ with $(COD)PtCl_2$ in a 2:1 ratio gave the square-planar platinum complex cis-$[Pt(Ph_2PCH_2NH^tBu)_2Cl_2]$, *(179)*. Complex *(179)* exhibits a signal in the $^{31}P-\{^1H\}$ nmr spectrum (see Table 6) at δ +4.0 ppm with platinum-195 satellites (J_{Pt-P} = 3710 Hz). The J_{Pt-P} coupling constants can be used to determine the stereochemistry of such complexes.[141-143] A J_{Pt-P} of 3710 Hz is typical of a phosphorus atom co-ordinated trans to chloride. It follows that the two phosphorus ligands are in a mutually cis configuration around the platinum metal centre. The ^1H nmr spectrum (see Table 6) displays a multiplet in the region δ 8.0-7.1 ppm due to the phenyl protons, a multiplet at δ 3.5 ppm due to the methylene protons as well as signals due to the tert-butyl and N-H protons. The $^{13}C-\{^1H\}$ nmr spectrum (see Table 6) displays a signal at δ 45 ppm corresponding to the methylene carbon as well as signals due to the tert-butyl and phenyl groups.

Reaction of the ligand Ph_2PCH_2NHp-tol with $(COD)PtCl_2$ gave a mixture of two products, as determined by $^{31}P-\{^1H\}$ nmr spectroscopy. It is probable that the signal observed at δ +5.9 ppm (see Table 6), J_{Pt-P} = 3693 Hz is due to complex *(180)*, cis-$[Pt(Ph_2PCH_2NHp\text{-tol})_2Cl_2]$, since the chemical shift and size of J_{Pt-P} are similar to those

found in complex *(179)*. The second signal at δ -6.1 ppm (J_{Pt-P} = 3417 Hz), see Table 6, is due to the chelated complex *(181)*, which was identified by comparison of its $^{31}P-\{^{1}H\}$ nmr spectrum with that of an independently prepared sample. This reaction involved the preparation of complex *(181)* from $(COD)PtCl_2$ and $Ph_2PCH_2N(p\text{-}tol)CH_2PPh_2$.

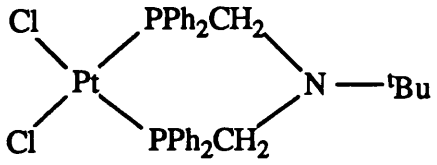


(181)

The $^{31}P-\{^{1}H\}$ nmr spectrum of *(181)* displays one signal at δ -6.1 ppm, J_{Pt-P} = 3417 Hz. The coupling constant indicates that the phosphine ligands are in a mutually cis configuration. The magnitude of J_{Pt-P} for complex *(181)*, which is smaller than that displayed for complex *(180)*, is typical for phosphorus-containing ligands in this type of six-membered chelate ring.[148] The ^{1}H nmr spectrum (Table 6) displays a broad multiplet, due to the methylene protons, and a multiplet due to the phenyl groups. A singlet at δ 5.2 ppm also indicates the presence of two molecules of dichloromethane of crystallisation. The simultaneous formation of cis-$[Pt\{Ph_2PCH_2NH(p\text{-}tol)\}_2Cl_2]$ *(180)* and cis-$[\overline{Pt\{Ph_2PCH_2N(p\text{-}tol)CH_2PPh_2\}}Cl_2]$ *(181)* is in contrast to the previous reaction, where R = ^{t}Bu when only the non-chelate complex cis-$[Pt(Ph_2PCH_2NH^{t}Bu)_2Cl_2]$ *(179)* is formed. The difference in reactivity of the two ligands may lie in the ability of the amine groups to act as leaving groups. The mechanism may go *via* nucleophilic attack of one co-ordinated ligand onto the amine of the second co-ordinated ligand. The electron-donating properties of the tert-butyl group, compared to p-tolyl, may make the t-butyl ligand more susceptible to this type of attack by a second ligand.

3.2.2 Reaction of complex *(179)* with formaldehyde

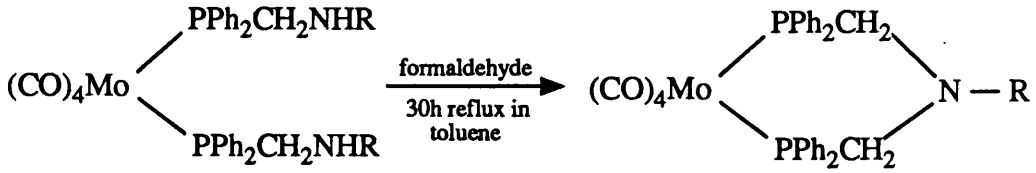
When complex *(179)*, cis-$[PtCl_2(Ph_2PCH_2NH^{t}Bu)_2$ was refluxed with formaldehyde for 24 hours, the chelate complex *(182)* was formed, having a $^{31}P-\{^{1}H\}$ nmr chemical shift of δ -5.9 ppm, J_{Pt-P} = 3427 Hz (Table 6).



(182)

The identity of *(182)* was confirmed by its independent preparation from the reaction of $(COD)PtCl_2$ with one equivalent of $Ph_2PCH_2N(^tBu)CH_2PPh_2$. The magnitude of J_{Pt-P} indicates that the phosphorus atoms are in a mutually cis arrangement, which is to be expected since it would not be possible for a six-membered ring to span the trans positions. The ^1H nmr spectrum of *(182)* exhibits multiplets at δ 3.4 ppm due to the methylene group and at δ 8.0-7.2 ppm due to the phenyl groups. There are also two singlets at δ 0.8 ppm, corresponding to the t-butyl protons and at δ 5.2 ppm due to a molecule of dichloromethane of crystallisation.

The differences in the $^{31}P-\{^1H\}$ nmr chemical shifts between the chelated and non-chelated complexes where R = ^{t}Bu and also where R = p-tol is in the region of 11-12 ppm. This compares well with the chemical shift differences between the analogous molybdenum complexes prepared by Healey,[123] Scheme 51. The mechanism of these reactions are uncertain, however, the carbonyl group of the formaldehyde may reduce the charge on one of the amine groups of complex *(179)*, making it more susceptible to attack by the amine of the other co-ordinated ligand.



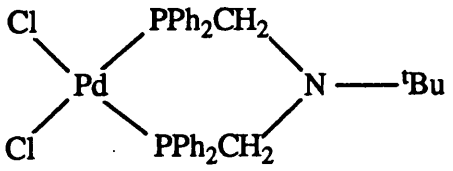
R=^{t}Bu; p-tol

Scheme 51

3.2.3 Reaction of $(COD)PdCl_2$ with $Ph_2PCH_2N^tBuCH_2PPh_2$

Reaction of the ligand $Ph_2PCH_2N^tBuCH_2PPh_2$ with $(COD)PdCl_2$ resulted in the formation of a bright yellow, insoluble complex which is tentatively proposed to be complex *(183)*.

The structure of complex *(183)* was assigned from its $^{31}P-\{^1H\}$ nmr spectrum



(183)

Table 6), which exhibits a single resonance at δ +11.3 ppm. The analogous complex $[\overline{Pd(Ph_2PCH_2NPhCH_2PPh_2)}Cl_2$ prepared by Balch *et al.*[112] has a similar $^{31}P-\{^1H\}$ nmr chemical shift (+10.4 ppm). However, complex *(183)* was not characterized fully due to its low solubility in organic solvents, making purification difficult, hence the reason why the elemental analysis is somewhat inaccurate. The ^1H nmr spectrum was obtained in a dilute solution of $CDCl_3$. The spectrum exhibits multiplets at δ 7.3-8.1 ppm, corresponding to the phenyl protons, and at δ 3.4 ppm corresponding to the methylene protons. A singlet at δ 0.8 ppm is also observed, which has been assigned to the t-butyl group.

3.2.4 Reaction of Pt and Pd with Ph_2PCH_2OH

The reaction of $(COD)PtCl_2$ with Ph_2PCH_2OH resulted in the formation of complex *(184)* cis-$[PtCl_2(Ph_2PCH_2OH)_2$. The $^{31}P-\{^1H\}$ nmr spectrum (Table 6) displays a singlet at δ +7.3 ppm, with corresponding platinum satellites having a J_{Pt-P} of 3687 Hz. As with complex *(179)*, the magnitude of the coupling constant indicates that the phosphine ligands are trans to chlorine, in a mutually cis configuration. The ^1H nmr spectrum (Table 6) exhibits a multiplet due to the phenyl protons at δ 7.6-7.0 ppm and a broad, unresolved multiplet at δ 4.5 ppm, which seems to display broad platinum satellites and is assigned to the methylene protons. A broad signal at δ 3.9 ppm, corresponding to the hydroxyl proton, is also displayed.

Crystals suitable for X-ray structure analysis were grown by diffusion of petroleum ether into a dichloromethane solution of complex *(184)*. A single crystal X-ray diffraction study of complex *(184)* was carried out to establish the molecular geometry and nature of bonding in the complex. A summary of important bond lengths and angles is given in Table 5. The molecular structure of *(184)* is illustrated in Fig. 3, together with the crystallographic numbering system.

The geometry around the platinum is effectively square planar. The molecule exists as the

TABLE 5

Selected Bond Lengths and Angles for the Complex cis-$[PtCl_2(Ph_2PCH_2OH)_2]$ *(184)*

Bond Length	(Å)	Bond Angle	(°)
Pt – P(1)	2.254 (2)	P(2) – Pt – P(1)	96.8 (1)
Pt – P(2)	2.248 (2)	Cl(2) – Pt – Cl(1)	86.3 (1)
Pt – Cl(1)	2.373 (2)	Cl(2) – Pt – P(2)	91.1 (1)
Pt – Cl(2)	2.357 (3)	Cl(1) – Pt – P(1)	85.9 (1)
P(1) – C(1)	1.865 (11)	C(1) – P(1) – Pt	109.7 (4)
P(2) – C(2)	1.860 (10)	C(2) – P(2) – Pt	115.5 (4)
C(1) – O(1)	1.389 (15)	P(1) – C(1) – O(1)	108.7 (7)
C(2) – O(2)	1.446 (17)	P(2) – C(2) – O(2)	112.7 (8)

Estimated standard deviations are given in parentheses

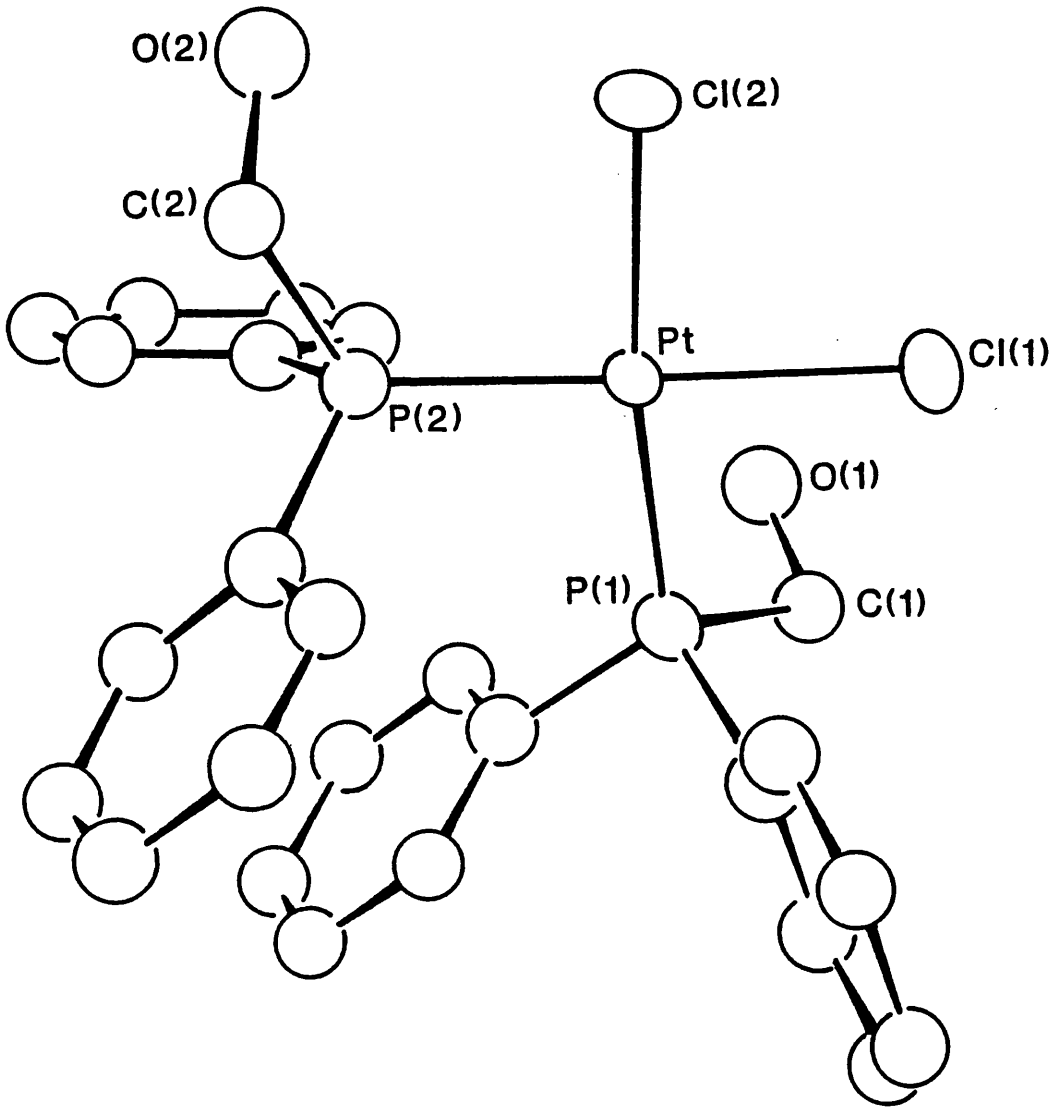


Figure 3(a)
Molecular Structure of cis-$[Pt(Ph_2PCH_2OH)_2Cl_2]$ *(184)*.

cis-isomer with the diphenyl hydroxymethyl phosphine ligands trans to the chloride ligands. The Pt-Cl and Pt-P bond lengths are of a similar magnitude to those reported for the complex cis-$[PtCl_2(PPh_3)_2]$,[145] which has average Pt-Cl and Pt-P bond lengths of 2.345(16) Å and 2.258(10) Å respectively. The Cl-Pt-Cl and P-Pt-P bond angles are slightly smaller than those recorded for cis-$[PtCl_2(PPh_3)_2]$ of 87.1(1)° and 97.8(1)° respectively.

The orientation of the complex in Fig. 3 suggests a possible interaction between the platinum and O(1). However, the non-bonded distance for O(1)-Pt (3.484 Å) is too large for such an interaction. Similarly, the diagram suggests a possible six-membered, hydrogen-bonded ring through the hydrogen of O(2) to Cl(2). Unfortunately, the hydrogens on O(1) and O(2) are not visible, which makes hydrogen bonding difficult to detect. However, the O(2)-Cl(2) non-bonded distance of 3.026 Å, which is similar to the O(1)-Cl(1) distance (3.212 Å), does not suggest any interaction.

The reaction of $(COD)PdCl_2$ with Ph_2PCH_2OH resulted in the formation of both cis and trans isomers of $[PdCl_2(Ph_2PCH_2OH)_2]$ *(185)*. The $^{31}P-\{^1H\}$ nmr spectrum (Table 6) displays two singlets at δ +28.4 ppm and +13.1 ppm, the signal at δ +28.4 ppm, assigned to the cis isomer, being almost four times the intensity of the signal at δ +13.1 ppm, assigned to the trans isomer. The ^1H nmr spectrum exhibits a multiplet at δ 7.6-7.0 ppm assigned to the phenyl protons, and two broad signals at δ 4.5 and 4.4 ppm. These two signals are assigned to the methylene protons, one singlet corresponding to the trans-isomer and the other to the cis. In total, the two singlets integrate to two protons with respect to the ten protons of the phenyl groups.

3.2.5 Reactivity of Co-ordinated Ligands

3.2.5.1 Towards Formation of Bimetallic Complexes

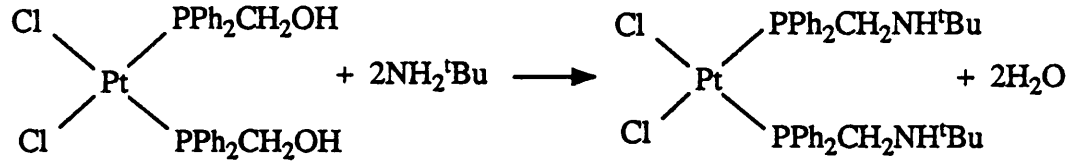
As mentioned in Section 3.1, the phosphine synthesis, Scheme 52, occurs rapidly at room temperature in diethylether solvent. This synthesis is based on the methods of Märkl[123] and

$$Ph_2PCH_2OH + NH_2{}^tBu \longrightarrow Ph_2PCH_2NH{}^tBu + H_2O$$

Scheme 52

Hoye[124-125] (see Section 2.1). Reaction of complex *(184)*, cis-$[PtCl_2(Ph_2PCH_2OH)_2]$ and

t-butylamine led to the formation of complex *(179)*, Scheme 53.

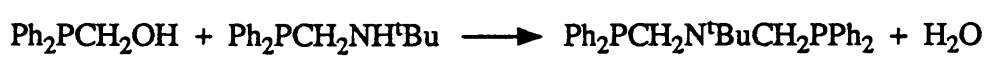


(184) *(179)*

Scheme 53

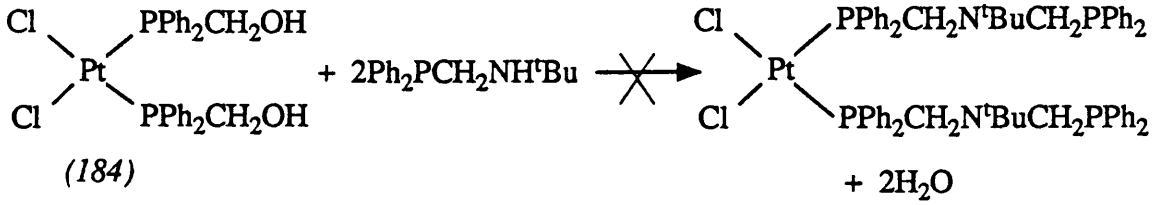
However, the reaction was less rapid than for the unco-ordinated ligand, Scheme 52, taking approximately 3h to go to completion. Complex *(179)* was identified on the basis of its $^{31}P-\{^{1}H\}$ nmr spectrum. The decreased rate of reaction of the co-ordinated Ph_2PCH_2OH compared to the unco-ordinated ligand is probably due to reduction of electron density on the OH group, on co-ordination of phosphorus.

As discussed previously, it was envisaged that this type of ligand may be used to link two different metal centres to form bimetallic complexes. The first strategy used was to apply the ligand synthesis, Scheme 54, to co-ordinated ligands. The ligand synthesis was developed by Healey[122] as an extension of the reactions of Hoye[124,125] and Märkl.[123] It was envisaged that



Scheme 54

a reaction such as that shown in Scheme 55 might occur when complex *(184)* was reacted with $Ph_2PCH_2NH^tBu$. It would then be possible to co-ordinate another metal to the unco-

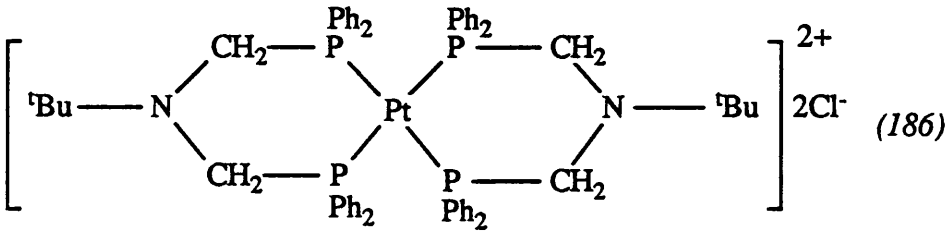


(184)

Scheme 55

ordinated phosphine groups of the ligand. However, this reaction did not give the predicted products. Reaction of complex *(184)*, cis-$[PtCl_2(Ph_2PCH_2OH)_2]$ with $Ph_2PCH_2NH^tBu$ led to the formation of complex *(186)*, cis-$[Pt(Ph_2PCH_2N^tBuCH_2PPh_2)_2]^{2+}$ $2Cl^-$. Presumably,

displacement of the chloride ions by the phosphine groups confers greater stability to the complex by way of the chelate effect. The condensation reaction may occur before or after this replacement of the chloride ions by the phosphine ligands. Complex *(186)* is insoluble in chloroform but slightly soluble in dichloromethane. The $^{31}P-\{^{1}H\}$ nmr spectrum (Table 6)



(186)

displays a signal at δ -15.1 ppm with platinum satellites, J_{Pt-P} = 2246 Hz. This coupling constant is typical of a phosphorus co-ordinated <u>trans</u> to another phosphorus atom. The chemical shift is typical for this type of chelate complex.

The ^{1}H nmr spectrum (Table 6) recorded in CD_2Cl_2, exhibits a multiplet in the region δ 8.0-7.0 ppm, assigned to the phenyl protons. In addition, a triplet at δ 4.3 ppm (J = 14 Hz) is also displayed. The ratio of the integration of the triplet is 1:4:1, suggesting that the triplet is observed due to coupling to platinum rather than phosphorus. A singlet at δ 0.8 ppm due to the t-butyl protons is also observed.

Due to the competitive co-ordination of phosphorus over the chloride ions in the previous reaction, an alternative approach to forming a bimetallic complex was considered. It was envisaged that reaction of two complexes [*(179)* and *(184)*] both having co-ordinated ligands, would result in a condensation reaction as described in Scheme 56. However, reaction of complexes *(179)* and *(184)* did not proceed as predicted. $^{31}P-\{^{1}H\}$ nmr spectroscopy was used to monitor the reaction and, as the reaction seemed to be proceeding slowly, different solvents, with progressively higher boiling points were used in order to increase the rate of reaction by refluxing at higher temperatures. The final product of the reaction was identified by $^{31}P-\{^{1}H\}$ nmr to be complex *(182)*, <u>cis</u>-$[\overline{PtCl_2(Ph_2PCH_2N^tBuCH_2PPh_2)}]$, spectrum (C) (Fig. 4).

The course of the reaction, as seen by $^{31}P-\{^{1}H\}$ nmr spectroscopy is described in Fig. 4. Spectrum (A) represents the $^{31}P-\{^{1}H\}$ nmr spectrum of the starting materials, complexes

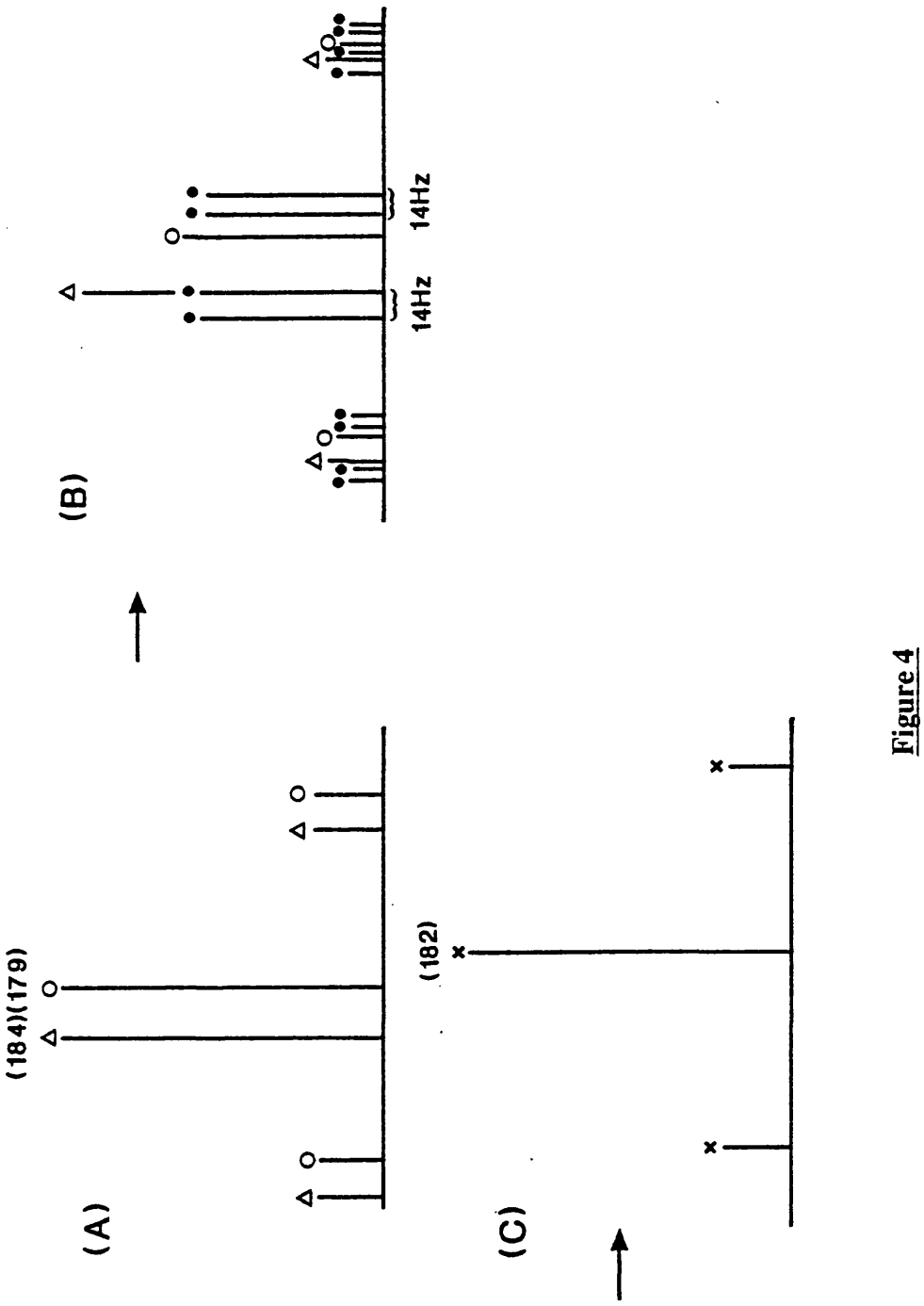
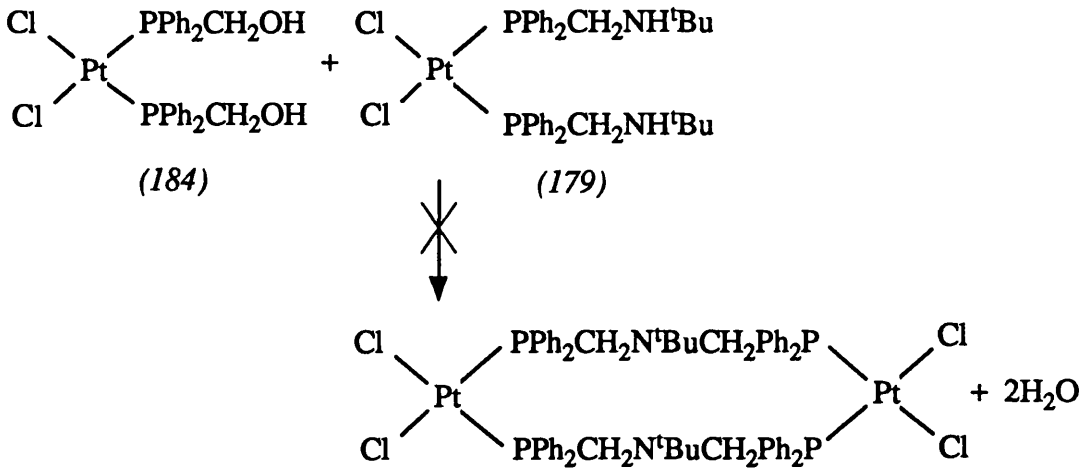
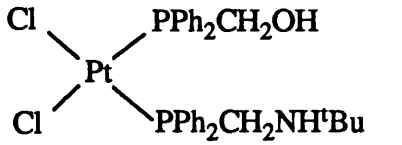


Figure 4



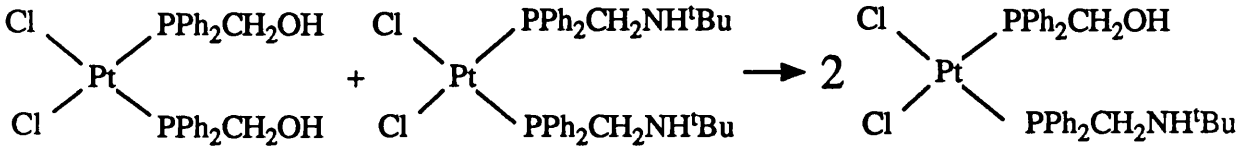
Scheme 56

(179) and *(184)*; spectrum (B) represents the $^{31}P-\{^1H\}$ nmr spectrum of the reaction after refluxing for 4 days, and spectrum (C) represents the $^{31}P-\{^1H\}$ nmr spectrum of the complex *(182)*, formed after refluxing at a higher temperature for a further 4h. In spectrum (A), complexes *(184)* and *(179)* can be identified, with their corresponding platinum satellites. After refluxing for 4 days in dichloromethane and then THF, the reaction mixture displayed the $^{31}P-\{^1H\}$ nmr spectrum (B). In this spectrum, both complexes *(184)* and *(179)* can be identified. However, there are also signals present which are not due to complexes *(179)* or *(184)*. A possible explanation of this spectrum is that the signals present, other than those assigned to complexes *(179)* and *(184)*, are two doublets and their corresponding platinum satellites. These doublets, which have been marked with a dark circle, ●, in spectrum (B), both have a $J_{(P-P)}$ of approximately 14 Hz. The overlapping of one signal from one of the doublets with the signal assigned to complex *(184)* could account for the greater intensity of this signal. Also, in a system of the type $M\begin{smallmatrix}P\\P\end{smallmatrix}$, the AB spectrum observed will have inner lines which are more intense than the outer lines. Therefore, it is suggested that spectrum (B) consists of three superimposed spectra from three different complexes, complex *(184)*, complex *(179)* and an unidentified complex, which displays two doublets and their corresponding platinum satellites. A possible structure for this latter complex is complex *(187)*. This structure would be consistent with a possible mechanism for this reaction, where one ligand, from each of complexes *(179)* and *(184)*, co-proportionate to give complex *(187)*.

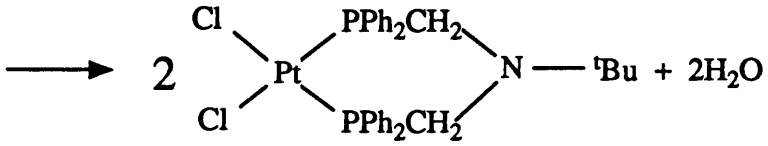


(187)

After further refluxing, a condensation reaction occurs, to give complex *(182)*, spectrum (C). Thus, the overall reaction is proposed to be that described in Scheme 57.



(184) *(179)* *(187)*



(182)

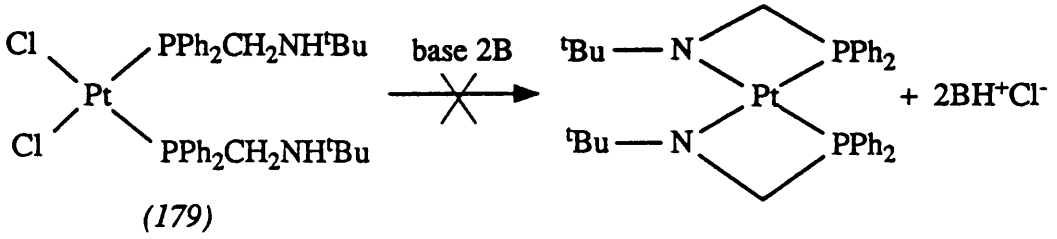
Scheme 57

It is evident, however, from both reactions described above that complexes of this type show a reluctance to form bimetallic species. In both approaches considered, the mononuclear complexes have preferred to rearrange to form species incorporating six-membered chelate rings. This is hardly surprising considering the stability that a six-membered chelate ring confers on a system. These results are also consistent with work done by Healey,[122] where reaction of molybdenum complexes of the type $(CO)_4Mo(PCX)_2$ (where X is NHR or OH) resulted in the formation of chelate complexes rather than bimetallic species.

3.2.5.2 Reactivity of Co-ordinated Ligands: Deprotonation Reactions

Although complexes containing four-membered chelate rings are not as stable as those containing five-membered rings, dppm does form chelate complexes in some circumstances, see Section 3.1. It was thought possible that the ligand $Ph_2PCH_2NH^tBu$ may also form

chelate complexes, if the secondary amine part of the ligand was deprotonated resulting in the formation of a metal-amide bond. Various reactions were therefore attempted with complex *(179)*, cis-$[PtCl_2(Ph_2PCH_2NH^tBu)_2]$, in order to deprotonate the amine, cause displacement of the chloride ions and so form a four-membered chelate ring, incorporating a platinum-amide bond, Scheme 58. However, attempts to deprotonate complex *(179)* using triethylamine, sodium methoxide and n-butyllithium all failed to produce any identifiable



(179)

Scheme 58

products. The $^{31}P-\{^1H\}$ nmr spectra of these reactions displayed a very large number of peaks and it was not possible to identify any of these. Reaction of complex *(179)* with sodium hydroxide produced a single peak in the $^{31}P-\{^1H\}$ nmr spectrum at δ +29.5 ppm, which had no platinum satellites. The phosphorus-containing product was not identified but is thought not to contain platinum.

3.3 EXPERIMENTAL

Experimental conditions were as for Chapter 2. Ligands were prepared from methods developed by Healey.[122] Platinum and palladium salts were on loan from Johnson Matthey. $(COD)PtCl_2$,[146] $(COD)PdCl_2$,[147] and $[Na\{N(SiMe_3)_2\}]$[148] were prepared by literature methods. Triethylamine, sodium methoxide, n-butyllithium and aqueous formaldehyde were used as supplied (Aldrich).

3.3.1 Reaction of $(COD)PtCl_2$ with $Ph_2PCH_2NH^tBu$

To a 0.99 mg solution of $Ph_2PCH_2NH^tBu$ (4.09 cm^3, 4.05 mmol) in toluene was added a solution of $(COD)PtCl_2$ (750 mg, 2.0 mmol) in dichloromethane (40 cm^3). The reaction mixture was stirred for 0.5h at room temperature after which time the solvents were removed

under vacuum to give a pale yellow solid. Crystallisation of the solid from dichloromethane and petroleum ether afforded pale yellow crystals of cis-$[Pt(Ph_2PCH_2NH^tBu)_2Cl_2]$ *(179)* (1.11g, 68.6%). The complex was identified on the basis of its ^1H, $^{31}P-\{^1H\}$ and $^{13}C-\{^1H\}$ nmr spectra (see Table 6) and its microanalysis (see Table 7).

3.3.2 Reaction of $(COD)PtCl_2$ with Ph_2PCH_2NH p-tol

To a solution of Ph_2PCH_2NH p-tol (461 mg, 1.51 mmol) in dichloromethane (40 cm^3) was added a solution of $(COD)PtCl_2$ (221 mg, 0.59 mmol) in dichloromethane (25 cm^3). The reaction mixture was stirred for 1h at room temperature, after which time the solvent was removed under vacuum affording a white solid. The solid consisted of a mixture of two complexes, as determined by $^{31}P-\{^1H\}$ nmr spectroscopy, cis-$[Pt(Ph_2PCH_2NH$ p-tol$)_2Cl_2]$ *(180)* and $[\overline{Pt(Ph_2PCH_2N(p\text{-tol})CH_2PPh_2)}Cl_2]$ *(181)* (See Table 6).

3.3.3 Reaction of $(COD)PtCl_2$ with $Ph_2PCH_2N(p\text{-tol})CH_2PPh_2$

To a solution of $(COD)PtCl_2$ (100 mg, 0.27 mmol) in dichloromethane (15 cm^3) was added a solution of $Ph_2PCH_2N(p\text{-tol})CH_2PPh_2$ (140 mg, 0.28 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 0.5h at room temperature, after which time the solvent was removed under vacuum giving a white solid. The solid was crystallised from dichloromethane and petroleum ether yielding white crystals of cis-$[\overline{Pt(Ph_2PCH_2N(p\text{-tol})CH_2PPh_2)}Cl_2]$ *(181)* with 2 molecules of CH_2Cl_2 of crystallisation (153 mg, 73.6%). The complex was identified on the basis of its $^{31}P-\{^1H\}$, ^1H nmr spectra (Table 6) and microanalysis (see Table 7).

3.3.4 Reaction of cis-$[Pt(Ph_2PCH_2NH^tBu)_2Cl_2]$ with aqueous formaldehyde

To a solution of cis-$[Pt(Ph_2PCH_2NH^tBu)_2Cl_2]$ (100 mg, 0.12 mmol) in toluene (30 cm^3) was added an aqueous solution (40%) of formaldehyde (0.044 cm^3, 0.58 mmol). The reaction mixture was refluxed for 24h at 115°C, after which time the solvents were removed under vacuum giving a pale yellow solid. $^{31}P-\{^1H\}$ nmr spectroscopy (Table 6) determined the presence of a single complex, cis-$[\overline{Pt(Ph_2PCH_2N(^tBu)CH_2PPh_2)}Cl_2]$ *(182)* which was not

isolated and was identified by comparison with the sample prepared by direct reaction of (COD)$PtCl_2$ with $Ph_2PCH_2NBu^tCH_2PPh_2$ (see Section 3.3.5).

3.3.5 Reaction of (COD)$PtCl_2$ with $Ph_2PCH_2N(^tBu)CH_2PPh_2$

To a solution of (COD)$PtCl_2$ (200 mg, 0.54 mmol) in dichloromethane (25 cm^3) was added a solution of $Ph_2PCH_2N(^tBu)CH_2PPh_2$ (251 mg, 0.54 mmol) in dichloromethane (30 cm^3). The reaction mixture was stirred for 1h after which time the solvent was removed under vacuum giving a white solid. The solid was crystallised from dichloromethane and petroleum ether affording white crystals of cis-[$Pt(Ph_2PCH_2N(^tBu)CH_2PPh_2)Cl_2$] *(182)* with 1 molecule of CH_2Cl_2 of crystallisation (313 mg, 78.8%) which was identified on the basis of its $^{31}P-\{^1H\}$ and ^1H nmr spectra (see Table 6) and its microanalysis (see Table 7).

3.3.6 Reaction of (COD)$PdCl_2$ with $Ph_2PCH_2N(^tBu)CH_2PPh_2$

To a solution of (COD)$PdCl_2$ (200 mg, 0.6 mmol) in dichloromethane (40 cm^3) was added a solution of $Ph_2PCH_2N(^tBu)CH_2PPh_2$ (282 mg, 0.6 mmol) in dichloromethane (30 cm^3). The mixture was stirred for 4h after which time a bright yellow precipitate cis-[$\overline{Pd(Ph_2PCH_2N(^tBu)CH_2PPh_2)}Cl_2$] *(183)* (298 mg, 76.8%) had formed which was filtered off and washed with dichloromethane. The complex was identified on the basis of its $^{31}P-\{^1H\}$ and ^1H nmr spectra (Table 6) and microanalysis (Table 7).

3.3.7 Reaction of (COD)$PtCl_2$ with Ph_2PCH_2OH

To a solution of Ph_2PCH_2OH (819 mg, 3.79 mmol) in dichloromethane (50 cm^3) was added a solution of (COD)$PtCl_2$ (650 mg, 1.79 mmol) in dichloromethane (50 cm^3). The mixture was stirred for 0.5h at room temperature, after which time the solvent was removed under vacuum giving a white solid. The solid was crystallised from dichloromethane and petroleum ether to give white crystals of cis-[$Pt(Ph_2PCH_2OH)_2Cl_2$] *(184)* (1.6 g, 84.8%). The complex was identified on the basis of its $^{31}P-\{^1H\}$ and ^1H nmr spectra (see Table 6) and its microanalysis (see Table 7).

3.3.8 Reaction of $(COD)PdCl_2$ with Ph_2PCH_2OH

To a solution of Ph_2PCH_2OH (366 mg, 1.54 mmol) in dichloromethane (30 cm^3) was added a solution of $(COD)PdCl_2$ (285 mg, 0.91 mmol) in dichloromethane (30 cm^3). The mixture was stirred for 3h at room temperature, after which time the solvent was removed under vacuum giving a bright yellow solid. The solid was crystallised from dichloromethane and petroleum ether affording bright yellow crystals of $[Pd(Ph_2PCH_2OH)_2Cl_2]$ *(185)* (460 mg, 82.9%). The complex was identified on the basis of its $^{31}P-\{^1H\}$ and ^1H nmr spectra (see Table 6) and its microanalysis (see Table 7).

3.3.9 Reaction of cis-$[Pt(Ph_2PCH_2OH)_2Cl_2]$ and $NH_2{}^tBu$

To a solution of t-butylamine (0.07 cm^3, 0.60 mmol) in dichloromethane (25 cm^3) was added a solution of cis-$[Pt(Ph_2PCH_2OH)_2Cl_2]$ (100 mg, 0.15 mmol) in dichloromethane (40 cm^3). The mixture was stirred for 3h at room temperature, after which time the solvent was removed under vacuum affording a pale yellow solid, cis-$[Pt(Ph_2PCH_2NH^tBu)_2Cl_2]$ *(179)*. The complex was not isolated and was identified on the basis of its $^{31}P-\{^1H\}$ nmr spectrum (see Table 6) by comparison with the sample prepared by direct reaction of $(COD)PtCl_2$ and $Ph_2PCH_2NH^tBu$.

3.3.10 Reaction of cis-$[Pt(Ph_2PCH_2OH)_2Cl_2]$ with $Ph_2PCH_2NH^tBu$

To a solution of $Ph_2PCH_2NH^tBu$ (194 mg, 0.72 mmol) in dichloromethane (20 cm^3) was added a solution of cis-$[Pt(Ph_2PCH_2OH)_2Cl_2]$ (250 mg, 0.36 mmol) in dichloromethane (50 cm^3). The mixture was stirred for 3 days at room temperature, after which time a white precipitate had formed. The precipitate was filtered and crystallised from a large volume of dichloromethane, giving white crystals of $[\overline{Pt(Ph_2PCH_2N(^tBu)CH_2PPh_2)_2}]Cl_2$ *(186)* with 2 molecules of dichloromethane of crystallisation (371 mg, 85.5%). The complex was identified on the basis of its $^{31}P-\{^1H\}$ and ^1H nmr spectra (Table 6) and its microanalysis (see Table 7).

3.3.11 Reaction of cis-[Pt(Ph_2PCH_2OH)$_2Cl_2$] with cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$]

To a solution of cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$] (202 mg, 0.25 mmol) in dichloromethane (30 cm^3) was added a solution of cis-[Pt(Ph_2PCH_2OH)$_2Cl_2$] (159 mg, 0.25 mmol) in dichloromethane (30 cm^3). The mixture was refluxed for 2 days in dichloromethane (40°C), for a further 2 days in THF (67°C) and for 4h in toluene (111°C), after which time the solvent was removed under vacuum giving an off-white solid, cis-[Pt($Ph_2PCH_2N(^tBu)CH_2PPh_2$)$Cl_2$] *(182)*. The complex was not isolated and was identified on the basis of its $^{31}P-\{^1H\}$ nmr spectrum, by comparison with the sample prepared in 3.3.5 above. The reaction was monitored at regular intervals by $^{31}P-\{^1H\}$ nmr spectroscopy - see Results and Discussion.

3.3.12 Deprotonation Reactions

A number of reagents were used to attempt deprotonation of cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$] *(179)*.

(i) Reaction of cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$] with Et_3N

To a solution of cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$] (427 mg, 0.70 mmol) in acetonitrile (50 cm^3) was added triethylamine (2 cm^3, 1.44 mmol). The mixture was refluxed for 3h at 90°C, after which time it was cooled to room temperature and the solvent removed under vacuum, giving a yellow solid. The $^{31}P-\{^1H\}$ nmr spectrum of the solid, when dissolved in dichloromethane, showed the presence of numerous phosphorus-containing products which were neither isolated nor identified.

(ii) Reaction of cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$] with sodium methoxide

To a solution of cis-[Pt($Ph_2PCH_2NH^tBu$)$_2Cl_2$] (120 mg, 0.15 mmol) in acetonitrile (40 cm^3) was added an excess of sodium methoxide (240 mg, 445 mmol). The mixture was stirred for 2 days at room temperature, after which time the excess sodium methoxide was filtered off and the solvent was removed under vacuum giving a yellow solid. The $^{31}P-\{^1H\}$ nmr spectrum of the solid showed the presence of numerous phosphorus-containing products which were neither isolated nor identified.

(iii) **Reaction of cis-[Pt($Ph_2PCH_2NH^tBu)_2Cl_2$] with n-butyllithium**

To a solution of cis-[Pt($Ph_2PCH_2NH^tBu)_2Cl_2$] (200 mg, 0.25 mmol) in THF (50 cm^3) at -78°C was added dropwise n-butyllithium (0.42 cm^3, 0.50 mmol). The mixture was stirred whilst warming to room temperature, after which time the solvent was removed under vacuum, yielding a yellow solid. The $^{31}P-\{^1H\}$ nmr spectrum of the solid showed the presence of numerous phosphorus-containing products which were neither isolated nor identified.

(iv) **Reaction of cis-[Pt($Ph_2PCH_2NH^tBu)_2Cl_2$] with sodium hydroxide**

To a solution of cis-[Pt($Ph_2PCH_2NH^tBu)_2Cl_2$] (140 mg, 0.175 mmol) in methanol (40 cm^3) was added an excess (~0.1g, 2.5 mmol) of sodium hydroxide pellets. The mixture was stirred for 3h, after which time the methanol was removed *in vacuo*. After a dichloromethane/water extraction, the product was dried with anhydrous magnesium sulphate to give an orange coloured solid. $^{31}P-\{^1H\}$ nmr spectrum; δ +29.5 ppm.

TABLE 6

^{31}P-{^{1}H} Nmr[a] and ^{1}H Nmr[b] Spectra of some Aminomethylphosphine Complexes of Pt and Pd

Complex	δ (^{31}P)/ppm	$J_{(Pt-P)}$/Hz	δ (^{1}H)
(179) *	+4.0	3711	1.00 (s, 9H, ^{t}Bu), 2.00 (s, br, 1H, NH), 3.50 (m, 2H, CH_2), 8.00 - 7.10 (m, 10H, Ph)
(180)	+5.9	3693	not isolated
(181) *	-6.1	3418	2.2 (s, 3H, Me), 3.9 (m, 4H, CH_2), 5.2 (s, 4H, CH_2Cl_2), 7.9 - 6.4 (m, 24H, Ph)
(182) *	-5.9	3428	0.8 (s, 9H, ^{t}Bu), 3.4 (m, 4H, CH_2), 5.2 (s, 2H, CH_2Cl_2), 8.0 - 7.2 (m, 20H, Ph)
(183)	+11.3	-	0.8 (s, 9H, ^{t}Bu), 3.4 (m, 4H, CH_2), 7.3 - 8.1 (m, 20H, Ph)
(184) *	+7.3	3687	3.9 (s, br, 1H, OH), 4.5 (m, 2H, CH_2), 7.6 - 7.0 (m, 10H, Ph)
(185)	+28.4 +13.1	- -	4.5 and 4.4 (s, br, 2H, CH_2), 7.6 - 7.0 (m, 10H, Ph)
(186) *	-15.1	2217	0.8 (s, 9H, ^{t}Bu), 4.3 [t, 4H, CH_2, J_{Pt-H} = 14 Hz], 8.0 - 7.0 (m, 20H, Ph)[c]

[a] in CH_2Cl_2; [b] in $CDCl_3$; [c] in CD_2Cl_2. * ^{1}H nmr spectra at 300 MHz.

TABLE 7

Elemental Analyses of some Aminomethylphosphine Complexes of Pt and Pd

Complex	Molecular Formula	Found (%)			Required (%)		
		C	H	N	C	H	N
(179)	$C_{34}H_{44}N_2Cl_2P_2Pt$	50.59	5.64	3.25	50.49	5.48	3.47
(181) **	$C_{35}H_{35}NCl_6P_2Pt$	45.23	3.43	1.52	44.76	3.76	1.49
(182) *	$C_{31}H_{35}NCl_4P_2Pt$	45.89	4.28	1.79	45.33	4.29	1.71
(184)	$C_{26}H_{26}Cl_2O_2P_2Pt$	44.49	3.66	< 0.2	44.71	3.75	0.00
(185)	$C_{26}H_{26}Cl_2O_2P_2Pd$	50.64	4.30	< 0.2	51.21	4.30	0.00
(186) **	$C_{62}H_{70}N_2Cl_6P_4Pt$	55.36	5.45	2.14	54.16	5.13	2.04

* Includes one molecule of dichloromethane of crystallisation
** " two molecules " " "

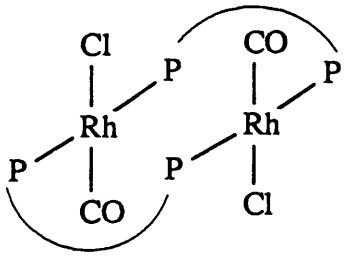
CHAPTER 4

Synthesis and Reactions of some Aminoalkylfunctionalised $Ph_2PCH_2CH_2NHR$ and $Ph_2PCH_2C(O)NHR$, Complexes of Pt and Pd

4.1 INTRODUCTION

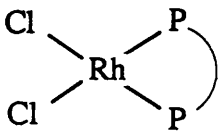
Transition metal complexes with tertiary phosphine ligands have been shown to act as versatile homogeneous catalysts.[1-3] Information concerning the stereochemistry of such complexes is easily obtained from $^{31}P-\{^{1}H\}$ nmr spectroscopy, particularly from metals which have magnetic nuclei, e.g. ^{195}Pt or ^{103}Rh. The catalytic properties of transition metal tertiary phosphine complexes can be accentuated by the use of chelating polyphosphine ligands. Ligands of this type provide more control over the number of phosphines co-ordinated to the metal than monophosphines and allow the stereochemistry to be predicted with greater ease.

The electronic and steric properties of polyphosphine ligands can be altered by systematically altering the substituents on phosphorus,[150] by varying the backbone length and by altering the number of donor atoms. For ligands of the type $Ph_2P(CH_2)_nPPh_2$ the tendency to chelate increases as the chain length decreases, up to a minimum when n = 2, when chelation is most likely. However, when n = 1 ligands tend to prefer bridging between two metals rather than chelation. For example, complexes of the type $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]$,[151] can either have a binuclear phosphine bridged structure, or a mononuclear structure with the phosphine chelated. The preferred structure depends on the size of n, see complexes *(188a-d)*.



(188a-c) where n = 1, 3, 4

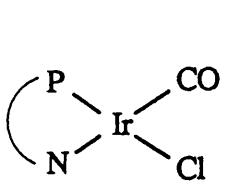
P P = $Ph_2P(CH_2)_nPPH_2$



(188d) where n = 2

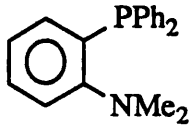
Hybrid functionalised phosphine ligands, containing both hard and soft donor atoms, can also chelate to a metal centre in a similar way. For example, the ligand $Ph_2PCH_2CH_2NMe_2$[59] forms a chelate complex with platinum. Hybrid ligands are thought to be useful as homogeneous catalysts since the hard donor atom is susceptible to displacement by substrate

molecules, but in the absence of the substrate the chelate effect stabilises the precursor. These ligands have become increasingly studied, partly due to their use in homogeneous catalysis. The iridium complexes *(189a-c)* have been shown to be more effective than $IrCl(CO)(PPh_3)_2$ for the isomerisation of hex-1-ene under hydrogenation conditions.[64]



P N = $Ph_2PCH_2CH_2NMe_2$ *(189a)*

P N = $Ph_2PCH_2CH_2CH_2NMe_2$ *(189b)*

P N = 

(189c)

Rhodium(I) complexes of the general formula $[Rh(Ph_2PCH_2CH_2SR)_2]^+$ (R = Ph, Et, Me) are found to catalyse air oxidation of terminal olefins to the corresponding methyl ketones, primary alcohols to acetals and secondary alcohols to ketones.[153] Also, a number of nickel chelate complexes, for example $[(\eta^3\text{-}C_8H_{13})\overline{Ni(Ph_2PCH_2COO)}]$, catalyse the oligomerization of ethylene (SHOP reaction).[109]

Hybrid ligands with a variety of hard donor functionalities and chelate bite angles have been prepared by Anderson *et al.*,[89] ligands *(190)* to *(193)*.

$Ph_2PCH_2CH_2OCH_3$ *(190)*

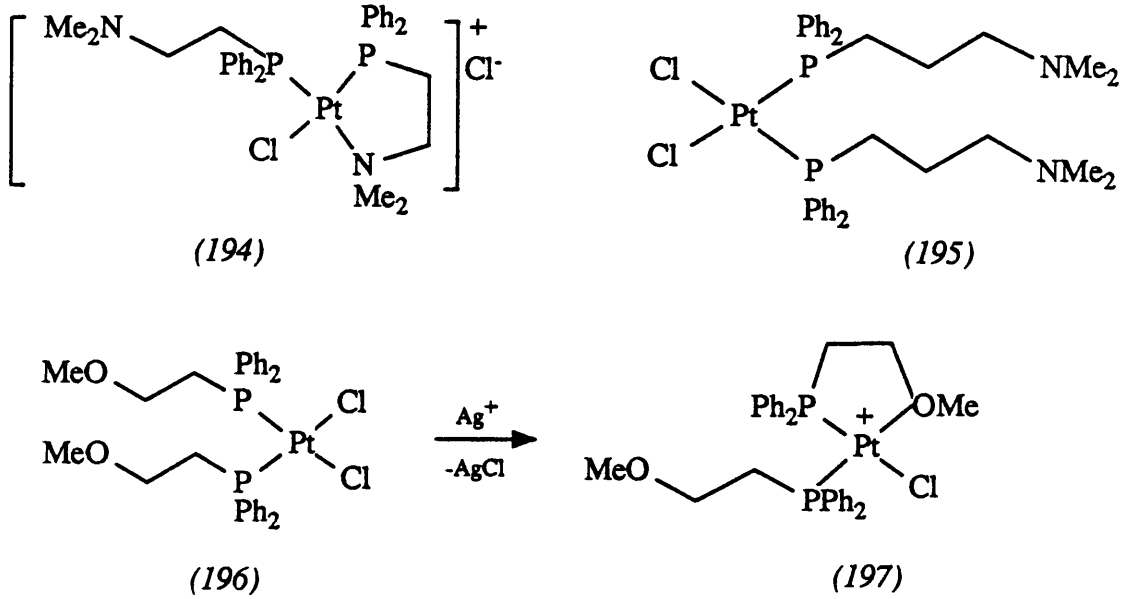
$Ph_2PCH_2CH_2N(CH_3)_2$ *(191)*

$Ph_2PCH_2CH_2CH_2N(CH_3)_2$ *(192)*

$Ph_2PCH_2CH_2SCH_3$ *(193)*

Ligand *(191)* reacts with $(COD)PtCl_2$ to form the chelate complex *(194)*, whereas ligand *(192)* does not chelate, forming complex *(195)*. Ligand *(192)* will only form a chelate complex with platinum on addition of silver tetrafluoroborate. Ligand *(190)* also forms chelate complexes, but only on the addition of silver perchlorate to complex *(196)*, Scheme 59.

Pringle *et al.*[95-99] have used the analogous hydroxyalkylphosphine ligands *(99)-(101)* to produce some interesting platinum and palladium alkoxide complexes. The three ligands behave slightly differently when co-ordinated to platinum, but all are found to be solvent

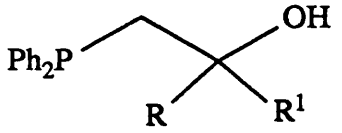


(194) *(195)*

(196) *(197)*

Scheme 59

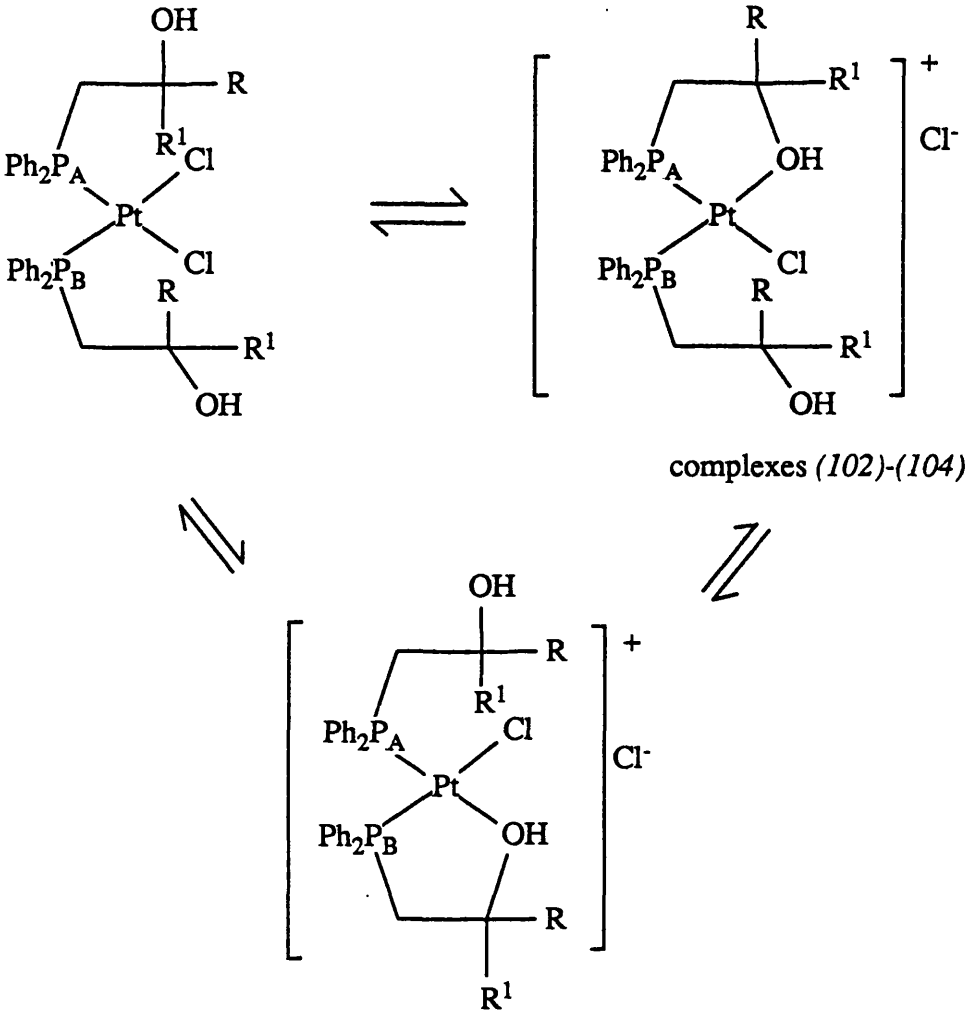
dependent. Pringle suggests that the fluxionality observed in solutions of the platinum complexes cis-$[Pt(Ph_2PCH_2CRR^1OH)_2Cl_2]$ *(102)-(104)*, formed with ligand *(99)-(101)*, may



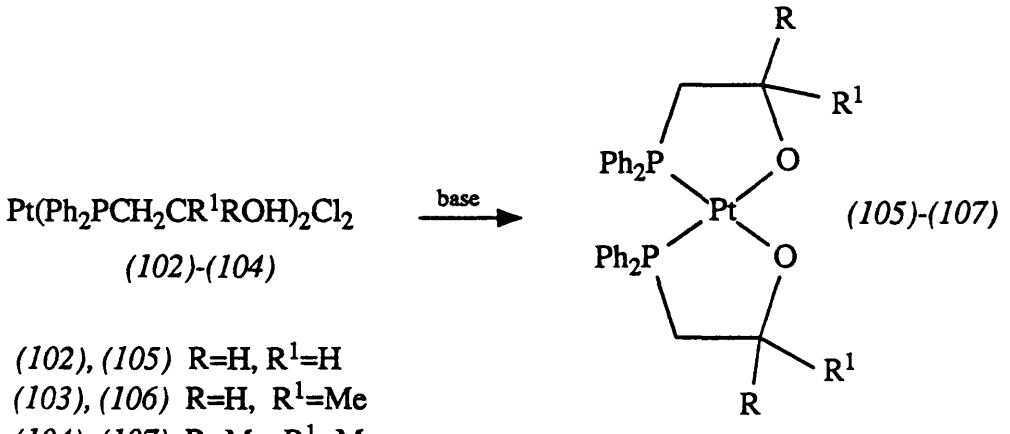
R=H, R^1=H *(99)*
R=H, R^1=Me *(100)*
R=Me, R^1=Me *(101)*

be due to rapid reversible chloride co-ordination, or intramolecular interchange of the OH donors, Scheme 60.

The ligand *(99)* reacted with $[PtCl_2(NC^tBu)_2]$ to give complex *(102)*, cis-$[Pt(Ph_2PCH_2CH_2OH)_2Cl_2]$, which in $CDCl_3$ solution at -50°C gave a sharp singlet with ^{195}Pt satellites in the $^{31}P-\{^1H\}$ nmr spectrum. This spectrum indicates that the neutral species, with both chlorides co-ordinated, exists in $CDCl_3$ solution at low temperatures. When complexes *(102)-(104)* were treated with base, Scheme 61, the chelate stabilised alkoxide complexes *(105)-(107)* were formed. These complexes can be reprotonated with dilute HCl to give complexes *(102)-(104)*. Pringle reports that these alkoxo complexes show that the Pt-O bonds are not inherently weak, but that the chelate ring stabilises the bond, by orientating the β-hydrogens away from the metal. This orientation of the β-hydrogens makes them kinetically stable towards β-hydrogen elimination. Pringle also reports[99] the formation of



Scheme 60

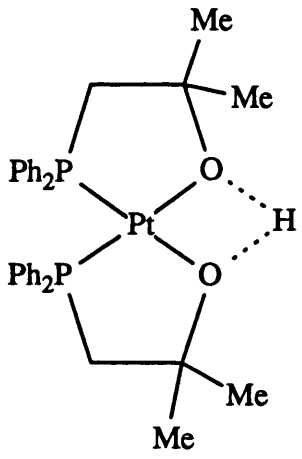


(102), (105) R=H, R^1=H
(103), (106) R=H, R^1=Me
(104), (107) R=Me, R^1=Me

Scheme 61

palladium alkoxo complexes, formed with ligands *(99)-(101)*.

In addition to the platinum alkoxo and alcohol complexes a mono-protonated species was also reported *(198)*. The complex was prepared from a mixture of the deprotonated alkoxo species *(107)* and the dication cis-$[Pt(Ph_2PCH_2CMe_2OH)_2]2ClO_4$. Pringle interprets the $^{31}P-\{^1H\}$ nmr spectrum as that of the mono-protonated species *(198)* formed from a rapid proton exchange equilibrium.



(198)

This Chapter describes the preparation of some aminoalkylphosphine ($Ph_2PCH_2CH_2NHR$ and $Ph_2PCH_2C(O)NHR$) complexes of platinum and palladium. The attempted deprotonation of these complexes, in a similar manner to the deprotonation of Pringle's cis-$[Pt(Ph_2PCH_2CR_2OH)_2Cl_2]$ complexes, will be described.

4.2 RESULTS AND DISCUSSION

4.2.1 Reaction of K_2PtCl_4 or $(COD)PtCl_2$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

Reaction of K_2PtCl_4 or $(COD)PtCl_2$ with two equivalents of *(166a)* affords cis-$[Pt(Ph_2PCH_2CH_2NH^tBu)(Ph_2PCH_2CH_2NH^tBu)Cl]Cl$ *(199)*, in which one ligand co-ordinates through just the phosphorus atom, while the other forms a five-membered chelate ring, co-ordinating through both the phosphorus and nitrogen atoms. Reaction of K_2PtCl_4 with one equivalent of *(166a)* led to a 50% yield of complex *(199)*. The co-ordination of the ligands is easily observed in the $^{31}P-\{^1H\}$ nmr spectrum of complex *(199)* (Table 9, Fig. 4). The spectrum shows two inequivalent phosphorus atoms as doublets (J_{P-P} = 20 Hz) at δ +32.7 and -2.2 ppm, each with ^{195}satellites. The signal to lower field

being the phosphorus incorporated into the five-membered chelate ring.[152,153] The Pt-P coupling constants of 3765 and 3203 Hz are as expected for phosphorus trans to chloride[141-143] and amine[71] respectively. Similar spectra have been observed for complexes obtained from the ligands $Ph_2PCH_2CH_2NMe_2$[89] and $Ph_2PCH_2CH_2NH(CH_2Ph)$,[90] although as discussed in Section 2.2, the latter actually contains $Ph_2PCH_2CH_2N(CH_2Ph)_2$.

Pringle *et al.*[95] have shown that the platinum species formed with the related hydroxyalkylphosphine, $Ph_2PCH_2CH_2OH$, was both solvent and temperature dependent. The $^{31}P-\{^1H\}$ nmr spectrum of *(199)* in $CDCl_3$ at room temperature displays two very broad signals, which may be indicative of an exchange process, Scheme 62, which is slow on the nmr time scale. The exchange process may be similar to that described by Pringle (Scheme 60) involving interchange of the NH donor and/or reversible chloride ion co-ordination. Complex *(199)* differs from the hydroxyalkylphosphine complex described by Pringle since the neutral species with both chlorides co-ordinated is not observed for *(199)*. Pringle isolated only the neutral complex, which was observed by $^{31}P-\{^1H\}$ nmr at -50°C. This is consistent with amines being better donors than alcohols and thus competing more effectively with chloride for one co-ordination site.

The ^1H nmr spectrum of complex *(199)* (see Table 11) in CD_3OD is very broad and signals due to the methylene protons are not well defined. However, two broad singlets, corresponding to the two inequivalent t-butyl substituents were observed, as well as signals due to the phenyl groups.

A single crystal X-ray diffraction study was carried out on complex *(199)*, which actually crystallised as the hydrochloride salt, i.e. the unco-ordinated nitrogen had been protonated by traces of acid, possibly from the dichloromethane solvent, and with one molecule of water of crystallisation. The molecular structure is illustrated in Fig. 6, together with the crystallographic numbering system. Selected bond lengths and angles for complex *(199)* are presented in Table 8. The geometry about the platinum atom is essentially square planar, although the P(1)-Pt-P(2) angle is greater than 90° (100.4°). The structure clearly shows the presence of one monodentate phosphine and one bidentate ligand. The bidentate ligand

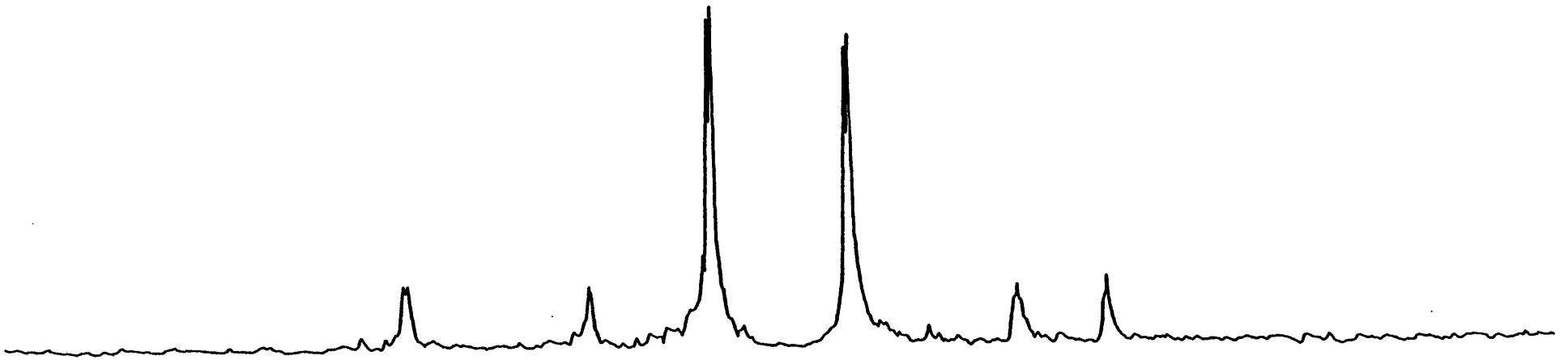


Figure 5
The $^{31}P-\{^{1}H\}$ nmr spectrum of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)Cl]Cl *(199)*.

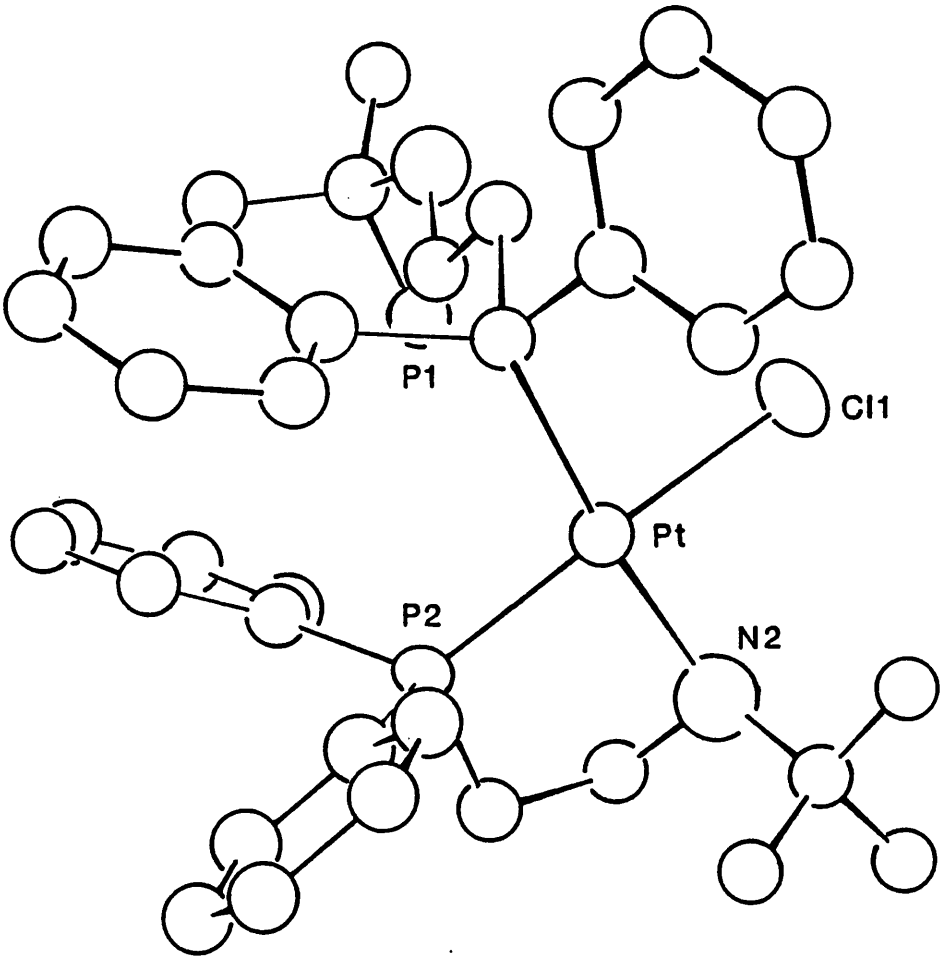


Figure 6

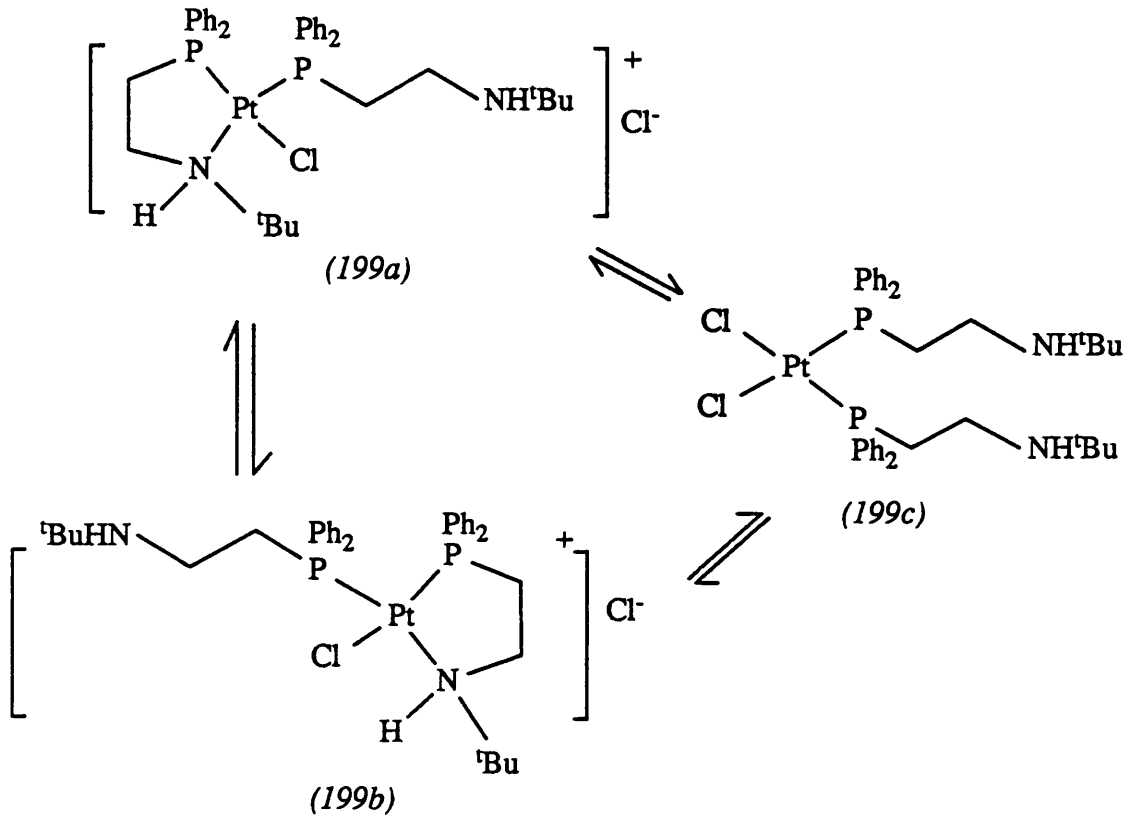
Molecular Structure of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)Cl]Cl *(199)*.

TABLE 8

Selected Bond Lengths and Bond Angles for the Complex cis-[Pt($Ph_2PCH_2CH_2NH^tBu$)($Ph_2PCH_2CH_2NH^tBu$•HCl)Cl]Cl•H_2O *(199)*

Bond Length	(Å)	Bond Angle	(°)
P(1) – Pt	2.260 (2)	P(2) – Pt – P(1)	100.4 (1)
Cl(1) – Pt	2.367 (3)	P(2) – Pt – N(2)	85.9 (3)
P(2) – Pt	2.226 (3)	P(1) – Pt – Cl(1)	87.0 (1)
N(2) – Pt	2.139 (8)	N(2) – Pt – Cl(1)	86.6 (3)
P(2) – C(3)	1.834 (11)	Pt – P(2) – C(3)	102.2 (4)
C(4) – C(3)	1.486 (18)	P(2) – C(3) – C(4)	111.1 (8)
C(4) – N(2)	1.526 (15)	C(3) – C(4) – N(2)	112.9 (10)
		C(4) – N(2) – Pt	107.2 (6)

Estimated standard deviations are given in parentheses.



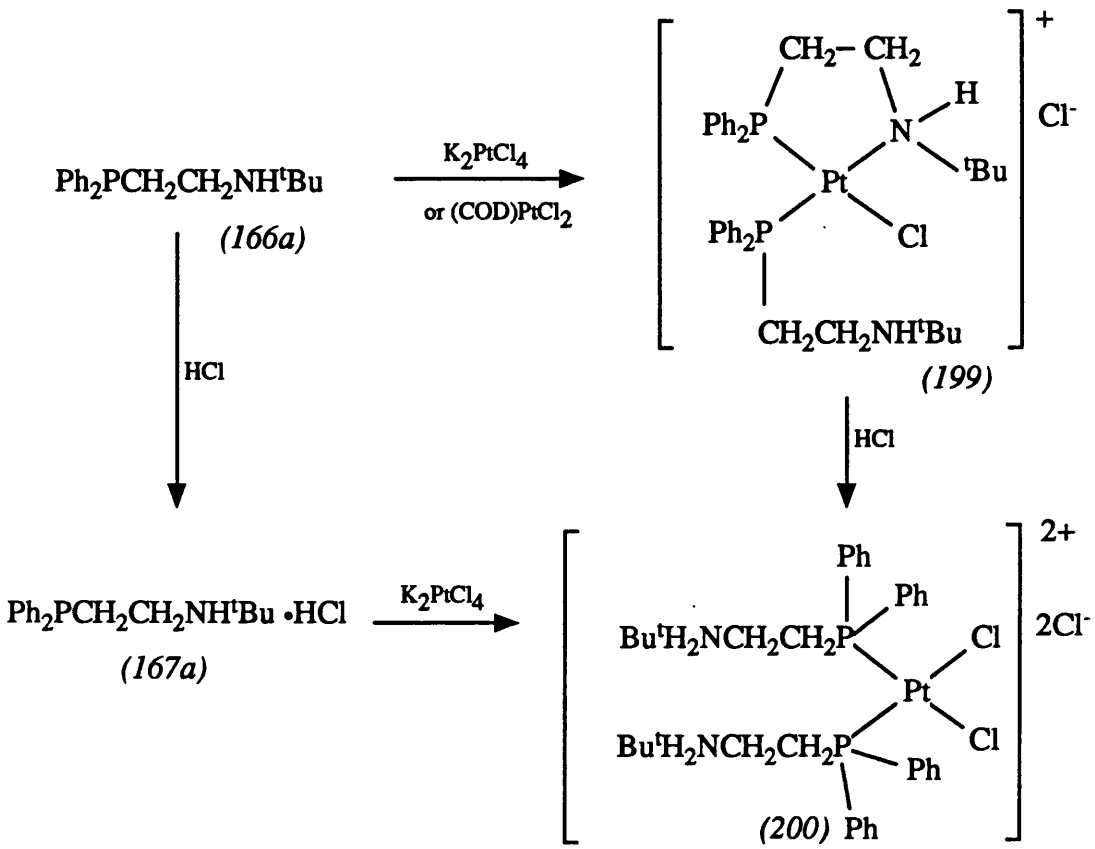
Scheme 62

co-ordinates to platinum in a five-membered chelate ring. The phosphorus atoms of the two ligands are shown to be in a cis configuration. The chelating ligand spans an angle of 85.9(3)° and has Pt-P and Pt-N bond lengths of 2.226(3) and 2.139(8) Å respectively which are similar to those of 86.4°, 2.245 and 2.12 Å respectively found for the o-diphenylphosphinoaniline ligand in the dication cis-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)_2]^{2+}$.[60,155]

4.2.2 Reaction of complex *(199)* with HCl

Treatment of complex *(199)* with HCl gas afforded complex *(200)*, Scheme 63, in which both ligands are co-ordinated through the phosphorus atom only. The complex was also prepared independently from the hydrochloride salt *(167a)* and K_2PtCl_4.

The $^{31}P\text{-}\{^1H\}$ nmr spectrum (Table 10) of complex *(200)* displays a single resonance at δ +3.6 ppm, with platinum satellites ($J_{Pt\text{-}P}$ = 3623 Hz). The chemical shift is typical for such a non-chelating phosphine complex[152,153] and the magnitude of $J_{Pt\text{-}P}$ is typical for phosphorus co-ordinated trans to chloride.[141-143] It follows that the phosphine ligands are in a mutually



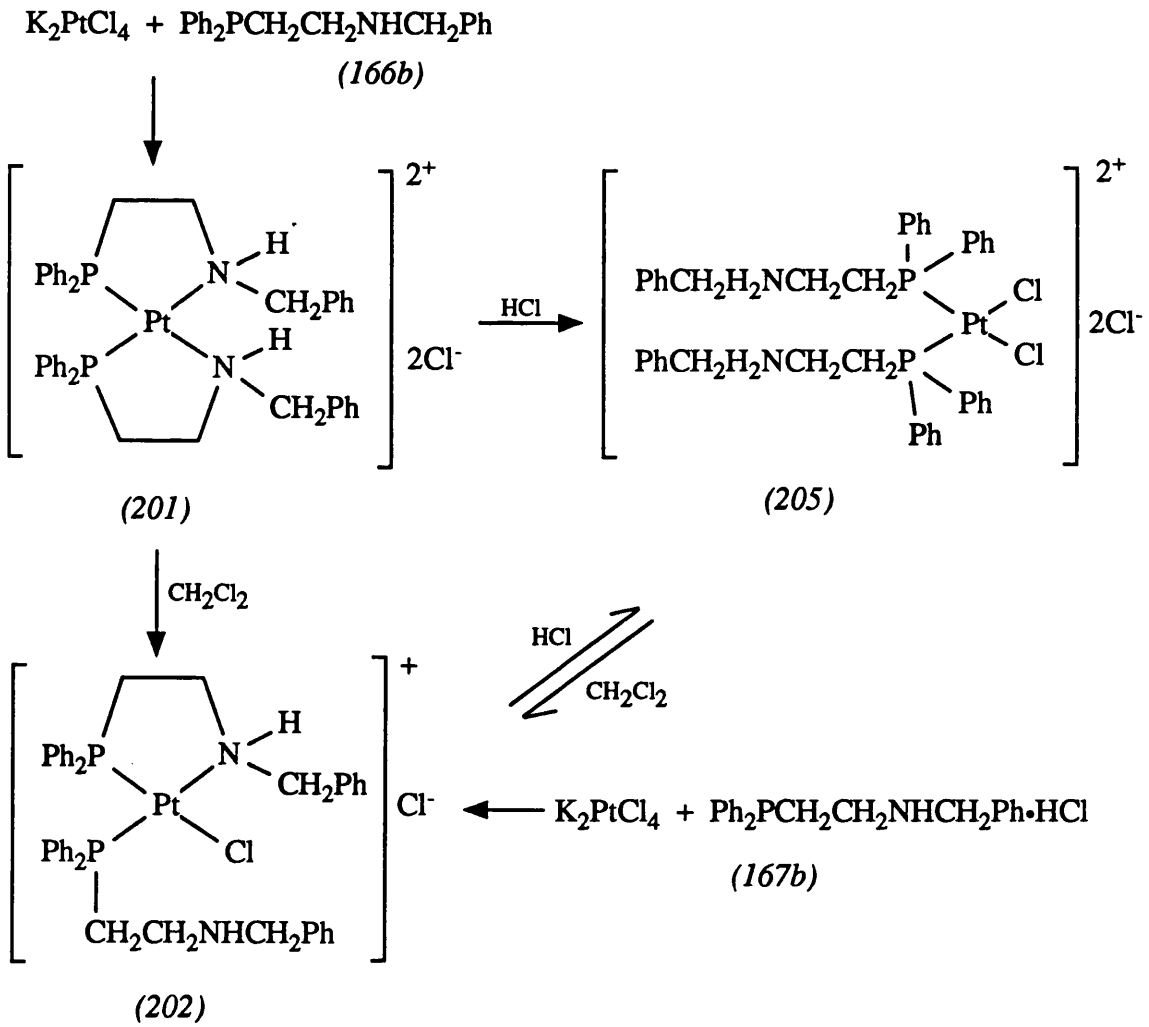
Scheme 63

cis configuration. The ^1H nmr spectrum (Table 11) of complex *(200)* displays broad signals due to the methylene protons (δ 3.4 ppm) and the NH_2 protons (δ 9.50 ppm), as well as signals due to the t-butyl and phenyl groups. On standing in air, it was found that complex *(200)* absorbed water in a similar manner to the free hydrochloride ligands *(167a-c)* (see Section 2.2). After one week it was noticeable that the signal at δ 9.50 ppm had broadened and integrated to less than two protons. The microanalysis of complex *(200)* is consistent with the presence of up to 0.5 equivalents of water.

4.2.3 Reaction of K_2PtCl_4 or $(COD)PtCl_2$ with ligands *(166b)*, *(166c)* and *(166d)*

Reaction of K_2PtCl_4 with $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)* leads to the formation of complex *(201)* which has been identified on the basis of its $^{31}P-\{^1H\}$ and ^1H nmr spectra (see Tables 10 and 11) as cis-[Pt($Ph_2PCH_2CH_2NCH_2Ph$)]2Cl (see Scheme 64). The $^{31}P-\{^1H\}$ nmr spectrum of *(201)* exhibits a single resonance at δ +28.4 ppm with platinum satellites (J_{Pt-P} =

3398 Hz). The $^{31}P-\{^1H\}$ nmr chemical shift is consistent with the phosphorus being incorporated into a five-membered chelate ring. The structure has been assigned on the basis of its $^{31}P-\{^1H\}$ nmr spectrum, since it is the only mononuclear structure possible in which both phosphorus atoms are equivalent and incorporated into chelate rings. The magnitude of J_{Pt-P} (3398 Hz) is different to the values observed for any of the other platinum complexes formed with this type of ligand. It is much smaller than the J_{Pt-P} values found in complexes *(199)*, *(200)*, *(202)*, *(203)* and *(204)* for phosphorus <u>trans</u> to chloride. The average value of these coupling constants is 3734 Hz. In addition, it is also larger (although nearer in value) than the J_{Pt-P} values for phosphorus <u>trans</u> to nitrogen in complexes *(199)*, *(202)*, *(203)* and *(204)* of, on average, 3220 Hz. However, the assigned structure is not directly comparable to any of these complexes since it contains two chelate rings.



Scheme 64

The ^1H nmr spectrum of *(201)* (Table 11) displays broad signals at δ 2.10 and 5.00 ppm in a 2:1 ratio. The broad signals centred around δ 2.10 ppm has been assigned to the methylene protons of the carbon backbone, whereas the broad signal at δ 5.00 ppm has been assigned to the benzyl protons. Signals were also observed in the phenyl region.

Attempts to crystallise complex *(201)* from dichloromethane led to its conversion to complex *(202)*, cis-[$\overline{Pt(Ph_2PCH_2CH_2NHCH_2Ph)}(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ (see Scheme 64). Complex *(202)* displays a $^{31}P-\{^1H\}$ nmr spectrum (Table 10) very similar to complex *(199)*, that is a sharp AX pattern, consisting of two doublets centred at δ -5.3 and +33.9 ppm, with their corresponding platinum satellites. The structure of *(202)* has been assigned principally on the basis of this $^{31}P-\{^1H\}$ nmr spectrum. The signal at δ +33.9 ppm (P_B), indicates that P_B is part of a five-membered chelate ring,[152,153] with a large $^1J(Pt-P_B)$ of 3779 Hz, consistent with P_B being situated trans to chloride.[141-143] The second signal is at a more normal shift, δ -5.3 ppm, consistent with a non-chelated ligand, and having a $^1J(Pt-P_A)$ value of 3189 Hz which is consistent with P_A being trans to the amine ligand.[71] The spectrum differs from that of *(199)* since it was recorded in dichloromethane, rather than the more polar methanol.

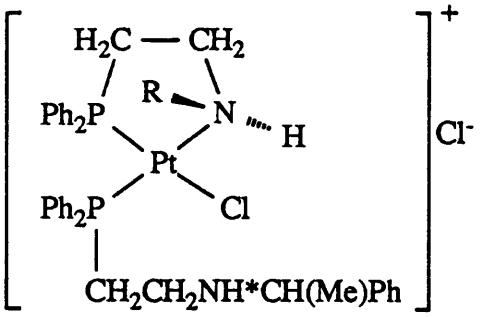
The formation of the bis-chelate complex *(201)* on reaction of K_2PtCl_4 with *(166b)* is in contrast to the formation of the mono-chelate complex *(199)* with ligand *(166a)*, $Ph_2PCH_2CH_2NH^tBu$. It is unlikely that the difference in basicities of the amine groups in the ligands affects the co-ordination of the amine to the metal. The tert-butyl moiety is more electron-donating than the benzyl group and hence would be expected to form more stable σ bonds to the metal. However, it is the benzyl ligand, *(166b)*, which is observed to form two chelate rings, whereas the tert-butyl ligand *(166a)* is only seen to form the monochelate complex *(199)*. However, a possible contributing factor is that the benzyl moiety confers greater 'softness' to the amine and therefore makes co-ordination to the soft platinum metal more favourable. Perhaps more importantly, steric factors could determine the number of chelate rings present in the complexes. Molecular models indicate that a metal complex such as *(201)*, with two chelate rings is more sterically attractive with benzyl substituents than

with tert-butyl.

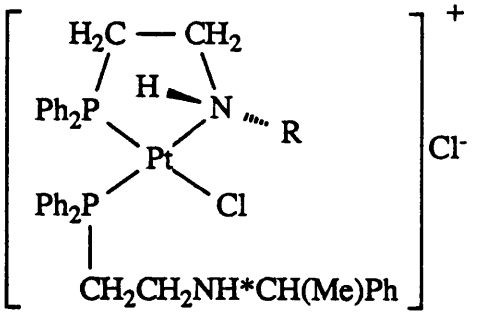
The preparation of complex *(201)* was carried out in a highly polar acetone/water solvent mixture which may have helped to stabilise the dicationic complex. However, standing in a solution of the less polar dichloromethane solvent, led to the formation of the monocation, complex *(202)*. Perhaps complex *(201)* is only stable in solutions of relatively greater polarity than dichloromethane. Similar solvent dependency has been demonstrated for iron complexes of these ligands (see Section 5.2).

Reaction of either K_2PtCl_4 or $(COD)PtCl_2$ with $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)* led to the formation of cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH(Me)Ph)}(Ph_2PCH_2CH_2NHCH(Me)Ph)Cl]Cl$, complex *(203)*. This complex has been identified on the basis of its $^{31}P-\{^1H\}$ nmr spectrum (Table 10) in methanol which displays an AX pattern similar to those observed for complexes *(199)* and *(202)*. Two broad signals, each with platinum satellites are observed, but the $^2J(P_A-P_B)$ coupling constant is not resolved. The signal at δ +37.0 ppm is typical for a phosphorus which is incorporated into a five-membered chelate ring[153,154] and is comparable[153,156] to the chemical shifts observed for complexes *(199)*, *(202)* and *(206)*. The $^1J(Pt-P_B)$ coupling constant is also similar to those observed in these complexes and is typical for a phosphorus atom co-ordinated trans to chloride.[141-143] The signal at δ -1.7 ppm is typical of a non-chelated ligand, and the $^1J(Pt-P_A)$ value of 3228 Hz is typical for a phosphorus atom co-ordinated trans to nitrogen.[71] The broadness of the two main signals may be due to fluxionality, or perhaps $^2J(P_A-P_B)$ is too small to be resolved. Another possibility may be the overlapping of signals from the two diastereoisomers of the complex, *(203a)* and *(203b)*.

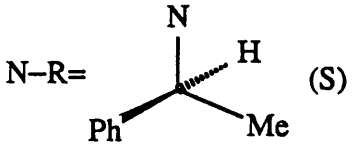
The two diastereoisomers are formed because the optically active ligand was prepared as a single enantiomer [the (S) form] from L-(-)-α-phenylethylamine. In common with complexes *(199)* and *(202)*, difficulty was found in crystallising complex *(203)*. After numerous attempts, it was crystallised from methanol and dichloromethane. The analysis suggests that the complex has crystallised with one molecule of water (possibly from the methanol solvent) and as the hydrochloride salt. Ligand *(166c)* has been observed to form



(203a)



(203b)



only this monochelate complex *(203)* on reaction with platinum, in contrast to the ligand $Ph_2PCH_2CH_2NHCH_2Ph$, *(166b)*, which has been observed to form both bis-chelate and monochelate complexes. The most favoured explanation for these observations is that steric constraints prevent the formation of two chelate rings for ligand *(166c)*.

Reaction of K_2PtCl_4 with $Ph_2PCH_2CH_2N(CH_2Ph)_2$ *(166d)* resulted in the formation of cis-$[\overline{Pt\{Ph_2PCH_2CH_2N}(CH_2Ph)_2\}\{Ph_2PCH_2CH_2N(CH_2Ph)_2\}Cl]Cl$, complex *(204)*. The complex was identified on the basis of its $^{31}P-\{^1H\}$ nmr spectrum (Table 10). The spectrum exhibited a sharp AX pattern, consisting of two doublets and their corresponding platinum satellites. The doublet at δ +33.8 ppm, indicative of a five-membered chelate ring,[153,154] displays a $^1J(Pt-P_B)$ value of 3789 Hz, indicating a phosphorus atom trans to chloride.[141-143] The lower field doublet at δ -2.2 ppm indicates that the ligand is not chelated, and the $^1J(Pt-P_A)$ value of 3223 Hz is indicative of phosphorus being co-ordinated trans to nitrogen.[71]

The $^{31}P-\{^1H\}$ nmr spectrum for the complex cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH_2Ph)}(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ reported by Kahn[90] displays an AX pattern with two doublets [$\delta(P_A)$ = -0.1 ppm, $\delta(P_B)$ = +34.0 ppm, $^2J(P_A-P_B)$ = 18 Hz] together with platinum satellites [$^1J(Pt-P_A)$ = 3259 Hz, $^1J(Pt-P_B)$ = 3768 Hz]. Comparison of the two spectra indicates that the complexes are, in fact, identical. This lends further support to the argument presented in Section 2.2 that the ligand prepared by Kahn and reported as $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)* is actually $Ph_2PCH_2CH_2N(CH_2Ph)_2$ *(166d)*.

4.2.4 Reaction of Complexes *(201)*, *(202)* and *(203)* with HCl gas

Reaction of solutions containing either complex *(201)* or *(202)* with HCl gas resulted in the formation of complex *(205)*, cis-$[Pt(Ph_2PCH_2CH_2NHCH_2Ph{\bullet}HCl)_2Cl_2]$ (see Scheme 64). The $^{31}P-\{^1H\}$ nmr spectrum of *(205)* displays a single resonance at δ +3.6 ppm, typical of a non-chelate complex and comparable to that displayed for cis-$[Pt(Ph_2PCH_2CH_2NH^tBu{\bullet}HCl)_2Cl_2]$ of δ +3.6 ppm. The J_{Pt-P} value of 3662 Hz is also indicative of phosphorus co-ordinated trans to chloride.[141-143] During attempts at crystallisation the complex was left standing in dichloromethane solution. It was found that this led to the conversion of complex *(205)* into complex *(202)*, the mono-chelated form. One explanation for this is that the benzyl moiety gives greater stability to the chelate complex *(205)* than to the hydrochloride complex *(203)*. An attempt was also made to prepare complex *(205)* from K_2PtCl_4 and $Ph_2PCH_2CH_2NHCH_2Ph{\bullet}HCl$ *(167b)*. However, this resulted in the formation of complex *(202)*, the mono-chelate, together with small amounts of complex *(205)*. This is in contrast to the reaction of K_2PtCl_4 with the tert-butyl containing ligand, *(167a)*, which produced only the non-chelated species *(200)*, cis-$[Pt(Ph_2PCH_2CH_2NH^tBu{\bullet}HCl)_2Cl_2]$. This may be due to the increased basicity of the amine in ligand *(167a)* which will help stabilise the hydrochloride salt. Perhaps more important is the smaller steric hindrance associated with ligand *(167b)* compared to *(167a)*. In the absence of steric restrictions, the stability of the chelate ring may make complex *(202)* more favourable than complex *(205)*. As with many of these complexes, *(202)* has proved difficult to crystallise and numerous attempts resulted only in the formation of oils.

Reaction of complex *(203)* cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH(Me)Ph)}(Ph_2PCH_2CH_2NHCH(Me)Ph)Cl]Cl$, with HCl gas resulted in the formation of the non-chelate complex *(206)*, cis-$[Pt(Ph_2PCH_2CH_2NHCH(Me)Ph{\bullet}HCl)_2Cl_2]$. The complex displayed a $^{31}P-\{^1H\}$ nmr spectrum very similar to that of complexes *(200)* and *(205)*. A single resonance was observed at δ +2.8 ppm, indicative of two non-chelated ligands, with a J_{Pt-P} of 3667 Hz. The value of J_{Pt-P} is again typical for a phosphorus atom co-ordinated trans to chloride.[141-143] Reaction of K_2PtCl_4 with ligand *(167c)*, $Ph_2PCH_2CH_2NHCH(Me)Ph{\bullet}HCl$ led to the

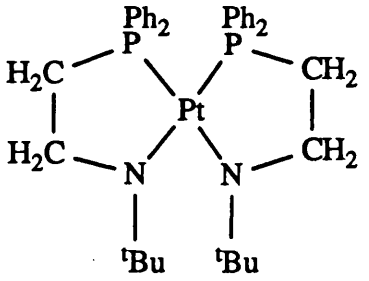
formation of the mono-chelate complex *(203)*, which was identified on the basis of its $^{31}P-\{^{1}H\}$ nmr spectrum. The non-chelate complex *(206)* was not observed by $^{31}P-\{^{1}H\}$ nmr spectroscopy as a product of this reaction.

4.2.5 Deprotonation reactions

Deprotonation reactions were carried out on both complex *(199)* and complex *(201)*. Reaction of cis-[Pt($Ph_2PCH_2CH_2NH^tBu$)($Ph_2PCH_2CH_2NH^tBu$)Cl]Cl *(199)* with either sodium hydroxide or sodium bis-trimethylsilylamide led to the formation of complex *(207)*. This complex has not been fully identified, although a number of possible products have been ruled out . $^{31}P-\{^{1}H\}$, ^{1}H and $^{13}C-\{^{1}H\}$ nmr spectra of complex *(207)* are presented in Tables 10, 11 and 12. The $^{31}P-\{^{1}H\}$ nmr spectrum displays a single resonance at δ +34.7 ppm, however, no platinum satellites are observed. The chemical shift is consistent with either a platinum complex with both ligands chelated or a free phosphine oxide ligand, e.g. $Ph_2P(O)CH_2CH_2NH^tBu$. The mass spectrum of the product indicates the presence of $Ph_2PCH_2CH_2NH^tBu$, but not of the phosphine oxide. In addition, the microanalysis of *(207)* indicates carbon and hydrogen contents far lower than those expected for the phosphine oxide. Also, in the course of this work numerous attempts, with many different oxidizing agents were made, without success, to prepare the phosphine oxide, $Ph_2P(O)CH_2CH_2NH^tBu$. The ligand $Ph_2PCH_2CH_2NH^tBu$ also failed to oxidize in air after prolonged periods. The ^{1}H nmr spectrum of *(207)* displays two triplets of doublets, corresponding to the methylene protons. Selective ^{1}H homodecoupling experiments were carried out on each of the triplet of doublets. The higher field triplet of doublets at δ 2.70 ppm was irradiated causing the lower field signal at δ 2.50 ppm to collapse into a doublet. This doublet displayed a J_{P-H} of 10.9 Hz. The lower field triplet of doublets was also irradiated, causing the triplet of doublets at δ 2.70 ppm to collapse into a doublet. This doublet displayed a J_{P-H} of 11.2 Hz. The values of J_{H-H} were then shown to be 7.3 Hz and 7.5 Hz respectively. The ^{1}H nmr spectrum also displayed one singlet, assigned to the tert-butyl group, indicating that if *(207)* is a platinum complex containing two ligands, then both tert-butyl moieties are equivalent. Signals due to the phenyl groups were also observed. The $^{13}C-\{^{1}H\}$ nmr spectrum of *(207)*

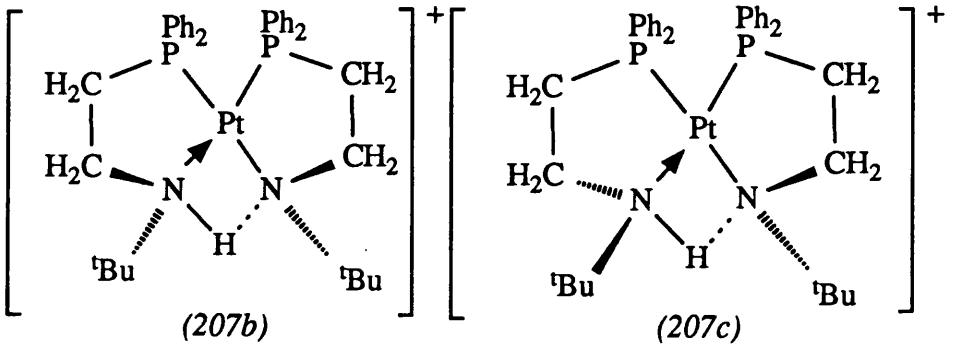
displays signals due to the methylene protons at δ 30.6 and 35.7 ppm. Both signals are singlets, compared to the ligand $Ph_2PCH_2CH_2NH^tBu$ which displays two doublets for the two methylene carbons. The chelated palladium complex cis-$[Pd(Ph_2PCH_2CH_2NH^tBu)Cl_2$ *(210)* (see Section 4.2.7) displays one doublet, assigned to the carbon atom adjacent to phosphorus and a singlet assigned to the carbon atom adjacent to nitrogen. Signals are also observed for the tert-butyl group, at δ 28.7 ppm, assigned to CMe_3 and at δ 50.5 ppm assigned to CMe_3. Phenyl signals were also observed in the region δ 125-134 ppm.

Both the ^1H and $^{13}C-\{^1H\}$ nmr spectra are consistent with complex *(207)* being either a platinum complex or the phosphine oxide. The anticipated product of the reaction, cis-$[Pt(Ph_2PCH_2CH_2N^tBu)_2]$ *(207a)* is not consistent with the microanalysis, however, the low carbon and hydrogen contents of the microanalysis suggests that *(207)* is a platinum



(207a)

complex rather than an organic ligand. Structure *(207a)* has not been completely ruled out, but the data could also be interpreted as representing a monoprotonated species in which one ligand exists as an amide and one an amine. The amide group could then form a hydrogen bond with the amine of the other ligand. Structural models indicate that two isomers of this complex are possible *(207b)* and *(207c)*.

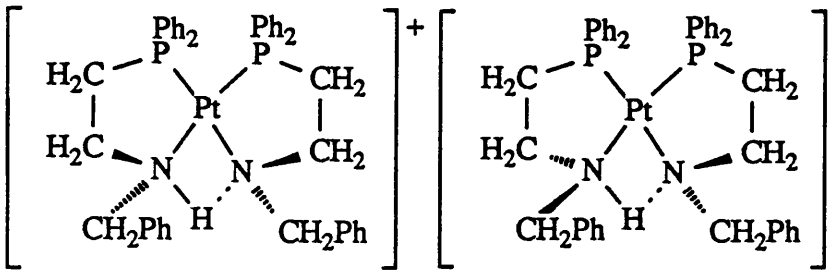


(207b) *(207c)*

In *(207b)* both tert-butyl groups are in a cis configuration, whereas in *(207c)* they are in a trans configuration. In each of the isomers, either of the nitrogens could be the amide or the amine. The $^{31}P-\{^{1}H\}$ nmr spectrum observed for this type of complex would depend on whether the hydrogen bond was symmetrical or unsymmetrical, and the rate of hydrogen transfer. An unsymmetrical bond might, in theory, produce two signals of close proximity, however, the observed spectrum would depend on the rate of hydrogen transfer from one nitrogen to the other. This transfer may be fast, resulting in only one signal being observed. Either or both the isomers *(207b)* and *(207c)* may be formed. Therefore, one of the isomers *(207b)* or *(207c)* may give a single $^{31}P-\{^{1}H\}$ nmr chemical shift of +34.7 ppm. However, the absence of platinum satellites has yet to be explained. Also, it would be expected that either the fully deprotonated complex *(207a)* or the monoprotonated complexes *(207b-c)* might reprotonate on addition of HCl. However, attempted reprotonation led to a large number of unidentified products, as seen by $^{31}P-\{^{1}H\}$ nmr spectroscopy. The equivalent alkoxide complexes prepared by Pringle *et al.*,[98] cis-$[\overline{Pt(Ph_2PCH_2CR_2O)_2}]$ react with carbon dioxide, carbon monoxide and methyliodide to form the corresponding insertion products. Complex *(207)* failed to react with CO, CO_2 or MeI. Although the data gathered on complex *(207)* is inconclusive, the mono-protonated complex is the preferred structure, although there are obviously still problems with this assignment.

Deprotonation of cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH_2Ph)}(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ *(202)* and cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH_2Ph)_2}]2Cl$ *(201)* were also carried out and led to the formation of two products, *(208a)* and *(208b)*. The $^{31}P-\{^{1}H\}$ nmr spectrum of the products displayed two singlets in very close proximity at δ +30.7 and +30.1 ppm in an almost 1:1 ratio. Neither of the signals displayed platinum satellites. This spectrum is obviously very similar to that displayed for complex *(207)*, except that there are two signals instead of one. The chemical shifts are indicative of the phosphorus atoms incorporated in a chelate ring. The presence of two signals also suggests that the product is not the phosphine oxide. Again, the preferred assignment is that the product is the mono-protonated complex, which can exist as two isomers, as described for *(207)*. Perhaps for steric reasons, the benzyl ligand is able to

form both isomers, whereas the tert-butyl can only form one. The two signals in the $^{31}P-\{^{1}H\}$ nmr spectrum may therefore be due to the two isomers, one in which the benzyl substituents are cis to each other *(208a)* and a second where the benzyl substituents are trans *(208b)*. As with complex *(207)*, attempts to reprotonate *(208)* failed, producing a large number of unidentified signals in the $^{31}P-\{^{1}H\}$ nmr spectrum.



(208a) *(208b)*

4.2.6 Reaction of $(COD)PtCl_2$ with $Ph_2PCH_2C(O)NH^tBu$

The ligand $Ph_2PCH_2C(O)NH^tBu$ was reacted with $(COD)PtCl_2$ to give complex *(209)*, cis-$[Pt(Ph_2PCH_2C(O)NH^tBu)_2Cl_2]$. The $^{31}P-\{^{1}H\}$ nmr spectrum of complex *(209)*, Table 9, displays a single resonance at δ +8.1 ppm, indicative of non-chelating ligands, with platinum satellites. The value of J_{Pt-P} (3750 Hz) is also typical for phosphorus co-ordinated trans to chloride. Complex *(209)* is non-chelating, in contrast to complex *(199)* where one $Ph_2PCH_2CH_2NH^tBu$ ligand is chelated. The difference is likely to be due to the carbonyl group which delocalises the lone pair of electrons on the amine, making them unavailable for bonding to the metal. Deprotonation of complex *(209)* was attempted using sodium methoxide or triethylamine producing a large number of products, which were not identified, since attempts at purification led to decomposition.

4.2.7 Reaction of $(PhCN)_2PdCl_2$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

When $(PhCN)_2PdCl_2$ was reacted with $Ph_2PCH_2CH_2NH^tBu$ in a 1:1 stoichiometric ratio, the resulting product was complex *(210)*, $[\overline{Pd(Ph_2PCH_2CH_2NH^tBu)Cl_2}]$, formed in good yield. The pale yellow solid is not very soluble in chlorinated organic solvents, but was crystallised from a large volume of dichloromethane to give pale yellow crystals. Complex

(210) was characterized on the basis of its $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ nmr spectra and microanalysis. The $^{31}P-\{^1H\}$ nmr spectrum (see Table 10) displays a single resonance at δ +50.8 ppm which is considerably down field from the monodentate complex *(223)* and therefore indicative of a phosphorus incorporated into a five-membered chelate ring.[153,154] The ^1H nmr spectrum of *(210)* (Table 11) exhibits three signals in the methylene region. The higher field signal, a multiplet at δ 2.65 ppm is assigned to the two methylene protons adjacent to phosphorus. This assignment is based on the lower electronegativity of phosphorus compared to nitrogen. The two lower field signals at δ 3.20 (a doublet of doublets) and δ 3.75 ppm (a multiplet) are assigned to the two methylene protons adjacent to nitrogen. Each signal integrates to one proton and the inequivalence of these protons can be explained by their proximity to the asymmetric nitrogen centre. However, of the two coupling constants in the doublet of doublets, the larger coupling of 48.0 Hz is not seen in the multiplet at δ 3.75 ppm and is therefore thought to be a J_{P-H} coupling. The N-H proton is also observed in the ^1H nmr at δ 5.88 ppm. Signals due to the tert-butyl and phenyl groups are also observed.

The $^{13}C-\{^1H\}$ nmr spectrum (Table 12) displays a doublet at δ 34.5 ppm ($^1H_{P-C}$ = 29 Hz) assigned to the methylene carbon adjacent to phosphorus. The methylene carbon adjacent to nitrogen has been assigned to the more down-field signal, a singlet at δ 50.4 ppm. The reason for the absence of phosphorus coupling for this methylene carbon is not clear, but it may lie in the positioning of the carbon away from the lone pair on the phosphorus, due to the constraint of the chelate ring. Other signals observed were assigned to the tert-butyl and phenyl carbons. The far IR spectrum of complex *(210)* indicated the presence of two ν(Pt-Cl) stretches at 325 and 280 cm^{-1}, confirming the cis-orientation of the chloride ligands.

An X-ray crystal structure determination was carried out on complex *(210)*. The molecular structure is illustrated in Fig. 7, together with the crystallographic numbering system. Selected bond angles and lengths for the complex are presented in Table 9. The structure clearly shows the presence of just one chelating ligand, which spans an angle of 85.9(3)° and has Pd-P and Pd-N bond lengths of 2.201(3) and 2.128(12) Å respectively. Two molecules of

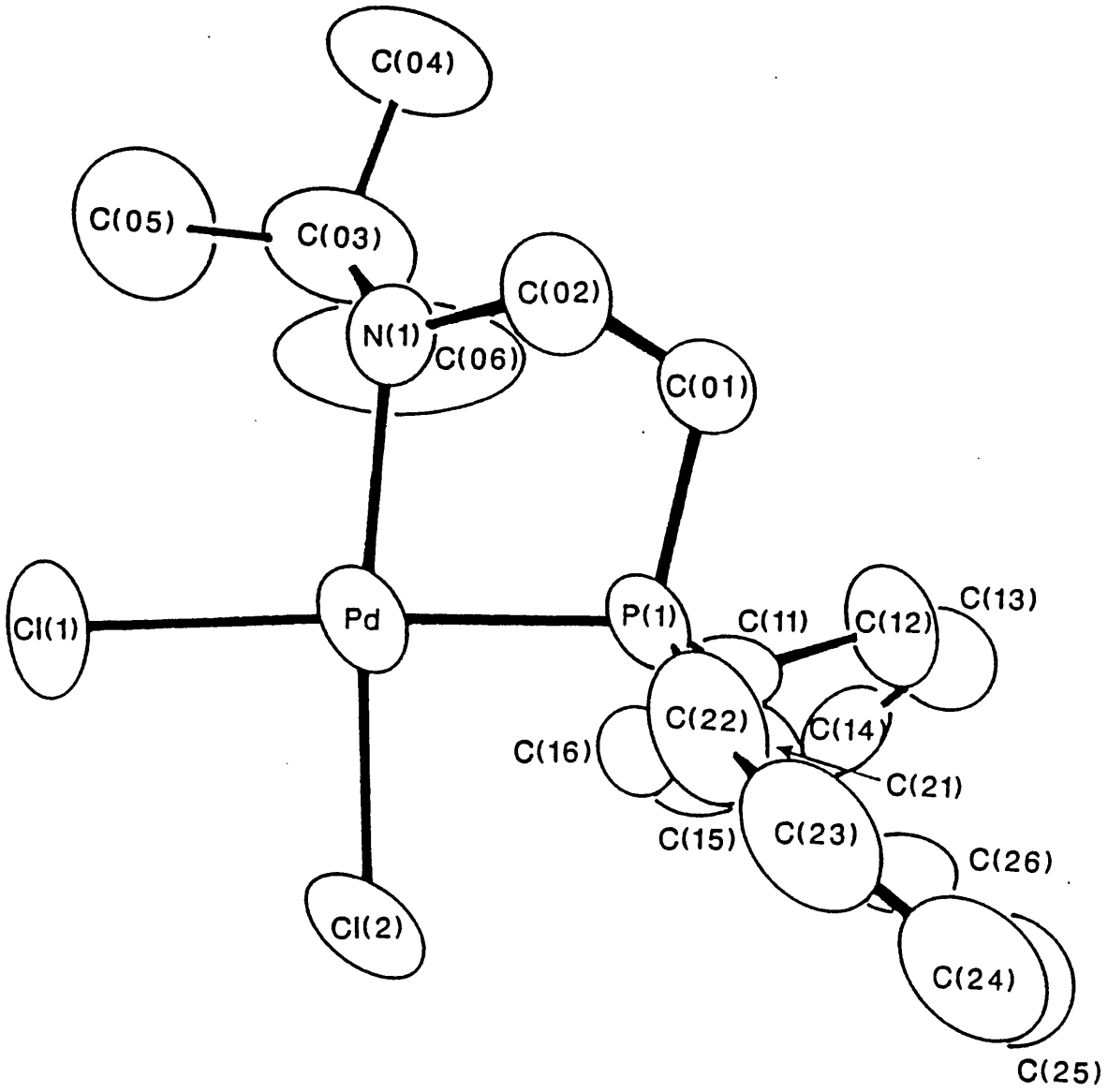


Figure 7

Molecular Structure of cis-[$\overline{Pd(Ph_2PCH_2CH_2NH^tBu)}Cl_2$] *(210).*

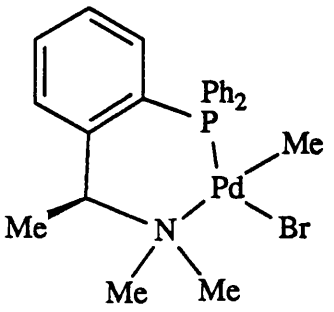
TABLE 9

Selected Bond Lengths and Angles for the cis-[$\overline{Pd(Ph_2PCH_2CH_2NH^tBu)Cl_2}$] *(210)*

Bond Length	(Å)	Bond Angle	(°)
P(1) – Pd	2.201 (3)	N(1) – Pd – P(1)	85.0 (3)
Cl(1) – Pd	2.375 (4)	N(1) – Pd – Cl(1)	97.7 (3)
Cl(2) – Pd	2.289 (4)	Cl(1) – Pd – Cl(2)	89.2 (1)
N(1) – Pd	2.128 (12)	Cl(2) – Pd – P(1)	88.1 (1)
N(1) – C(02)	1.482 (19)	Pd – N(1) – C(02)	104.9 (11)
C(02) – C(01)	1.335 (25)	N(1) – C(02) – C(01)	122.4 (20)
C(01) – P(1)	1.820 (12)	C(02) – C(01) – P(1)	108.6 (11)
		Pd – P(1) – C(01)	102.9 (5)

Estimated standard deviations are given in parentheses.

the complex were found to have crystallised in the asymmetric unit. The Pd-N bond length of 2.128(12) Å is within the normal range (1.94-2.13 Å) and is also comparable to that found in the complex $[\overline{Pd(Ph_2PC_6H_{12}CH(Me)N}Me_2)(Me)(Br)]$ *(95)* of 2.220(6) Å.[75] The Pd-P bond distance also has a normal value and is comparable to that found in complex *(95)*



(95)

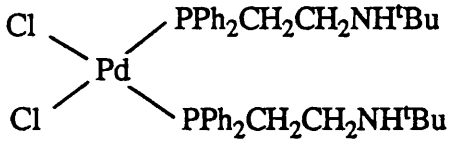
of 2.207(3) Å. The geometry around the palladium is effectively square planar, however the P-Pd-N angle is somewhat less than 90° [85.0(3)°] probably due to the constraint of the chelate ring. This angle is also less than the P-Pd-N angle of 93.1(2)° in the six-membered chelate ring of complex *(95)*. However, the P-Pd-N angle is greater than those found in the bis-chelate, zero-valent palladium complex $[\overline{Pd(o\text{-}Ph_2PC_6H_4N}C(O)Ph)_2]$,[68] where the P,N chelate bite angles are 76.4(2)° and 82.1(3)°.

The formation of this type of palladium chelate complex *(210)* with only one ligand is in contrast to the reaction of 1:1 stoichiometric ratios of *(166a)* with K_2PtCl_4 or $(COD)PtCl_2$. With platinum the bis-phosphine complex is always formed (in 50% yield with one equivalent of phosphine). This difference in the reactivity of platinum and palladium may be due to a number of factors. The palladium chelate complex is presumably formed because co-ordination of the amine to palladium is more favourable than in the platinum complex. This may be due to the relative 'softness' of platinum and palladium. Alternatively, the well known thermodynamic and kinetic instability of palladium complexes compared to platinum[158] may make the monophosphine chelate complex more favourable for palladium. Also, the greater spatial extension of the 5d electrons in platinum compared to the 4d electrons in palladium may effect the tendency for the metals to form chelate rings.

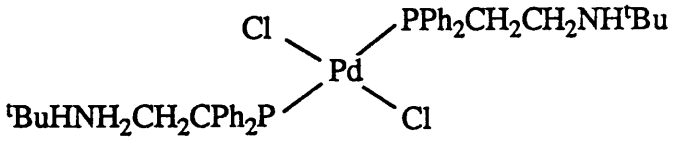
Reaction of $(PhCN)_2PdCl_2$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)* in a 1:2 ratio led to the

formation of two products, which exhibited singlets at δ +31.1 and +21.8 ppm in the $^{31}P-\{^{1}H\}$ nmr spectrum. These two complexes have been tentatively assigned as the cis and trans isomers of $[Pd(Ph_2PCH_2CH_2NH^tBu)_2Cl_2]$, complex *(223)*. The signal at δ +31.1 ppm is thought to be the cis isomer and the signal at δ +21.8 ppm the trans isomer. This assignment has been made on comparison of the shifts with those exhibited by other phosphine complexes of the type $PdCl_2(PR_3)_2$. For example, cis-$[Pd(PPh_2Me)_2Cl_2]$[159] has a $^{31}P-\{^{1}H\}$ nmr shift of δ +19.1 ppm, compared to +7.8 ppm for the trans isomer. More importantly, the observed co-ordination shift, Δ_{obs}, between the free phosphine and the complex is +47.2 ppm for the cis isomer and +35.5 ppm for the trans. These compare well to the co-ordination shifts between ligand *(166a)* and the complex *(223)*. For the signal at δ +21.8 ppm, Δ_{obs} is +42.4 ppm and for the signal at δ +31.1 ppm, the shift on co-ordination is +51.7 ppm.

The presence of both isomers compared to the formation of only cis-isomers in the platinum complexes can be explained by the greater kinetic and thermal stability of platinum complexes. Addition of excess phosphine altered the ratio of cis and trans isomers as seen by $^{31}P-\{^{1}H\}$ nmr, increasing the peak at δ +31.1 ppm, which has been assigned to the cis-isomer. Addition of $Ph_2PCH_2CH_2NH^tBu$ *(166a)* to complex *(210)* also led to the formation of a mixture of cis and trans isomers of complex *(223)*. Crystallisation gave yellow crystals, thought to be just the cis-isomer, *(223a)*, displaying a single $^{31}P-\{^{1}H\}$ nmr resonance at δ +31.1 ppm. On standing in dichloromethane solution the complex reverted to a mixture of cis and trans isomers.

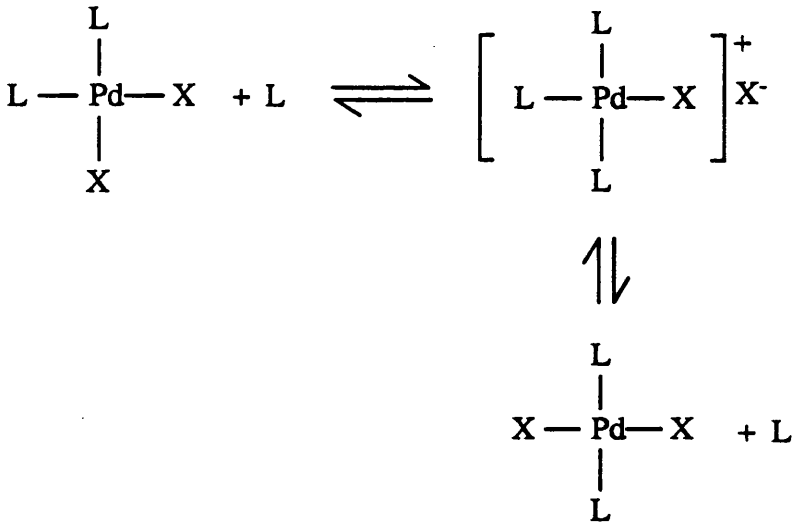


cis *(223a)*



trans *(223b)*

This cis-trans isomerization is typical of $PdX_2(PR_3)_2$ complexes. In solution a cis-trans equilibrium is quickly established, though usually only one isomer is isolated in the solid state.[160,161] The mechanism of cis-trans isomerisation is thought to be one of consecutive displacement, Scheme 65, which is accelerated by excess phosphine.[162] Alternatively, excess

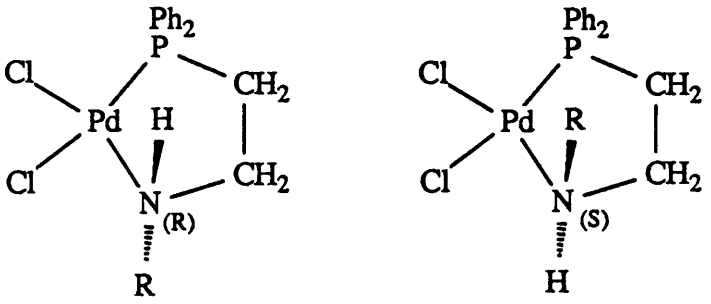


Scheme 65

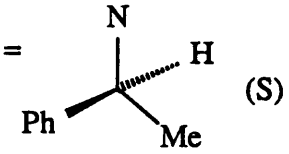
phosphine, L or solvent molecules could add to give five co-ordinate intermediates.[163a] The cis-isomers are generally more stable than trans-isomers,[163b] further supporting our identification of the isolated yellow solid and the cis-isomer. The far IR spectrum displays only a single stretching frequency at ν 300 cm^{-1}, indicating the trans-isomer is present. However, this is rather low compared to trans-$[Pd(PPh_3)_2Cl_2]$ which has a stretching frequency of 357 cm^{-1}. It may be that the sample was too weak for the cis-stretching frequencies to be observed. The ^1H nmr spectrum of complex *(223)* displays a singlet at δ 1.30 ppm assigned to the tert-butyl protons, a broad signal at δ 3.15 ppm, assigned to the methylene protons and a multiplet at δ 7.60 ppm, assigned to the phenyl groups.

4.2.8 Reaction of $(PhCN)_2PdCl_2$ with $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*

Reaction of $(PhCN)_2PdCl_2$ with ligand *(166c)* in a 1:1 ratio led to the formation of complex *(224)*. The chiral nitrogen centre, which occurs when the ligand is co-ordinated to the metal, results in the existence of two diastereoisomers, *(224a)* and *(224b)*. The ligand *(166c)* has been prepared as the (S) enantiomer, however, the nitrogen chiral centre can be either (S) or (R). Therefore, there are two possible diastereoisomers, (SS) or (SR). The existence of two diastereoisomers is suggested by the $^{31}P-\{^1H\}$ nmr spectrum (Table 10), which displays two singlets at δ +56.0 and +55.3 ppm, in a 1:1 ratio. These signals are in the same region as the signal displayed by complex *(210)*, at δ +50.8 ppm, and indicate that the



(224a) *(224b)*

where N–R =  (S)

phosphorus atoms are incorporated into a five-membered chelate ring. The ^{1}H nmr spectrum (Table 11) exhibits several overlapping multiplets in the region δ 2.60-3.80, which integrate to a total of eight protons. These multiplets are assigned to the methylene protons, four from each isomer. Signals corresponding to the methyl and C-H protons of the chiral substituents are observed for both isomers. The two doublets at δ 1.75 and 1.85 ppm are assigned to the methyl protons of each isomer, each signal integrating to three protons. The two multiplets at δ 5.45 and 5.70 ppm integrate to one proton each and have been assigned to the CH(Me)Ph protons. The $^{13}C-\{^{1}H\}$ nmr spectrum (Table 12) also displays signals for both isomers. One doublet and one singlet assigned to the $-CH_2-CH_2-$ backbone are observed for each isomer. The doublets at δ 31.8 and 32.8 ppm have been assigned to the methylene carbons adjacent to the phosphorus atoms, as with complex *(210)*. The singlets at δ 43.6 and 42.6 ppm are assigned to the methylene carbons adjacent to the nitrogen atoms. Two singlets assigned to CHMe, at δ 58.9 and 59.4 ppm and a further two singlets, assigned to CHMe, at δ 17.6 and 17.8 ppm were also observed.

CONCLUSIONS

A number of metal complexes of ligands *(166a-d)* and *(167a-c)* have been prepared. Problems were encountered since it seems particularly easy for these ligands to pick up trace amounts of acid (probably HCl in the dichloromethane solvent) when co-ordinated to platinum. This was shown in the crystal structure of cis-[Pt($Ph_2PCH_2CH_2NH^tBu$)(Ph_2PCH_2

$CH_2NH^tBu)Cl]Cl$ *(199)* in which the unco-ordinated nitrogen clearly exists as the hydrochloride salt. This uncertainty as to the degree of protonation of the ligands has been a problem throughout the work. The complexes formed from the reaction of K_2PtCl_4 and ligands *(166b)* and *(167b)* were difficult to isolate due to their ease of interconversion from one complex to another. Again, this may be due to the amine being protonated by traces of HCl in the solvent. Problems with crystallisation of the complexes was also encountered, particularly with complexes which have salt structures. Numerous attempts at crystallisation in different solvents often failed, leading to the formation of oils. Deprotonation reactions of these complexes have been difficult to interpret, but it is thought that complexes *(207)* and *(208)* are the monoprotonated species, in which one ligand exists as an amide, the other as an amine. Reaction of ligand *(166a)* and *(166c)* with $(PhCN)PdCl_2$ in a 1:1 ratio led to the formation of chelate complexes containing only one aminoalkylphosphine ligand. Further reaction with two equivalents of *(166a)* produced cis and trans isomers of the bis-phosphine complex *(224)*.

4.3 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. Table 10 shows the $^{31}P-\{^1H\}$ nmr spectrum for compounds *(199)-(210)*, *(223)* and *(224)*. ^1H and $^{13}C-\{^1H\}$ nmr spectra are displayed in Tables 11 and 12 respectively. IR spectra were recorded on a Perkin Elmer 580 spectrophotometer as a Nujol Mull on polythene discs. The compounds $(PhCN)_2PdCl_2$,[157] $[NaCN(SiMe_3)_2]$[148] and $(COD)PtCl_2$[147] were prepared as described in the literature. The ligand $Ph_2PCH_2C(O)NH^tBu$ was prepared from the method of Healey.[123] The ligands $Ph_2PCH_2CH_2NHCH_2Ph$ and $Ph_2PCH_2CH_2NHCH$ (Me)Ph were stored as 2M solutions in toluene. The toluene solvent was removed before addition of the ligands to reaction mixtures. The platinum and palladium metal salts were obtained on loan from Johnson Matthey p.l.c.

4.3.1 Reaction of K_2PtCl_4 with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of K_2PtCl_4 (500 mg, 1.2 mmol) in water (8 cm^3) was added a solution of

$Ph_2PCh_2CH_2NH^tBu$ (700 mg, 2.45 mmol) in acetone (25 cm^3). The solution, which changed from red to yellow on addition of the phosphine, was stirred at room temperature for 0.5h. The solvent was removed *in vacuo* and the residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane gave a yellow solid cis-[Pt($Ph_2PCH_2CH_2NH^tBu$)($Ph_2PCH_2CH_2NH^tBu$)Cl]Cl *(199)* (915 mg, 91%). Recrystallisation gave the hydrochloride salt with one molecule of water of crystallisation. Found: C, 47.94; H, 5.87; N, 2.64. $C_{36}H_{51}N_2Cl_3OP_2Pt$ requires C, 48.51; H, 5.77; N, 3.14. The complex was identified by $^{31}P-\{^1H\}$ and ^1H nmr spectra (Tables 10 and 11).

4.3.2 Reaction of $(COD)PtCl_2$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of $(COD)PtCl_2$ (300 mg, 0.8 mmol) in dichloromethane (25 cm^3) was added a solution of $Ph_2PCH_2CH_2NH^tBu$ (480 mg, 1.68 mmol) in dichloromethane (25 cm^3). The reaction mixture was stirred for 0.5h, after which time the solution was reduced in volume and petroleum ether was added to precipitate a yellow solid, cis-[Pt($Ph_2PCH_2CH_2NH^tBu$)($Ph_2PCH_2CH_2NH^tBu$)Cl]Cl *(199)* (506 mg, 75%). The complex was identified by $^{31}P-\{^1H\}$ nmr spectrum (Table 10) and by comparison to the sample prepared from the reaction of K_2PtCl_4 and *(166a)*.

4.3.3 Reaction of K_2PtCl_4 with $Ph_2PCH_2CH_2NH^tBu{\cdot}HCl$ *(167a)*

To a solution of K_2PtCl_4 (260 mg, 0.63 mmol) in water (5 cm^3) was added a solution of $Ph_2PCH_2CH_2NH^tBu{\cdot}HCl$ (404 mg, 1.26 mmol) in methanol (30 cm^3). The solution, which changed from red to white on addition of the hydrochloride *(167a)* was stirred for 2h at room temperature. The solvents were removed under vacuum and the residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane gave a white solid, cis-[Pt($Ph_2PCH_2CH_2NH^tBu{\cdot}HCl)_2Cl_2$] *(200)* (360 mg, 68%). The complex was crystallised from dichloromethane and petroleum ether. Found: C, 46.86; H, 6.00; N, 2.85. $C_{36}H_{56}N_2Cl_4P_2Pt$ requires C, 47.53; H, 5.54; N, 3.08. Complex *(200)* was identified by its $^{31}P-\{^1H\}$ and ^1H nmr spectra (Tables 10 and 11).

4.3.4 Reaction of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)Cl]Cl *(199)* with HCl gas

Hydrogen chloride gas was bubbled through a solution of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)Cl]Cl *(199)* (196 mg, 0.023 mmol) in methanol (25 cm^3) for five minutes, after which time the solvent was removed under vacuum to give a white solid, cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu•HCl)$_2$Cl$_2$] *(200)*. The complex was identified by its ^{31}P-{^{1}H} nmr spectrum (Table 10) and by comparison to the sample prepared from the reaction of K_2PtCl_4 with Ph$_2$PCH$_2$CH$_2$NH^{t}Bu•HCl.

4.3.5 Reaction of K_2PtCl_4 with Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph *(166b)*

To a solution of K_2PtCl_4 (500 mg, 1.2 mmol) in water (10 cm^3) was added a solution of Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph (2.6 mmol) in acetone (25 cm^3). The reaction mixture was stirred for 0.5h at room temperature, after which time the solvents were removed under vacuum. The residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the solvent afforded an orange solid cis-[Pt(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)$_2$]2Cl$_2$ *(201)*, (94.1 mg, 86.7%). The complex was identified by its ^{31}P-{^{1}H} and ^{1}H nmr spectra (Tables 10 and 11). On standing in dichloromethane solution it was found that cis-[Pt(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)$_2$2Cl *(201)* converted into cis-[Pt(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)Cl]Cl *(202)*. This complex was identified by its ^{31}P-{^{1}H} nmr spectrum (see Table 10).

4.3.6 Reaction of K_2PtCl_4 with Ph$_2$PCH$_2$CH$_2$NHCH(Me)Ph *(166c)*

To a solution of K_2PtCl_4 (500 mg, 1.20 mmol) in water (8 cm^3) was added a solution of Ph$_2$PCH$_2$CH$_2$NHCH(Me)Ph (2.56 mmol) in acetone (25 cm^3). The mixture was stirred for 0.5h at room temperature, after which time the solvents were removed under vacuum. The residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane afforded a yellow solid, cis-[Pt(Ph$_2$PCH$_2$CH$_2$NHCH(Me)Ph)(Ph$_2$PCH$_2$CH$_2$NHCH(Me)Ph)Cl]Cl *(203)*, (893 mg, 82%). The complex was crystallised from methanol and dichloromethane to give the hydrochloride salt with one

molecule of water. Found: C, 52.52; H, 5.19; N, 2.77. $C_{44}H_{48}N_2Cl_2P_2Pt$ requires C, 56.65; H, 5.19; N, 3.00. The complex was identified by its $^{31}P-\{^1H\}$ nmr spectrum (Table 10).

4.3.7 Reaction of K_2PtCl_4 with $Ph_2PCH_2CH_2N(CH_2Ph)_2$ *(166d)*

To a solution of K_2PtCl_4 (250 mg, 0.60 mmol) in water (10 cm^3) was added a solution of $Ph_2PCH_2CH_2N(CH_2Ph)_2$ (1.21 mmol) in acetone (25 cm^3). The reaction mixture, which turned from red to yellow on addition of the phosphine, was stirred at room temperature for 3h. The solvents were then removed under vacuum and the residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane gave a yellow solid, cis-$[\overline{Pt(Ph_2PCH_2CH_2N}(CH_2Ph)\}\{Ph_2PCH_2CH_2N(CH_2Ph)_2\}Cl]Cl$ *(204)*, (530 mg, 81%), which was identified by its $^{31}P-\{^1H\}$ nmr spectrum (Table 10).

4.3.8 Reaction of cis-$[\overline{Pt(Ph_2PCH_2CH_2N}HCH_2Ph)(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ *(202)* with HCl

Hydrogen chloride gas was bubbled through a solution of cis-$[Pt(Ph_2PCH_2CH_2NHCH_2Ph)(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ *(203)* (400 mg; 0.44 mmol) in methanol (20 cm^3) for 5 minutes. The solvent was removed under vacuum affording a white solid, cis-$[Pt(Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl)_2Cl_2]$ *(205)* (333 mg, 77%) which was identified by its $^{31}P-\{^1H\}$ nmr spectrum (see Table 10). Attempts to crystallize this complex failed, since on standing in a solution of dichloromethane, the complex converted to cis-$[\overline{Pt(Ph_2PCH_2CH_2N}HCH_2Ph)(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ *(202)*, which was identified by its $^{31}P-\{^1H\}$ nmr spectrum (Table 10).

4.3.9 Reaction of cis-$[Pt(Ph_2PCH_2CH_2NHCH_2Ph)_2]2Cl$ *(201)* with HCl

Hydrogen chloride gas was bubbled through a solution of cis-$[\overline{Pt(Ph_2PCH_2CH_2N}HCH_2Ph)_2]2Cl$ *(201)* (400 mg, 0.46 mmol) in methanol (20 cm^3) for 5 minutes. The solvent was removed under vacuum affording a white solid, cis- $[\overline{Pt(Ph_2PCH_2CH_2N}HCH_2Ph{\cdot}HCl)_2Cl_2]$ *(205)* (370 mg, 82%) which was identified on the basis of its $^{31}P-\{^1H\}$ nmr spectrum (see Table 10). As in the previous reaction, on standing in a dichloromethane solution, during crystallisation attempts, complex *(205)* converted into cis-$[Pt(Ph_2PCH_2CH_2NHCH_2Ph)$

$(Ph_2PCH_2CH_2NHCH_2Ph)Cl]Cl$ *(202)*, which was identified by its $^{31}P-\{^1H\}$ nmr spectrum (Table 10).

4.3.10 Reaction of K_2PtCl_4 with $Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl$ *(167b)*

To a solution of K_2PtCl_4 (400 mg, 0.96 mmol) in water (8 cm^3) was added a suspension of $Ph_2PCH_2CH_2NHCH_2Ph{\cdot}HCl$ (600 mg, 1.92 mmol) in acetone (30 cm^3). The solution changed from red to yellow on addition of the hydrochloride and was stirred at room temperature for 0.5h. The solvents were removed under vacuum and the residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane afforded a yellow solid, cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH_2Ph)}(Ph_2PCH_2CH_2NH-CH_2Ph)Cl]Cl$ *(204)*, (622 mg, 82%), which was identified by its $^{31}P-\{^1H\}$ nmr spectrum (see Table 10).

4.3.11 Reaction of cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH(Me)Ph)}(Ph_2PCH_2CH_2NHCH(Me)Ph)Cl]Cl$ *(203)* with HCl gas

Hydrogen chloride gas was bubbled through a solution of *(203)* (240 mg; 0.26 mmol) in methanol (25 cm^3) for five minutes, after which time the $^{31}P-\{^1H\}$ nmr spectrum indicated the complete conversion of *(203)* into cis-$[Pt(Ph_2PCH_2CH_2NHCH(Me)Ph{\cdot}HCl)_2Cl_2]$ *(206)* (210 mg, 80%). The complex was identified by its $^{31}P-\{^1H\}$ nmr spectrum (see Table 10). Attempted crystallisation in dichloromethane solution resulted in the conversion of *(206)* into complex *(203)*, which was identified by its $^{31}P-\{^1H\}$ nmr spectrum.

4.3.12 Reaction of K_2PtCl_4 and $Ph_2PCH_2CH_2NHCH(Me)Ph{\cdot}HCl$ *(167c)*

To a solution of K_2PtCl_4 (250 mg, 0.60 mmol) in water (8 cm^3) was added a solution of $Ph_2PCh_2CH_2NHCH(Me)Ph{\cdot}HCl$ *(167c)* (444 mg, 1.2 mmol) in acetone (25 cm^3). The reaction mixture was stirred at room temperature for 0.5h, after which time the solvents were removed under vacuum. The residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane afforded a yellow solid *(203)*, cis-$[\overline{Pt(Ph_2PCH_2CH_2NHCH(Me)Ph)}(Ph_2PCH_2CH_2NHCH(Me)Ph)Cl]Cl$ (498 mg,

89%), which was identified by its $^{31}P-\{^1H\}$ nmr spectrum (Table 10).

4.3.13 Reaction of $(COD)PtCl_2$ with $Ph_2PCH_2C(O)NH^tBu$

To a solution of $Ph_2PCH_2C(O)NH^tBu$ (235 mg, 0.95 mmol) in dichloromethane (30 cm^3) was added $(COD)PtCl_2$ (150 mg, 4.00 mmol) in dichloromethane (25 cm^3). The reaction mixture was stirred for 0.5h at room temperature, after which time the solvent was removed under vacuum. The resulting white solid was crystallised from dichloromethane and petroleum ether to give cis-$[Pt(Ph_2PCH_2C(O)NH^tBu)_2Cl_2]$ *(209)* (645 mg, 89%). Found: C, 48.34; H, 4.72; N, 2.58. $C_{35}H_{44}N_2Cl_2O_2P_2Pt$ requires C, 50.02; H, 5.13; N, 3.24. The complex was identified by its $^{31}P-\{^1H\}$ and ^1H nmr spectra (see Tables 10 and 11).

4.3.14 Reaction of cis-$[Pt(Ph_2PCH_2C(O)NH^tBu)_2Cl_2]$ *(209)* with sodium methoxide

To a solution of complex *(209)* (225 mg, 0.28 mmol) in acetonitrile (30 cm^3) was added an excess of sodium methoxide (100 mg, 1.9 mmol). The reaction mixture was stirred at room temperature for 24h, after which time the excess sodium methoxide was removed by filtration. The solvent was removed under vacuum to give a yellow solid. The $^{31}P-\{^1H\}$ nmr of the solid in dichloromethane displayed a large number of signals. The products were not identified since attempts at purification led to further decomposition.

4.3.15 Reaction of cis-$[Pt(Ph_2PCH_2C(O)NH^tBu)_2Cl_2]$ *(209)* with triethylamine

To a solution of *(209)* (250 mg, 0.31 mmol) in acetonitrile (40 cm^3) was added triethylamine (0.092 cm^3, 0.65 mmol). The reaction mixture was refluxed for 3h at 90°C, after which time it was cooled to room temperature and the solvent was removed under vacuum yielding a yellow solid. The $^{31}P-\{^1H\}$ nmr of the solid in dichloromethane displayed numerous signals which were not isolated or identified.

4.3.16 Reaction of cis-$[\overline{Pt(Ph_2PCH_2CH_2NH^tBu)}(Ph_2PCH_2CH_2NH^tBu)Cl]Cl$ *(199)* with $Na[N(SiMe_3)_2]$

To a solution of cis-$[\overline{Pt(Ph_2PCH_2CH_2NH^tBu)}(Ph_2PCH_2CH_2NH^tBu)Cl]Cl$ (600 mg, 0.72

mmol) in THF (20 cm^3) was added $Na[N(SiMe_3)_2]$ (275 mg, 1.5 mmol). The solution changed from yellow to brown on addition of the base and was stirred for 0.5h at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in diethylether and filtered. Evaporation of the diethylether afforded a dark yellow/brown solid, complex *(207)* (376 mg). Found: C, 53.07; H, 6.06; N, 3.29. The $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ nmr spectra of complex *(207)* are displayed in Tables 10, 11 and 12.

4.3.17 Reaction of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)Cl]Cl *(199)* with NaOH

To a solution of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)(Ph$_2$PCH$_2$CH$_2$NH^{t}Bu)Cl]Cl (235 mg, 0.28 mmol) in methanol (25 cm^3) was added sodium hydroxide pellets (300 mg, 7.5 mmol). The mixture was stirred for 2h, after which time the solvent was removed under vacuum. The residue was dissolved in diethylether and filtered affording a dark yellow/brown solid, complex *(207)* (160 mg). The $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ nmr spectra for *(207)* are displayed in Tables 10, 11 and 12.

4.3.18 Reaction of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)$_2$]2Cl *(201)* with NaOH

To a solution of *(201)* (250 mg, 0.27 mmol) in methanol (25 cm^3) was added sodium hydroxide pellets (330 mg, 8.3 mmol). The reaction mixture was stirred for 2h, after which time the solvent was removed under vacuum. The residue was dissolved in diethylether and filtered to give a yellow/brown solid, complex *(208)* (182 mg). The $^{31}P-\{^1H\}$ nmr spectrum of *(208)* is displayed in Table 10.

4.3.19 Reaction of cis-[Pt(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)(Ph$_2$PCH$_2$CH$_2$NHCH$_2$Ph)Cl]Cl *(202)* with NaOH

Complex *(202)* was reacted with NaOH in the same way as complex *(208)* above, to give complex *(208)*. $^{31}P-\{^1H\}$ nmr spectrum of *(208)* is displayed in Table 10.

4.3.20 Reaction of Complex *(207)* with carbon monoxide

Carbon monoxide was bubbled through a solution of complex *(207)* (125 mg) in

chloroform (25 cm^3) for 10h. Evaporation of the solvent afforded a brown solid, which was shown by $^{31}P-\{^1H\}$ nmr spectroscopy to contain unreacted *(207)*.

4.3.21 Reaction of Complex *(207)* with methyliodide

To a solution of complex *(207)* (130 mg) in THF (30 cm^3) was added methyliodide (22 µl, 0.35 mmol). The reaction mixture was stirred at room temperature for 2h, after which time the solvent was evaporated to give a brown solid, which was shown by $^{31}P-\{^1H\}$ nmr spectroscopy to contain unreacted *(207)*.

4.3.22 Reaction of Complex *(207)* with carbon dioxide

To a solution of complex *(207)* (150 mg) in THF (30 cm^3) was added a large excess of frozen carbon dioxide pellets. The reaction mixture was stirred for 3h, with additional pellets added every half an hour. Evaporation of the solvent afforded a brown solid, which was shown by $^{31}P-\{^1H\}$ nmr spectroscopy to contain unreacted *(207)*.

4.3.23 Reaction of $(PhCN)_2PdCl_2$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of $(PhCN)_2PdCl_2$ (250 mg, 0.65 mmol) in dichloromethane (20 cm^3) was added a solution of $Ph_2PCH_2CH_2NH^tBu$ (186 mg, 0.65 mmol) in dichloromethane (10 cm^3). The mixture was stirred at room temperature for 2h, after which time the solvent was removed under vacuum to give a pale yellow solid. Crystallisation from dichloromethane and petroleum ether yielded pale yellow crystals of cis-$[\overline{Pd(Ph_2PCH_2CH_2NH^tBu)Cl_2}]$ *(208)* (252 mg, 83.6%). Found: C, 46.69; H, 5.16; N, 3.14. $C_{18}H_{24}NCl_2PPd$ requires C, 46.73; H, 5.23; N, 3.03. The complex was identified by its $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ nmr spectra (Tables 10, 11 and 12) and its IR spectrum: ν(Pd-Cl) 325 and 280 cm^{-1}.

4.3.24 Reaction of $(PhCN)_2PdCl_2$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of $(PhCN)_2PdCl_2$ (1.0g, 2.6 mmol) in dichloromethane (30 cm^3) was added a solution of $Ph_2PCH_2CH_2NH^tBu$ (1.49 mg, 5.3 mmol) in dichloromethane (30 cm^3). The reaction mixture was stirred for 3h, after which time the volume of solvent was reduced and petroleum ether was added to precipitate an orange solid containing cis and trans

[$Pd(Ph_2PCH_2CH_2NH^tBu)_2Cl_2$] *(223)* (1.51g, 78%). The complex was crystallised from dichloromethane and petroleum ether to give cis-[$Pd(Ph_2PCH_2CH_2NH^tBu)_2Cl_2$]. Found: C, 60.91; H, 7.16; N, 3.87. $C_{36}H_{44}N_2Cl_2P_2Pd$ requires C, 57.80; H, 6.47; N, 3.75. Complex *(223)* was identified by its $^{31}P-\{^1H\}$ and ^1H nmr spectra (Tables 10 and 11) and its IR spectrum: ν(Pd-Cl) 300 cm^{-1}.

4.3.25 Reaction of $(PhCN)PdCl_2$ with $Ph_2PCH_2CH_2NHCHMePh$ *(166c)*

To a solution of $(PhCN)_2PdCl_2$ (95 mg, 0.25 mmol) in dichloromethane (15 cm^3) was added a solution of $Ph_2PCH_2CH_2NHCHMePh$ (300 mg, 0.89 mmol) in dichloromethane (15 cm^3). The reaction mixture was stirred for 0.5h at room temperature, after which time the solvent was removed under vacuum, giving a pale yellow solid. Crystallisation of the solid from dichloromethane and petroleum ether afforded pale yellow crystals of [$\overline{Pd(Ph_2PCH_2CH_2NHCHMePh)Cl_2}$] *(212)* (114 mg, 91%). Found: C, 50.90; H, 5.01; N, 2.32. $C_{22}H_{24}NCl_2PPd$ requires C, 51.73; H, 4.74; N, 2.74. Complex *(224)* was identified by its $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ nmr spectra (Tables 10, 11 and 12).

TABLE 10

^{31}P-{^{1}H} Nmr data[a] for some Aminoalkylphosphine Complexes

Complex	δ (P_A)	^{1}J(Pt-P_A)	δ (P_B)	^{1}J(Pt-P_B)	^{2}J(P_A-P_B)
(199)[b]	-2.2	3203	+32.7	3765	20
(200)[c]	+3.6	3623			
(201)	+28.4	3398			
(202)	-5.3	3189	+33.9	3779	20
(203)[b]	-1.7	3228	+37.0	3784	–*
(204)[b]	-2.2	3223	+33.8	3789	20
(205)	+3.6	3662			
(206)	+2.8	3667			
(207)	+34.7	–**			
(208)	+30.9 +30.1	–**			
(209)	+8.1	3750			
(210)	+50.8				
(223)	+31.1 +21.8				
(224)	+56.0 +55.3				

[a] in dichloromethane;
[b] in methanol;
[c] in chloroform.

* see Section 4.2.3
** see Section 4.2.5

TABLE 11

^{1}H nmr data[a] for some Aminoalkylphosphine Complexes

Complex	δ (^{1}H)
(199) [b] *	1.35 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 2.60-3.50 (m, br, 8H, CH_2), 7.50 (m, 20H, Ph)
(200) *	1.40 (s, 9H, ^{t}Bu), 3.45 (m, 2H, CH_2), 7.30 (m, 10H, Ph), 9.50 (br, 2H, NH_2)
(201) *	2.10 (m, br, 2H, CH_2), 5.00 (s, br, 2H, CH_2Ph), 7.30 (m, 15H, Ph)
(207) *	1.05 (s, 9H, ^{t}Bu), 2.50 (td, 2H, CH_2, $J_{(HH)} = 7.3$, $J_{(PH)} = 10.9$), 2.70 (td, 2H, CH_2, $J_{(HH)} = 7.5$, $J_{(PH)} = 11.2$), 7.40-7.80 (m, 10H, Ph)
(209) *	1.45 (s, 9H, ^{t}Bu), 3.45 (m, 2H, CH_2), 7.30 (m, 10H, Ph)
(210) *	1.45 (s, 9H, ^{t}Bu), 2.65 (m, 2H, CH_2), 3.20 (dd, 1H, CH_2), 3.75 (m, 1H, CH_2), 5.9 (s, 1H, NH), 7.6 (m, 10H, Ph)
(223) *	1.30 (s, 9H, ^{t}Bu), 3.15 (m, br, 4H, CH_2), 7.60 (m, 10H, Ph)
(224) *	1.75 (d, 3H, CH_3), 1.85 (d, 3H, CH_3), 2.60-3.80 (m, 8H, CH_2), 5.50 (m, 1H, CH), 5.70 (m, 1H, CH), 7.60 (m, 30H, Ph)

[a] In $CDCl_3$; [b] In CD_3OD.

* At 300 MHz
* At 90 MHz

TABLE 12

^{13}C-{^{1}H} nmr data[a] for some Aminoalkylphosphine Complexes

Complex	δ (^{13}C)
(207)	28.7 ($C\underline{Me}_3$), 30.6 ($\underline{C}H_2$), 35.7 ($\underline{C}H_2$), 50.5 ($\underline{C}Me_3$), 125-134 (Ph)
(210)	31.0 ($C\underline{Me}_3$), 34.5 [d, C_1, $J_{P\text{-}C}$ = 29], 50.4 (C_2), 59.9 ($\underline{C}Me_3$), 129-134 (Ph)
(224)	17.6, 17.8 } $C\underline{Me}_3$, 31.8 [d, C, $J_{P\text{-}C}$ = 30], 43.6, 32.8 [d, C, $J_{P\text{-}C}$ = 30], 42.6 } C_2, 58.9, 59.4 } $\underline{C}Me_3$, 125-139 (Ph)

[a] In $CDCl_3$.

CHAPTER 5

Synthesis of some Aminoalkylphosphine, $Ph_2PCH_2CH_2NHR$, Complexes of Fe(II) and Ru(II)

5.1 INTRODUCTION

Although iron(II) and ruthenium(II) can be classed as 'borderline' rather than 'soft' acids, examples of amide complexes of these metals are relatively rare. The recent interest in amides of the late transition metals has resulted in the preparation of many more amide complexes, particularly with ruthenium. However, an example of an iron amide, $Fe[N(SiMe_3)_2]_3$ was reported as early as 1963 by Bürger *et al.*,[164] Scheme 66. The two

$$2FeCl_3 + 3Na[N(SiMe_3)_2] \longrightarrow Fe[N(SiMe_3)_2]_3 + Na_3FeCl_6$$

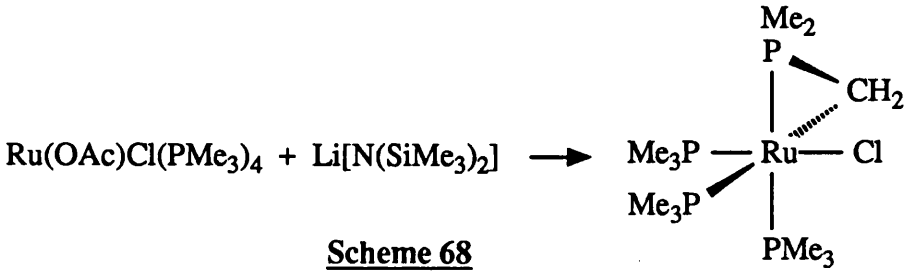
Scheme 66

co-ordinate iron amide $Fe[N(SiMePh_2)_2]_2$ has also been prepared.[165] The ligand $-N(SiMe_3)_2$, which is stable with respect to β-elimination, was also used to prepare the first example of a ruthenium amide complex, $RuH(PPh_3)_2[N(SiMe_3)_2]$, *via* a metal exchange reaction,[39] Scheme 67. However, other ruthenium complexes such as cis-$[Ru(OAc)Cl(PMe_3)_4]$ or cis-

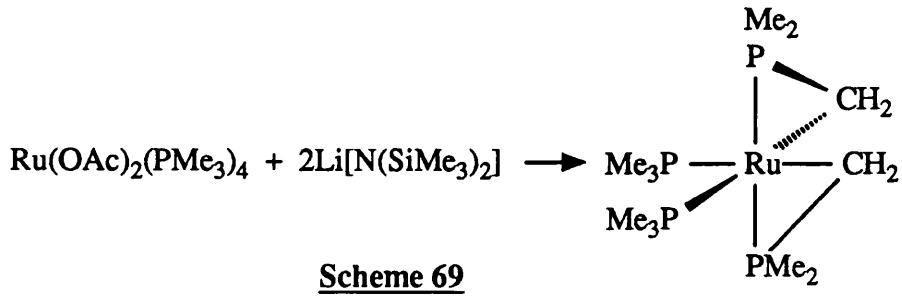
$$Ru(H)Cl(PPh_3)_3 + Li[N(SiMe_3)_2] \longrightarrow Ru(H)(PPh_3)_2[N(SiMe_3)_2]$$

Scheme 67

$[Ru(OAc)_2(PMe_3)_4]$ did not react with $Li[N(SiMe_3)_2]$, instead metallacyclic complexes of the type shown in Schemes 68 and 69 were formed.[166] It is suggested that the amides were not



Scheme 68



Scheme 69

formed due to the greater electron density at the metal in the case of the PMe_3 complexes, compared to the PPh_3 complex, Scheme 67, making nucleophilic substitution relatively slow, or to the greater acidity of alkyl relative to aryl C-H bonds in phosphines.

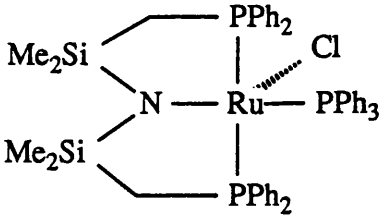
Ruthenium amides have also been prepared by metal exchange reactions using LiNRPh (R = H or Ph) and $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ in THF,[32] as described in Chapter 1, Scheme 13. However, the use of $LiNH^tBu$ leads to the formation of a metallacyclic complex, $(\eta^5\text{-}C_5H_5)\text{-}Ru(PMe_3)(CH_2PMe_2)$,[32] similar to that shown in Scheme 68. Reactions with other primary amide salts led to intractable product mixtures. However, primary and secondary amines have been used successfully to produce ruthenium amides *via* exchange with ruthenium hydroxo complexes, Scheme 70.

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(OH) + HNRPh \rightleftharpoons (\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NRPh) + H_2O$$
(R = H or Ph)

Scheme 70

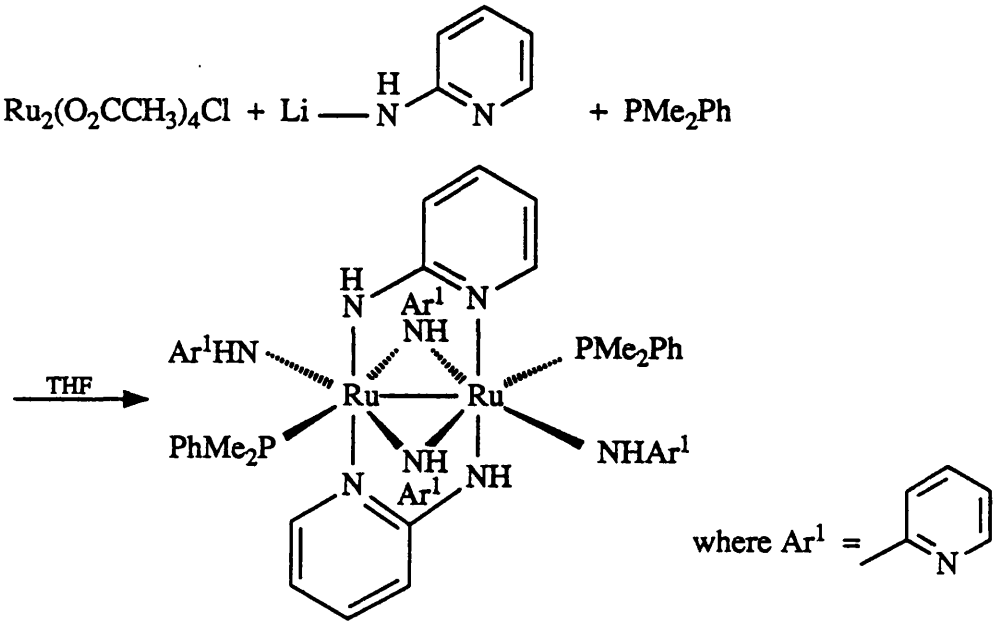
A whole range of late transition metal amide complexes have been prepared using the chelating ligand, $LiN(SiMe_2CH_2PPh_2)_2$, which contains phosphine and amide donor groups. A five co-ordinate ruthenium amide complex, Scheme 71, has been prepared with this

$$RuCl_2(PPh_3)_2 + LiN(SiMe_2CH_2PPh_2)_2 \xrightarrow[(-LiCl)\ (-PPh_3)]{THF}$$



Scheme 71

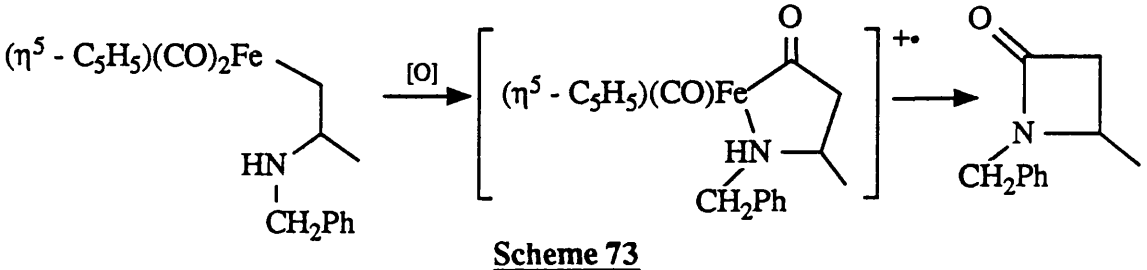
ligand.[167] Reactions of this complex with electrophiles and nucleophiles have been reported, however, the metal amide bond does not react. Another chelating ligand, 2-aminopyridine, has been used to prepare a binuclear ruthenium complex in which the amido co-ordinates in a terminal and bridging position, Scheme 72.[168]



Scheme 72

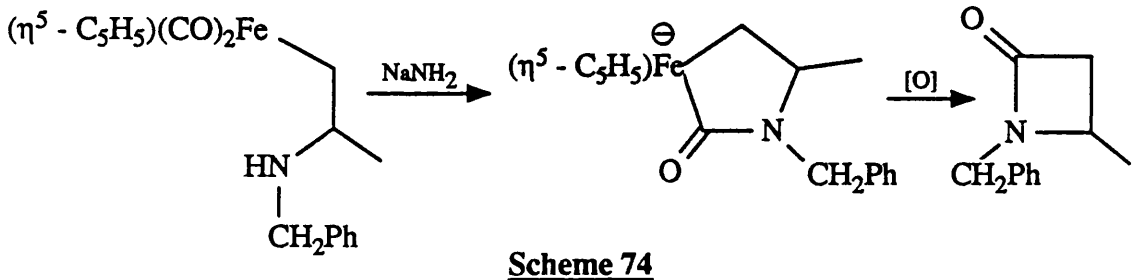
Relatively few iron or ruthenium complexes have been reported with functionalised phosphine ligands, but Khan[90] prepared a number of ruthenium complexes with the ligand $Ph_2PCH_2CH_2NHCH_2Ph$, such as the five co-ordinate ruthenium(II) complex, $[\overline{Ru(Ph_2PCH_2CH_2NHCH_2Ph)_2}Cl]Cl$. However, the ligand used has been shown to be $Ph_2PCH_2CH_2N(CH_2Ph)_2$ (see Chapter 2).

The synthesis of the important antibiotics, β-lactams, by the rhodium catalyzed ring expansion of aziridines was discussed in Chapter 1. However, β-lactams have also been prepared *via* a number of other transition metal complexes, including some β-aminoalkyl iron complexes. The oxidative degradation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CH_2CHMeNH(CH_2Ph)\}]$ results in the formation of β-lactams and Rosenblum[169] suggests that the reaction proceeds *via* an iron(III) radical cation intermediate, Scheme 73. The β-lactam formed from this



Scheme 73

radical cation results from the formation of a C-N bond. However, Giering[170] has shown that the radical cation is not the immediate precursor of the β-lactam, and reports that the reaction can go *via* deprotonation and cyclisation to form an anionic aminocarbonyl complex, Scheme 74. Presumably, the reaction proceeds through deprotonation of the amine, which then attacks a carbonyl group. The anion then eliminates the β-lactam, which involves C-C bond formation.



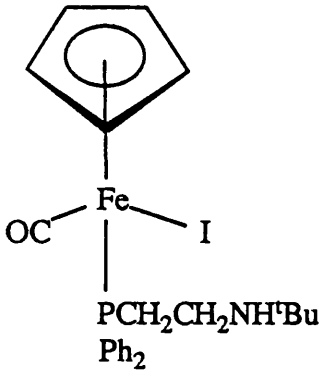
Scheme 74

This Chapter discussed the formation of some iron and ruthenium complexes of the ligands $Ph_2PCH_2CH_2NHR$ (R = ^{t}Bu, CH_2Ph, CH(Me)Ph) and $Ph_2PCH_2C(O)NH^tBu$. The attempted deprotonation of these complexes to form chelate-stabilised iron or ruthenium amides is also reported.

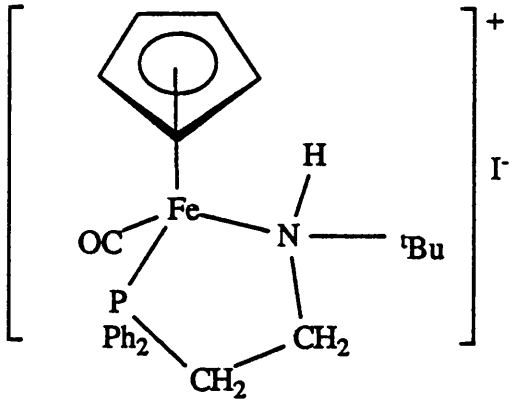
5.2 RESULTS AND DISCUSSION

5.2.1 Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NH^tBu$ in the presence of the catalyst $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ led to a mixture of two complexes, *(211)* and *(212)*, in a 5:1 ratio. Complex *(211)* is the dark green complex $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NH^tBu)I$ and complex *(212)* is the brown coloured chelate complex $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NH^tBu)}]I$, where iodide has been displaced by amine. The $^{31}P\text{-}\{^1H\}$ nmr spectrum of *(211)* (Table 13) exhibits a single chemical shift at δ +59.1 ppm, whereas the chemical shift of complex *(212)* is further downfield at δ +80.7 ppm, indicating the presence of a five-membered chelate ring.[153,154] Complex *(212)* contains two chiral centres, one at iron and the other at nitrogen. Similar iridium and rhodium cyclopentadienyl and ruthenium arene complexes incorporating amino acids have been reported.[171] In these complexes only one configuration at nitrogen is



(211)



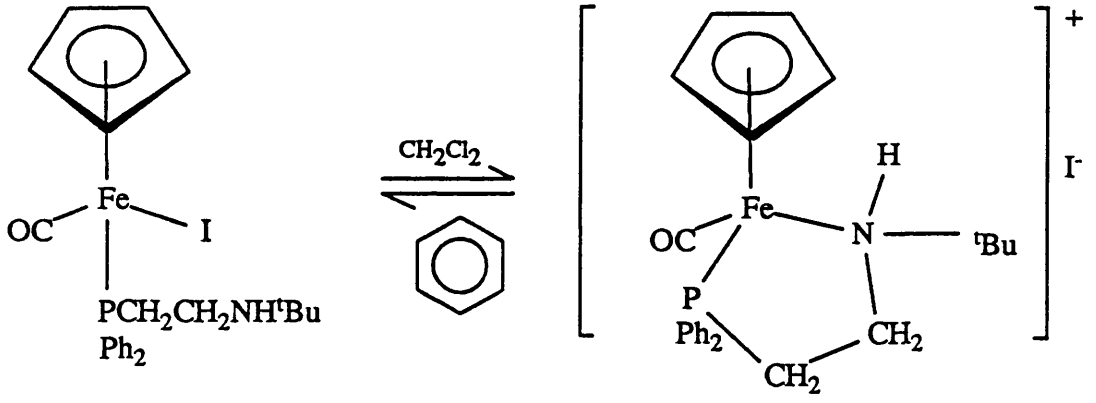
(212)

observed, consistent with the hydrogen being orientated towards the cyclopentadienyl or arene ring, and the more bulky substituent being orientated away from the ring. It is therefore probable that the tert-butyl group in complex *(212)* is orientated away from the cyclopentadienyl ring to give the most sterically favoured configuration. This situation allows only two possible combinations of the chiral centres, resulting in two enantiomers, (RR) and (SS), which will not be distinguishable by $^{31}P-\{^{1}H\}$ nmr spectroscopy. This is consistent with the observed single peak in the $^{31}P-\{^{1}H\}$ nmr spectrum.

Complex *(211)* is soluble in benzene, whereas complex *(212)* is insoluble. Crystallisation of *(211)* from benzene gave dark green crystals which were used for microanalysis and ^{1}H nmr spectroscopy. The ^{1}H nmr spectrum (Table 13) exhibits a singlet at δ 0.85 ppm, assigned to the tert-butyl protons and a multiplet in the region δ 2.30-2.90 ppm assigned to the methylene protons. A singlet at δ 4.00 ppm was also observed, assigned to the cyclopentadienyl protons, as well as multiplets (δ 6.90-7.80 ppm) corresponding to the phenyl groups. It was observed that the ^{1}H nmr spectrum of *(211)* broadened and indicated the presence of *(212)*, as well as *(211)*, even if the sample was left in solution for short periods of time. Complex *(212)* was isolated by filtering the brown solid *(212)* from the green solution of *(211)* in benzene. The ^{1}H nmr spectrum of *(212)* (Table 13) was broad, although signals were observed similar to those displayed by complex *(211)*, but shifted further downfield. A singlet at δ 1.30 ppm is assigned to the tert-butyl protons and the multiplets in the region δ 2.60-3.40 ppm are assigned to the methylene protons. The

cyclopentadienyl protons are assigned to a singlet observed at δ 4.85 ppm, whilst the multiplets in the region δ 7.20-7.80 ppm are assigned to the phenyl groups. The broadness of any spectra containing complex *(212)* is thought to be due to paramagnetic properties of the complex, resulting from the iron existing in a high spin state. The infrared spectra of complexes *(211)* and *(212)* were recorded in solution, however, this was not found to be a useful technique in distinguishing between the two complexes since the difference between their ν(C=O) stretching frequencies is very small (1960 cm^{-1} and 1975 cm^{-1} respectively).

Complexes *(211)* and *(212)* equilibrate in solution. The equilibrium is solvent dependent, lying towards the non-chelate complex *(211)* in benzene solution and towards the chelate complex *(212)* in the more polar dichloromethane solution, Scheme 75. Presumably, more



(211) *(212)*

Scheme 75

polar solvents stabilise the salt structure of *(212)*. After refluxing the reaction mixture of the two complexes in benzene for two days, the $^{31}P-\{^{1}H\}$ nmr spectrum indicated that complex *(212)* had been completely converted into complex *(211)*. Refluxing the reaction mixture in dichloromethane for two days pushed the equilibrium in the opposite direction and led to a 1:1 mixture of complexes *(211)* and *(212)*, as seen by $^{31}P-\{^{1}H\}$ nmr spectroscopy. Further refluxing in dichloromethane did not alter the ratio of the two complexes.

The reaction of $(\eta^5-C_5H_5)Fe(CO)_2I$ with ligand *(166a)*, $Ph_2PCH_2CH_2NH^tBu$ in the presence of the dimer $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ as a catalyst is thought to proceed *via* a free radical chain mechanism. The thermal dissociation of this dimer, Scheme 76, and other

similar dimers such as $Mn_2(CO)_{10}$ into radicals is well precedented.[172-175] The reaction of

$$[(\eta^5 - C_5H_5)Fe(CO)_2]_2 \longrightarrow 2(\eta^5 - C_5H_5)Fe(CO)_2^{\bullet}$$

Scheme 76

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)]$ with phosphines and phosphites is reported to proceed, in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, *via* a free radical chain mechanism,[177] Scheme 77. The dimer dissociates to give the radical $(\eta^5\text{-}C_5H_5)Fe(CO)_2\bullet$, which then reacts, substituting a carbonyl with the phosphine or phosphite, P. The new radical $(\eta^5\text{-}C_5H_5)Fe(CO)P\bullet$ then reacts with $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ to give the product and regenerate the radical

$$[(\eta^5 - C_5H_5)Fe(CO)_2]_2 \longrightarrow 2(\eta^5 - C_5H_5)Fe(CO)_2^{\bullet}$$

$$(\eta^5 - C_5H_5)Fe(CO)_2^{\bullet} + P \longrightarrow (\eta^5 - C_5H_5)Fe(CO)P^{\bullet} + CO$$

$$(\eta^5 - C_5H_5)Fe(CO)P^{\bullet} + (\eta^5 - C_5H_5)Fe(CO)_2(\eta^1 - C_5H_5) \longrightarrow$$

$$(\eta^5 - C_5H_5)Fe(CO)P(\eta^1 - C_5H_5) + (\eta^5 - C_5H_5)Fe(CO)_2^{\bullet}$$

Scheme 77

$(\eta^5\text{-}C_5H_5)Fe(CO)_2\bullet$ which will react with further molecules of phosphine or phosphite. However, the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with ^{t}BuNC, in the presence of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ dimer, is proposed by Colville *et al.*[176,178] to proceed *via* a 'non-chain' radical mechanism, to form $(\eta^5\text{-}C_5H_5)Fe(CO)(^t\text{BuNC})I$. This mechanism involves electron transfer, and is thought to involve an active catalyst species (A), which induces ligand activation and subsequently product formation, Scheme 78. The species (A) may correspond

$$[(\eta^5 - C_5H_5)Fe(CO)_2]_2 \overset{h\nu/\Delta}{\rightleftharpoons} (A)$$

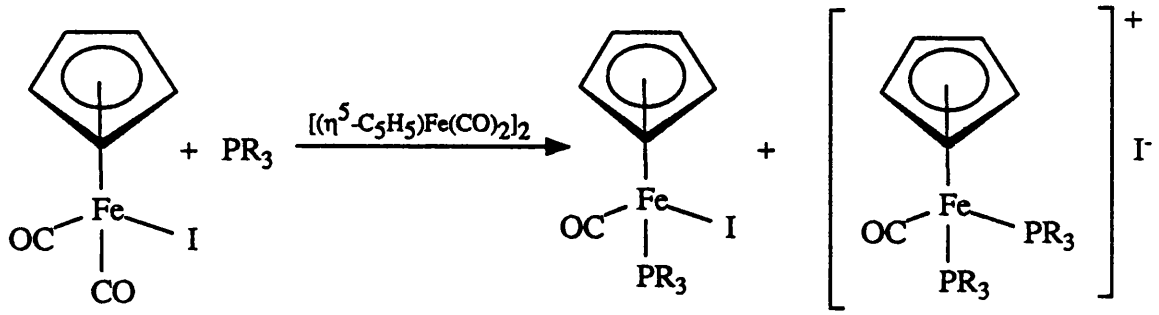
$$(A) + [(\eta^5 - C_5H_5)Fe(CO)_2I] \rightleftharpoons (A) - [(\eta^5 - C_5H_5)Fe(CO)_2I]$$

$$(A) - [(\eta^5 - C_5H_5)Fe(CO)_2I] + RNC \rightleftharpoons (A) - [(\eta^5 - C_5H_5)Fe(CO)(CNR)I] + CO$$

$$(A) - [(\eta^5 - C_5H_5)Fe(CO)(CNR)I] \rightleftharpoons (A) + [(\eta^5 - C_5H_5)Fe(CO)(CNR)I]$$

Scheme 78

to the $(\eta^5\text{-}C_5H_5)Fe(CO)_2\bullet$ radical. Colville also reports the use of this type of reaction with phosphine donor ligands (PR_3) with both iron and ruthenium complexes,[176] Scheme 79. The



Scheme 79

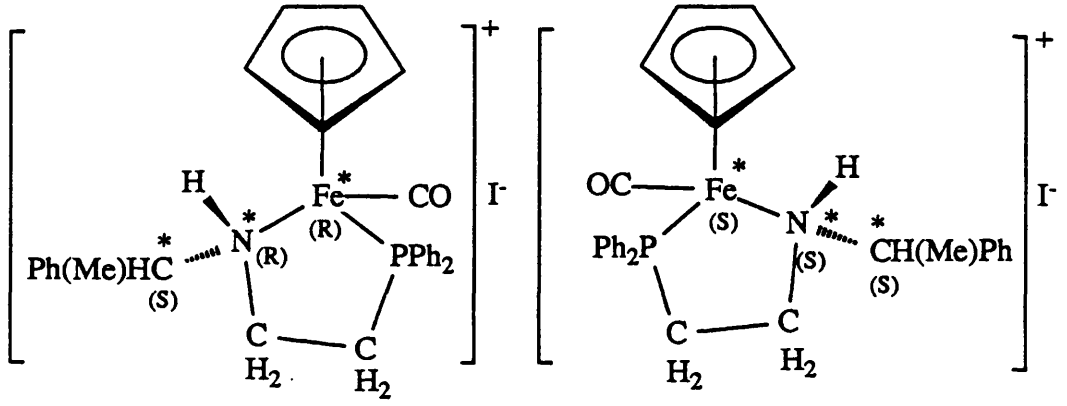
use of the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as a catalyst in the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NH^tBu$ was found to be very effective at increasing the rate of reaction. The reaction time of 0.75h in the presence of the dimer can be compared to 3h in its absence.

5.2.2 Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)* and $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with either $Ph_2PCH_2CH_2NHCH_2Ph$ or $Ph_2PCH_2CH_2NH$ CH(Me)Ph, in the presence of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalyst, gave similar products to those formed with $Ph_2PCH_2CH_2NH^tBu$ (Section 5.2.1). $Ph_2PCH_2CH_2NHCH_2Ph$ reacts to give two products, the dark green $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHCH_2Ph)I$, *(213)* and the brown chelate complex $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NHCH_2Ph)}]I$, *(214)*. Similarly, the ligand $Ph_2PCH_2CH_2NHCH(Me)Ph$ reacted to give the dark green $(\eta^5\text{-}C_5H_5)Fe(CO)$ $(Ph_2PCH_2CH_2NHCH(Me)Ph)I$ *(215)* and the brown chelate complex $[(\eta^5\text{-}C_5H_5)$ $\overline{Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)}]I$ *(216)*. As was the case with complex *(212)*, *(214)* will exist as diastereoisomers, due to the two chiral centres at iron and nitrogen. However, steric factors will result in the hydrogen being orientated towards the cyclopentadienyl ring, allowing only two enantiomers, (RR) and (SS), which will not be distinguishable by $^{31}P\text{-}\{^1H\}$ nmr spectroscopy. The $^{31}P\text{-}\{^1H\}$ nmr spectrum of *(214)* (Table 13) displays a single chemical shift at δ +83.3 ppm, similar to that of complex *(212)* at δ +80.7 ppm. The non-chelate complex *(213)* also display a $^{31}P\text{-}\{^1H\}$ nmr chemical shift (δ +57.7 ppm) similar

to that of complex *(211)*, δ +59.1 ppm. The downfield $^{31}P-\{^{1}H\}$ nmr shift of complex *(214)* compared to that of *(213)* suggests that the phosphorus atom in complex *(214)* is incorporated in a five-membered chelate ring.[153,154]

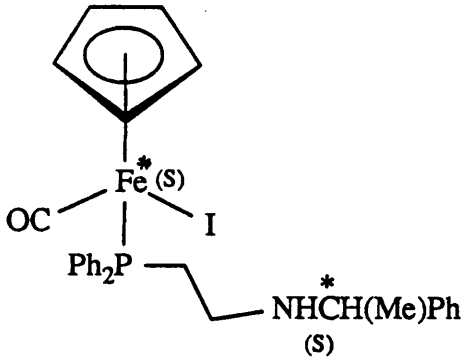
Complexes *(215)*, $(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)I$, and *(216)*, $[(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)]I$ differ from *(213)* and *(214)*, since they contain a chiral substituent on the nitrogen ligand. This results in complex *(216)* containing three chiral centres, one at iron, one at nitrogen and one at the carbon of the -CH(Me)Ph group, which has a fixed (S) configuration. The two chiral centres at nitrogen and iron can either



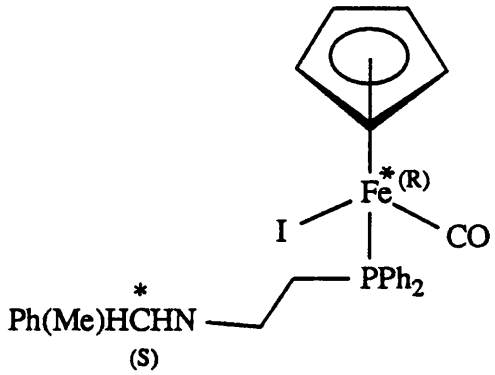
(216a) (RRS) *(216b)* (SSS)

have configurations of (SS) or (RR), in the same way as complexes *(212)* and *(214)*, since the hydrogen will always be orientated towards the cyclopentadienyl ring. This results in the three chiral centres combining to give two possible diastereoisomers *(216a)* which has an (RRS) configuration and *(216b)* which has an (SSS) configuration. The two diastereoisomers can be seen in the $^{31}P-\{^{1}H\}$ nmr spectrum (Table 13) as two singlets at δ +80.6 and +81.4 ppm. Due to the chiral CH(Me)Ph group, complex *(215)*, $(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)I$ has two chiral centres, one at iron and one at the carbon of the -CH(Me)Ph group. The latter has a fixed (S) configuration, resulting in two possible diastereoisomers, *(215a)* which has a (SS) configuration and *(215b)* which has a (RS) configuration. However, the $^{31}P-\{^{1}H\}$ nmr spectrum of *(215)* displays only one signal at δ +56.7 ppm. The observation of only one signal can be explained by the distance between the two chiral centres. In

complex *(216)* the chiral centres are in close proximity, resulting in two $^{31}P-\{^1H\}$ nmr chemical shifts being observed, however, the chiral centres in complex *(215)* may be too far apart to effect each other's magnetic environment.



(215a) (SS)



(215b) (RS)

Both pairs of complexes *(213)/(214)* and *(215)/(216)* equilibrate in solution, in a similar manner to complexes *(211)* and *(212)*. Full conversion of just one complex was not achieved for either pair of complexes, although the percentage of the non-chelate complexes increased on refluxing in benzene. Conversely, the percentage of the chelate complexes increased on refluxing the mixtures in dichloromethane. Isolation of these complexes proved difficult, due to the equilibria between each pair. Filtration and flash column chromatography were used to attempt to separate the complexes, but standing, even for short periods of time in solution, led to the formation of a mixture of both chelate and non-chelate complexes. This has made collection of nmr data difficult and all $^{31}P-\{^1H\}$ and ^1H nmr spectra recorded represent a mixture of either complexes *(213)* and *(214)* or complexes *(215)* and *(216)*.

5.2.3 Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)I$ with $Ph_2PCH_2C(O)NH^tBu$

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2C(O)NH^tBu$ led to the formation of one product, the green coloured, non-chelate complex, $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2C(O)NH^tBu)I$, *(217)*. The corresponding chelate complex was not observed. This is presumably due to the carbonyl group of the ligand, which delocalises the nitrogen lone pair, making them unavailable for co-ordination to the metal. The monodentate nature of this ligand was also observed in the complex cis-$[Pt(Ph_2PCH_2C(O)NH^tBu)_2Cl_2]$ *(209)* in Chapter 4, where the

ligand co-ordinates to the platinum only through the phosphorus atom.

The $^{31}P-\{^1H\}$ nmr spectrum (Table 13) of complex *(217)* exhibits a single resonance at δ +61.5 ppm, slightly downfield to that exhibited by $(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NH^tBu)I$ at δ +59.1 ppm. The ^1H nmr spectrum (Table 13) displays singlets at δ 1.1 and 4.3 ppm, assigned to the tert-butyl and cyclopentadienyl protons respectively, as well as signals in the region δ 6.90-7.80 ppm due to the phenyl groups. Two doublets of doublets observed at δ 3.45 and 3.65 ppm are assigned to the two protons of the CH_2 group (Fig. 8). The more downfield signal (A) has two coupling constants of 13.4 and 9.9 Hz, whereas the higher field signal (B) has coupling constants of 13.1 and 9.9 Hz. The coupling constants have not been assigned, but both are within the normal ranges for $^2J_{P-H}$ and geminal J_{H-H}.

5.2.4 Reaction of $(\eta^5-C_5H_5)Ru(CO)_2Cl$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*, $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*

$(\eta^5-C_5H_5)Ru(CO)_2Cl$ reacted with the ligand $Ph_2PCH_2CH_2NH^tBu$, in the presence of the $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ dimer to form the yellow chelate complex $[(\eta^5-C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NH^tBu)}]Cl$ *(219)* as the major product and a small amount of the brown non-chelate complex $(\eta^5-C_5H_5)Ru(CO)(Ph_2PCH_2CH_2NH^tBu)I$, *(218)*. Complex *(219)* was isolated by flash column chromatography, but complex *(218)* was produced in such small amounts that it was found to be very difficult to purify. The $^{31}P-\{^1H\}$ nmr spectra (Table 13) of complexes *(218)* and *(219)* exhibit signals at δ +40.5 and +66.6 ppm respectively. The difference in $^{31}P-\{^1H\}$ nmr chemical shift between complexes *(218)* and *(219)*, suggests that the phosphorus atom in complex *(219)* is incorporated in a five-membered chelate ring.[153,154] Complex *(219)* can be compared to complex *(212)*, since it also contains two chiral centres, one at ruthenium and one at nitrogen. The only possible configurations of the complex are (SS) and (RR), due to the orientation of the hydrogen towards the cyclopentadienyl ring. The two isomers, *(219a)* and *(219b)*, are enantiomers and therefore indistinguishable in the $^{31}P-\{^1H\}$ nmr spectrum. The ^1H nmr spectrum of *(219)* exhibits a singlet at δ 1.30 ppm, assigned to the tert-butyl protons and a singlet at δ 5.00 ppm, assigned to the cyclopentadienyl protons, as well as signals due to the phenyl groups. A multiplet, in the region

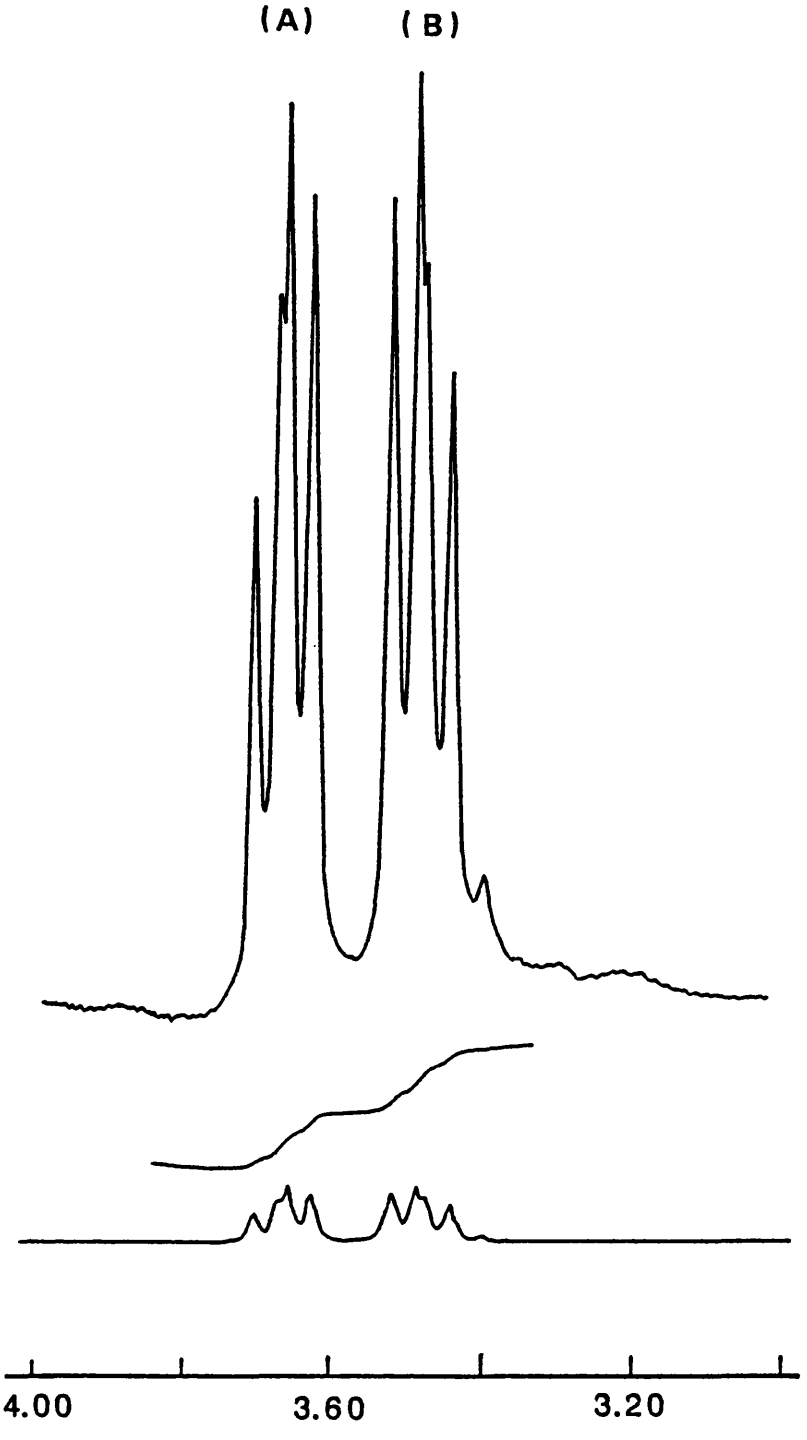
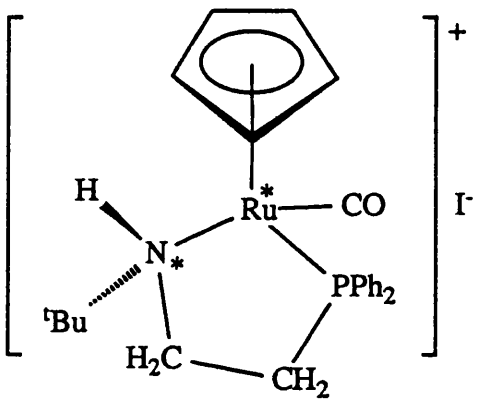


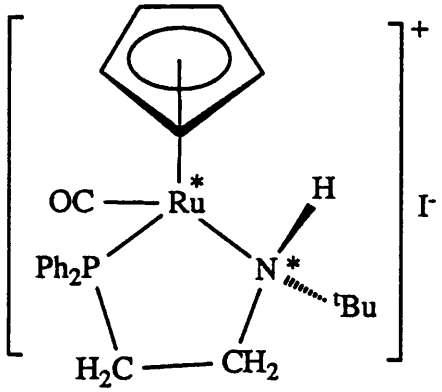
Figure 8

The two doublets of doublets observed in the ^{1}H nmr spectrum of complex *(217)*.

δ 2.60-3.40 ppm, was also observed and assigned to the CH_2 protons. This signal is in the same region as the CH_2 multiplet observed in the ^1H nmr spectrum of complex *(212)*, $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NH^tBu)}]I$, and is further downfield than the CH_2 multiplet observed for $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NH^tBu)I$ *(211)*. The FAB mass spectrum of complex *(219)* displays ions at m/e 480, corresponding to the molecular mass of the cation $[(\eta^5\text{-}C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NH^tBu)}]^+$.



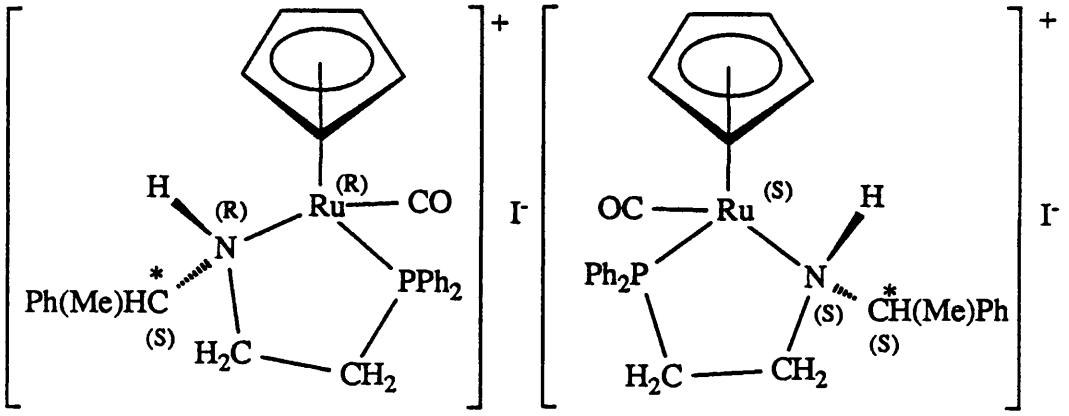
(219a) (RR)



(219b) (SS)

$(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$ reacted with $Ph_2PCH_2CH_2NHCH(Me)Ph$, in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, to give complex $[(\eta^5\text{-}C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)}]Cl$ *(220)*. The corresponding non-chelate complex was not observed in the $^{31}P\text{-}\{^1H\}$ nmr spectrum. The structure of complex *(220)* has primarily been assigned on the basis of its $^{31}P\text{-}\{^1H\}$ nmr chemical shifts (δ +66.8 and +67.1 ppm) which are very close to those observed for the similar complex $[(\eta^5\text{-}C_5H_5)\overline{Ru(CO)_2(Ph_2PCH_2CH_2NH^tBu)}]Cl$ *(219)* at δ +66.6 ppm. The two signals observed in the $^{31}P\text{-}\{^1H\}$ nmr spectrum are presumably due to two diastereoisomers, similar to those formed for complex *(217)*, $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)}]I$, which have configurations (RRS) or (SSS). The ^1H nmr spectrum of complex *(220)* exhibits signals for both diastereoisomers. Two doublets at δ 1.70 and 1.75 ppm are seen, assigned to the CHMePh protons, together with two cyclopentadienyl signals at δ 4.40 and 5.00 ppm. Signals due to the phenyl protons (δ 7.20-8.20 ppm) and multiplets due to the methylene protons (δ 2.60-3.80 ppm) were also observed. The absence of the non-chelated complex may be due to steric factors, since the

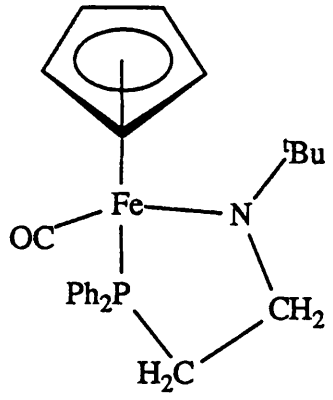
more stable chelate complex will be less sterically hindered when the R substituent in the ligands $Ph_2PCH_2CH_2NHR$ is -CH(Me)Ph rather than tert-butyl.



(220a) (RRS) *(220b)* (SSS)

5.2.5 Deprotonation Reactions

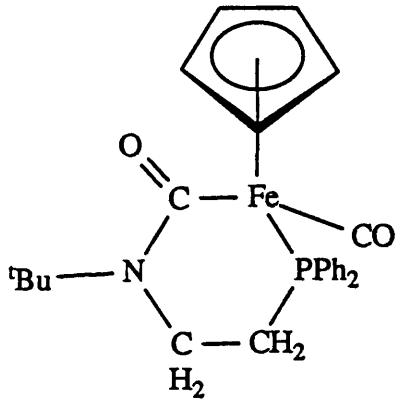
Reaction of a mixture of complexes *(211)* and *(212)* with $Na[N(SiMe_3)_2]$, in an attempt to form a chelated iron amide, led to a single phosphorus containing product *(221)*, as seen by $^{31}P-\{^1H\}$ nmr spectroscopy. The observed $^{31}P-\{^1H\}$ nmr chemical shift was at δ +50.2 ppm, upfield from both the chelate and non-chelate complexes *(212)* and *(211)*. The anticipated product *(221a)* would be expected to display a $^{31}P-\{^1H\}$ nmr shift more downfield than



(221a)

δ +50.2 ppm, probably closer to that displayed by complex *(212)* (δ +80.7 ppm). In addition, the i.r. spectrum of *(221a)* would be expected to exhibit an absorption only in the terminal CO stretching region. However, the product displays two absorptions, one at 1960 cm^{-1} and another at 1730 cm^{-1}. The absorption at 1960 cm^{-1} is typical for a terminal carbonyl and is

the same as, or very near to, the absorptions observed for complexes *(211)* and *(212)*. The second absorption at 1730 cm^{-1} is typical of an acyl carbonyl or a bridging carbonyl group. A possible product of the reaction is complex *(221b)* which would be the result of a disproportionation reaction, where a carbonyl has inserted into the Fe-N bond. The IR spectrum of this complex would be expected to show two absorptions, one for the terminal CO and another for the acyl carbonyl, which corresponds to the spectrum observed for complex *(221)*. The $^{31}P-\{^{1}H\}$ nmr spectrum of *(221)* suggests that it does not contain a

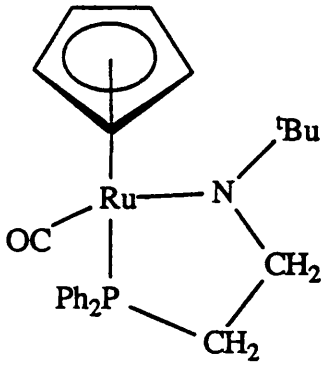


(221b)

five-membered chelate ring, but the spectrum would be consistent with the presence of a four- or six-membered chelate ring, which result in $^{31}P-\{^{1}H\}$ nmr chemical shifts similar to those of non-chelated ligands.[153,154] If *(221b)* was produced as a result of a disproportionation reaction, another phosphorus-containing product would also be formed, however no other signals were observed in the $^{31}P-\{^{1}H\}$ nmr spectrum.

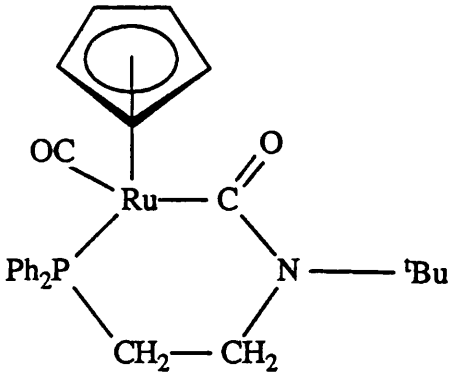
Reaction of complex *(219)*, $[(\eta^5-C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NH^tBu)}]Cl$, with sodium hydroxide, resulted in the formation of complex *(222)*, which has a $^{31}P-\{^{1}H\}$ nmr spectrum indicated that only about 30% of complex *(219)* had reacted, and addition of more sodium hydroxide and further stirring did not affect the reaction composition. The i.r. spectrum of the mixture of complexes *(222)* and *(219)* displayed two absorptions, similar to those observed for complex *(221)*, at 1960 and 1710 cm^{-1}. The absorption at 1960 cm^{-1} is typical of a terminal CO, but may be due only to the presence of complex *(219)*. The second absorption at 1710 cm^{-1} is typical of either an acyl or bridging carbonyl. Due to the presence of complex *(219)* it is difficult to detect whether *(222)* contains both terminal carbonyls and

acyl/bridging carbonyls or just acyl/bridging carbonyls. The expected product of the reaction, *(222a)*, contains only terminal carbonyls, with no acyl or bridging carbonyls.



(222a)

Complex *(222a)* also would be expected to give a $^{31}P-\{^{1}H\}$ nmr shift more downfield than the observed δ +30.9 ppm, probably closer to that observed for complex *(219)* at around δ +66.6 ppm. It can therefore be inferred from the i.r. and $^{31}P-\{^{1}H\}$ nmr data that complex *(222)* is not the chelated amide *(222a)*. As with the iron complex *(221)*, a possible product of



(222b)

the reaction may be complex *(222b)*, however, it is impossible to deduce from the IR spectrum whether the complex contains a terminal carbonyl group. The proposed complex *(222b)* might result from a disproportionation reaction, as described for the iron complex *(221)*. This type of reaction would result in the formation of another phosphorus-containing product, but no other signals were observed in the $^{31}P-\{^{1}H\}$ nmr spectrum.

CONCLUSIONS

The ligands *(166a-c)* react with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ to give mixtures of chelate and non-chelate complexes of the type $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NHR)}]I$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHR)I$. The chelate and non-chelate complexes equilibrate in solution and the equilibrium was found to be solvent dependent. The ligand $Ph_2PCH_2C(O)NH^tBu$ reacts with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ to give only the non-chelate complex $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2C(O)NH^tBu)I$ *(217)*. The ligands *(166a)* and *(166c)* also react with $(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$ to give chelate complexes of the type $[(\eta^5\text{-}C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NHR}]Cl$ and small amounts of the non-chelate complex in the case of ligand *(166a)*. The ruthenium complexes were more easily isolated than their iron analogues since they did not seem to equilibrate in solution. The iron and ruthenium complexes $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NH^tBu)}]I$ *(212)* and $[(\eta^5\text{-}C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NH^tBu)}]Cl$ *(219)* were reacted with base, but both failed to produce the desired metal amide complexes containing a five-membered chelate ring.

5.3 EXPERIMENTAL

5.3.1 Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (307 mg, 1.01 mmol) in benzene (25 cm^3) was added $Ph_2PCH_2CH_2NH^tBu$ (316 mg, 1.11 mmol) in benzene (25 cm^3) and a catalytic amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (12 mg). The reaction mixture was refluxed at 80°C for 0.75h, during which time the solution turned from black to dark green and a brown precipitate was formed. The reaction mixture was filtered to a green solution of $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NH^tBu)I$ *(211)* and a brown solid $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NH^tBu)}]I$ *(212)* (72 mg, 12%). The solvent was evaporated from the solution of *(211)* to give a green solid (368 mg, 65%), which was crystallised from benzene and petroleum ether to give green crystals of *(211)*. Found: C, 51.62; H, 5.43; N, 2.54. $C_{24}H_{29}NFeIOP$ requires C, 51.36; H, 5.21; N, 2.50. Complexes *(211)* and *(212)* were identified by their $^{31}P\text{-}\{^1H\}$ and ^1H nmr spectra (Table 13) and their IR spectra: *(211)* ν(C=O) 1960 cm^{-1}, *(212)* ν(C=O) 1975 cm^{-1}.

5.3.2 Reflux of complexes *(211)* and *(212)* in dichloromethane and benzene solvents

A 3:1 mixture of complexes *(211)* and *(212)* (200 mg, 0.36 mmol) was refluxed in dichloromethane (40 cm^3) at 40°C for two days. The mixture was monitored by $^{31}P-\{^1H\}$ nmr spectroscopy at regular intervals over the two days. It was observed that the ratio of *(211):(212)* changed until the two complexes were present in approximately equal quantities. At this point further refluxing in dichloromethane did not alter the ratio of *(211):(212)*, as seen by $^{31}P-\{^1H\}$ nmr spectroscopy. The dichloromethane solvent was removed under vacuum and replaced with benzene (40 cm^3). The mixture was then refluxed at 80°C and monitored by $^{31}P-\{^1H\}$ nmr spectroscopy at intervals. After two days the $^{31}P-\{^1H\}$ nmr spectrum indicated only the presence of complex *(211)*, $(\eta^5-C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2NH^tBu)I$.

5.3.3 Reaction of $(\eta^5-C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NHCH_2Ph$ *(166b)*

To a solution of $(\eta^5-C_5H_5)Fe(CO)_2I$ (290 mg, 0.96 mmol) in benzene (25 cm^3) was added $Ph_2PCH_2CH_2NHCH_2Ph$ (0.96 mmol) in benzene (25 cm^3) and a catalytic amount of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ (12 mg). The reaction mixture was refluxed at 80°C for 0.75h after which time the mixture was cooled to room temperature and the solvent removed under vacuum to give a mixture of the green $(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHCH_2Ph)]$ *(213)* and brown $[(\eta^5-C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2N}HCH_2Ph)]I$ *(214)* (433 mg, 73%). Complexes *(213)* and *(214)* were identified by their $^{31}P-\{^1H\}$ nmr spectra (Table 13), which indicated that the complexes were present in a 7:1 ratio. Separation of the complexes by flash column chromatography was unsuccessful. Refluxing the mixture in dichloromethane (40 cm^3) at 40°C resulted in an increased proportion of complex *(214)* in the solution. Conversely, refluxing the mixture in benzene (40 cm^3) at 80°C, resulted in an increased proportion of *(213)*, but full conversion to just one complex was not achieved.

5.3.4 Reaction of $(\eta^5-C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*

To a solution of $(\eta^5-C_5H_5)Fe(CO)_2I$ (228 mg, 0.75 mmol) in benzene (25 cm^3) was added $Ph_2PCH_2CH_2NHCH(Me)Ph$ (0.75 mmol) in benzene (25 cm^3) and a catalytic amount of

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (12 mg). The reaction mixture was refluxed at 80°C for 0.75h after which time the mixture was cooled to room temperature and the solvent evaporated to give a mixture of the green complex $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)I$ *(215)* and the brown $[(\eta^5\text{-}C_5H_5)\overline{Fe(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)}]I$ *(216)* (346 mg, 76%). Complexes *(215)* and *(216)* were identified by their $^{31}P\text{-}\{^1H\}$ nmr spectra (Table 13), which indicated that the complexes were present in a 3:10 ratio. Separation by flash column chromatography proved unsuccessful. Refluxing the mixture in dichloromethane (40 cm^3) at 40°C resulted in an increased proportion of complex *(216)* compared to *(215)*, as seen by $^{31}P\text{-}\{^1H\}$ nmr spectroscopy. Conversely, refluxing in benzene (40 cm^3) at 80°C, resulted in an increased proportion of *(215)* compared to *(216)*, however full conversion to just one complex was not achieved.

5.3.5 Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $Ph_2PCH_2C(O)NH^tBu$

To a solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (306 mg, 1.0 mmol) in benzene (25 cm^3) was added $Ph_2PCH_2C(O)NH^tBu$ (358 mg, 1.2 mmol) in benzene (25 cm^3) and a catalytic amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (12 mg). The reaction mixture was refluxed at 80°C for 0.75h, after which time it was cooled to room temperature, and the solvent was removed to give a dark green solid $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2C(O)NH^tBu)I$ *(217)* (425 mg, 78%). Found: C, 50.03; H, 5.57; N, 2.38. $C_{24}H_{27}NFeIO_2P$ requires C, 50.12; H, 4.73; N, 2.44. Complex *(217)* was identified by its $^{31}P\text{-}\{^1H\}$ and ^1H nmr spectra (Table 13) and its IR spectrum: $\nu(C{=}O)$ 1960 cm^{-1}.

5.3.6 Reaction of $(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$ with $Ph_2PCH_2CH_2NH^tBu$ *(166a)*

To a solution of $(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$ (140 mg, 0.60 mmol) in benzene (25 cm^3) was added $Ph_2PCH_2CH_2NH^tBu$ (172 mg, 0.60 mmol) in benzene (25 cm^3) and a catalytic amount of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (12 mg). The reaction mixture was refluxed at 80°C for 0.75h, after which time it was cooled to room temperature and the solvent removed to give a yellow-brown solid, a mixture of $[(\eta^5\text{-}C_5H_5)Ru(CO)(Ph_2PCH_2CH_2NH^tBu)]I$ *(219)* and $(\eta^5\text{-}C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NH^tBu)}I$ *(218)* (0.198 mg, 66%). Complex *(219)* was

purified by column chromatography and crystallised from dichloromethane and petroleum ether to give yellow crystals. Found: C, 56.10; H, 6.40; N, 2.10. $C_{24}H_{29}NClOPRu$ requires C, 55.97; H, 5.64; N, 2.72. Complexes *(219)* was identified by its $^{31}P-\{^1H\}$ and ^1H nmr spectra (Table 13) and its IR spectrum: $\nu(C{=}O)$ 1958 cm^{-1}.

5.3.7 Reaction of $(\eta^5-C_5H_5)Ru(CO)_2Cl$ with $Ph_2PCH_2CH_2NHCH(Me)Ph$ *(166c)*

To a solution of $(\eta^5-C_5H_5)Ru(CO)_2Cl$ (140 mg, 0.60 mmol) in benzene (25 cm^3) was added $Ph_2PCH_2CH_2NHCH(Me)Ph$ (0.60 mmol) in benzene (25 cm^3) and a catalytic amount of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ (12 mg). The reaction mixture was refluxed at 80°C for 0.75h, after which time the solvent was removed under vacuum to give a yellow solid, $[(\eta^5-C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NHCH(Me)Ph)}]I$ (320 mg, 72%). Found: C, 54.40; H, 5.00; N, 2.00. $C_{28}H_{29}NClOPRu$ requires C, 53.75; H, 4.82; N, 2.16. Complex *(219)* was identified by its $^{31}P-\{^1H\}$ and ^1H nmr spectra (Table 13) and its IR spectrum: $\nu(C{=}O)$ 1958 cm^{-1}.

5.3.8 Reaction of $(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NH^tBu)I$ *(211)* and $[(\eta^5-C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NH^tBu)]I$ *(212)* with $Na[N(SiMe_3)_2]$

To a mixture of complexes *(211)* and *(212)* (500 mg, 0.89 mmol) in THF (15 cm^3) was added sodium bis-trimethylsilylamide (366 mg, 2.0 mmol) in THF (10 cm^3). There was no observed colour change on addition and the reaction mixture was stirred at room temperature for 2h. The solvent was removed under vacuum to give a brown solid, complex *(221)*, which has not been identified. $^{31}P-\{^1H\}$ nmr spectrum $\delta(P)$ +50.2 ppm, IR spectrum: $\nu(C{=}O)$ 1960, 1730 cm^{-1}.

5.3.9 Reaction of $[(\eta^5-C_5H_5)Ru(CO)(Ph_2PCH_2CH_2NH^tBu)]I$ *(219)* with NaOH

To a solution of $[(\eta^5-C_5H_5)\overline{Ru(CO)(Ph_2PCH_2CH_2NH^tBu)}]I$ *(219)* (200 mg, 0.37 mmol) in methanol (30 cm^3) was added a 5% methanolic solution of sodium hydroxide (5 mls, 6.25 mmol). The reaction mixture was stirred at room temperature for 24h, after which time the solvent was removed under vacuum. The residue was dissolved in dichloromethane and filtered. Evaporation of the solvent gave a brown solid containing a mixture of the starting material *(219)* and complex *(222)*, in a 7:3 ratio. Complex *(222)* was not identified.

^{31}P-{^{1}H} nmr spectrum of the mixture of *(219)* and *(222)*: δ(P) +66.6, +30.9 ppm, IR spectrum of *(219)* and *(222)*: ν(C=O) 1960, 1710 cm^{-1}.

TABLE 13

^{31}P-{^{1}H} nmr[a] and ^{1}H nmr[b] Spectra of some Iron and Ruthenium Aminoalkylphosphine Complexes

Complex	δ (^{31}P)	δ (^{1}H)
(211)[c]	+59.1	0.85 (s, 9H, ^{t}Bu), 2.30-2.90 (m, 4H, CH_2), 4.00 (s, 5H, Cp), 6.90-7.80 (m, 10H, Ph)
(212)	+80.7	1.30 (s, 9H, ^{t}Bu), 2.60-3.40 (m, 4H, CH_2), 4.85 (s, 5H, Cp), 7.20-7.80 (m, 10H, Ph)
(213)	+57.7	——
(214)	+83.3	——
(215)	+56.7	——
(216)	+80.6 +81.4	——
(217)	+60.3	1.10 (s, 9H, ^{t}Bu), 3.45 (dd, 1H, CH_2), 3.65 (dd, 1H, CH_2), 4.40 (s, 5H, Cp), 7.30-7.90 (m, 10H, Ph)
(219)	+66.6	1.30 (s, 9H, ^{t}Bu), 2.60-3.40 (m, 4H, CH_2), 5.00 (s, 5H, Cp), 7.20-7.80 (m, 10H, Ph)
(220a) *(220b)*	+67.1 +66.8	1.70 (d, 3H, CHMePh), 2.60-3.80 (m, 8H, CH_2), 4.40 (s, 5H, Cp), 7.20-8.20 (m, 20H, Ph) 1.75 (d, 3H, CHMePh), 5.00 (s, 5H, Cp)

[a] in CH_2Cl_2; [b] in $CDCl_3$ at 300 MHz; [c] in C_6D_6 at 300 MHz.

REFERENCES

REFERENCES

1. J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley CA, 1980, Section 3.4 and Chapter 11.

2. R. F. Heck, 'Organotransition Metal Chemistry', Academic Press, New York, 1974, Chapter 2.

3. G. W. Parshall, 'Homogeneous Catalysis', Wiley, New York, 1980, Chapters 2-5.

4. L. S. Hegedus, L. M. Schultze, J. Toro and C. Yiju, *Tetrahedron*, 1985, **41**, 5833.

5. C. Borel, L. S. Hegedus, J. Krebs and Y. Satoh, *J. Am. Chem. Soc.*, 1987, **109**, 1101.

6. A. G. M. Barrett, C. P. Brock amd M. A. Sturgess, *Organometallics*, 1985, **4**, 1903.

7. H. Alper and C. P. Perera, *J. Am. Chem. Soc.*, 1981, **103**, 1289.

8. H. Alper and F. Urso, *J. Am. Chem. Soc.*, 1983, **105**, 6737.

9. H. Alper, F. Urso and S. Calet, *J. Am. Chem. Soc.*, 1989, **111**, 931.

10. H. Alper and N. Hamel, *Tetrahedron Lett.*, 1987, **28**, 3237.

11. H. Alper and D. Roberto, *Organometallics*, 1984, **3**, 1767.

12. G. S. Hartley and T. F. West, 'Chemicals for Pest Control', Pergamon Press, New York, 1969, pp.86-87, 174-1843.

13. S. Fukuoka, M. Chono and M. Kohno, *J. Chem. Soc., Chem. Commun.*, 1984, 399.

14. S. Fukuoka, M. Chono and M. Kohno, *J. Org. Chem.*, 1984, **49**, 1458.

15. H. Alper and F. W. Harstock, *J. Chem. Soc., Chem. Commun.*, 1985, 1141.

16. H. Alper, G. Vasapollo, F. W. Harstock and M. Miekuz, *Organometallics*, 1987, **6**, 2391.

17. F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto and A. Yamamoto, *J. Am. Chem. Soc.*, 1985, **107**, 3235.

18. J. Chen and A. Sen, *J. Am. Chem. Soc.*, 1984, **106**, 1506.

19. T. Kobayashi and M. Tanaka, *J. Organomet. Chem.*, 1982, **233**, C64.

20. M. Tanaka, T. Kobayashi and T. Sakakura, *J. Chem. Soc., Chem. Commun.*, 1985, 837.

21. B. Fell and W. Kohl, *Chem. Ztg.*, 1986, **110**, 401.

22. S. Murahashi, Y. Mitsue and K. Ike, *J. Chem. Soc., Chem. Commun.*, 1987, 125.

23. P. Giannoccara, *J. Organomet. Chem.*, 1987, **336**, 271.

24. A. Schoenberg and R. F. Heck, *J. Org. Chem.*, 1974, **39**, 3327.

25. M. Mori, K. Chiba and Y. Ban, *J. Org. Chem.*, 1978, **43**, 1684.

26. M. D. Fryzuk and P. A. MacNeil, *Organometallics*, 1983, **2**, 355.

27. M. D. Fryzuk and P. A. MacNeil, *Organometallics*, 1983, **2**, 682.

28. G. P. Pez and J. E. Galle, *Pure Appl. Chem.*, 1985, **57**, 1917.

29. D. R. Stull, E. F. Westrum, Jr. and G. C. Surke, 'The Chemical Thermodynamics of Organic Compounds', Wiley, New York, 1969, pp.636-652.

30. A. E. Schweiser, R. L. Fowlkes, J. H. McHahin and T. E. Whyte, Jr., 'Encylopedia of Chem. and Tech.', Vol. 2, 3rd. Edn., pp.272-283.

31. H. E. Bryndza, *Organometallics*, 1985, **4**, 406.

32. H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 1444.

33. R. L. Cowan and W. C. Trogler, *Organometallics*, 1987, **6**, 2451.

34. R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.

35. R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 643.

36. F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Publishers Ltd., London, p.13.

37. M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, 'Metal and Metalloid Amides', Ellis Horwood Ltd., Chichester, pp.468 and 488.

38. S. E. Diamond and F. Mares, *J. Organomet. Chem.*, 1977, **142**, C55.

39. B. Cetinkaya, M. F. Lappert and S. Torrini, *J. Chem. Soc., Chem. Commun.*, 1979, 843.

40. (a) H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam and J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 4805.
(b) H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163.

41. (a) M. D. Fryzuk and C. D. Montgomery, *Coord. Chem. Rev.*, 1989, **95**, 1.
(b) H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163.

42. H. E. Bryndza, W. C. Fultz and W. Tam, *Organometallics*, 1985, **4**, 939.

43. S. Park, D. M. Roundhill and A. L. Rheingold, *Inorg. Chem.*, 1987, **126**, 3972.

44. F. G. A. Stone, M. Green, J. L. Spencer and J. Fornies, *J. Chem. Soc., Dalton Trans.*, 1977, 1006.

45. T. Yoshida, T. Matsuda, T. Okana, T. Kitani and S. Otsuka, *J. Am. Chem. Soc.*, 1979, **101**, 2027.

46. D. Braga, P. Sabatino, C. Di Bugno, P. Leoni and M. Pasquali, *J. Organomet. Chem.*, 1987, **334**, C46.

47. D. M. Roundhill, *Inorg. Chem.*, 1970, **9**, 254.

48. T. Yamamoto, K. Sano and A. Yamamoto, *Chem. Lett.*, 1982, 907.

49. J. H. Nelson, D. L. Schmitt, R. A. Henry, D. W. Moore and H. B. Jonassen, *Inorg. Chem.*, 1970, **9**, 2678.

50. A. L. Casalnuovo, J. C. Calabrese and D. Milstein, *Inorg. Chem.*, 1987, **26**, 971.

51. A. L. Casalnuovo, J. C. Calabrese and D. Milstein, *J. Am. Chem. Soc.*, 1988, **110**, 6738.

52. R. A. Michelin, M. Napoli and R. Ros, *J. Organomet. Chem.*, 1979, **175**, 239.

53. W. Beck and M. Bauder, *Chem. Ber.*, 1970, **103**, 583.

54. W. Beck, M. Bauder, G. La Monica, R. Cenini and R. Ugo, *J. Chem. Soc. (A)*, 1971, 113.

55. S. Okaya, H. Yoshimatsu, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 483.

56. (a) S. Cenini and G. LaMonica, *Inorg. Chim. Acta*, 1976, **18**, 279.
(b) S. Cenini, M. Pizzotti, F. Porta and G. LaMonica, *J. Organomet. Chem.*, 1975, **88**, 237.

57. H. D. Empsall, E. M. Hyde and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1975, 1690.

58. H. D. Empsall, P. N. Heys, W. S. McDonald, M. C. Norton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1978, 1119.

59. B. Storhoff and A. J. Infante, *Inorg. Chem.*, 1974, **13**, 3043.

60. T. B. Rauchfuss, F. T. Patino and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 652.

61. T. B. Rauchfuss and D. M. Roundhill, *J. Organomet. Chem.*, 1973, **59**, C30.

62. T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1974, **96**, 3098.

63. T. B. Rauchfuss, J. L. Clements, S. F. Agnew and D. M. Roundhill, *Inorg. Chem.*, 1977, **16**, 775.

64. D. M. Roundhill, R. A. Bechtold and S. G. N. Roundhill, *Inorg. Chem.*, 1980, **19**, 284.

65. D. Hedden, D. M. Roundhill, W. C. Fultz and A. L. Rheingold, *J. Am. Chem. Soc.*, 1984, **106**, 5014.

66. D. Hedden and D. M. Roundhill, *Inorg. Chem.*, 1985, **24**, 4152.

67. D. Hedden and D. M. Roundhill, *Inorg. Chem.*, 1986, **25**, 9.

68. S. Park, D. Hedden, A. L. Rheingold and D. M. Roundhill, *Organometallics*, 1986, **5**, 1305.

69. S. Park, D. Hedden and D. M. Roundhill, *Organometallics*, 1986, **5**, 2151.

70. S. Park, M. Pontier-Johnson and D. M. Roundhill, *Organometallics*, 1989, **8**, 1700.

71. M. K. Cooper and J. M. Downes, *Inorg. Chem.*, 1978, **17**, 880.

72. C. W. G. Ansell, M. McPartlin, P. A. Tasker, M. K. Cooper and P. A. Duckworth, *Inorg. Chim. Acta*, 1983, **76**, L135.

73. M. K. Cooper, J. M. Downes, H. J. Goodwin, M. McPartlin and J. M. Rosalky, *Inorg. Chim. Acta*, 1983, **76**, L155.

74. G. J. Organ, M. K. Cooper, K. Hendrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1984, 2377.

75. W. de Graaf, S. Harder, J. Boersma and G. Vankozen, *J. Organomet. Chem.*, 1988, **358**, 545.

76. B. N. Storhoff, *J. Organomet. Chem.*, 1972, **43**, 197.

77. H. D. Empsall, E. M. Hyde, D. Pawson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1977, 1292.

78. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 299.

79. A. R. Sanger and R. W. Day, *Inorg. Chim. Acta*, 1982, **62**, 99.

80. A. R. Sanger, *Can. J. Chem.*, 1983, **61**, 2214.

81. L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 1968, **7**, 1419.

82. P. Rigo, *Inorg. Chim. Acta*, 1980, **44**, L223.

83. M. D. Fryzuk, P. A. McNeil and S. J. Rettig, *Organometallics*, 1986, **5**, 2469.

84. M. D. Fryzuk, P. A. McNeil and S. J. Rettig, *Organometallics*, 1985, **4**, 1145.

85. M. D. Fryzuk, P. A. McNeil and N. T. McManus, *Organometallics*, 1987, **6**, 882.

86. M. D. Fryzuk and P. A. McNeil, *J. Am. Chem. Soc.*, 1981, **103**, 3592.

87. M. D. Fryzuk, P. A. McNeil and S. J. Rettig, *J. Organomet. Chem.*, 1987, **332**, 345.

88. W. J. Knebel, R. J. Angelici and D. J. Darensbourg, *J. Organomet. Chem.*, 1974, **66**, C11.

89. G. K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.

90. M. M. Taqui Khan and A. P. Reddy, *Polyhedron*, 1987, **6**, 2009.

91. M. M. Taqui Khan, V. Vijay Sen Reddy and H. C. Bajaj, *Polyhedron*, 1987, **6**, 921.

92. M. M. Taqui Khan, H. C. Bajaj, R. H. Siddiqui, B. Taqui Khan, M. S. Reddy and K. V. Reddy, *J. Chem. Soc., Dalton Trans.*, 1985, 2603.

93. M. M. Taqui Khan and V. Vijay Sen Reddy, *Inorg. Chem.*, 1986, **25**, 208.

94. M. M. Taqui Khan and Md. K. Nazeruddin, *Inorg. Chim. Acta*, 1988, **147**, 33.

95. N. W. Alcock, A. W. G. Platt and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1989, 139.

96. N. W. Alcock, A. W. G. Platt and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1987, 2273.

97. N. W. Alcock, A. W. G. Platt and P. G. Pringle, *Inorg. Chim. Acta*, 1987, **128**, 215.

98. N. W. Alcock, A. W. G. Platt, H. H. Powell and P. G. Pringle, *J. Organomet. Chem.*, 1989, **361**, 409.

99. A. W. G. Platt and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1989, 1193.

100. R. T. Boere , C. D. Montgomery, N. C. Payne and C. J. Willis, *Inorg. Chem.*, 1985, **24**, 3680.

101. C. D. Montgomery, N. C. Payne and C. J. Willis, *Inorg. Chem.*, 1987, **26**, 519.

102. C. D. Montgomery, N. C. Payne and C. J. Willis, *Inorg. Chim. Acta*, 1986, **117**, 103.

103. H. E. Bryndza, J. C. Calabrese and S. S. Wreford, *Organometallics*, 1984, **3**, 1603.

104. H. E. Bryndza, *Organometallics*, 1985, **4**, 406.

105. D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, 1980, **199**, 119.

106. D. P. Klein, J. C. Hayes and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 3704.

107. M. K. Cooper, J. M. Downes, K. Hendrick, H. J. Goodwin and M. McPartlin, *Inorg. Chim. Acta*, 1983, **76**, L159.

108. W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 466.

109. M. Peuckert and W. Keim, *Organometallics*, 1983, **2**, 594.

110. A. R. Sanger, *Canad. J. Chem.*, 1982, **60**, 1363.

111. J. T. Mague and A. R. Sanger, *Inorg. Chem.*, 1979, **18**, 2060.

112. C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 1641.

113. C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 3637.

114. E. W. Stern and P. K. Maples, *J. Catal.*, 1972, **27**, 120.

115. E. W. Stern and P. K. Maples, *J. Catal.*, 1972, **27**, 134.

116. T. P. Dang and H. B. Kagan, *J. Chem. Soc., Chem. Commun.*, 1971, 481.

117. K. Issleib and R. Rieschel, *Chem. Ber.*, 1965, **98**, 2086.

118. W. J. Knebel and R. J. Angelici, *Inorg. Chim. Acta*, 1973, **7**, 713.

119. D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc.*, 1970, **92**, 5351.

120. G. R. Dobson, R. C. Taylor and T. D. Walsh, *Inorg. Chem.*, 1967, **6**, 1929.

121. K. Kashiwabara, I. Kinoshita, T. Ito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 725.

122. Von G. Märkl and B. Merkel, *Tet. Letts.*, 1981, **22**, 4459.

123. I. Healey, Ph.D. Thesis, Leicester University.

124. Von G. Märkl, G. Yu Jin and Ch. Schoerner, *Tet. Letts.*, 1980, **21**, 1845.