The Synthesis and Reactions of Metal Complexes of Bis(Diphenylphosphino)amine Monoxides

> A Thesis submitted by Clive Proctor for the Degree of Doctor of Philosophy in the Faculty of Science



University of Leicester Department of Chemistry LEICESTER England

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STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy is based on work conducted by the author in the Department of Chemistry of the University of Leicester between October 1990 and November 1993.

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

Signed:

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The Synthesis and Reactions of Metal Complexes of Bis(diphenylphosphino)amine Monoxides

Author: Clive Proctor

ABSTRACT

Chapter 1 reviews the literature concerning the principal synthetic routes to the bis(diphosphino)alkane monoxide ligands, their metal complexes and the use of these complexes in catalysis and formation of heterobimetallic metal complexes.

Chapter 2 describes the synthesis of novel bis(diphenylphosphino)amine monoxide ligands, the data indicating both similarities and differences to related ligands. The isolation of a novel triphosphazane monoxide has also been achieved.

Chapter 3 is concerned with the preparation and characterisation of transition metal complexes of the bis(diphenylphosphino)amine monoxides with palladium, rhodium, iridium, ruthenium, molybdenum and tungsten. The molecular structures of the complexes cis-[RhCl(CO){Ph}2PN(R)P(O)Ph}] (R=C_6H_4OMe-4) and [Rh(COD){Ph}2PN(Ph)P(O)Ph}][PF_6] establish the presence of a slightly puckered five-membered chelate ring in both complexes. The complexes cis-[Mo(CO)_4{Ph}2PN(Ph)P(O)Ph}2] and cis-[W(CO)_4(Ph}2PN(Ph)P(O)Ph}2] have been shown to contain non-chelating monodentate ligands from ³¹P-{¹H} n.m.r. data.

In Chapter 4 the reactions of the bis(diphosphino)amine monoxide metal complexes are discussed with particular reference to the oxidative addition reactions of the rhodium and iridium analogues. Attempts to form water-soluble complexes by the use of the biologically important Etmal and Memal ligands led to an investigation of the novel rhodium(I) complexes of these ligands and comparison with similar complexes in the literature containing the acac ligand.

The final chapter describes the preparation of some metal complexes of the triphosphazane monoxide ligand $(Ph_2PNPh)_2P(O)Ph$ with platinum, palladium, molybdenum and tungsten. Reactions of the platinum complexes and complexes of the type $[PtCl_2(P-P)]$ with esters of acetone dicarboxylic acid and amides containing activated hydrogen atoms in the presence of silver(I) oxide, leads to a variety of four-membered ring platinacycles. The $^{195}Pt-\{^{1}H\}$ n.m.r. spectra of some of the complexes are presented.

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ABBREVIATIONS AND SYMBOLS

General and Physical:

Å	= Angstrom unit
br	= Broad
°C	= Centigrade
cm ³	= Cubic centimetres
d	= Doublet
decomp.	= Decomposition
δ	= Chemical shift
(°)	= Degrees
FAB	= Fast Atom Bombardment
g	= Gramme
Δ	= Heat
Hz	= Hertz
h	= Hour
i.r.	= Infrared
K	= Kelvin
m	= Medium (i.r.); Multiplet (n.m.r.)
M+	= Molecular ion
MHz	= Megahertz
m.p.	= Melting point
mmol	= Millimole
n.m.r.	= Nuclear magnetic resonance
p.p.m.	= Parts per million
{ ¹ H}	= Proton decoupled
q	= Quartet
S	= Strong (i.r.); Singlet (n.m.r.)
t	= Triplet
td	= Triplet of doublets
vs	= Very strong
vt	= Virtual triplet
cm ⁻¹	= Wave number

ABBREVIATIONS AND SYMBOLS (Continued)

Chemical:

<u>Chemicai</u> .	
acac	= Anion of pentane-2,4-dione
acacH	= Pentane-2,4-dione
bipy	= 2,2'-bipyridine
COD	= cis, cis-Cyclo-octa-1,5-diene
COT	= Cyclooctatetraene
Ср	= Cyclopentadienyl anion
cym	= <i>p</i> -cymene
depe	= 1,2-Bis(diethylphosphino)ethane
depeO	= 1,2-Bis(diethylphosphino)ethane monoxide
dmad	= Dimethyl acetylenedicarboxylate
dmpm	= Bis(dimethylphosphino)methane
DMSO	= Dimethyl sulphoxide
dppb	= 1,4-Bis(diphenylphosphino)butane
dppe	= 1,2-Bis(diphenylphosphino)ethane
dppm	= Bis(diphenylphosphino)methane
dppp	= 1,3-Bis(diphenylphosphino)propane
dppeO	= 1,2-Bis(diphenylphosphino)ethane monoxide
dppmO	= Bis(diphenylphosphino)methane monoxide
dppmS	= Thio analogue of dppmO
DMF	= N,N-Dimethylformamide
Et	= Ethyl
EtmalH	= Ethylmaltol
Me	= Methyl
mes	= Mesitylene $(1,3,5-Me_3C_6H_3)$
MemalH	= Methylmaltol
nap	= Napthalene
NBD	= Bicyclo[2.2.1] hepta-2,5-diene
opmpp	=
Ph	= Phenyl
pip	= Piperidine
ⁱ Pr	= <i>iso</i> -Propyl
TCNE	= Tetracyanoethylene
THF	= Tetrahydrofuran
p-tol	= p-Tolyl

CHAPTER 1

Synthesis of Bis(Diphosphino)alkane Monoxides and Their Metal Complexes

1.1 Introduction

The chemistry of both monodentate and chelating phosphines is extensive, and phosphines as soft bases are well known for the stabilisation of low oxidation state metals. A phosphine oxide is a harder base and the presence of a soft, and a relatively hard base in the same ligand should bestow some interesting properties on the metal complexes.

The first transition metal complexes containing coordinated phosphine-phosphine oxide ligands appeared in 1975 as part of an n.m.r. study by Grim *et al.*^{1,27} A complex had, however, been previously reported of a phosphine-phosphine oxide with an uncoordinated phosphoryl group.²

The earliest example of a ligand which contained a phosphine-phosphine oxide backbone was reported in 1960 when Issleib *et al.*³ observed that chlorodiphenylphosphine reacted with moist diazomethane solution to form $Ph_2P(O)CH_2PPh_2$ which, has since been extensively used as a ligand in metal chemistry.⁴⁻⁶ The series of these bis(diarylphosphino)alkane monoxides, $Ph_2P(O)\{CH_2\}_nPPh_2, n=1-6, (1)$ have also been synthesised.⁷

Besides the direct combination of the ligands themselves with the metal containing precursor, such complexes have also been prepared by the action of various oxidants *in situ*, on "dangling" trivalent phosphino moieties. Such instances include oxidation by adventitious oxygen,⁸ and hydrogen peroxide.⁹ One particularly interesting example has been observed where coordinated NO acted as a source of oxygen to monoxygenate a coordinated diphosphine.^{10,53}

The complexes of phosphine-phosphine oxide ligands with rhodium have been widely used as catalysts^{11,82} for carbonylation and hydroformylation reactions, and many patents have been published in this area.^{12,13}

This first chapter thus comprises an overview of the preparation of phosphine-phosphine oxide ligands, their numerous metal complexes, and uses of these complexes both in catalysis, and in the formation of heterobimetallic complexes.⁶

The properties of the bis(diphenylphosphino)amine monoxide ligands,

-1-

 $Ph_2P(O)N\{R\}PPh_2$, (R=Ph, C₆H₄OMe-4) (2), which are similar to bis(diphenylphosphino)methane monoxide, and their metal complexes have been investigated in the subsequent chapters.

<u>1.2 Synthesis of bis(diphosphino)alkane monoxides by the use of organo-lithium and</u> -magnesium reagents

In 1964 Seyferth *et al.*¹⁴ reported that the reaction of RCH_2Li in diethyl ether, or of RCH_2MgBr in refluxing tetrahydrofuran with triphenylphosphine oxide resulted in the formation of benzene and $Ph_2P(O)CH(R)M$ (M=Li and MgBr respectively; R=H, alkyl), (3). The mechanism of formation of these reagents was shown to involve a very rapid exchange step, which was followed by a relatively rapid metalation reaction when M was lithium, Scheme 1.

 $Ph_{3}PO + RCH_{2}M \longrightarrow Ph_{2}P(O)CH_{2}R + PhM$ $Ph_{2}P(O)CH_{2}R + PhM \longrightarrow C_{6}H_{6} + Ph_{2}P(O)CH\{R\}M$

Scheme 1

It was also noted that the phosphorylalkyllithium reagent must be added to an excess of the chlorodiphenylphosphine, otherwise low yields were obtained. If the phosphorylalkyllithium was in excess, the desired products were metalated and complicated reaction mixtures were obtained, Scheme 2.

 $Ph_2P(O)CHRLi + Ph_2P(O)CHRPPh_2$

 $Ph_2P(O)CH_2R + Ph_2P(O)C\{R\}LiPPh_2$

Scheme 2

When M=MgBr it was observed that both the exchange and metalation steps were slower than when M=Li. During these studies Seyferth¹⁴ also noted that (3), (R=H, M=Li) could be treated with chlorodiphenylphosphine followed by elemental sulphur, to yield Ph₂P(O)CH₂PMe₂. This procedure was later modified to yield the new ligands (1;

n=1), $Ph_2P(O)CH_2PMe_2$, and $(nap)_2P(O)CH_2P(nap)_2$ by elimination of the sulphur addition step.¹⁵

1.3 Synthesis of bis(diphosphino)alkane monoxides by alkaline hydrolysis of phosphonium salts

It has been shown by one group of workers⁷ that the alkaline hydrolysis of phosphonium salts leads to the isolation of the ligands (1; n=1-6), Scheme 3.

 $Ph_2P(CH_2)_nPPh_2 + PhCH_2Br \longrightarrow [Ph_2P(CH_2)_nPPh_2(CH_2Ph)] [Br]$ aq.NaOH

Scheme 3

$Ph_2P(CH_2)_nP(O)Ph_2$

(1; n=1-6)

The ligand $Ph_2P(CH_2)_2P(O)Ph_2$ (1; n=2), has also been synthesised^{16,25} by alkaline hydrolysis of cyclic diphosphonium salts. Several mechanisms were postulated for the decomposition of these phosphonium salts, one of which was later deemed^{24,25} to be most likely, due to relief of steric strain and charge repulsion.

1.4 Synthesis of bis(diphosphino)alkane monoxides by partial oxidation

In a few cases partial oxidation of a diphosphine has yielded the relevant diphosphine monoxides.^{17,18,83} In one case the reaction was achieved by the storage of a hydrochloric acid solution¹⁸ of ¹³C labelled (4) in air, however, the product was mixed with the corresponding dioxide. The oxidation of the hydrochloric acid solution with dilute alkaline hydrogen peroxide gave exclusively the dioxide.

In the case of $Me_2P(CH_2)_2PMe_2$ (4), preparation of the monoxide¹⁷ was best achieved by partial oxidation of a 2M hydrochloric acid solution of (4) with hydrogen peroxide, followed by neutralisation.

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1.5 Synthesis of bis(diphenylphosphino)ethane monoxide by the use of vinyldiphenylphosphine oxide and its synthons

Diphenylphosphine has been treated with both $H_2C=CHP(O)Ph_2^{19}$ and its synthetic equivalent, $Ph_2P(O)CH_2CH_2OH^{20}$ to give (1; n=2) in good yields.

1.6 Miscellaneous routes to bis(diphosphino)alkane monoxide ligands

The earliest reported method for the formation of bis(diphenylphosphino)ethane monoxide was that of Aguiar and Daigle in 1964.²¹ Previously it had been stated that cis-1,2-bis(diphenylphosphino)ethene was resistant to catalytic hydrogenation²² but it was later observed that cis-1,2-bis(diphenylphosphino)ethene reacted with hydrogen bromide in hot glacial ethanoic acid, affording (1; n=2) by aqueous workup, Scheme 4.

(1); n=2

The i.r. spectrum of (1; n=2) showed a strong band at 1190 cm⁻¹ which was attributed to the phosphoryl group.

A new method for the synthesis of bis(diarylphosphino)methane monoxides was reported in 1991 by Tsvetkov *et al.*²³ This involved the reaction of diarylphosphines with formic acid in the presence of concentrated hydrochloric acid, to give the desired products in high yield, Scheme 5.

1.7 Synthesis of metal complexes by direct combination of the ligand with a metal complex²⁶

As part of a wide ranging n.m.r. study encompassing coupling between chemically different phosphorus atoms, Grim *et al.*^{1,27} synthesised the ligands $Ph_2P(O)CHPRPh_2$ (R=H, CH₃ and Pr) and from these directly made the complexes [HgBr₂{Ph₂PCH₂P(O)Ph₂}], [HgBr₂{Ph₂PCH(Pr)P(O)Ph₂}] and the analogous cadmium

-4-



complexes. This was accomplished on stirring the ligand and metal halide in ethanol. The complexes $[M(CO)_4{Ph_2PCH(Pr)P(O)Ph_2}]$ (M=Cr, Mo, and W) were also prepared on refluxing $[Mo(CO)_6]$ and the ligand in diglyme. In all cases the ³¹P-{¹H} n.m.r. showed two doublets with the phosphine end appearing further downfield than the phosphoryl moiety. The tungsten complex exhibited ³¹P-¹⁸³W coupling to one of the ³¹P signals which was assigned to the coordinated phosphino moiety.

A series of complexes were synthesised by Shaw *et al.*⁵ from [PtCl₂(COD)] with the ligands $Ph_2P(CH_2)_nP(O)Ph_2$ (n=1-4). The complexes formed were always of the type *cis*-[PtCl₂{Ph₂P(CH₂)_nP(O)Ph₂}₂]. *Trans* complexes were only obtained by reaction of [Hg(C=CPh)₂] with *cis*-[PtCl₂(dppmO)₂].

In these complexes the phosphine oxide moiety was not coordinated to the metal, and coordination was achieved on refluxing ethanolic solutions of cis-[PtCl₂{Ph₂P(CH₂)_nP(O)Ph₂}] (n=1,2), and of cis-[PdCl₂(dppmO)₂] with silver nitrate, Scheme 6.

In 1991, a four-coordinate platinum complex containing dppmO was synthesised



<u>Scheme</u> 6

where the P=O group was not coordinated, and the complex also contained a tridentate phosphorus ligand,⁴ Scheme7.



Scheme 7

It has been reported¹⁹ that dppeO reacted with $PdCl_2$ in a mixture of DMF and dichloromethane to afford $[PdCl_2(dppeO)_2.5H_2O]$, in which the phosphoryl group was also uncoordinated. This was explained by the fact that Pd(II) can be classed as a soft acid. It was also claimed that $[PdCl_2(dppeO)_4.8H_2O]$ had been formed in this reaction although the complexes had identical ³¹P chemical shift values and other data were not conclusive.

The specific complexing properties of the phosphine-phosphine oxide ligands have been employed in the spectrophotomeric determination of the platinum metals.²⁸ In this publication it was claimed that palladium and rhodium complexed with dppeO whereas platinum and iridium did not! Thus, dppeO was used to detect palladium and rhodium in the presence of platinum and iridium. The palladium was found to react with dppeO with formation of 1:2 and 1:4 complexes^{19,28} and rhodium formed a 1:6 complex. The palladium complex formation was also used to detect this metal in the presence of a 25,000-fold excess of copper, and a 1000-fold excess of nickel and cobalt, without interference.

In 1992, trans-dichlorobis((2-diphenylphosphinoethyl)diphenylphosphine oxide)

palladium was shown to contain palladium in square planar coordination.²⁹ Presumably this was the complex used for the sensitive detection of palladium in the earlier paper.²⁸ Once again the phosphoryl group was not bound to the metal centre.

A further comprehensive study of the ligands dppmO and dppeO was undertaken recently by Davis *et al.*²⁶ This study wished to examine the relative ease of formation of chelated complexes, and those containing unidentate ligands for a series of transition metals. Various complexes were formed with platinum, palladium, rhodium, iridium, chromium, molybdenum, tungsten, and manganese to complement the previous studies by other groups. One interesting observation was that it was possible to achieve coordination of dppeO to a molybdenum carbonyl unit via the [P] donor atom, and an η^6 -aromatic ring rather than by [P,O] chelation, (5).



Mayer *et al.*³⁰ have observed an interesting oxygen atom transfer from a phosphoryl group to tungsten. It was found that $[WCl_2(PMePh_2)_4]$ reacted rapidly with dppeO to give the substitution complex (6), Scheme 8. If (6) was heated at 80°C for 8h, a rearrangement occurred, Scheme 9.

This reaction was the first example of an intramolecular oxygen atom transfer from a phosphoryl group to a metal centre. The reaction was remarkable in itself due to the strength of the phosphoryl bond.³¹ The compound $[WCl_2(PMe_3)_4]$ was also found to deoxygenate (6) but no intermediate complex was observed. Further studies with non-chelating phosphine oxides showed these to be unreactive, and suggested that the chelating nature of (6) was required to assist the oxygen atom transfer. The presence of the oxygen atom transfer step was confirmed by the use of ¹⁸O labelling studies.

The ligand dppmO has been used to synthesise rhenium(V) metallacyclic

-7-



complexes.³² The reaction of dppmO with the $[\text{ReOCl}_4]^-$ anion, which was generated *in* situ by the action of NH₄ReO₄ and concentrated HCl, led to the isolation of $[\text{Re}(O)\text{Cl}_3\{\text{PPh}_2\text{CH}_2\text{P}(O)\text{Ph}_2\}]$ (7). By performing the reaction in ethanol the monoethoxy derivative, $[\text{Re}(O)(\text{OEt})\text{Cl}_2\{\text{PPh}_2\text{CH}_2\text{P}(O)\text{Ph}_2\}]$ (8) was obtained, Scheme 10.

An X-ray crystal structure of (7) was obtained and the complexes were further characterised by analytical and spectroscopic methods.

An extension to the work of Grim et al. was undertaken by Dixon et al.³³ The



(7); X=Cl, (8); X=OEt

ligand dppmO was reacted with the chloro-bridged dimer $[Pt_2Cl_4(PEt_3)_2]$ in the presence of NaClO₄ or NaBF₄ to yield perchlorate and fluoroborate salts of the complex cations *cis*- and *trans*- $[PtCl_2(PEt_3){Ph_2PCH_2P(O)Ph_2}]^+$. Initially through ³¹P-{¹H} n.m.r. studies it was established that the initial product of the reaction was the *trans* isomer which contained a "dangling" phosphoryl group. Further phosphorus n.m.r. studies showed that during purification this complex converted to the corresponding *cis* isomer. In the presence of NaClO₄ one chloride ligand, labilized by the *trans*-effect of phosphorus was displaced by the "dangling" phosphoryl moiety. Thus, the ultimate product was *cis*- $[PtCl(PEt_3){Ph_2PCH_2P(O)Ph_2}][ClO_4]$, Scheme 11

An analogous displacement of chloride by the phosphine oxide group of dppmO also occurred in its reaction with $[Pt_2Cl_2(PEt_3)_4][ClO_4]_2$, which produced the chelate complex *cis*- $[Pt(PEt_3)_2{Ph_2PCH_2P(O)Ph_2}][ClO_4]_2$ under ambient conditions.

1.8 Formation of complexes containing phosphine-phosphine oxide ligands by *in situ* oxidation of "dangling" trivalent diphosphino moieties

1.8.1 Oxidation by adventitious oxygen and hydrogen peroxide

Leigh *et al.*³⁴ showed that the reaction of $[Mo(N_2)_2(depe)_2]$ with anhydrous HCl in benzene did not lead to the isolation of any nitrogen-containing complex. The molybdenum-containing product was shown by analysis to contain less than two moles



of depe per. molybdenum atom. On standing, crystals were deposited from the reaction mixture, and an X-ray structure analysis⁸ showed these to be $[MoCl_3O\{depeO\}]$, formed by the action of adventitious oxygen.

Muir et al.⁹ found that the reaction of $[Pt(O_2CCF_3)_2(dppm)]$ with CO/H₂O at 100°C gave the 58-electron cluster cation $[Pt_4(\mu-H)(\mu-CO)_2(\mu-dppm)_3(dppm-P)]^+$ whose crystal structure was determined as the $[PF_6]^-$ salt. This showed the compound to contain a Pt₄ core in a butterfly geometry. The monodentate dppm-P ligand of the cluster was easily oxidised by O₂ or H₂O₂ to give the new cluster cation $[Pt_4(\mu-H)(\mu-CO)_2(\mu-dppm)_3\{Ph_2PCH_2P(O)Ph_2\}]^+$, which contained a non-coordinated phosphine oxide group. The ³¹P-{¹H} n.m.r. of this new cluster provided chemical shift evidence for this change in valency at phosphorus.

Another crystal structure of a similar platinum "butterfly" cluster was also solved

by the same group of co-workers.³⁵ During catalysis of the water gas shift reaction, by the binuclear complex $[Pt_2H_2(\mu-H)(\mu-dppm)_2][PF_6]$, the catalytic solutions were shown to contain $[Pt_4(\mu-CO)_2(\mu-dppm)_3\{Ph_2PCH_2P(O)Ph_2\}]$, Scheme 12.



Scheme 12

The new diplatinum(I) complex, $[Pt_2(\mu-S)(\mu-dppm)(\eta^1-dppm)_2]$ (9) was also prepared³⁶ by the reaction of $[Pt_2(\mu-dppm)_3]$ with COS, Scheme 13. On exposure of (9)



Scheme 13

to air, oxygenation of the "dangling" dppm ligands occurred to produce (10), Scheme 14.



Scheme 14

An unstable rhenium carbonyl complex containing a monodentate dppmO ligand was obtained³⁷ by reaction of *cis-mer*-[ReBr(CO)₂(dppm-P)(dppm-P,P')], (11), with oxygen in xylene at room temperature, Scheme 15. A crystal structure of the compound



Scheme 15

(12) was determined on a mixture containing crystals of (11) and (12) in the ratio 1:0.43. The fluxional monodentate dppm complexes, *trans*-[Pt(CCR)₂{Ph₂PCH₂PPh₂}₂]
(13), (R=C₆H₄Me-4, Ph, or Me) have been oxidised³⁸ by the use of H₂O₂ to give the non-fluxional phosphine oxide complexes (14), Scheme 16. At room temperature, the



Scheme 16

³¹P-{¹H} n.m.r. spectra of complexes (13a)-(13c) were broad due to rapid exchange between free and coordinated phosphorus but were well resolved at -20°C showing two "virtual triplet" resonances with associated ¹⁹⁵Pt satellites.

On refluxing a mixture of $[Co(NO)_2{Ph_2P(CH_2)_2PPh_2}][PF_6]$ and $[Et_4N]I$, crystals of the complex $[Co(NO)_2{PPh_2(CH_2)_2PPh_2(O)}]$ appeared.³⁹ The crystal structure was determined and the complex found to be distorted tetrahedral in geometry, with a non-coordinated phosphine oxide moiety. The P-O distance was in good agreement with the sum of the double-bond covalent radii.⁴⁰

An interesting publication⁴¹ was concerned with the self-reactivity of $[CpCo(P-P)I]^+$ complexes, $(P-P= Ph_2P(CH_2)_nPPh_2; n=1-4)$ which, led to oxidised "dangling" P-P species. It was observed that the stability of these complexes was in the order (n=4<<1<2,3) as expected from the relief of chelate ring strain upon dissociation of one end of the chelating diphosphine. The organometallic products were (15a)-(15d). These complexes were formed via a neutral complex which contained a "dangling" P-P ligand, Scheme 17. It appeared evident that the formation of the final species was consistent with oxidation initiated by photolysis of the Co-I bond, which required the presence of light and adventitious O_2/H_2O .

Osmium complexes containing phosphine oxide groups have also been formed by oxidation of pendant diphenylphosphino groups.⁴² Thus, heating $[Os_2(CO)_6(\mu-O_2CMe)_2]$ with two equivalents of dppm yielded (16), Scheme 18, which on treatment with two molar equivalent of H₂O₂ resulted in oxidation of the two diphenylphosphino groups which were not coordinated to the metal centre.

During the u.v. irradiation of a mixture of $[CpMn(CO)_3]$ and dppe,⁴³ the complex $[CpMn(CO)_2\{\mu-dppeO\}]$ was isolated as a minor product from the reaction mixture and was proof for a stepwise mechanism for the photochemical replacement of carbonyl groups in this system.

The complexes mer-[ReCl₃(dppm-P,P'){dppmO-P}] (17), and [ReCl₄(dppmO-P,O)] (18) were obtained by the reaction of [ReOCl₃(PPh₃)₂] or [AsPh₄][ReOCl₄] with dppm under different conditions.⁴⁴ A crystal structure of (18)





(16)





(17)



-14-

showed that the P-O bond length of 1.523(8)Å was longer than the corresponding distance of 1.485(7)Å for the monodentate ligand in (17), where the phosphoryl group remained uncoordinated.⁴⁵ In order to obtain a pure sample of (17) it was necessary to use a two molar equivalent of dppm and the starting compound, [ReOCl₃(AsPh₃)₂], in hot benzene, otherwise a mixture of both complexes was obtained. The tribromide analogue of (17) was also obtained on heating [ReOBr₃(dppm-P,P')] with excess dppm.

Another example of a rhenium complex containing a phosphine-phosphine oxide ligand was published in 1967.⁴⁶ Reaction of $\text{Re}_2(\text{CO})_{10}$ with dppe at high temperature gave *cis*-[Re(CO)₂(dppe)₂], which exhibited two infra-red bands. On reaction with I₂ in benzene, (19) was obtained, and on treatment of (19) with 0.1M NaOH, in benzene, the diamagnetic rhenium(I) complex, (20), was synthesised, Scheme 19. Complex (20) was identified by two infra-red frequencies due to v(P=O) at 1190 and 1178cm⁻¹.





Scheme 19

An interesting reaction of dppe occurred on its combination with the alkylidyne complex $[NEt_4][Mo(CC_6H_4Me-4)(CO)_2{\eta^5-C_2B_9H_9Me_2}]^{47}$ This yielded two products one of which contained the carborane cage acting as a counter-ion in a protonated form. The X-ray crystal structure of the complex showed that the coordination geometry about the molybdenum atom was approximately octahedral, with the phosphine oxide group *trans* to the alkylidyne group, (21). This was rationalised by the fact that the P=O ligand

is a σ -donor with no π -acid properties, and that the alkylidyne group is a stronger π -acceptor than either carbonyl or phosphine ligands.⁴⁸



Darensbourg *et al.*⁴⁹ found evidence for a *fac* to *mer* isomerisation followed by oxidation of a monodentated dppm ligand attached to a tungsten metal centre, Scheme 20.



The isomerisation process was prolonged and adventitious oxygen oxidised the free phosphino group. The presence of the *fac* isomer before isomerisation was confirmed by ${}^{31}P{-}{}^{1}H$ n.m.r. as only one resonance was observed at -11.1 p.p.m. whereas the *mer* isomer would be expected to display two resonances.⁵⁰

A hexarhodium cluster derived from the photoreaction of $Rh_6(CO)_{16}$ with dppe has been shown to give two products, one of which $[Rh_6(CO)_{15}{\eta^1-Ph_2P(CH_2)_2P(O)Ph_2}]^{51}$ contained a non-coordinated phosphoryl group. In contrast the reaction of $Rh_6(CO)_{16}$ with dppe under thermal conditions has been shown to yield another complex in which only one phosphorus is coordinated to rhodium.⁵² The other one was connected to the oxygen atom of the (μ^3 -CO) group, which was confirmed by the considerable low-field shift of the (μ^3 -CO) group in its ¹³C-{¹H} n.m.r. spectrum.

1.8.2 Coordinated NO as a source of oxygen in the presence of dppe

The nitrosyl dimer $[Fe(NO)_2Cl]_2$ on reaction with dppe, yielded the binuclear complex $[Fe(NO)_2Cl]_2(\mu$ -dppe)^{10,53} which in the presence of excess dppe, resulted in the NO substitution complex $[Fe(NO)Cl_2\{dppeO\}]$ besides the expected $[Fe(NO)_2\{dppe\}]$. It was clear that the diphosphine had been monooxygenated by NO. This indicated that the active cycle occurring was an Fe-NO/Fe-ONO₂ oxygen shuttle, after which oxygen was transferred to the diphosphine.

1.9 Phosphine-phosphine oxide ligands as by-products or as minor products

There have been numerous examples where phosphine-phosphine oxide ligands have been observed as very minor products or as by-products in reactions. A minor product⁵⁴ of the reaction of ruthenium(III) chloride with opmpp analysed as *trans*-[RuCl₂{(\pm)-2-C₆H₄(PMePh)₂}{(\pm)-2-C₆H₄(PMePh)(P(O)MePh) }] which was shown to contain a co-ordinated phosphine oxide group by an X-ray crystal structure determination.

Several instances have been observed where the ligands have been seen as by-products due to partial hydrolysis of reaction mixtures or exposure to oxygen.^{55-59,79,80} In all cases the presence of the species have been confirmed by the ³¹P- $\{^{1}H\}$ n.m.r. spectra.

A minor product, $[(\mu^3-CMe)Co_3(CO)_8\{Ph_2PCH_2P(O)Ph_2\}]$ (23) was isolated in 5% yield from the reaction between the alkylidyne cluster $[(\mu^3-CMe)Co_3(CO)_9]$ (22), and dppm,⁶⁰ Scheme 21. The presence of the uncoordinated phosphoryl group was confirmed by i.r. and ³¹P-{¹H} n.m.r. spectra. At room temperature the ³¹P-{¹H}



spectrum was broad, and cooling to -40°C gave a well resolved spectrum due to the increased quadrupolar relaxation of the ⁵⁹Co nuclei allowing observation of the complete coupling pattern.⁶¹

Other cobalt cluster compounds synthesised, which contained such ligands, were $\label{eq:ch2} [Co_6(\mu^3-S)_8\{Ph_2CH_2P(O)Ph_2\}_6]^{62} \quad \text{and} \quad [(\mu^3-CCl)Co_3(CO)_8\{Ph_2(CH_2)_nP(O)Ph_2\}], \\ (n=1-4).^{81}$

1.10 The use of phosphine-phosphine oxide complexes in catalysis

The title complexes have been used in a wide variety of catalytic processes. In 1993 a Russian paper appeared⁶³ where dppmO and dppeO were used in a study of the influence of such ligands and their thiophosphoryl analogues on the rate and regioselectivity of hydrocarboxylation of α -olefins using PdCl₂ catalysts. It was observed that with dppeO a high regioselectivity (>80%) was achieved.

The chelation of such phosphine-phosphine oxide ligands could be expected to confer stability on the resulting complexes. The introduction of a suitable reagent can then lead to cleavage of the weak M-O bond and creation of an "active" site at the metal which is a necessary prerequisite for catalysis.²⁶ This idea has been used by the major researchers in this area, Wegman *et al.* who have studied the use of rhodium complexes on a wide variety of systems. They reported in several patents that, $[RhCl(CO)_2]_2$ in the presence of dppeO was an active catalyst for the carbonylation of methanol to acetic acid

and to acetate esters. In a paper by the same group,¹¹ it was also found that under a 1 atmosphere pressure of CO the phosphoryl group of [RhCl(CO){dppeO}] was cleaved from the metal allowing CO to co-ordinate at the "active" site, Scheme 22. At 80°C and



Scheme 22

3 atmospheres of CO a turnover of $400h^{-1}$ was observed for the carbonylation of methanol. Methyl iodide was present in the reaction in order to aid the conversion of (25) back to (24). The analogous complex [RhCl(CO){dppmO}] (26), did not react with CO at 1 atmosphere and requires 80°C and 30 atmospheres for (26) to be produced. A ¹⁰³Rh-³¹P coupling constant of 4.8 Hz was observed for the [Rh-O=P] linkage, and a larger decrease in v(P=O) was noted for the dppmO ligand on coordination as compared to dppeO. This and the lower reactivity of (26) towards CO suggested a stronger phosphine oxide-metal bond for (26) than (24). The X-ray crystal structure of (26) was determined and the phosphine oxide bond was found to be longer than both the P-O bond length in Ph₃PO and Me₃PO.⁶⁸ The data for these ligands and rhodium complexes are given in Table 1.

Compound	δP	δP=O	J(RhP)	J(RhOP)	J(PPO)	υ _{P=O}
dppmO	-28 .7	27.4	—		49.5	1200
dppeO	-12 .4	34.3		-	48.3	1190
cis-[RhCl(CO)dppmO]	43.8	58.6	162.4	4.8	29.0	1065
cis-[RhCl(CO)dppeO]	34.2	41.6	16.7		12.1	1150

 δ /ppm ; J/Hz ; υ / cm $^{-1}$

Table 1

One group have carried out a study of comparisons of phosphine and phosphine oxide ligands in hydroformylation reactions.¹¹⁴ Few cases have been reported of the use

of mixed bidentate ligands in such reactions, the best catalytic activity being observed using bisphosphine monoxide ligands.¹¹ The discovery that the related phosphine oxide derivative, (27) formed an even more active rhodium catalyst led to further investigation. Derivatives like (27) showed exceptional reactivity and regioselectivity under mild conditions and simple work-up.



1.11 The formation of homo- and heterobimetallic metal complexes containing diphosphine ligands

The use of dppm as a bridging ligand for formation of homo- and heterobimetallic complexes has been well documented. Shaw⁶⁹⁻⁷¹ showed that monodentate dppm complexes of platinum(II) acetylides, (28), could be used in the synthesis of bimetallic complexes of the type $[Pt(CCR)_2{\mu-dppm}_2MX_n]^{y+}$, (R=alkyl or aryl, M=Pt,Rh,Ir,W,Ag,Au,Cd or Hg, X=ligand or radical and y=0 or 1).



During further studies to find ligands which would prevent initial chelation of the free phosphorus in complexes like (28), the complexes with cyanide ligands were also synthesised,⁷² (29). These were found to stabilise the fluxional η^1 -dppm complexes, and heterobimetallic complexes were thus synthesised with silver, mercury or rhodium (30)-(32). Shaw *et al.*⁷³ also used dppm to synthesise a heterobimetallic rhenium-rhodium complex.

The main object in heterobimetallic complexes is to obtain different reactivities at



both metal sites. A useful method of enhancement of this character was the inclusion of a hard donor atom such as oxygen on the ligand site accomodating the adjacent metal. Oxidation of the terminal end of a monodentate diphosphine ligand has achieved this objective.³⁸ Air oxidation of $[Pd_2Cl_2(dmpm)_2]$ has been shown to give (33) although oxidation of Pd(I) to Pd(II) accompanied this process, making it a little less straightforward.⁷⁴ Thus the pendant functionalities of (33) would then serve as useful

$$Cl \qquad Pd \qquad P = O \\ P \qquad P = O \\ P \qquad P = O \\ P \qquad P = O \\ Me_2 \qquad P = O \\ Me_2 \qquad Me_2 \qquad O$$

$$(33)$$

reagents for the formation of heterobimetallics with a metal able to coordinate to phosphine oxide.⁷⁵

Heterobimetallic complexes incorporating neodymium have been prepared in which phosphoryl groups have been coordinated to the lanthanide centre and a free phosphine moiety to other metals.⁶ It was possible to coordinate either the phosphino or the phosphoryl group first, Scheme 23.

The coordination to neodymium was confirmed by a lowering of v(P=O) and a large shift to low field of the phosphoryl resonance in ³¹P-{¹H} n.m.r. spectra.

In the same paper, $[Mo(CO)_4(NBD)]$ was added to a solution of the adduct $[Nd(BH_4)_3dppmO{THF}]$, and the reaction followed by phosphorus n.m.r. spectroscopy. Two sharp doublets were observed of equal intensity which confirmed the presence of a heterobimetallic adduct formed in the presence of $[(COT)NdCl{THF}_2]$. The adduct



was therefore assigned to $[(COT)NdCl{dppmO}]_2Mo(CO)_4$ by analogy with other neodymium and molybdenum phosphine systems.

Two instances have appeared of tungsten carbonyl complexes acting as ligands.^{76,77} The complex, (35), was used to form (36), (37), and (38). The complexes





were identified by the use of phosphorus n.m.r. although this was complicated by coupling to ¹⁹⁵Pt and ¹⁹⁹Hg respectively.

In both of these papers the complex, (35), with the terminal phosphorus oxidised to a phosphoryl group was obtained and this could hold potential for formation of heterobimetallic complexes although this was not investigated.

A bimetallic complex which contained molybdenum and gold has been observed,78

but the diphosphine was coordinated only to the molybdenum centre, Scheme 24.



Scheme 24

As mentioned briefly earlier, the related bis(diphosphino)amine monoxide ligands and metal complexes will be discussed in the subsequent chapters. These could show both similar and strikingly different properties to compounds discussed in this chapter.

CHAPTER 2

Synthesis of Some Bis(Diphenylphosphino)amine Monoxides
2.1 Introduction

Compounds which contain either a trivalent or pentavalent phosphine oxide species directly bound to nitrogen are of interest as potential ligands, and many examples which can act both as monodentate or bidentate systems exist. A bidentate ligand incorporating both types of phosphorus moieties bonded to nitrogen opens up further interesting possibilities.

Only one such ligand, $Ph_2P(O)NHPPh_2$ (38) has been observed previously, the compound being reported by two different groups of workers. In a patent published by Hiroshi *et al.*⁸⁴ (38) was treated with various substrates to produce phosphinamide derivatives. These derivatives were used in bacteria control of cucumber seedlings. In the second instance, (38) was observed as an intermediate in the reaction of diphenylphosphinyl azide with diphenylphosphine, Scheme 1.⁸⁵

$$Ph_{2}P(O)N_{3} + Ph_{2}PH \longrightarrow Ph_{2}P(O)NHPPh_{2} + N_{2}$$
(38)
$$Ph_{2}P(O)N_{3} + Ph_{2}P(O)NHPPh_{2} \longrightarrow Ph_{2}P(O)NHPPh_{2} = NP(O)PPh_{2} + N_{2}$$
(39)

Scheme 1

The product (39) tautomerised to $Ph_2P(O)[N=PPh_2]_2OH$ (40) and it was thought conceivable that an excess of diphenylphosphine was required to act as a proton transfer agent. The ligand (38) was only isolated in small quantities which indicated that it was preferentially oxidised by diphenylphosphinyl azide to yield (40). No metal complexes of (38) have ever been synthesised although these would be very interesting compounds.

The bonding in P-N bonded ligands has been postulated⁸⁶ to incorporate much delocalisation of electrons by $p\pi$ -d π orbital overlap betweeen nitrogen and phosphorus. In order to investigate this, a study of CO infra-red frequencies of metal carbonyls was undertaken knowing that these are highly sensitive to the amount of π -bonding in the carbon-oxygen bond⁸⁷ and hence the π -bonding of attached ligands. The relevant study undertaken looked at a series of *cis*-[Mo(CO)₄{Ph₂PN(R)PPh₂}] (R= alkyl) complexes and the results showed the carbonyl frequencies to be very similar to those for complexes

where phosphorus is bonded to carbon only (e.g. dppm⁸⁸), in which there is no possibility of π -bonding between phosphorus and the bridging atom. This indicated that the replacement of CH₂ or CHR by NR does not greatly change the ability of phosphorus to accept electrons from the metal. Calculation of the apparent force constants⁸⁹ confirmed that there is no great difference between the amount of π -bonding in the CO group in the aminophosphine ligands, and that in simple phosphine complexes.

The elaboration of phosphorus ligands has usually been performed by using the reactivity of phosphorus-chlorine bonds⁹⁰ which is very important in phosphorus ligand chemistry. The chemistry of nitrogen and chlorine bound to phosphorus has been much less studied than that of phosphorus-oxygen linkages despite having more potential interest, for instance in the *in situ* formation of ligands. The ready hydrolysis of P-N bonds however is one problem associated with this type of chemistry. The P-N bond has been readily formed by the elimination of hydrogen halide from a halogenophosphine and a primary or secondary amine in benzene or diethyl ether at room temperature or below.⁹¹ The replacement of the second chlorine atom of dichlorophosphines is slower than the first, and this allows isolation of the intermediate monochloro compound.

Much scope exists for further studies on ligands containing nitrogen bridging two phosphorus atoms in contrast to oxygen bridges, due to the possibility for variation of substituents at both phosphorus and nitrogen. Attendant changes in the P-N-P bond angle, and the conformation around the phosphorus centres can cause significant differences in the coordination behaviour and structural features of the resulting complexes.⁹² The synthesis of the bis(diphenylphosphino)amine monoxide ligands in this chapter and their metal complexes in later chapters further broadens this scope. The novel ligand (41) has also been investigated to observe if it could exhibit variable modes of coordination to metal centres.

$$\begin{array}{c}
 O \\
 Ph \\
 P$$

2.2 Preparation of bis(diphenylphosphino)amine monoxide ligands, (2a,b)

The preparation of the ligands was carried out via a two step process which involved the isolation of the intermediate phosphinamides.^{93,94} These phosphinamides have been synthesised previously, for use as acid labile protecting group reagents for peptides.⁹⁵ This acid lability is known to involve initial protonation of the nitrogen atom followed by solvent attack at this site.

Reaction of the phosphinamides (42) and (43) at room temperature with a slight molar excess of chlorodiphenylphosphine in the presence of triethylamine as base, led to



the isolation of (2a) and (2b) in high yield. These moisture sensitive white solids were stored under a dry nitrogen atmosphere.



An attempt to make the corresponding ligand containing a 4-nitrophenyl substituent led only to the isolation of $Ph_2PP(O)Ph_2$ along with unreacted phosphinamide, as shown by a ³¹P-{¹H} n.m.r. spectrum. The interesting ligand $Ph_2PP(O)Ph_2$ has been observed previously and a few metal complexes are known.^{99,100} The compound was easily identified by its large phosphorus-phosphorus coupling constant of 224 Hz.^{97,98}

The spectroscopic properties of (2a) and (2b) were in accordance with the proposed structures.

2.2.1 N.m.r. spectra of the ligands (2a) and (2b)

The ${}^{31}P{-}{}^{1}H$ n.m.r. of the ligands exhibited an AX spin system, Figure 1. Similar spin systems have been observed in the related bis(diphenylphosphino)alkane monoxide ligands⁵ and other ligands containing two distinctly different phosphorus atoms.^{101,108} Comparison of the ${}^{31}P{-}{}^{1}H$ n.m.r. data for dppmO with (2a) and (2b), Table 1, show

Ligand	J(PP)	δΡ	δP=O
dppmO	50	-28.7	27.4
(2a)	86	55.7	30.3
(2b)	88	55.8	30.4

J/Hz; δ/p.p.m.

Table 1

that there was no significant difference in the chemical shift of the phosphine oxide moiety. However, the comparable shift for the diphenylphosphino moiety was observed to be 84 p.p.m. different in ligands (2a) and (2b) than in dppmO. This important difference has been attributed to the effect of the greater electronegativity of an N(R) group as compared to that of a methylene group. A study of a series of P-N bonded aminophosphines¹⁰² was carried out to elucidate information on the P(III)-N bond. This confirmed that phosphorus n.m.r. shifts of P-N bonded compounds appear at much lower field due to this electronegativity difference. Comparison of the ³¹P-{¹H} n.m.r. shifts of the ligands Ph₂PNMe₂¹⁰² and Ph₂PCH₃¹⁰³ also confirmed this general trend, Table 2.

Ligand	δP∖p.p.m.
Ph ₂ PNMe ₂	63.9
Ph ₂ PCH ₃	27.2

Table 2

In P-N bonded systems $p\pi$ - $d\pi$ bonding is important and it has also been shown that the correct geometry for such overlap occurs in compounds which incorporate a phosphine oxide moiety directly bonded to nitrogen.⁸⁶ An X-ray crystal structure determination on Ph₂P(O)NMe₂ suggested the nitrogen lone pair to be in the N-P-O plane, and that the geometry at nitrogen was a flattened tetrahedron.⁹⁶ It was therefore obvious that the system which contained the O-P-N-P backbone, as synthesised during this work, allowed good π -overlap along the whole backbone. This effective overlap also explains the greatly increased phosphorus-phosphorus coupling constant observed in these systems when compared to that of dppmO.

2.2.2 Infra-red spectra of ligands (2a) and (2b)

Compounds which contain a phosphoryl group have been easily identified by their characteristic, and very strong infra-red stretching frequency which is generally observed between 1350-1100 cm⁻¹.^{104,105} In general more electronegative substituents attached to the phosphoryl moiety increase the amount of π -bonding between the phosphorus 'd' orbitals and appropriately aligned 'p' orbitals on oxygen.¹⁰⁶ This has the effect of increasing the stretching frequency of the phosphoryl group. Despite the presence of the greater electronegativity of the nitrogen substituent in (2a) and (2b) as compared to dppmO, no difference was observed in v(P=O), which was located at 1200 cm⁻¹ in both cases. Thus other factors must also be important in determining the position of v(P=O) besides the electron withdrawing effects of attached groups. Infra-red bands of phosphoryl groups often appear as doublets.^{106,107} This feature was also shown by ligands (2a) and (2b).

2.2.3 ¹H n.m.r. and mass spectra of (2a) and (2b)

The ¹H n.m.r spectra showed the expected aromatic proton resonances, this including the expected AA'BB' pattern for the para-disubstituted aromatic ring in ligand (2b) where ${}^{4}J_{PH}$ was observed as 1.3 Hz. The EI mass spectra of the ligands showed the respective molecular ions, Figure 2.

³¹P-{¹H} n.m.r. spectrum of Ph₂PN(Ph)P(O)Ph₂ (2a)







Figure 2

2.3 Preparation of the novel chelating diphosphine, (41)

Using the general method described by Cross *et al.*⁹¹, the diphosphine (41) was obtained as a white solid in high yield via the intermediate (44), Scheme 2.

$$PhP(O)Cl_{2} + 4PhNH_{2} \xrightarrow{-2PhNH_{3}^{+}Cl^{-}} PhP(O)\{NHPh\}_{2}$$

$$(44)$$

$$PhP(O)\{NHPh\}_{2} \xrightarrow{CH_{2}Cl_{2}} (41)$$

Scheme 2

2.3.1 ³¹P-{¹H} n.m.r. spectrum of (41)

The ligand (41) showed the expected ${}^{31}P{}_{1}$ n.m.r. spectrum characteristic of an A₂X type spin system. The data obtained have been summarised in Table 3. The data for the starting material, (44) have also been given for comparison. The spectrum is given in Figure 3.

Ligand	J(PP)	δP	δP=O
(41)	78.1	55.6(d)	26.2(t)
(44)			10.0

J/Hz; δ/p.p.m.

<u>Table 3</u>

As in the case of (2a) and (2b) the diphenylphosphino resonances appeared downfield from P-C bonded ligands due to the greater electronegativity of the attached nitrogen substituents. The observed J(PP) value was similar to that of (2a) and (2b).

2.3.2 Infra-red spectrum of (41)

The infra-red spectrum confirmed the presence of the phosphoryl group due to an intense band at 1220 cm^{-1} .

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³¹P-{¹H} n.m.r. spectrum of PhP(O){N(Ph)PPh₂}₂ (41)

Figure 3

2.4 Preparation of a diphosphine containing a sulphuryl group

The ligand (41) which was discussed earlier incorporates at least three possible sites for coordination to metal centres. For comparative purposes the diphosphine ligand (45) was also synthesised by treating diphenylsulphamide with two molar equivalents of chlorodiphenylphosphine in the presence of an excess of triethylamine. The creamy



coloured product was identified by its ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum which showed a single peak at 69 p.p.m. Though stored under an inert atmosphere (45) showed surface discolouration after a short period and rapidly became a sticky paste. The ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum of this paste also contained numerous other resonances in the region

expected for oxidation and breakdown of (45). Attempts to synthesise metal complexes as detailed in Chapter 5 were frustrated by the instability of (45) as was full characterisation.

2.5 Attempted preparation of a chiral bis(diphenylphosphino)amine monoxide, (46)

In an attempt to extend the work to prepare the ligand (46), it was first necessary to prepare the intermediate phosphinanilide, (47). The attempted synthesis of (47) was

$$\begin{array}{ccc}
O & & O \\
\parallel & & \parallel \\
Ph_2P & & PPh_2 & Ph_2P & N & SR \\
& & & & & | \\
SR & & & H & H
\end{array}$$

(46) $R=C_6H_3\{NO_2\}_2-2,4$ (47)

carried out by refluxing RSNH₂ (R=C₆H₃{NO₂}₂-2,4) with Ph₂P(O)Cl in dichloromethane for 2h. After this time a ³¹P-{¹H} n.m.r. spectrum of the reaction mixture was taken. This showed two singlet resonances at 43.9 and 28.6 p.p.m. attributed to unreacted Ph₂P(O)Cl and (47) respectively. Further refluxing did not change the observed ratio of starting to product phosphoryl moieties of 40:60 and separation was not possible. It was thought that a higher reflux temperature in pyridine, as for other phosphinanilides⁹³ might be necessary and constitutes future work.

2.6 Conclusion

The novel bis(diphenylphosphino)amine monoxide ligands, (2a) and (2b), and the chelating diphosphine ligand (41) have been made in order to investigate their coordination chemistry and this is presented in the subsequent chapters.

Further work which would merit consideration would be the synthesis of similar ligands by variation of the substituents at both nitrogen and phosphorus. It may be possible by using chiral amines to obtain chiral ligands for synthesising chiral metal complexes for catalysts.

One final avenue which could be investigated would be to try to synthesise the

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thio- analogues of (2a) and (2b) and further extend the range of available metal complexes to produce analogues of dppmS.

2.7 Experimental

Microanalytical results, m.p.'s, i.r., mass spectral and n.m.r. data are presented for the newly isolated compounds. Microanalyses were carried out by Butterworth Laboratories Ltd., 54-56, Waldegrave Road, Teddington, Middlesex, TW11 8LG. M.p's were recorded on a Gallenkamp apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer as KBr discs. The ¹H n.m.r. spectra were recorded at room temperature in [²H₁]-chloroform on a JEOL EM390 spectrometer operating at 90 MHz with SiMe₄ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field). Coupling constants J are in Hz. The ³¹P-{¹H} n.m.r. spectra were recorded in dichloromethane on a JEOL JNM-FX90 spectrometer operating at 36.2 MHz, with [P(OH)₄]⁺ in [²H₂]-water (0.0 p.p.m.) as external reference and positive values to high frequency (low field). Mass spectra were recorded on a Kratos Concept Double Focussing Sector Mass Spectrometer.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use, from the following drying agents: dichloromethane (calcium hydride); diethyl ether (sodium/benzophenone). The compound chlorodiphenylphosphine (Aldrich) was distilled before use, and diphenylphosphinic chloride (Aldrich), aniline (Lancaster), and sulphamide (Lancaster) were used as supplied by commercial sources. The compounds diphenylsulphamide,¹¹³ N,N,P-Triphenylphosphinic diamide,¹⁰⁹⁻¹¹² N-(phenyl)diphenylphosphinamide^{93,94} and N-(4-methoxyphenyl)diphenylphosphinamide^{93,94} were prepared as described in the literature.

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2.7.1 Preparation of phosphine-phosphine oxide ligands

(i) Ph2P(O)N(Ph)PPh2 (2a)

Ph₂PCl (0.90g, 0.73 cm³, 4.1 mmol) and triethylamine (1.71g, 2.4 cm³, 17 mmol) were added to a solution of Ph₂P(O)NHPh (1.0g, 3.41 mmol) in dichloromethane (50 cm³) under a nitrogen atmosphere. The solution which gradually became pale yellow was stirred at room temperature for 3h. The solvent was then reduced in volume, and diethyl ether added to precipitate amine hydrochloride as a white solid. This solid was removed by filtration under nitrogen and the filtrate evaporated to dryness to yield the product as a fluffy white solid which was dried *in vacuo*, (1.12g, 69%).

(Found: C, 73.4; H, 5.69; N, 2.44. C₃₀H₂₅NOP₂ requires C, 73.0; H, 5.11; N, 2.83%), m.p. 102-4°C.

 v_{max} at 1430s (v_{P-Ph}) and 1200s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CDCl₃): ¹H (90 MHz), δ 6.9-8.1 p.p.m. [m, 25H, Ph].

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 30.3 [d, P_X, ²J(P_AP_X) 86], δ 55.7 p.p.m. [d, P_A, ²J(P_XP_A), 86].

Mass spectrum (EI High Res), [M]⁺ 477.

(ii) Ph₂P(O)N(C₆H₄OMe-4)PPh₂ (2b)

Triethylamine (1.57g, 2.2 cm³, 15.5 mmol) was added with stirring to a solution of $Ph_2P(O)NH(C_6H_4OMe-4)$ (1.0g, 3.10 mmol) and Ph_2PCl (0.82g, 0.67 cm³, 3.72 mmol) in dichloromethane. Work-up as above yielded the product as a creamy coloured solid which was dried *in vacuo*, (1.13g, 72%).

(Found: C, 73.7; H, 5.60; N, 2.70. C₃₁H₂₇NOP₂ requires C, 73.4; H, 5.40; N, 2.80%), m.p. 125-27°C.

 v_{max} at 1430m (v_{P-Ph}), 1200s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 3.57 [s, 3H, OMe], 5.30 [s, 2H, CH₂Cl₂], 6.33 [d, 2H, ¹J_{a'b'} 8.9], 6.58 [dd, 2H, ¹J_{a'b'} 9.0, ⁴J_{PH} 1.3], 7.26-7.44 p.p.m. [m, 20H, Ph]. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 29.7 [d, P_X, ²J(P_AP_X) 88], δ 55.7 p.p.m. [d, P_A, $^{2}J(P_{X}P_{A})$ 88].

Mass spectrum (EI Res), [M]⁺ 507.

(iii) PhP(O){N(Ph)PPh₂}₂ (41)

Triethylamine $(1.65g, 2.27 \text{ cm}^3, 16.3 \text{ mmol})$ was added with stirring to a suspension of PhP(O){NHPh}₂ (1.0g, 3.25 mmol) in dichloromethane (50 cm³). Two molar equivalents of Ph₂PCl (1.43g, 1.16 cm³, 6.50 mmol) were added and the resulting pale yellow solution was stirred under a nitrogen atmosphere for a further 3h. The solvent was rotary evaporated *in vacuo* and diethyl ether was added. The amine hydrochloride was removed by filtration the remaining solvent was removed to give a fluffy white solid which was dried *in vacuo*, (1.43g, 65%).

(Found: C, 70.8; H, 5.56; N, 3.71. C₄₂H₃₅N₂OP₃ requires C, 71.2; H, 4.98; N, 3.95%), m.p. 117-19°C.

 v_{max} at 1420s (v_{P-Ph}), 1210s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CDCl₃, 36.2 MHz), δ 26.2 [t, P_X, ²J(P_AP_X) 78], δ 55.6 p.p.m. [d, P_A, ²J(P_XP_A) 78].

2.7.2 Preparation of other ligands

(i) $SO_{2}{N(Ph)PPh_{2}}_{2}$ (45)

As above triethylamine (2.02g, 2.78 cm³, 20 mmol), Ph₂PCl (1.06g, 0.86 cm³, 4.8 mmol) and SO₂(NHPh)₂ (1.0g, 4.0 mmol) a sticky white solid which was dried *in vacuo*, (1.48g, 60%).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 69.0 p.p.m. [s, PPh₂].

(ii) Attempt to prepare Ph₂P(O)NH{SC₆H₃(NO₂)₂-1,3} (47)

A solution of $Ph_2P(O)Cl$ (0.22g, 0.18 cm³, 0.93 mmol) and $H_2NSC_6H_3(NO_2)_2$ -1,3 (0.2g, 0.93 mmol) in dichloromethane (20 cm³) was refluxed for 2h under a nitrogen atmosphere. A ³¹P-{¹H} n.m.r. spectrum of the reaction mixture showed two singlet

resonances at δ 28.6 and δ 43.9 p.p.m.

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CHAPTER 3

Synthesis of Some Transition Metal Complexes of Bis(Diphenylphosphino)amine Monoxides

3.1 Introduction

There have been no examples which have appeared in the literature to date of metal complexes of aminebis(diphosphine) monoxide ligands, which themselves have only appeared on two occasions as mentioned previously, with Ph₂PNHP(O)PPh₂ (38), Chapter 2.

Grim and co-workers have previously investigated the coordination chemistry of dppmO, but the most recent and wide-ranging study of its chemistry was carried out by Davies *et al.*²⁶ It was realised during these studies that the use of simple ideas like the absolute hardness values ^{115,116} of transition metals and the donor atoms of the ligands, were not sufficient to account for the observed coordination behaviour. A good illustration of this point was the fact that none of the metal carbonyl complexes reported showed [P,O] chelation. However, in the study by Grim *et al.*¹ complex (48) was prepared which contained a chelated derivative of dppmO despite only a subtle variation in the ligand. During the course of our studies with the ligands Ph₂PN(Ph)P(O)Ph₂ (2a) and Ph₂PN(C₆H₄OMe-4)P(O)Ph₂ (2b) similar variations have been observed.



(48)

Davis *et al.* successfully synthesised complexes of dppmO with Cr(0), Rh(I) and Ir(I), the rhodium complex being cationic and containing a [P,O] chelated ligand. Such cationic rhodium complexes which contain a chelating olefin have been shown to be active hydrogenation and isomerisation catalysts^{117,118} such as the Monsanto asymmetric catalysts. These complexes are catalytically active only after the removal by hydrogenation of the chelating olefin to form solvent coordinated complexes *in situ*.¹¹⁵ It has been postulated that such catalytic solutions contained hemilabile [P,O] chelates, where dissociation of the "hard" ligand component generates a vacant site for substrate binding. This hemilability can be initiated by other ligands or solvent molecules. Depending on the relative strength of the P-metal or O-metal bonds, equilibria can exist

in which the ligand bite opens up,¹¹⁹ Scheme 1. Several reactions have been attempted in the subsequent chapter to determine if metal complexes containing the ligands $Ph_2PN(Ph)P(O)Ph_2$ (2a) and $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (2b) could show this hemilabile behaviour, and have applications in catalysis.





The chelating nature of these [P,O] bonded metal complexes renders the phosphines more rigid than their freely rotating analogues. This in turn renders the ligands more stereochemically discriminating and enhances the stereoselectivity of the catalytic systems. Such systems have been demonstrated for Pd(II), Rh(I), Rh(III) and Ru(II) complexes.^{11,115,119}

3.2 Preparation of cis-[PdX₂{Ph₂PN(Ph)P(O)Ph₂}] complexes (X=Cl, Br and R=Ph, C₆H₄OMe-4

The complexes (50)-(53) were prepared in the present study by treatment of a dichloromethane solution of $[PdCl_2(COD)]$ or $[PdBr_2(COD)]$ with a stoichiometric amount of the relevant ligand, Scheme 2.



Scheme 2

The compounds were isolated as orange solids in yields of 67-85%, and were all highly soluble in dichloromethane and chloroform. The complexes (50) and (51) could

also be isolated by using $[PdCl_2(PhCN)_2]$ as starting precursor, but the ligands $Ph_2PN(Ph)P(O)Ph_2$ (2a) and $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (2b) did not displace Bipy from $[PdCl_2(Bipy)]$, with a ³¹P-{¹H} n.m.r. spectrum on the reaction mixture showing species due to oxidised ligand and ligand itself. The complexes (50)-(53) were identified by their ³¹P-{¹H} n.m.r. spectra which exhibited two doublets at approximately 63 and 83 p.p.m. with a $J(P_AP_X)$ value of 46 Hz, due to the expected AX spin system. The reduced J(PP) value along with the large downfield shift of both resonances in comparison with the free ligands confirmed complex formation. The resonance at 63 p.p.m. was assigned to the P_X moiety, this being the metal-coordinated phosphoryl group. The infra-red spectra of the metal complexes (50)-(53) showed a doublet absorption at 1108 and 1130 cm⁻¹ and an upfield shift from the free ligand vibration of 1200 cm⁻¹ thus assigned to $v_{P=0}$.^{106,107} This shift was concurrent with lengthening of the P-O bond due to electron donation to metal 'd' orbitals. The FAB mass spectra were used to confirm formation of (50)-(53), these showing [M-Cl]⁺ or [M-Br]⁺ as the highest observed ions.

The reported complexes crystallise with dichloromethane, the amount being dependent upon the speed of crystallisation, and also the extent of drying time *in vacuo*.

In all observed examples of complexes between palladium and bis(diphosphino)alkane monoxides discussed in Chapter 1, the phosphoryl groups were always uncoordinated except when AgNO₃ was employed as a dual halide remover and counter ion provider. This is in contrast to the complexes (50)-(53) where phosphoryl coordination was observed to be facile. Thus the use of absolute hardness values of transition metals and donor atoms once again fails, with Pd(II) having been classed as a soft metal and oxygen donors as hard ligands.

Crystals of complex (50) were grown but were found to be solvent dependent and would require a low temperature X-ray study to determine their structure.

3.3 <u>Preparation of $cis-[Mo(CO)_4{Ph_2PN(Ph)P(O)Ph_2}_2]$ (54) and $cis-[W(CO)_4(pip){Ph_2PN(Ph)P(O)Ph_2}]$ (55) complexes</u>

The complexes (54) and (55) were prepared by standard methods¹²³ involving displacement of relatively weakly bonded piperidine from metal carbonyl complexes.

Reaction of cis-[Mo(CO)₄(pip)₂] with a 2 molar equivalent of Ph₂PN(Ph)P(O)Ph₂ (2a) in refluxing dichloromethane resulted in the formation of the corresponding cis-[Mo(CO)₄{Ph₂PN(Ph)P(O)Ph₂}₂] complex (54). This is in contrast to the observation of Darensbourg that for normal phosphine ligands there is a slight thermodynamic preference for the *trans* isomer of [Mo(CO)₄{phosphine}₂].¹²⁰

For the cis-[W(CO)₄(pip)₂] complex, the displacement of the second piperidine ligand is known to be a more difficult process than for the analogous reaction with molybdenum,¹²¹ and consequently requires more forcing conditions in refluxing benzene or toluene. Thus the reaction of cis-[W(CO)₄(pip)₂] with a 2 molar equivalent of Ph₂PN(Ph)P(O)Ph₂ (2a) was attempted in refluxing benzene, but was unsuccessful as shown by a ³¹P-{¹H} n.m.r. spectrum on the crude reaction mixture, which showed oxidation and breakdown of (2a).

The analogous reaction of cis-[W(CO)₄(pip)₂] and a one molar equivalent of Ph₂PN(Ph)P(O)Ph₂ (2a) in refluxing dichloromethane, however yielded the mixed complex (55), Scheme 3. The complexes (54) and (55) were isolated as bright yellow solids in 52-65% yield.

$$cis-[Mo(CO)_4(pip)_2] \xrightarrow{2Ph_2PN(Ph)P(O)Ph_2} CH_2Cl_2,\Delta(2h) \xrightarrow{OC} \begin{array}{c} CO & Ph_2 & Ph \\ \downarrow & P- & N- & P(O)Ph_2 \\ OC & \downarrow & P- & N- & P(O)Ph_2 \\ OC & \downarrow & P- & N- & P(O)Ph_2 \\ CO & Ph_2 & Ph \end{array}$$

(54)



Scheme 3

The spectroscopic properties of (54) and (55) were in accord with the proposed

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structures. Thus the ³¹P-{¹H} n.m.r. spectra of both complexes exhibit two doublets shifted downfield from free ligand (2a) and with a reduced $J(P_AP_X)$ value. For the tungsten complex the satellite peaks due to coupling to ¹⁸³W (I= $\frac{1}{2}$, 14.3%) were not observed. Both complexes were too insoluble in common organic solvents for ¹³C-{¹H} n.m.r., and both crystallised with solvent of crystallisation, this being dichloromethane and observed in the ¹H n.m.r. spectra.

An attempt to obtain the complex (56) containing chelated $Ph_2PN(Ph)P(O)Ph_2$ (2a) by the use of more forcing conditions in refluxing benzene was unsuccessful as shown by ³¹P-{¹H} n.m.r. with no evidence for coordination of the phosphine oxide moiety.



(56)

For a cis-[M(CO)₄L₂] complex with C_{2V} symmetry, group theory predicts four infrared-active stretching vibrations comprising 2a₁, b₁ and b₂. A *trans* complex of D_{4h} symmetry on the other hand only shows one infrared-active band and so these isomers are easily distinguishable, although additional bands can be observed for *trans* complexes. These other bands are noticeable when the asymmetry of the ligand lowers the overall symmetry of the entire molecule and consequently, previously inactive bands become weakly active, Figure 1.¹²²





Infrared spectra in the v_{CO} region for two metal carbonyl complexes

<u>Figure 1</u>

Thus the KBr disc infra-red spectra of complexes (54) and (55) each showed three

bands, with the band for the symmetry element b_2 only observed as an unresolved shoulder. These spectra confirmed the assignment of the *cis* stereochemistry at the metal centres.

3.4 Reactions of (2a) and (2b) with ruthenium

3.4.1 <u>Preparation of [RuCl(R){Ph₂PN(R')P(O)Ph₂}][Cl] complexes (R=p-cym, mes and R'=Ph, C₆H₄OMe-4)</u>

There has only been one instance of a phosphine-phosphine oxide ligand ruthenium metal complex and this only occurred as a minor product in another reaction, between ruthenium(III) chloride and opmpp.⁵⁴

By far the most commonly observed method for the synthesis of ruthenium metal complexes of both mono and bidentate ligands has been the use of $[RuCl_2(\eta^6-arene)]_2$ starting materials (arene= *p*-cymene, benzene, mesitylene and hexamethylbenzene) which are readily available from ruthenium(III) chloride.¹²⁴⁻⁶ The reaction of monodentate ligands commonly yields neutral dichloro species, (57) whilst bidentate ligands produce ionic salt complexes, (58).



The reaction of ligands $Ph_2PN(Ph)P(O)Ph_2$ (2a) and $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (2b) have been carried out to yield the title complexes (59)-(62) by reaction with $[RuCl_2(\eta^6\text{-}arene)]_2$ (arene= *p*-cymene, mesitylene) in refluxing ethanol. The products were isolated as orange-brown solids in 59-62% yield, Scheme 4. The ³¹P-{¹H} n.m.r. spectra of the complexes (59)-(62) all exhibited two doublets as expected, with the resonances for the complexes containing mesitylene appearing several p.p.m. further downfield than those containing *p*-cymene due to the character of these arene rings. The FAB mass spectra of all the complexes exhibited as the two highest peaks, [M-Cl]⁺ and [M-2Cl]⁺ respectively with no molecular ion being seen.

The 300 MHz ¹H n.m.r. spectra of complexes (59) and (60) showed a broad singlet at 1.28 p.p.m., a broad multiplet at 2.77 p.p.m. for the -CHMe₂ group, and a singlet at 2.08 p.p.m. corresponding to the arene -CH₃ group. Two broad singlets were also



Scheme 4

observed for the ring protons of the arene moiety. The 1 H n.m.r. spectra of complexes (61) and (62) exhibited singlets at 2.13 p.p.m. and 5.11 p.p.m. which were attributed to the methyl and arene ring protons of the mesitylene moiety respectively.

3.4.2 Reaction of $[RuCl_2(R)]_2$ (R=p-cymene) with Ph₂PN(Ph)P(O)Ph₂ in refluxing benzene

The reaction of bidentate diphosphine ligands in refluxing benzene with $[RuCl_2(\eta^6-C_6H_6)]_2$ has been previously investigated and complexes of the type $[RuCl_2(\eta^6-C_6H_6)]_2{\mu-Ph_2P(CH_2)_nPPh_2}$ (n=2-4) were prepared.¹²⁶ Hence, the reaction of the phosphine-phosphine oxide ligand Ph_2PN(Ph)P(O)Ph_2 (2a) was carried out with $[RuCl_2(p-cymene)]_2$ in refluxing benzene. A ³¹P-{¹H} n.m.r. spectrum of the reaction mixture exhibited two doublet resonances appearing at 60 and 140 p.p.m. respectively. A FAB mass spectrum of the yellow-brown solid obtained from this reaction mixture exhibited a pattern characteristic of complexes (59) and (60).

3.5 Synthesis of rhodium complexes of ligands (2a) and (2b)

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3.5.1 <u>cis-[RhCl(CO){Ph₂PN(R)P(O)Ph₂}] (R=Ph, C₆H₄OMe-4)</u>

It has been known for many years that the use of the rhodium carbonyl chloride dimer (64) provides a convenient method for the preparation of Rh(I) monodentate complexes by reaction with both bidentate and monodentate ligands via bridge splitting reactions.¹²⁷ The reaction of (64) with chelating bidentate ligands results in stereospecific formation of *cis*-[RhCl(CO){LL}] complexes.¹²⁸ These complexes can be formed by direct reaction of previously prepared (64)¹²⁹ or from (64) formed *in situ* by the passage of carbon monoxide through a dichloromethane or benzene solution of [RhCl(CO)]₂ (65) for a short period. The reaction of (64) (formed *in situ*) with two

$$_{\rm OC}^{\rm OC}$$
 >Rh $<_{\rm Cl}^{\rm Cl}$ >Rh $<_{\rm CO}^{\rm CO}$

molar equivalents of ligands $Ph_2PN(Ph)P(O)Ph_2$ (2a) and $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (2b) in dichloromethane at room temperature afforded the title complexes (66) and (67), as orange microcrystalline solids in good yields, Scheme 5. The ³¹P-{¹H} n.m.r. spectra

$$[RhCl(CO)_2]_2 \xrightarrow{Ph_2PN(R)P(O)Ph_2}_{CH_2Cl_2,2h} \qquad \qquad \begin{array}{c} Ph_2 \\ P \\ P \\ Ph_2 \\ \end{array} \xrightarrow{P} \\ Ph_2 \\ Cl \\ Ph_2 \\ Cl \\ Ph_2 \\ Cl \\ Ph_2 \\ Cl \\ Ph_2$$

Scheme 5

of (66) and (67) were consistent with an AMX spin system containing two chemically and magnetically distinct phosphorus nuclei also coupling to spin active rhodium-103 $(I=\frac{1}{2}, 100\%)$.¹³⁰ The spectra consisted of two sets of doublet of doublet resonances from which ¹J(RhP_A), ²J(RhP_X) and ²J(P_AP_X) were obtained. The low frequency doublet of doublets appeared as a virtual doublet¹³¹ because the value of ²J(RhP_X) was only 3.2 Hz, and this resonance was assigned to the P(O)Ph₂ moiety, Figure 2. This value of ²J(RhP_X) corresponds favourably with that observed for [RhCl(CO){Ph₂PCH₂P(O)Ph₂}] (25),

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Chapter 1 of 4.8 Hz.¹¹ The resonance for the PPh₂ (P_A) moiety in complex (66) appeared at 109 p.p.m. this being considerably downfield (65 p.p.m.) from the analogous resonance for complex (25), the reasons for this having been discussed previously with respect to the ligands themselves, Chapter 2. The FAB mass spectra of (66) and (67) exhibited as the highest species [M-CO]⁺ and [M-Cl]⁺. A ¹³C-{¹H} n.m.r. spectrum of the complexes did not exhibit a resonance for the carbonyl moieties, this being attributed to the intensity of the aromatic signals and also to the coupling expected to phosphorus and rhodium nuclei. The KBr disc i.r. spectra exhibited a strong absorption at 1980 cm⁻¹ attributed to the v_{CO} stretching band.

3.5.2 Structural properties of cis-[RhCl(CO){Ph2PN(C6H4OMe-4)P(O)Ph2}] (67)

The molecular structure of complex (67) is illustrated in Figure 3 which also gives the crystallographic numbering system, and a summary of selected bond lengths and angles is given in Table 1. Bond lengths and angles for the complex cis-[RhCl(CO)dppmO] (25)¹¹ are also given for comparison in Table 2.

The view of (67) in Figure 3 shows that the geometry about the rhodium atom is essentially square planar, although the P(1)-Rh-O(3) angle is slightly less than 90°(85.4°). The ligand (2b) coordinates to rhodium in a five-membered cis chelate in which the carbonyl group is trans to the phosphoryl moiety and the chloride is trans to the diphenylphosphino moiety as expected on the basis of π -bonding of the ligands. The five-membered chelate ring is essentially planar with a deviation of 0.1Å from this plane at the rhodium atom. The P=O bond length of 1.511(3)Å is longer than the P=O bond length in triphenylphosphine oxide (1.46Å),¹⁴⁴ and is comparable to the P=O bond cis-[RhCl(CO)dppmO] of (25) (1.514Å)¹¹ length and of that cis-[RhCl(CO)₂{Cy₃PO}].¹⁴⁹ This confirms that there is no difference in the character of the P=O bond of both complexes as was mentioned previously, Chapter 2. As can be observed, all the important bond lengths of the complexes (67) and (25) are of the same order, Table 1. Complex (67) crystallises with three moles of chloroform from which X-ray quality crystals were grown.

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Figure 3

(a) Molecular structure of *cis*-[RhCl(CO){Ph₂PN(C₆H₄OMe-4)P(O)Ph₂}] (67) with all hydrogen atoms omitted.

(b) View showing the slight deviation from planarity of the chelate ring.

Bond	(67) (Å)	<i>cis-</i> [RhCl(CO)dppmO] (Å)
Rh - Cl(1)	2.371(2)	2.382
Rh - C(1)	1.799(5)	1.787
Rh - P(1)	2.192(1)	2.220
Rh - O(3)	2.108(3)	2.109
P(2) - O(3)	1.511(3)	1.514
C(1) - O(1)	1.140(6)	
P(1) - N(1)	1.725(3)	
P(2) - N(1)	1.679(3)	

<u>Table 1</u>
Selected bond lengths for the complex
cis -[RhCl(CO){Ph ₂ PN(C ₆ H ₄ OMe-4)P(O)Ph ₂ }] (67)
compared to data for cis-[KhUI(UU)dppmU] (25).11

Bond Angle	(67) (°)
O(3) - Rh - C(1)	176.9(22)
P(1) - Rh - C(1)	91.6(20)
P(1) - Rh - O(3)	85.4(9)
Cl - Rh - C(1)	93.7(20)
Cl - Rh - O(3)	89.4(9)
Cl - Rh - P(1)	174.7(4)
P(1) - N(1) - P(2)	117.1(21)
Rh - O(3) - P(2)	120.6(15)
N(1) - P(2) - O(3)	107.4(16)

 Table 2

 Selected bond angles for the complex

 cis-[RhCl(CO){Ph2PN(C6H4OMe-4)P(O)Ph2}] (67)

3.6 Preparation of [Rh(COD){Ph2PN(R)P(0)Ph2}][PF6] (R=Ph, C6H4OMe-4)

Complexes of the type $[Rh(diene)L_2][X]^-$, where X⁻ is a non-coordinating counter ion and L is a monodentate tertiary phosphine or L₂ is a chelating diphosphine, have been shown to be versatile and easily prepared catalyst precursors.^{132,133}

The complexes (68) and (69) were prepared by treating a system of $[RhCl(COD)]_2$ and KPF₆ in dichloromethane with the phosphine-phosphine oxide ligands (2a) and (2b) at room temperature, Scheme 6. The products were precipitated as bright yellow-orange

$$[RhCl(COD)]_{2} + 2KPF_{6} \xrightarrow{2Ph_{2}PN(R)P(O)Ph_{2}}{CH_{2}Cl_{2},2h} \left[(COD)Rh \xrightarrow{Ph_{2}}{O} = PPh_{2} \right] [PF_{6}]$$

$$R=Ph (68)$$

$$R=C_{6}H_{4}OMe-4 (69)$$

Scheme 6

microcrystalline solids in good yields and were air-stable. The ³¹P-{¹H} n.m.r. spectra of the complexes exhibited one set of doublet of doublets to low field (δ P) and to high field a closely spaced doublet of doublets (δ P=O) which at 24 MHz appeared as a virtual doublet, this due to the small observed value of ²J(Rh-O=P).¹³¹ Both sets of doublet of doublets exhibited a ¹J(RhP) coupling constant of 161 Hz. The PF₆⁻ counter ion was observed at -144 p.p.m. with the expected ¹J(PF) value of 711 Hz. The signals were observed as septets with the outer lines not being observed. The observed values of ¹J(RhP) agrees with the value in the analogous complex with dppmO, [Rh(COD)dppmO][PF₆] (70) of 162.4 Hz.²⁶ The observed value in the i.r. spectrum of (68) and (69) of ν (P=O) of 1130 cm⁻¹ is also in agreement with the literature values for complex (70).²⁶ The FAB mass spectra of (68) and (69) exhibited [M-PF₆]⁺ as the highest species. In the 300 MHz ¹H n.m.r. spectra of the complexes the unsymmetrical nature of the overall molecule caused two separate resonances to be seen for both the methylene and alkene protons of the COD moieties.

3.6.1 Structural properties of [Rh(COD){Ph2PN(Ph)P(O)Ph2}][PF6] (68)

The molecular structure of complex (68) is illustrated in Figure 4 which also gives the crystallographic numbering system, and a summary of selected bond lengths and angles is given in Table 3. Bond lengths and angles for the complex $[Rh(COD){Ph_2PCH(CH_3)CH(CH_3)PPh_2}][ClO_4].THF$ are also given for comparison in Table 4.¹⁸⁶

The view of (68) in Figure 4 shows that the geometry about the rhodium atom is essentially square planar with the P(2)-Rh-O(1) angle slightly less than 90°(85.9°) with the bisecting angles of the double bonds of the COD moiety and this is in agreement with the literature values.^{186,187} Once again as in the structure of (67) the five-membered chelate ring is essentially planar with a small deviation from this plane at the rhodium atom of 0.095Å but puckering of the overall plane.

The P=O bond length of 1.504(4)Å is similar to that of complex (67) of 1.511(3)Å where the phosphine oxide moiety is also bound to rhodium. The two coordinated C=C double bond lengths are 1.398(10)Å and 1.357(10)Å and are comparable to the bond lengths observed for the COD ligand in the literature in other structures.¹⁸⁶ It is observed that the Rh(1)-C(1) and Rh(1)-C(2) distances at 2.102(6)Å and 2.108(6)Å respectively are significantly shorter than the Rh(1)-C(5) and Rh(1)-C(6) distances at 2.220(7)Å and 2.253(6)Å respectively, and this is a consequence of the greater back bonding in the case of the phosphoryl moiety. The Rh(1)-P(2) distance is 2.250(1)Å in agreement with other such distances.^{186,187}



Figure 4

Molecular structure of cis-[Rh(COD){Ph₂PN(Ph)P(O)Ph₂}] [PF₆] (68) with all hydrogen atoms omitted

Bond	(68) (Å)	[Rh(COD){Ph2PCH(CH3)CH(CH3)PPh2}][CI04].THF	(67) (Å)
Rh(1) - P(2)	2.250(1)	2.266(1)	2.192(1)
Rh(1) - O(1)	2.095(3)		2.108(3)
Rh(1) - C(1)	2.102(6)	2.241(4)	
Rh(1) - C(2)	2.108(6)	2.338(6)	
Rh(1) - C(5)	2.220(7)	2.247(5)	
Rh(1) - C(6)	2.253(6)	2.247(5)	
C(1) - C(2)	1.398(10)	1.362(8)	
C(5) - C(6)	1.357(10)	1.357(8)	
P(1) - O(1)	1.504(4)		

Table 3

Selected bond lengths for the complex cis-[Rh(COD){Ph_2PN(Ph)P(O)Ph_2}] [PF₆] (68) compared to relevant literature data.¹⁸⁶

3.6.2 Preparation of [Rh(NBD){Ph2PN(Ph)P(O)Ph2}][PF6] (71)

An analogous method to that for complexes (68) and (69), afforded the complex (71) with the diene being bicyclo[2.2.1] hepta-2,5-diene. The complex was isolated in 88% yield as an orange microcrystalline solid. The ³¹P-{¹H} n.m.r. spectrum of (71) exhibited like (68) and (69), a low field doublet of doublets, a high field virtual doublet and a septet with the two outer lines not being observed. The value of ¹J(RhP) for (71) at 183 Hz was \approx 20 Hz larger than that in either (68) or (69), this being caused by the lower *trans*-influence of NBD compared to that of COD enhancing the bonding of the diphenylphosphino moiety to the metal.¹⁶⁶ A ¹⁹F n.m.r. spectrum of (71) displayed a



doublet resonance at -74 p.p.m. and a FAB mass spectrum exhibited $[M-PF_6]^+$ as the highest observed ion at m/z 672.

3.7 Preparation of [RhCl(Cp*){Ph2PN(Ph)P(O)Ph2}][PF6]

The complex $[RhCp*Cl_2]_2$ (72) possesses labile ligands as well as a strong C_5Me_5 -metal bond. This allows useful reactions to occur for the design of new homogeneous catalysts, such that the metal-ligand bonds will be capable of surviving the necessary changes of oxidation state and coordination number during any catalytic cycle.¹³⁴ It is known that chloride bridge cleavage reactions occur very easily with tertiary phosphines to yield the monomeric Rh(III) species, $[Rh(Cp*)Cl_2L]$ and so the reaction of the bis(diphenylphosphino)amine monoxide ligand (2a) was carried out with (72) to afford the ionic complex salt (73) as a bright orange microcrystalline solid, Scheme 7. The ³¹P-{¹H} n.m.r. spectrum of (73) exhibited two doublet of doublet resonances centred at 54.4 and 93.2 p.p.m. as well as the septet for the PF₆⁻ counter ion. A ¹H n.m.r. spectrum exhibited besides the resonances of the aromatic region, a doublet



Scheme 7

at 1.48 p.p.m. with a ${}^{2}J(RhH)$ coupling constant of 3.8 Hz. Similarly, the ${}^{13}C-{}^{1}H$ n.m.r. spectrum contained a doublet at 100.4 p.p.m. with a ${}^{1}J(RhC)$ value of 4.8 Hz. These resonances were assigned to the metal-coordinated pentamethylcyclopentadienyl moiety.

3.8 Preparation of cis-[IrCl(CO){Ph2PN(Ph)P(O)Ph2}] (75)

The reactions of chelating diphosphines with complexes of the type $[IrCl(CO)_2NH_2R]$ have been shown to afford complexes of the type (74).



(74)

The reaction of $Ph_2PN(Ph)P(O)Ph_2$ (2a) with [IrCl(CO)₂{H₂NC₆H₄Me-4}] was carried out in dichloromethane at room temperature to afford the complex (75) as a pale yellow microcrystalline solid, Scheme 8.

$$[IrCl(CO)_{2}\{H_{2}NC_{6}H_{4}Me-4\}] \xrightarrow{Ph_{2}PN(Ph)P(O)Ph_{2}} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{Ph_{2}} \xrightarrow{P} \xrightarrow{CO} \xrightarrow{CO} \xrightarrow{CH_{2}Cl_{2},2h} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{CO} \xrightarrow{CO} \xrightarrow{CO} \xrightarrow{CH_{2}Cl_{2},2h} \xrightarrow{Ph} \xrightarrow{$$



Scheme 8



Often, iridium phosphine complexes react irreversibly with O_2 via oxidative addition.¹³⁷ Complex (75) showed no changes on prolonged exposure in air. The ³¹P-{¹H} n.m.r. spectrum of (75) exhibited two doublets with identical coupling constants and an i.r. spectrum contained an intense band attributed to the carbonyl group at 2020 cm⁻¹.

3.9 Miscellaneous reactions of Ph2PN(Ph)P(O)Ph2 (2a)

The reaction of (2a) in dichloromethane with $[IrCl(COD)]_2$ (76) in the presence of KPF₆ was attempted. Reaction of the related ligand dppmO with (76) has been shown to afford the complex [IrCl(COD)dppmO] (77) as an orange solid without KPF₆ present.^{26a} The complex (77) contained unidentate [P]-bound dppmO, and no evidence of [P,O] chelation was observed. A ³¹P-{¹H} n.m.r. spectrum of the reaction mixture from reaction of (2a) and (76) exhibited two distinct sets of resonances each appearing as two doublets. These resonances were tentatively assigned to the species (78) and (79). It



was not possible to separate the complexes present in the mixture. A FAB mass spectrum on the yellow solid obtained from the reaction mixture exhibited $[M-PF_6]^+$ at m/z 778 for (78) but $[M-Cl]^+$ for (79) could not be discerned.

Attempts to obtain cobalt and nickel complexes of the phosphine-phosphine oxide ligands were carried out by reaction with anhydrous $CoCl_2$ and $NiCl_2$ respectively, knowing that the hydrated species of these compounds would cause hydrolysis of the ligand itself. The ³¹P-{¹H} n.m.r. spectra of the reaction mixtures indicated that no complex had been formed in either case, and that the ligand had broken down under the reaction conditions employed.

The reaction of dppmO with [PtCl₂(COD)] has been shown to afford the complex

 $[PtCl_2(dppmO)_2]$ (80) containing non-chelated dppmO ligands.⁵ Similarly, the reaction of a two molar amount of ligand Ph₂PN(Ph)P(O)Ph₂ (2a) with $[PtCl_2(COD)]$ in dichloromethane was carried out in our study. On addition of the ligand a slight darkening of the solution was observed and after stirring for 2h at room temperature a $^{31}P-{^{1}H}$ n.m.r. spectrum indicated the presence of two compounds in the mixture only one of which was observed with associated ^{195}Pt satellites. A singlet resonance was observed at 28.9 p.p.m. and also a singlet at 67.3 p.p.m. with a ¹J(PtP) coupling constant of 2974 Hz. The compounds observed were attributed to the compounds (81) and (82), Scheme 9. With both resonances appearing as singlets it was evident that each species contained only one type of phosphorus atom due to the lack of an observed J(P_AP_X)

$$[PtCl_{2}(COD)] \xrightarrow{2Ph_{2}PN(Ph)P(O)Ph_{2}} PhN \xrightarrow{Ph_{2}} Pt \xrightarrow{Cl} Ph_{2}Pt \xrightarrow{O} O \qquad O \\ P \\ Ph_{2}Pt \xrightarrow{Cl} Ph_{2}Pt \xrightarrow{O} Pt \xrightarrow{O} Ph_{2}Pt \xrightarrow{O} Pt \xrightarrow{$$

Scheme 9

coupling constant. The chemical shifts observed are consistent with the proposed products, with phosphine oxide resonances characteristically appearing in the lower frequency region and the lack of ¹⁹⁵Pt satellites confirming the assignment of (82).

Shaw *et al.* observed that the reaction of dppmO with [PtCl₂(COD)] afforded [PtCl₂(dppmO)₂] which was isolated.⁵ By analogy it would appear that the intermediate complex (83) was formed initially, this then undergoing further reaction intramolecularly in order to afford the more stable thermodynamically favoured chelate ring of (81) with concurrent elimination of (82), Scheme 10. A similar type of intramolecular reaction Pho. Ph. Pho.

Scheme 10

under the same conditions has been previously observed by Davies et al. with platinum

coordinated aminomethylphenyl phosphine ligands, with both chelate and monodentate species observed by ³¹P-{¹H} n.m.r.¹⁶⁷ In contrast in the same work, it was seen that the conversion of the bis-monodentate molybdenum tetracarbonyl species was only achieved in refluxing toluene at high temperature and the non-chelate species was isolated which is in agreement with the isolation of the complex cis-[Mo(CO)₄{Ph₂PN(Ph)P(O)Ph₂}₂] (54), Chapter 3.

3.10 Conclusion

It has been demonstrated that the bis(diphenylphosphino)amine monoxide ligands (2a) and (2b) are versatile ligands for the formation of metal complexes with several different metals. These ligands have been observed cooordinating as chelating bidentate or as non-chelating monodentate ligands, this being dependent on the metal involved Similar behaviour has been seen in the literature for the for the analogous carbon bridged ligand dppmO. Further work involves attempted coordination of the ligands to other metals to extend the range of complexes.

3.11 Experimental

General experimental techniques were as described in Chapter 2. The ${}^{31}P{-}{}^{1}H$ n.m.r. spectra were recorded on a JEOL JNM-FX90 spectrometer operating at 36.2 MHz or on a Bruker AM300 spectrometer operating at 121.5 MHz with $[P(OH)_4]^+$ in $[{}^{2}H_2]$ -water (0.0 p.p.m.) as external reference with positive values to high frequency (low field). The ${}^{19}F{-}{}^{1}H$ n.m.r. spectra were recorded in dichloromethane on a Bruker AM300 spectrometer operating at 282.41 MHz with CFCl₃ as external reference and positive values to high frequency (low field). The ${}^{13}C{-}{}^{1}H$ n.m.r. spectra were recorded along with DEPT spectra in $[{}^{2}H_{1}]$ -chloroform on a Bruker AM300 spectrometer operating at 75.47 MHz with SiMe₄ (0.0 p.p.m.) as internal reference.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use, from the following drying agents: toluene, light petroleum (sodium); ethanol (magnesium/iodine). Light petroleum refers to the fraction boiling in the range 40-60°C. The compounds anhydrous NiCl₂, anhydrous CoCl₂, Mo(CO)₆, W(CO)₆ (Aldrich) and KPF₆ (Ventron) were all used as supplied by commercial sources. The compounds $[PtCl_2(COD)]$,¹³⁹ $[PdCl_2(COD)]$,¹⁴⁰ $[PdCl_2(PhCN)_2]$,¹⁴¹ $[PdCl_2bipy]$,¹⁴² $[Mo(CO)_4pip_2]$,¹²¹ $[W(CO)_4pip_2]$,¹²¹ $[W(CO)_4pip_2]$,¹²¹ $[RhCl(COD)]_2$,¹⁴³ $[IrCl(CO){H_2NC_6H_4Me}]$,¹⁴⁰ $[IrCl(COD)]_2$,¹⁴⁵ $[RhCl(NBD)]_2$,¹⁴⁶ $[RuCl_2(mes)]_2$,¹⁴⁷ $[RuCl_2(p-cym)]_2$,¹⁴⁷ $[RhCl_2(C_5Me_5)]_2$ ¹⁴⁸ and $[PdBr_2(COD)]$ ¹⁴⁰ were all prepared as described in the literature. Precious metals were obtained on loan from Johnson Matthey plc.

3.11.1 Preparation of cis-[PdX₂{Ph₂PN(R)P(O)Ph₂}] complexes

(i) X=Cl, R=Ph (50)

A solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.34g, 0.70 mmol) in dichloromethane (10 cm³) was added to a stirred solution of $[PdCl_2(COD)]$ (0.2g, 0.70 mmol) also in dichloromethane whereupon the resulting dark orange solution was stirred for 3h. The volume of solvent was reduced *in vacuo* before the addition of light petroleum afforded an orange microcrystalline solid which was recrystallised from dichloromethane-diethyl ether and dried *in vacuo* (0.34g, 74%)

(Found: C, 50.7; H, 3.76; N, 1.74. C₃₀H₂₅Cl₂NOP₂Pd.CH₂Cl₂ requires C, 50.3; H, 3.75; N, 1.89%), m.p. 185-7°C(decomp.).

 v_{max} at 1440s (v_{PPh}), 1130s ($v_{P=O}$) and 1110s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 62.8 [d, P_X, ²J(P_AP_X) 43.9] and δ 83.5 p.p.m. [d, P_A, ²J(P_XP_A) 43.9].

Mass spectrum (FAB), [M-Cl]⁺ 620, [M-2Cl]⁺ 583.

(ii) X=Cl, R=C₆H₄OMe-4 (51)

As above, a solution of $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (0.36g, 0.70 mmol) in dichloromethane was added to $[PdCl_2(COD)]$ (0.2g, 0.70 mmol) in dichloromethane and the solution stirred for 3h. Work-up as above afforded the title product (51) as an orange microcrystalline solid which was dried *in vacuo* (0.32g, 67%).
(Found: C, 53.7; H, 4.06; N, 2.36. C₃₁H₂₇Cl₂NO₂P₂Pd requires C, 54.3; H, 3.97; N, 2.05%), m.p. 182-4°C(decomp.).

 v_{max} at 1440m (v_{PPh}), 1130s ($v_{P=O}$) and 1108s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 62.6 [d, P_X, ²J(P_AP_X) 46.4] and δ 82.6 [d, P_A, ²J(P_XP_A) 46.4].

Mass spectrum (FAB), [M-Cl]⁺ 648, [M-2Cl]⁺ 613.

(iii) X=Br, R=Ph (52)

As above, a solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.25g, 0.53 mmol) in dichloromethane (10 cm³) was added with stirring to one of $[PdBr_2(COD)]$ (0.2g, 0.53 mmol) and the solution stirred for 2h. Work-up as above afforded the product identified as (52) as a dark orange solid which was recrystallised from dichloromethane-diethyl ether and dried *in vacuo* (0.34g, 85%).

(Found: C, 46.1; H, 3.18; N, 1.64. C₃₀H₂₅Br₂NOP₂Pd.0.5 CH₂Cl₂ requires C, 46.6; H, 3.33; N, 1.78%), m.p. 172-4°C.

 v_{max} at 1430s (v_{PPh}), 1130s ($v_{P=O}$) and 1108s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 62.2 [d, P_X, ²J(P_AP_X) 46.4] and δ 83.3 p.p.m. [d, P_A, ²J(P_XP_A) 46.4].

Mass spectrum (FAB), [M-Br]⁺ 664, [M-2Br]⁺ 583.

(iv) X=Br, R=C₆H₄OMe-4 (53)

A solution of $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (0.31g, 0.53 mmol) was added to a stirred solution of $[PdBr_2(COD)]$ (0.2g, 0.53 mmol) in dichloromethane (15 cm³) and the resulting dark orange solution stirred for 3h. Work-up as above afforded the title product (53) as a dark orange solid which was recrystallised from dichloromethane-diethyl ether and dried *in vacuo* (0.31g, 79%).

(Found: C, 44.9; H, 3.40; N, 1.70. C₃₁H₂₇Br₂NO₂P₂Pd requires C, 44.8; H, 3.40; N, 1.63%), m.p. 230-2°C.

 v_{max} at 1420s (v_{PPh}), 1130s ($v_{P=O}$) and 1115s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 61.2 [d, P_X, ²J(P_AP_X) 47.7] and δ 84.4 p.p.m. [d, P_A, ²J(P_XP_A) 47.7].

Mass spectrum (FAB), [M-Br]⁺ 694, [M-2Br]⁺ 613.

3.11.2 Preparation of cis-[RhCl(CO){Ph₂PN(Ph)P(O)Ph₂}] complexes

(i) **<u>R=Ph (66)</u>**

After the passage of a slow stream of CO through a dichloromethane solution of $[RhCl(COD)]_2$ (0.25g, 0.51 mmol) for 0.5h, a solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.49g, 1.03 mmol) also in dichloromethane was added, and the orange solution stirred for 2h. The volume of solvent was reduced and the addition of light petroleum afforded the title product (66) as an orange microcrystalline solid which was recrystallised from dichloromethane-diethyl ether and dried *in vacuo* (0.41g, 62%).

(Found: C, 55.4; H, 4.04; N, 1.98. $C_{31}H_{25}CINO_2P_2Rh.0.5CH_2Cl_2$ requires C, 55.1; H, 3.82; N, 2.04%), m.p. 197-9°C.(decomp.).

 υ_{max} at 1980s (υ_{CO}), 1440s (υ_{PPh}) and 1130s ($\upsilon_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), δ 54.8 [dd, P_X, ²J(P_AP_X) 52.9, ²J(RhP_X) 3.2] and δ 109 p.p.m. [dd, P_A, ²J(RhP_A) 169.3, ²J(P_XP_A) 52.9].

 $^{13}C-\{^{1}H\}$ (CDCl₃, 75.47 MHz), δ 126.1-133.9 p.p.m. [m, Ph]; carbonyl resonance not observed.

Mass spectrum (FAB), [M-CO]⁺ 615, [M-Cl]⁺ 608, [M-Cl-CO]⁺ 580.

(ii) <u>R=C₆H₄OMe-4 (67)</u>

Similarly to above, $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (0.69g, 1.36 mmol) was added to $[RhCl(COD)]_2$ (0.25g, 0.68 mmol) in dichloromethane after the passage of CO for 0.5h. After stirring the resulting solution for 2h, reduction of the volume was followed by the addition of light petroleum to afford (67) as an orange microcrystalline solid which was recrystallised from dichloromethane-diethyl ether and dried *in vacuo* (0.6g, 65%).

(Found: C, 55.3; H, 3.79; N, 1.96. C₃₂H₂₇ClNO₃P₂Rh.0.5CH₂Cl₂ requires C, 54.7; H, 3.83; N, 1.90%), m.p. 255-7°C(decomp.).

 u_{max} at 1980s (u_{CO}), 1440 (u_{PPh}) and 1130s ($u_{P=O}$) cm⁻¹ (KBr). N.m.r. ³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), δ 54.6 [dd, P_X, ²J(P_AP_X) 56.4, ²J(RhP_X) 3.2] and δ 109 p.p.m. [dd, P_A, ¹J(RhP_A) 169, ²J(P_XP_A) 56.4]. Mass spectrum (FAB), [M-CO]⁺ 645, [M-Cl]⁺ 638, [M-Cl-CO]⁺ 610.

3.11.3 Preparation of cis-[IrCl(CO)Ph₂PN(Ph)P(O)Ph₂] (75)

A solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.24g, 0.52 mmol) in dichloromethane (15 cm³) was added with stirring to [IrCl(CO)₂{H₂NC₆H₄Me-4}] (0.2g, 0.51 mmol), in dichloromethane and the resulting solution stirred for 2h. Reduction of the solvent volume and the addition of light petroleum afforded the title product (75) as a pale yellow solid which was recrystallisd from dichloromethane-diethyl ether (0.25g, 67%). (Found: C, 49.1; H, 3.47; N, 1.89. C₃₁H₂₅ClIrNO₂P₂.0.5CH₂Cl₂ requires C, 48.8; H, 3.38; N, 1.81%), m.p. 210-2°C.(decomp.).

 υ_{max} at 2020s ($\upsilon_{CO}),$ 1440s ($\upsilon_{PPh})$ and 1130s ($\upsilon_{P=O})$ cm^{-1} (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), δ 57.7 [d, P_X, ²J(P_AP_X) 47.6] and δ 76.8 p.p.m. [d, P_A, ²J(P_XP_A) 47.6].

Mass spectrum (FAB), [M]⁺733, [M-CO]⁺705, [M-C1]⁺698, [M-C1-CO]⁺670.

3.11.4 Preparation of cis-[Rh(COD){Ph2PN(R)P(O)Ph2}][PF6] complexes

(i) <u>**R=Ph (68)**</u>

Ph₂PN(Ph)P(O)Ph₂ (0.39g, 0.81 mmol) was added to a suspension containing [RhCl(COD)] (0.2g, 0.41 mmol) and KPF₆ (0.19g, 1.01 mmol) and the resulting mixture stirred for 2h. The suspension was filtered and the volume of solvent reduced and diethyl ether added to afford the product (68) as an orange microcrystalline solid which was dried *in vacuo* and recrystallised from dichloromethane-light petroleum (0.41g, 61%). (Found: C, 54.6; H, 4.44; N, 1.51; F, 12.3. $C_{38}H_{37}F_6NOP_3Rh$ requires C, 54.8; H, 4.48; N, 1.68; F, 13.6%), m.p. 171-3°C.

 v_{max} at 1440s (v_{PPh}), 1130s ($v_{P=O}$) and 840s (v_{PF}) cm⁻¹ (KBr).

N.m.r. (CDCl3): 1H (300.13 MHz), 82.07-2.20 [m, 4H, CH2, COD], 2.41-2.62 [m, 4H,

C<u>H</u>₂, COD], 3.20 [m, 2H, C<u>H</u>=CH, COD], 5.74 [m, 2H, C<u>H</u>=CH, COD] and δ 7.47-7.75 p.p.m. [m, 25H, Ph].

¹⁹F-{¹H} (282.41 MHz), δ -74.0 p.p.m. [d, PF₆, ¹J(PF) 712].

³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), δ -143.8 [s, PF₆, ¹J(PF) 712], 59.8 [d, P_X, ²J(P_AP_X) 55.2] and δ 99.0 p.p.m. [dd, P_A, ¹J(RhP_A) 161, ²J(P_XP_A) 55.1]; ²J(RhP_X) not observed. Mass spectrum (FAB), [M-PF₆]⁺ 688.

(ii) <u>R=C₆H₄OMe-4 (69)</u>

As above $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (0.41g, 0.82 mmol) was added to a suspension of $[RhCl(COD)]_2$ (0.2g, 0.41 mmol) and KPF₆ (0.19g, 1.01 mmol) in dichloromethane (20 cm³) and the mixture stirred for 2h. After filtration of the mixture, removal of the solvent and the addition of diethyl ether afforded the product (69) as an orange solid which was dried *in vacuo* (0.45g, 64%).

(Found: C, 53.8; H, 4.55; N, 1.73; F, 12.6. C₃₉H₃₉F₆NO₂P₃Rh requires C, 54.2; H, 4.55; N, 1.62; F, 13.2%), m.p. 235-°C(decomp.).

 υ_{max} at 1440s (υ_{PPh}), 1130s ($\upsilon_{P=O}$) and 845s (υ_{PF}) cm⁻¹ (KBr).

N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 2.07-2.20 [m, 4H, C<u>H</u>₂, COD], 2.43-2.60 [m, 4H, C<u>H</u>₂, COD], 3.20 [m, 2H, C<u>H</u>=CH, COD], 3.64 [s, 3H, OC<u>H</u>₃], 5.74 [m, 2H, C<u>H</u>=CH, COD], 5.98 [d, 2H, ³J(H_aH_b) 8.88], 6.37 [d, 2H, ³J(H_a'H_{b'}) 8.88] and δ 7.48-7.75 p.p.m. [m, 20H, Ph].

¹⁹F-{¹H} (282.41 MHz), δ -74.0 p.p.m. [d, PF₆, ¹J(PF) 712].

³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), δ -143.8 [s, PF₆, ¹J(PF) 712], 59.8 [d, P_X, ²J(P_AP_X) 58.4] and δ 99.0 p.p.m. [d, P_A, ¹J(RhP_A) 161, ²J(P_XP_A) 58.4]; ²J(RhP_X) not observed. Mass spectrum (FAB), [M-PF₆]⁺ 718.

3.11.5 Preparation of cis-[Rh(NBD){Ph₂PN(Ph)P(O)Ph₂}][PF₆] (71)

A dichloromethane solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.41g, 0.87 mmol) was added with stirring to a suspension of $[RhCl(NBD)]_2$ (0.2g, 0.43 mmol) and KPF_6 (0.2g, 1.1 mmol) and the mixture stirred for 2h. Filtration followed by removal of the solvent and the addition of diethyl ether afforded the product (71) as an orange microcrystalline solid which was recrystallised from dichloromethane-diethyl ether and dried *in vacuo* (0.63g, 88%).

(Found: C, 49.4; H, 3.96; N, 1.55; F, 10.3. C₃₇H₃₃F₆NOP₃Rh.1.5CH₂Cl₂ requires C, 48.9; H, 3.84; N, 1.48; F, 12.0%), m.p. 173-5°C(decomp.).

 v_{max} at 1440s (v_{PPh}), 1125s ($v_{P=O}$) and 850s (v_{PF}) cm⁻¹ (KBr).

N.m.r. ¹⁹F-{¹H} (282.41 MHz), δ -74.0 p.p.m. [d, ¹J)PF) 712].

³¹P-{¹H} CH₂Cl₂, 121.5 MHz), δ -144.6 [s, PF₆, ¹J(PF) 712], 56.6 [vd, P_X, ²J(P_AP_X) 51.3] and δ 99.9 p.p.m. [dd, P_A, ¹J(RhP_A) 183, ²J(P_XP_A) 51.3]; ²J(RhP_X) not observed. Mass spectrum (FAB), [M-PF₆]⁺ 672.

3.11.6 Preparation of [RhCl(Cp*){Ph2PN(Ph)P(O)Ph2}][PF6] (73)

 $Ph_2PN(Ph)P(O)Ph_2$ (0.31g, 0.65 mmol) was added to a suspension in dichloromethane (25 cm³) of [RhCl₄(Cp*)₂] (0.2g, 0.32 mmol) and KPF₆ (0.15g, 0.81 mmol) and the resulting mixture stirred for 2h. The suspension was filtered and the volume of solvent reduced before the addition of light petroleum afforded the title product as a bright orange solid which was dried *in vacuo* (0.35g, 61%).

(Found: C, 49.1; H, 4.03; N, 1.69; F, 12.8. $C_{40}H_{40}F_6NOP_3Rh.1.5CH_2Cl_2$ requires C, 48.8; H, 4.24; N, 1.37; F, 11.2%), m.p. 132-4°C(decomp.).

 v_{max} at 1440s (v_{PPh}), 1135s ($v_{P=O}$), 850 (v_{PF}) cm⁻¹. (KBr).

N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 1.48 [d, 15H, CH₃, ²J(RhH) 3.76], 5.30 [s, 2H, CH₂Cl₂] and 7.02-7.85 [m, 25H, Ph].

¹⁹F-{¹H} (282.41 MHz), δ -74.0 p.p.m. [d, PF₆, ¹J(PF) 712].

¹³C-{¹H} (75.47 MHz), δ 8.95 [s, <u>C</u>H₃], 100.4 [d, <u>C</u>₅Me₅, ¹J(RhC) 4.80] and δ 123.2-137.2 p.p.m. [m, Ph].

 $^{31}P-\{^{1}H\}$ (121.5 MHz), δ -144.6 [s, PF₆, $^{1}J(PF)$ 712], 54.4 [dd, $P_{X},~^{2}J(P_{A}P_{X})$ 42.5,

 2 J(RhP_X) 4.9] and 93.2 p.p.m. [dd, P_A, 1 J(RhP_A) 151.4, 2 J(P_XP_A) 42.5].

Mass spectrum (FAB), [M-PF₆]⁺ 750, [M-PF₆-Cl]⁺ 714.

3.11.7 Preparation of cis-[Mo(CO)₄{Ph₂PN(Ph)P(O)Ph₂}₂] (54)

A solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.51g, 1.06 mmol) in dichloromethane (15 cm³) was added to a suspension of $[Mo(CO)_4pip_2]$ (0.2g, 0.53 mmol) also in dichloromethane, and the reaction mixture heated to reflux for 2h. The resulting yellow solution was concentrated *in vacuo* to *ca*. 10 cm³ and the addition of methanol afforded the title product (54) as a bright yellow microcrystalline solid which was dried *in vacuo* (0.32g, 52%).

(Found: C, 56.6; H, 3.74; N, 1.19. C₆₄H₅₀MoN₂O₆P₄.3CH₂Cl₂ requires C, 56.8; H, 3.98; N, 0.99%), m.p. 190-2°C(decomp.).

 v_{max} at 2020s (v_{CO}), 1910s (v_{CO}), 1840s (v_{CO}), 1440s (v_{PPh}) and 1205s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 50.3 [d, P_X, ²J(P_AP_X) 66] and 102.5 p.p.m. [d, P_A, ²J(P_XP_A) 66].

3.11.8 Preparation of cis-[W(CO)₄(pip){Ph₂PN(Ph)P(O)Ph₂}] (55)

A solution of $Ph_2PN(Ph)P(O)Ph_2$ (0.21g, 0.45 mmol) in dichloromethane was added to a stirred suspension of $[W(CO)_4pip_2]$ (0.2g, 0.43 mmol) in dichloromethane (15 cm³) and the mixture heated to reflux for 2h before reduction of the solvent volume and the addition of diethyl ether afforded the product identified as (55) as a bright yellow microcrystalline solid which was dried *in vacuo* (0.24g, 65%).

(Found: C, 51.1; H, 3.19; N, 1.90. $C_{39}H_{36}N_2O_5P_2W.CH_2Cl_2$ requires C, 50.9; H, 4.05; N, 2.90%), m.p. 165-7°C.

 v_{max} at 2015s (v_{CO}), 1880s (v_{CO}), 1840s (v_{CO}), 1435m (v_{PPh}) and 1200s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r.³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 52.8 [d, P_X, ²J(P_AP_X) 63.5] and δ 96.6 p.p.m. [d, P_A, ²J(P_XP_A) 63.5].

3.11.9 Preparation of [RuCl(R){Ph2PN(R')P(O)Ph2}][C1] complexes

(i) <u>R=p-cym, R'=Ph (57)</u>

A suspension of $Ph_2PN(Ph)P(O)Ph_2$ (0.31g, 0.66 mmol) in ethanol (10 cm³) was added to a stirred solution of $[RuCl_2(p-cym)]_2$ (0.2g, 0.33 mmol) also in ethanol, and the red solution heated to reflux for 2h. After removal of the solvent, dichloromethane (5 cm³) was added to dissolve the red oily residue and the addition of diethyl ether afforded an orange-brown solid identified as the title product (57) which was dried *in vacuo* (0.31g, 61%).

(Found: C, 52.7; H, 5.09; N, 1.51. C₄₀H₃₉Cl₂NOP₂Ru.2CH₂Cl₂ requires C, 52.9; H, 4.55; N, 1.47%), m.p. 165-7°C(decomp.).

 v_{max} at 1440s (v_{PPh}) and 1140s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CDCl₃): ¹H(300.13 MHz), δ 1.28 [s, 6H, C(H)<u>Me</u>₂], 2.08 [s, 3H, C<u>H</u>₃], 2.77 [m, 1H, C(<u>H</u>)Me₂], 5.30 [s, 2H, CH₂Cl₂], 5.44 [s, 2H, *p*-cym(ring)], 5.63 [s, 2H, *p*-cym(ring)] and δ 6.84-7.79 p.p.m. [m, 25H, Ph].

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 59.2 [d, P_X, ²J(P_AP_X) 44] and δ 98.8 p.p.m. [d, P_A, ²J(P_XP_A) 44].

Mass spectrum (FAB), [M-Cl]⁺748.

(ii) <u>R=p-cym, R=C₆H₄OMe-4 (58)</u>

Similarly, a suspension of $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (0.33g, 0.67 mmol) in ethanol (10 cm³) was added to a stirred solution of $[RuCl_2(p-cym)]_2$ (0.2g, 0.33 mmol) also in ethanol, and the mixture heated to reflux for 2h. Work-up as above the afforded product identified as (58) as an orange microcrystalline solid which was dried *in vacuo* (0.33g, 60%).

(Found: C, 54.3; H, 5.09; N, 1.67. C₄₁H₄₁Cl₂NO₂P₂Ru.1.5CH₂Cl₂ requires C, 54.2; H, 4.71; N, 1.49%), m.p. 175-7°C(decomp.).

 v_{max} at 1440s (v_{PPh}) and 1130s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 1.27 [s, 6H, C(H)<u>Me</u>₂], 2.08 [s, 3H, C<u>H</u>₃], 2.77 [m, 1H, C(<u>H</u>)Me₂], 3.67 [s, 3H, OC<u>H</u>₃], 5.30 [s, 2H, C<u>H</u>₂Cl₂], 5.44 [s, 2H, *p*-cym(ring)], 5.61 [s, 2H, *p*-cym(ring)], 6.26 [d, 2H, ³J(H_aH_b) 8.1], 6.44 [d, 2H, ³J(H_a'H_b') 8.1] and δ

6.67-8.07 p.p.m. [m, 20H, Ph].

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 59.9 [d, P_X, ²J(P_AP_X) 51.3] and δ 97.6 p.p.m. [d, P_A, ²J(P_XP_A) 51.3].

Mass spectrum (FAB), [M-Cl]⁺ 778, [M-2Cl]⁺ 743.

(iii) <u>R=mes, R'=Ph (59)</u>

Similarly, a suspension of $Ph_2PN(Ph)P(O)Ph_2$ (0.33g, 0.68 mmol) in ethanol (10 cm³) was added to one of $[RuCl_2(mes)]_2$ (0.2g, 0.34 mmol) and the resulting mixture heated to reflux for 2h. Following work-up as above the title product was obtained as an orange-brown microcrystalline solid which was dried *in vacuo*, (0.31g, 59%).

(Found: C, 55.3; H, 5.12; N, 1.80. C₃₉H₃₇Cl₂NOP₂Ru.1.25CH₂Cl₂ requires C, 55.2; H, 4.55; N, 1.60%), m.p. 132-4°C.

 υ_{max} at 1440m ($\upsilon_{PPh})$ and 1130s ($\upsilon_{PPh})~cm^{-1}$ (KBr).

N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 2.13 [s, 9H, C<u>H</u>₃], 5.11 [s, 3H, C(<u>H</u>)(ring)], 5.30 [s, 2H, C<u>H</u>₂Cl₂] and 7.01-7.75 p.p.m. [m, 25H, Ph].

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 61.6 [d, P_X, ²J(P_AP_X) 44.3] and δ 103.3 p.p.m. [d, P_A, ²J(P_XP_A) 44.3].

Mass spectrum (FAB), [M-Cl]⁺ 734 and [M-2Cl]⁺ 699.

(iv) <u>R=mes, R'=C₆H₄OMe-4 (60)</u>

A suspension of $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (0.35g, 0.69 mmol) in ethanol was added to one of $[RuCl_2(mes)]_2$ (0.2g, 0.34 mmol) in ethanol, and the mixture heated to reflux for 2h. Work-up as above afforded the title complex (60) as an orange-brown solid which was dried *in vacuo*, (0.34g, 62%).

(Found: C, 54.4; H, 5.21; N, 1.65. C₄₀H₃₉Cl₂NO₂P₂Ru.1.25CH₂Cl₂ requires C, 54.6; H, 4.62; N, 1.54%), m.p. 165-7°C(decomp.).

 v_{max} at 1440s (v_{PPh}) and 1130s (v_{PPh}) cm⁻¹ (KBr).

N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 2.12 [s, 9H, C<u>H</u>₃], 3.69 [s, 3H, OC<u>H</u>₃], 5.09 [s, 3H, C(<u>H</u>)(ring)], 5.30 [s, 2H, C<u>H</u>₂Cl₂], 6.23 [d, 2H, ³J(H_a'H_b') 8.6], 6.46 [d, 2H, ³J(H_a'b') 8.6]

and 7.27-7.75 p.p.m. [m, 20H, Ph]. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 60.8 [d, P_X, ²J(P_AP_X) 48.8] and δ 103.2 p.p.m. [d, P_A, ²J(P_XP_A) 48.8]. Mass spectrum (FAB), [M-Cl]⁺ 764, [M-2Cl]⁺ 729.

3.11.10 Miscellaneous reactions of Ph₂PN(Ph)P(O)Ph₂ (2a)

(i) With [PdCl₂Bipy]

Reaction of (2a) with $[PdCl_2Bipy]$ in dichloromethane afforded a residue after removal of the solvent which exhibited numerous resonances in its ³¹P-{¹H} n.m.r. spectrum.

(ii) With [W(CO)₄pip₂] in benzene

A suspension which contained $[W(CO)_4pip_2]$ (0.2g, 0.43mmol) and (2a) (0.41g, 0.86 mmol) in benzene was heated to reflux for 3h affording a dirty yellow suspension. A ³¹P-{¹H} n.m.r. spectrum exhibited numerous resonances.

(iii) With [Mo(CO)4pip2] in benzene

In an attempt to chelate the ligand (2a) to the metal, a solution containing $[Mo(CO)_4pip_2]$ (0.1g, 0.26 mmol) and Ph₂PN(Ph)P(O)Ph₂ (0.13g, 0.26 mmol) in benzene was heated to reflux for 2h. A ³¹P-{¹H} n.m.r. spectrum on the reaction residue indicated that the only species present was *cis*-[Mo(CO)₄{Ph₂PN(Ph)P(O)Ph₂}₂] (54).

(iv) With [RuCl₂(p-cym)]₂ in benzene

A solution containing $[RuCl_2(p-cym)]_2$ (0.1g, 0.16 mmol) and (2a) (0.08g, 0.16 mmol) in benzene (25 cm³) was heated to reflux for 3h. A ³¹P-{¹H} n.m.r. spectrum was taken on the reaction residue.

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 60 [d, P_X] and δ 140 p.p.m. [d, P_A].

(v) With [IrCl(COD)]2

 $Ph_2PN(Ph)P(O)Ph_2$ (0.30g, 0.6 mmol) was added to a stirred suspension in dichloromethane of $[IrCl(COD)]_2$ (0.20g, 0.3 mmol) and KPF_6 (0.14g, 0.75 mmol) added before stirring the suspension for 2h. A ${}^{31}P-{}^{1}H$ n.m.r. was taken on the reaction residue which indicated the presence of two species.

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), Complex (79), δ 45.5 [d, P_X, ²J(P_AP_X) 39] and δ 70.6 p.p.m. [d, P_A, ²J(P_XP_A) 39]; Complex (78), δ 65.3 [d, P_X, ²J(P_AP_X) 51] and δ 87.2 p.p.m. [d, P_A, ²J(P_XP_A) 51].

Mass spectrum (FAB), [M-PF₆]⁺ 778.

(vi) With [PtCl2(COD)]

A solution in dichloromethane of $[PtCl_2(COD)]$ (0.1g, 0.27 mmol) and $Ph_2PN(Ph)P(O)Ph_2$ (0.26g, 0.54 mmol) was stirred for 2h before a ³¹P-{¹H} n.m.r. spectrum on the reaction residue indicated the presence of two species.

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), Complex (82), δ 28.6 p.p.m. [s, <u>P</u>(O)]; Complex (81), δ 67.8 p.p.m. [s, <u>PPh₂</u>, ¹J(PtP) 2974].

(vii) With CoCl₂ and NiCl₂

Stirring a suspension in acetonitrile of $Ph_2PN(Ph)P(O)Ph_2$ (2a) and the respective metal salt showed no reaction with a ³¹P-{¹H} n.m.r. spectrum in each case indicating only the presence of oxidised ligand (2a).

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<u>CHAPTER 4</u>

Reactions of The Bis(Diphenylphosphino)amine Monoxide Metal Complexes

4.1 Introduction

The most widely investigated reactions of planar rhodium(I) and iridium(I) complexes are those involving the oxidative addition of small molecules (A-B), resulting in the formation of octahedral compounds, Scheme 1. Such additions have been trans-[MX(CO)L₂] + A-B \longrightarrow [MX(CO)A(B)L₂]

M=Rh,Ir; X=halide; L,L₂=phosphine

Scheme 1

achieved with a wide range of substrates including halogens, organic halides, oxygen and hydrogen.

Many complexes $[MX_3(CO)L_2]$ have been synthesised by the oxidative addition of halogens X_2 to *trans*- $[MX(CO)L_2]$ and occur with both Rh(I) and Ir(I) complexes.¹⁵⁰⁻¹⁵³ The $[MX_3(CO)L_2]$ have octahedral geometry and various geometric isomers are theoretically possible.^{154,155} For addition of mixed halogens a greater range of isomers is possible and the stereochemistry of individual isomers have been assigned by interpretation of their n.m.r. and far i.r. spectra.¹⁵⁶

Other inorganic molecules may be oxidatively added to trans-[MX(CO)L₂] complexes including thionyl halides (X-SOX), carbon disulphide and certain oxidising metal salts (L_X'M'-Y). The oxidative addition of thionyl chloride to trans-[IrX(CO)L₂] gives Ir(III) complexes which contain the chlorosulpinyl moiety, Scheme 2.^{157,158} The



Scheme 2

S-Cl bond reacts with methanol to yield a methoxy-sulphinyl group.

The oxidative addition of silanes and boranes (R_2B -H) to metal centres have been found to proceed stereoselectively, under kinetic control, with one major preferred

diastereoisomer.159,160

Some substrates which possess mulitiple bonds add oxidatively to *trans*- $[MX(CO)L_2]$ complexes, and these reactions proceed with retention of the bond between the substrate fragments, thus yielding products containing a three-membered ring. Examples of this type of behaviour include the substrates CS_2^{161} and tetracyanoethylene.¹⁶² If the substrate adds with no rupture of the A-B linkage then A and B will have a *cis* configuration in the product, (84) but if the components of A-B separate upon reaction, the product can have *cis* (85-87) or *trans* (88) stereochemistry.



Generally, the final product will be the isomer (or mixture of isomers) which is most stable thermodynamically under the reaction conditions. Difficulty in assigning the stereochemistry of the initially formed product has prompted confusion of the mechanisms involved, and it is accepted that several mechanistic pathways are possible.¹⁶⁸

In several instances, coordination of a metal has been achieved by oxidative addition of HgX₂ (X=Cl, Br) with *trans*-[IrCl(CO)L₂]^{163,164} to yield products with distorted octahedral geometry by *trans* oxidative addition.

White *et al.* in a recent publication¹⁶⁵ provided evidence which indicated that rhodium(I) catalysed Kharasch reactions may proceed *via* oxidative addition of perhalocarbon to rhodium followed by stepwise transfer to a coordinated alkene. A

crystal structure of $[RhBrCl(CCl_3)(CO)(PMe_3)_2]$ was obtained as evidence for this mechanism.

Water soluble transition metal phosphine complexes have uses in catalysis and water soluble organometallic complexes in general are of great pharmacological importance for the removal of certain metals from the body,¹⁶⁹ and for the ease of recovery of metals after catalysis. One way of attempting to enhance water solubility of phosphine complexes is by incorporating biological water soluble ligands on the metal or as counter ions in a complex as these can confer the solubility required on the resulting metal species. Such uses have been found for methyl maltol (89) and ethyl maltol (90) which are natural products, and a neutral water soluble aluminium complex of (89) with neurological interest was synthesised in 1986.¹⁷⁰ The numbering systems of (89) and



(90) are indicated with reference to n.m.r. spectra assigned later. Both (89) and (90) possess a ketonic oxygen atom *ortho* to a hydroxy group albeit in a heteronuclear ring system, and this hydroxy group readily deprotonates thus allowing formation of complexes of the monoanion function as an O,O' chelate¹⁷¹ in an analogous manner to the monoanion of pentane-2,4-dione (acacH). An X-ray crystal structure of Al(malt)₃ showed that the rings retain planarity in the complex.

Much work has been carried out with the complex [Rhacac(COD)] (91) which, would be expected to be very similar to the complexes [Rh(Memal)(COD)] and [Rh(Etmal)(COD)] which are not known. The only previusly mentioned complex of maltol with rhodium is [Rh(malt)₃].¹⁷¹ Complex (91), has been a versatile starting material reacting with both monodentate phosphines and bidentate chelating phosphines with displacement of the 1,5-COD or the acac moieties to afford new rhodium complexes. Complex (91) was first mentioned in 1957 by Chatt and Venanzi¹⁴⁷ but later





in 1964¹⁷³ it was observed that (91) could also be synthesised by the displacement of both carbonyl groups from [Rhacac(CO)₂] (92) by the diene COD at room temperature. At the same time it was observed that (92) reacted immediately with triphenylphosphine and triphenylarsine with the replacement of one carbonyl group. Complex (91) reacted with CO and Ph₃P with the displacement of COD.¹⁷⁴ An improved method for the synthesis of [Rh(β -diketone)COD] complexes was reported in 1989 starting from [RhCl(COD)]₂, which greatly improved on yields from previous methods, Scheme 3.¹⁷⁵

$$[RhCl(COD)]_{2} + 2 \beta \text{-diketone} + KOH$$

$$\downarrow$$

$$\downarrow$$

$$2[Rh(\beta \text{-diketone})(COD)] + 2KCl + 2H_{2}O$$

Scheme 3

The close electronic and structural similarity of square-planar d⁸ *cis*-rhodium(I) complexes such as [RhCl(NH₃)COD] and [Rhacac(COD)] (91) to *cis*-platinum(II) complexes showing antitumour activity has led to the screening of several of these derivatives.¹⁷⁶ Complex (91) was found to inhibit the growth of lung carcinoma with the same level of activity as *cis*-dichlorodiamminoplatinum(II) but with only slight nephrotoxicity.

Various addition reactions of complexes (91) and (92) have been investigated. A publication by Kemmitt *et al.*¹⁷⁷ showed that hexafluorobut-2-yne reacted with the β -ketoenolate rhodium(I) complex (91) to give complexes in which the fluorocarbon added 1,4 to the rhodium(I) acetylacetonate ring. Much work has been carried out on the

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oxidative addition of methyl iodide to [Rhacac(CO)(Ph₃P)] with kinetic studies being used to attempt to determine the mechanism of such reactions.¹⁷⁸ A spectral investigation on the same reaction by another group of co-workers revealed that in the reaction mixture there were actually two methylcarbonyl complexes of rhodium(III) which were assigned to isomers of [RhacacI(Me)(CO)(Ph₃P)], as well as a third product of an acetyl complex presumed to be the dimer [RhacadI(Ph₃P)(MeCO)]₂.¹⁷⁹

This chapter covers the isolation of the methyl maltol complex (93) and ethyl maltol derivative (94) together with their addition reactions, with emphasis on their oxidative addition reactions. The reaction of (94) with the ligand $Ph_2PN(Ph)P(O)Ph_2$,



Chapter 2 has also been attempted to try to obtain a water soluble complex of these phosphine-phosphine oxide ligands. The oxidative addition reactions of cis-[RhCl(CO){Ph_2PN(Ph)P(O)Ph_2}] (66) and cis-[IrCl(CO){Ph_2PN(Ph)P(O)Ph_2}] (75), Chapter 3 have also been investigated along with miscellaneous reactions of metal complexes from Chapter 3.

4.2 Preparation of [Rh(R)(COD)] (R=Memal, Etmal) complexes

The complex [Rhacac(COD)] (91) has been extensively studied previously and a similar method to the synthesis of (91) by Potgeiter *et al.* has been employed to obtain (93) and (94) in good yields. Hence, the reaction of $[RhCl(COD)]_2$ with ethyl and methyl maltol respectively at low temperature in the presence of in diethyl ether afforded the products as pale yellow solids, Scheme 4. The ¹H n.m.r. spectra of complexes (93) and (94) exhibit two doublets at 6.4 and 7.6 p.p.m. respectively which are assigned to the olefinic protons of the maltol moieties, the shift to higher frequency from the free ligands themselves being indicative of complexation.¹⁷¹ The FAB mass spectra of the complexes

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exhibit the respective molecular ions.

4.3 Preparation of [Rh(R)(CO)(Ph₃P)] (R=Memalt, Etmalt) complexes

The complexes (95) and (96) were formed by the facile displacement of one CO ligand from the *bis*-carbonyl analogues of (93) and (94) in dichloromethane at room temperature by triphenylphosphine. The *bis*-carbonyl analogues were formed *in situ* by the passage of CO through solutions of (93) and (94). The products were isolated as orange solids in reasonable yields, Scheme 5. The products exhibit carbonyl stretching



Scheme 5

frequencies at 1980 cm⁻¹ in their i.r. spectra, typical of the complex [Rhacac(CO)(Ph₃P)]. The ¹³C-{¹H} n.m.r. spectra were recorded in order to observe the CO moiety of the complexes but these were not observed probably because the coupling which would be expected with the ¹⁰³Rh and ³¹P nuclei makes the peaks indiscernible from the

background noise. The ${}^{31}P-{}^{1}H$ n.m.r. spectra of the complexes (95) and (96) exhibit two sets of doublet resonances of different intensities at 47.8 and 49.7 p.p.m. respectively and with different values of ${}^{1}J(RhP)$ coupling constants. These observations have been attributed to the presence in the reaction mixtures of both of the possible geometric isomers of the products, Figure 1. One isomer has a ${}^{1}J(RhP)$ value of 181 Hz





and the other has a value of 165 Hz the isomers being present in a ratio of 6:1 but they were not separable and the complexes have been characterised as a mixture. The FAB mass spectra of the complexes exibit [M]⁺ and also [M-CO]⁺ as the highest observed fragments.

4.4 Reactions of [Rh(R)(CO)(Ph₃P)] (R=Etmal), (96) with MeI, TCNE, I₂ and Br₂ (i) With MeI

The oxidative addition of an organic halide, R-X to a metal substrate provides a convenient synthesis of alkyl (or aryl) complexes of rhodium(III) and Ir(III). Thus, the addition of MeI to a solution of (96) in dichloromethane afforded (98). Mechanistic



studies have shown that a kinetically controlled *trans* addition of the alkyl halide occurs, with nucleophilic attack by the metal by an $S_N 2$ mechanism.^{172,180} A polar transition



Scheme 6

29.8 p.p.m. with a ¹J(RhP) coupling constant of 122 Hz. The decrease in this coupling in conjunction with the shift to lower frequency from that of (96) is indicative of oxidative addition. The observed values are in good agreement with those of the related complex [RhacacI(Me)(CO)(Ph₃P)],¹⁷⁹ and confirm the assignment of the product although only one geometric isomer was observed in our study. The ¹H n.m.r. spectrum exhibited a doublet of doublets at 1.90 p.p.m. corresponding to the rhodium-coordinated methyl group with a ²J(RhH) coupling constant of 2.0 Hz and a ³J(PH) value of 3.6 Hz. The carbonyl region for complex (98) in its ¹³C-{¹H} n.m.r. spectrum exhibited a doublet of doublets with a ¹J(RhC) value of 60 Hz and a ²J(PC) value of 10 Hz, once again in agreement with the literature values.¹⁷⁹ The FAB mass spectrum of (98) showed [M-CO]⁺ and [M-I]⁺ at m/z 647 and 547 respectively.

(ii) With TCNE

Tetracyanoethylene forms a large number of stable adducts with many rhodium and iridium complexes.^{162,181} The treatment of complex (96) with a one molar equivalent of TCNE afforded complex (100). The spectroscopic data are consistent with





the formulation of the complex in which the metal has a formal oxidation state of (III).

The v_{CO} band is seen in the i.r. spectrum at 2080 cm⁻¹ which is significantly higher than that for complex (96) which has a v_{CO} at 1980 cm⁻¹. A value of v_{CN} was also seen at 2210 cm⁻¹. These values are in accord with the values observed for the complex [Rhacac(CO)(Ph₃P)(TCNE)].¹⁸³ The complex (100) was not soluble enough for ¹³C-{¹H} n.m.r. or for ¹H n.m.r. spectra, and a ³¹P-{¹H} n.m.r. spectrum was only obtained from the reaction solution before isolation of the reaction product. This exhibited a doublet at 26.2 p.p.m. with a ¹J(RhP) coupling constant of 124.5 Hz.

X-ray crystal structure studies have shown that the organic fragment adds sideways to the metal.¹⁸² On coordination, the C-C distances in the ligating alkene are lengthened. This behaviour along with the stabilising effect of the electronegative substituents is in accord with the back donation of electron density from the metal to the π^* orbitals on the ligand.

(iii) With X_2 (X=Br, I)

The addition of iodine and bromine to [Rhacac(CO)(Ph₃P)] has been shown to lead to the formation of octahedral complexes of rhodium(III). In a number of instances the reactions are accompanied by removal of the acac ligand from the coordination sphere or its extensive halogenation.¹⁸⁴ Another publication by the same group of co-workers investigated an approximate correlation of δ (¹³CO) chemical shifts with carbonyl group stretching frequencies, v_{CO} . On oxidative addition, the increase in the v_{CO} value reflects the diminished electron density on the central atom and the lower values of ¹J(RhP) are due to the reduced contribution of the rhodium 5s orbital in the Rh-CO bond.¹⁸⁵

Thus the addition of a molar equivalent of iodine to (96) in dichloromethane led to the isolation of (99) as a brown microcrystalline solid. The possibility of obtaining



(99)

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geometric isomers exists in the complex but the ³¹P-{¹H} n.m.r. spectrum exhibits only one doublet indicating the presence of one major isomer. The ¹H n.m.r. spectrum exhibited the expected doublets for the olefinic maltol protons H_5 and H_6 which indicated that the double bond had not been halogenated. The FAB mass spectrum also confirmed this, exhibiting [M]⁺ at m/z 787.

The analogous reaction of (96) with a molar equivalent of bromine however did not occur with simple oxidative addition. The FAB mass spectrum showed a molecular ion at m/z 771, which corresponded to hydrobromination of the olefinic bond of the ethyl maltol moity as well as simple *trans* oxidative addition to the metal centre. Such halogenation has been observed previously with related complexes.¹⁸⁴ A ¹H n.m.r. spectrum was not possible due to the almost total insolubility of the product (101) in all solvents. It was hoped to have been able to observe the loss of the resonances in the olefinic proton region for the maltol protons H₅ and H₆. The ³¹P-{¹H} n.m.r. spectrum



on the reaction solution containing (101) exhibits two doublets indicating the presence of two isomers, each with a slightly different ${}^{1}J(RhP)$ coupling constant.

4.5 Miscellaneous reactions of complex (96)

(i) With DMAD

The reaction of (96) with DMAD in dichloromethane showed no change as evidenced by a ${}^{31}P{}^{1}H$ n.m.r. spectrum on the reaction mixture after 2h.

(ii) With HgCl₂ and HgBr₂

The treatment of (96) with a molar equivalent of $HgCl_2$ or $HgBr_2$ respectively in acetone afforded residues which showed the presence of numerous signals in a ³¹P-{¹H}

n.m.r. spectrum.

(iii) With SO₂

After the passage of SO₂ through a dichloromethane solution of (96) for 2h a $^{31}P-{^{1}H}$ n.m.r. spectrum indicated the presence of unchanged starting material.

(iv) With HCl

Similarly, after the passage of HCl through a solution of (96) a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum indicated numerous resonances around 30 p.p.m.

(v) With SOCl₂

The addition of a molar equivalent of $SOCl_2$ to a solution of (96) in dichloromethane caused an immediate colour change from orange to blood-red. However a ³¹P-{¹H} n.m.r. spectrum showed a complex mixture of signals.

(vi) With Cl₂

The passage of Cl_2 through a solution of (96) in dichloromethane afforded a residue which showed a complex mixture of signals in the ³¹P-{¹H} n.m.r. spectrum.

4.6 Reaction of complex (94) with TCNE

The reaction of (94) with a molar equivalent of TCNE afforded complex (97) whose geometry can be tentatively predicted as shown in the absence of X-ray crystal structure data, the organic fragment known to undergo sideways addition to the metal centre.¹⁸² A band in the i.r. spectrum at 2220 cm⁻¹ was observed for v_{CN} , and in the FAB mass spectrum the molecular ion was observed at m/z 479. The 300.13 MHz ¹H n.m.r. spectrum contained four separate multiplets each of equal integration corresponding to the four olefinic protons of the COD moiety. This feature arises due to the highly unsymmetrical nature of the overall molecule, and the multiplicity arises due to coupling of these distinct protons to ¹⁰³Rh and the different ¹H nuclei.



4.7 Miscellaneous reactions of complex (94)

It has been observed previously^{173,174} that [Rhacac(CO)₂] (92) reacts with Ph₃P or Ph₃As with the displacement of one of the carbonyl groups by the incoming ligand, whereas the reaction with Ph₃Sb afforded the octahedral complex [Rhacac(CO)(Ph₃Sb)₃].¹⁷³ The reactions of (94) with the same ligands, and also with Ph₂PN(Ph)P(O)Ph₂ (2a), Chapter 2, were hence attempted.

(i) With Ph₃As

On passage of CO followed by the addition of Ph_3As to a dichloromethane solution of (94) the colour darkened but a FAB mass spectrum showed numerous peaks, and a ¹H n.m.r. spectrum indicated the loss of the ethyl maltol moiety from the metal.

(ii) With Ph₃Sb

Similarly the reaction with Ph_3Sb/CO also indicated the loss of ethyl maltol and numerous peaks in the FAB mass spectrum.

(iii) With Ph₂PN(Ph)P(O)Ph₂ (2a)

After the passage of CO through a solution of (94), a molar equivalent of (2a) was added, and darkening of colour observed. However, a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum on the reaction solution indicated the breakdown of the ligand.

4.8 <u>Reactions of cis-[RhCl(CO){Ph2PN(Ph)P(O)Ph2}]</u> (66) with TCNE, X2 (X=Cl,

Br, I) and SOCl₂

(i) With TCNE

The treatment of (66) with a molar equivalent of TCNE afforded the octahedral complex (105) which exhibited bands corresponding to v_{CO} at 2085 cm⁻¹ and v_{CN} at 2220 cm⁻¹ in accord with similar literature values.¹⁸³ The ³¹P-{¹H} n.m.r. spectrum of





(105) exhibited a doublet of doublets centred at 91.5 p.p.m., and a virtual doublet at 63.5 p.p.m. with the value of ${}^{2}J(RhP_{X})$ being too small to be observed. The FAB mass spectrum of the complex showed [M-TCNE]⁺ as the highest ion at m/z 643 as expected.

(ii) With SOCl₂

The oxidative addition of thionyl chloride to iridium(I) complexes is known to give octahedral iridium(III) complexes.^{157,158} Thus, the addition of $SOCl_2$ to a solution of (66) in dichloromethane afforded (106) as a pale yellow solid. In the i.r. spectrum of the



complex, in addition to the expected v_{CO} band at 2085 cm⁻¹ a band for $v_{S=O}$ was observed at 1100 cm⁻¹, characteristic of such complexes. The ³¹P-{¹H} n.m.r. data are shown in Table 1 for the purpose of comparison with the other oxidative addition products. In previous cases it has been shown that on refluxing in methanol the S-Cl

bond is converted to a methoxy-sulpinyl group.¹⁵⁷ This has not yet been attempted with (106) and constitutes future work. In the FAB mass spectrum of (106), the highest observed species is $[M-SOCL]^+$ at m/z 678.

(iii) With X2 (X=Cl, Br, I)

Rhodium and iridium complexes generally undergo facile oxidative addition reactions with the dihalogen to produce octahedral Rh(III) and Ir(III) complexes. Thus, (66) was reacted with chlorine to afford the products (102), with the probable major geometric isomer shown. In the case of the oxidative addition of chlorine, the ${}^{31}P{}-{}^{1}H$



(102); X=Cl

n.m.r. spectrum indicates the presence of only one geometric isomer, this being obviously the most thermodynamically favoured under the reaction conditions.¹⁶⁸ In the case of both the addition of bromine and that of iodine, more geometric isomers are theoretically possible due to the presence of two different halogen atoms in the product. In the product from the reaction with chlorine there are only three possible geometric isomers, Figure 2. The X-ray crystal structure of complex



Figure 2

cis-[RhCl(CO){Ph₂PN(C₆H₄OMe-4)P(O)Ph₂}] (67), Chapter 3, indicates the favoured geometry before oxidative addition to be that where Cl is in a *trans* position with respect

to the diphenylphosphino moiety and carbonyl *trans* to the phosphoryl moiety. It should be possible hence to assume that Isomer A would be the favoured one for complex (102).

When the oxidative addition of Br_2 and I_2 were carried out with (66) the ³¹P-{¹H} n.m.r. spectra indicated the presence of two different geometric isomers, each with slightly different chemical shift values and coupling constants. In the case of Br_2 and I_2 addition there are seven theoretically possible geometric isomers, Figure 3. In each case,



Figure 3 (X=Br,I)

the two observed isomers are present in an approximate 2:1 ratio. The FAB mass spectra of both products (103; X=Br and 104; X=I) exhibited [M-X]⁺ as the highest ions.

4.9 Reactions of cis-[IrCl(CO){Ph₂PN(Ph)P(O)Ph₂}] (75) with TCNE and I₂

(i) With TCNE

The treatment of (75) with a molar equivalent of TCNE afforded (107) which exhibited an infra-red band at 2060 cm⁻¹ corresponding to v_{CO} , and exhibited two doublets in the ³¹P-{¹H} n.m.r. spectrum. In contrast to the rhodium analogue (105) which exhibits an AMX spin system pattern due to coupling of the two distinct ³¹P

nuclei with ¹⁰³Rh (I= $\frac{1}{2}$), the iridium complex exhibits an AX spin spectrum, the central iridium atom being spin-inactive. In a ¹³C-{¹H} n.m.r. spectrum of (107) a doublet was observed corresponding to the carbonyl group with a ²J(PC) coupling constant of 9.3 Hz. An unresolved multiplet was observed between 112-116 p.p.m. for the carbon atoms of the cyano groups.

(ii) With I₂

The treatment of (75) with iodine in dichloromethane afforded (108) as an orange microcrystalline solid. Complex (108) was present as only one major geometric isomer



(108)

as shown by the ³¹P-{¹H} n.m.r. spectrum which exhibited two doublets. As for the



(107)

other similar complexes the FAB mass spectrum exhibited [M-Cl]⁺ as the highest ion at m/z 952.

4.10 Miscellaneous reactions of complex (66)

Numerous attempts were made to undertake reactions with various other molecules with the complexes (66) and (75).

(i) Thus the treatment of dichloromethane solutions of (66) with air, HCl gas, excess

Complex	δ(P)	δ(P=O)	$^{2}J(P_{A}P_{X})$	¹ J(RhP _A)	$^{2}J(RhP_{X})$
(102)	93.9	59.3	41.5	94.0	2.4
(103);Isomer A	96.1	59.1	41.3	95.0	
(103);Isomer B	94.0	60.0	41.5	95.3	
(104);Isomer A	89.7	59.9	46.4	95.3	
(105)	91.5	65.3	51.0	120.0	
(106)	74.2	51.3	34.2	128.2	
(107)	68.1	64.2	44.9		
(108)	61.1	58.4	29.3		—

$P_A=PPh_2$; $P_X=P(O)Ph_2$; δ /p.p.m.; J /Hz

³¹P-{¹H} n.m.r. data for complexes (102)-(108)

Complex	δ(Ρ)	¹ J(RhP)	
(95);Isomer A	47.8	165	
(95);Isomer B	49.7	181	
(96);Isomer A	48.4	167	
(96);Isomer B	50.4	183	
(98)	29.8	122	
(99)	30.5	105	
(100)	26.2	124.5	
(101);Isomer A	29.2	105	
(101);Isomer B	28.3	102	

<u>Table 1</u>

³¹P-{¹H} n.m.r. data for complexes (95)-(101)

Table 2

DMAD, tetraethylethylenetetracarboxylate, SO₂, CO, CS₂ and $H_2NC_6H_4Me$ -4 all resulted in only unreacted (66) as evidenced by ³¹P-{¹H} n.m.r. spectra of the reaction mixtures.

(ii) The addition of excess MeI to a solution of (66) in dichloromethane afforded an orange oil which exhibited numerous signals in its ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum.

(iii) The treatment of an acetone solution of (66) with HgX₂ (X=Cl, Br) afforded only

unreacted starting complex.

(iv) The addition of a two molar excess of Ph_3P or a molar equivalent of dppb to a dichloromethane solution of (66) caused the displacement of the ligand (2a) from the metal complex as shown by ³¹P-{¹H} n.m.r. spectra of the reaction mixture.

4.11 Miscellaneous reactions of cis-[PdCl₂{Ph₂PN(Ph)P(O)Ph₂}] (50)

(i) The reactions of complex (50) in dichloromethane solution with CO, HCl, HCl/MeOH, H₂NC₆H₄Me-4, ¹BuNC, AgOCOCH₃, MeCN, pyridine, dimethyl 1,3-acetonedicarboxylate/Ag₂O, Ph₃P (1 mole) and DMSO all showed the presence of only unreacted starting complex in the ³¹P-{¹H} n.m.r. spectra.

(ii) The reactions of complex (50) with Ph_3P (2 moles), dppp, dppe and 2,2'-dipyridyl in dichloromethane solution all caused the displacement of $Ph_2PN(Ph)P(O)Ph_2$ (2a) from the complex as evidenced by ³¹P-{¹H} n.m.r. spectra of the reaction mixtures.

(iii) The reaction of (50) in acetone with a two molar equivalent of KBr afforded the dibromide derivative (52) by comparison of FAB mass and ${}^{31}P{-}{}^{1}H$ n.m.r. spectra with those of the authentic sample, Chapter 3.

4.12 Miscellaneous reactions of cis-[Mo(CO)₄{Ph₂PN(Ph)P(O)Ph₂}] (54)

(i) The reaction of (54) in dichloromethane and methanol with HCl gas resulted in unchanged starting complex as evidenced by a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum.

(ii) It has been shown in the literature that uncoordinated phosphoryl groups can be coordinated to other metal centres with the formation of heterobimetallic complexes.⁶ Hence, complex (54) was reacted with molar equivalents of $[PdCl_2(COD)]$, $[PdCl_2(PhCN)_2]$ and $HgCl_2$ solutions in dichloromethane or acetone respectively, and ³¹P-{¹H} n.m.r. spectra taken on the reaction mixtures after several hours. In each case,

the coordination of the P=O groups to the other metal was confirmed by new sets of signals in the ³¹P-{¹H} spectra slightly to higher frequency than the starting material. In all cases however unchanged complex (54) was also present in a 2:1 ratio with the new products, and separation could not be achieved. Refluxing the reaction mixtures had no effect on the final ratio. The ³¹P-{¹H} n.m.r. data are summarised, Table 3.

Complex	δ(P)	δ(P=O)	$^{2}J(P_{A}P_{X})$
(54)	102.6	50.3	65.9
$(54)(P=O)_2 \rightarrow PdCl_2$	110.5	55.6	56.5
$(54)(P=O)_2 \rightarrow HgCl_2$	124.7	57.9	54.0

 $P_A=PPh_2$; $P_X=P(O)Ph_2$; $\delta/p.p.m.$; J/Hz

<u>Table 3</u>

(iii) The addition of an excess of BF₃.Et₂O to a CH_2Cl_2 solution of (54) showed unreacted starting material in a ³¹P-{¹H} n.m.r. spectrum.

4.13 Reaction of [RuCl(p-cym){Ph₂PN(Ph)P(O)Ph₂}][Cl] (58) with KPF₆

The reaction of (58) with KPF_6 in dichloromethane exchanged the chloride anion for the hexafluorophosphate anion as shown in a ³¹P-{¹H} n.m.r. spectrum of the product, (113).

4.14 Conclusion

Simple oxidative addition reactions of the Rh(I) and Ir(I) complexes occur readily to afford the corresponding octahedral Rh(III) and Ir(III) complexes. Reactions with certain reagents were unsucessful, and it is clear that these complexes do not undergo such reactions with all reagents perhaps due to a lack of electron density at the metal centre. Complexes which contain two phosphino groups attached to a metal have a more electron rich nucleophilic metal centre and can undergo oxidative addition reactions more readily. The phosphoryl moiety being more distant from the metal and more weakly bonded means that there is potentially less electron density at the metal, hence the lower reactivity. Further work constitutes further investigations of the reactions of these metal complexes isolated in Chapter 3.

4.15 Experimental

General experimental techniques were as described in Chapter 2. The ¹H n.m.r. spectra were recorded in [²H₁]-chloroform unless otherwise stated on a Bruker AM300 spectrometer operating at 300.13 MHz, or on a JEOL EM390 spectrometer at 90 MHz with SiMe₄ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field). The ¹³C-{¹H} n.m.r. spectra were recorded along with DEPT spectra in [²H₁] chloroform on a Bruker AM300 spectrometer operating at 75.47 MHz with SiMe₄ (0.0 p.p.m.) as internal reference. The compounds iodomethane, p-toluidine, potassium bromide, potassium hydroxide, triphenylphosphine, carbon disulphide, dimethylsulphoxide, pyridine and tetraethylethylenetetracarboxylate (Lancaster), iodine, thionyl chloride, bromine, dimethylacetylenedicarboxylate, methanol, mercury(II) bromide, mercury(II) chloride, tetracyanoethylene, 2,2'-dipyridyl, triphenylarsine, triphenylantimony, 3-hydroxy-2-methyl-4-pyrone, 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane (Aldrich), 3-hydroxy-2-ethyl-4-pyrone (Pfizer), hydrogen chloride (Argo International), carbon monoxide (B.O.C.), sulphur dioxide (B.D.H.) and chlorine (B.O.C.) were all used as supplied by commercial sources.

4.15.1 Preparation of [Rh(R)(COD)] complexes

(i) <u>R=Memalt (93)</u>

Methyl maltol (0.21g, 1.7 mmol) was added to a solution of $[RhCl(COD)]_2$ (0.4g, 0.82 mmol) in diethyl ether (10 cm³) and this solution cooled to -80°C. A solution of KOH (0.28g, 5 mmol) in H₂O (2 cm³) was added dropwise and the resulting mixture warmed to room temperature and stirred for 0.25h before the addition of diethyl ether (10 cm³). The product separated as a bright yellow solid which was removed by filtration, dissolved in dichloromethane, and the organic layer dried over anhydrous magnesium sulphate. After filtration to remove the drying agent, the filtrate was evaporated to dryness *in vacuo* to afford the product as a yellow microcrystalline solid (0.34g, 62%).

(Found: C, 47.9; H, 4.95. C₁₄H₁₇O₃Rh.0.25CH₂Cl₂ requires C, 47.9: H, 4.94%), m.p. 140-2°C.

N.m.r. (CDCl₃): ¹H (90 MHz), δ 1.4-1.8 [m, 8H, CH₂(COD)], 2.4 [s, 3H, Me], 4.2 [m, 4H, (<u>H</u>)C=C (COD)], 5.3 [s, 2H, CH₂Cl₂], 6.4 [d, 1H, H₅, ³J(H₆H₅) 4.5], and δ 7.6 p.p.m. [d, 1H, H₆, ³J(H₅H₆) 4.5].

Mass spectrum (FAB), [M]⁺ 336.

(ii) <u>R=Etmalt (94)</u>

Similarly, ethyl maltol (0.23g, 1.6 mmol) was added to a solution of $[RhCl(COD)]_2$ (0.4g, 0.82 mmol) in diethyl ether (10 cm³) and the resulting solution cooled to -80°C. After the addition of a solution of KOH (0.28g, 5 mmol) in H₂O (5 cm³) dropwise, the mixture was warmed with stirring to room temperature and further diethyl ether added (10 cm³). After an analogous work-up procedure the title product was obtained as a yellow microcrystalline solid (0.35g, 63%).

(Found: C, 51.6; H, 5.45. $C_{15}H_{19}O_3Rh$ requires C, 51.4; H, 5.47%), m.p. 152-4°C. N.m.r. (CDCl₃): ¹H (90 MHz), δ 1.2 [t, 3H, C<u>H</u>₃], 1.5-2.5 [m, 8H, C<u>H</u>₂ (COD)], 2.8 [q, 2H, C<u>H</u>₂], 4.2 [m, 4H, (<u>H</u>)C=C (COD)], 6.5 [d, 1H, H₅, ³J(H₆H₅) 4.5], and δ 7.7 p.p.m. [d, 1H, H₆, ³J(H₅H₆) 4.5].

Mass spectrum (FAB), [M]⁺ 350.

4.15.2 Preparation of [Rh(R)(CO)(Ph₃P)] complexes

(i) <u>R=Memalt (95)</u>

After the passage of a slow stream of CO through a solution of [Rh(Memalt)(COD)] (93) (0.2g, 0.59 mmol) in dichloromethane (20 cm³) for 0.25h, triphenylphosphine (0.16g, 0.6 mmol) was added with stirring whereupon the solution immediately darkened to orange, and effervescence was observed. After further stirring for 2h the volume of the solvent was reduced *in vacuo*, and light petroleum added slowly. The orange microcrystalline solid identified as (95) was removed by filtration, and recrystallised from dichloromethane-light petroleum (0.21g, 69%).

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(Found: C, 52.8; H, 3.88. C₂₅H₂₀O₄PRh.CH₂Cl₂ requires C, 52.1; H, 3.68%), m.p. 182-4°C.

 υ_{max} at 1975s ($\upsilon_{CO})$ and 1460s ($\upsilon_{PPh})~cm^{-1}$ (KBr).

N.m.r. (CDCl₃): ¹H (90 MHz), δ 2.2 [s, 3H, Me], 5.3 [s, 2H, CH₂Cl₂], 6.6 [d, 1H, H₅,

 $^3J(H_6H_5)$ 5] and δ 7.2-7.9 p.p.m. [m, 16H, Ph+H_6].

³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), Isomer A, δ 47.8 p.p.m. [d, PPh₃, ¹J(RhP) 165]; Isomer B, δ 49.7 p.p.m. [d, PPh₃, ¹J(RhP) 181].

Mass spectrum (FAB), [M]⁺ 518, [M-CO]⁺ 490.

(ii) <u>R=Etmalt (96)</u>

Similarly, triphenylphosphine (0.15g, 0.57 mmol) was added with stirring to a CO treated dichloromethane solution of [Rh(Etmalt)(COD)] (94) (0.2g, 0.57 mmol) and the resulting orange solution stirred for a further 2h. An analogous work-up afforded the product identified as (94) as an orange solid which was removed by filtration, and dried *in vacuo* (0.2g, 66%).

(Found: C, 53.0; H, 3.96. C₂₆H₂₂O₄PRh.CH₂Cl₂ requires C, 52.9; H, 3.92%), m.p. 183-5°C.

 υ_{max} at 1980s ($\upsilon_{CO})$ and 1460s ($\upsilon_{PPh})$ cm^{-1} (KBr).

N.m.r. (CDCl₃): ¹H (300 MHz), Isomer A, δ 1.05 [t, 3H, Me, ³J(HH) 7.5], 2.55 [q, 2H, C<u>H</u>₂, ³J(HH) 7.5], 5.3 [s, 2H, CH₂Cl₂], 6.35 [d, 1H, H₅, ³J(H₆H₅) 5] and δ 7.3-7.8 p.p.m. [m, 16H, Ph+H₆]; Isomer B, δ 1.25 [t, 3H, Me, ³J(HH) 7.5], 3.05 [q, 2H, C<u>H</u>₂, ³J(HH) 7.5], 6.65 [d, 1H, H₅, ³J(H₆H₅) 5] and δ 7.3-7.8 p.p.m. [m, 16H, Ph+H₆].

³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), Isomer A, δ 48.4 p.p.m. [d, PPh₃, ¹J(RhP) 167]; Isomer B, δ 50.4 p.p.m. [d, PPh₃, ¹J(RhP) 183].

Mass spectrum FAB), [M]⁺ 532, [M-CO]⁺ 504.

4.15.3 Reaction of complex (94)

(i) With TCNE

Tetracyanoethylene (0.07g, 0.6 mmol) was added to a stirred solution of

[Rh(Etmal)(COD)] (94) (0.2g, 0.6 mmol) at room temperature whereupon the resulting solution had darkened to brown-yellow. After stirring for a further 2h, the solvent volume was reduced *in vacuo*, and light petroleum added to afford the product as a dark brown microcrystalline solid which was recrystallised from dichloromethane-light petroleum, dried *in vacuo* and identified as (97), [Rh(Etmal)(TCNE)(COD)], (0.2g, 75%).

(Found: C, 51.9; H, 3.79; N, 11.5. $C_{21}H_{19}N_4O_3Rh$ requires C, 52.6; H, 4.0; N, 11.7%), m.p. 180-2°C.

 υ_{max} at 2220s (υ_{CN}), 1600s (υ_{C-O}) and 1540s (υ_{ring}) cm^{-1} (KBr).

N.m.r. (CDCl₃): ¹H (300 MHz), δ 1.15 [t, 3H, Me, ³J(HH) 7.6], 1.7-2.5 [m, 8H, C<u>H</u>₂ (COD)], 2.80 [q, 2H, C<u>H</u>₂CH₃, ³J(HH) 7.6], 4.20 [m, 1H, COD], 4.70 [m, 1H, COD], 5.50 [m, 1H, COD], 5.70 [m, 1H, COD], 6.40 [d, 1H, H₅, ³J(H₆H₅) 5.6] and δ 7.75 p.p.m. [d, 1H, H₆, ³J(H₅H₆) 5.6].

Mass spectrum (FAB), [M]⁺ 479, [M-TCNE]⁺ 350.

4.15.4 Reactions of complex (96)

(i) With MeI

An excess of MeI (0.08g, 0.56 mmol, 0.04 cm³) was added to a stirred solution of (96) (0.2g, 0.38 mmol) in dichloromethane (20 cm³). The colour of the solution changed from orange to yellow-brown and was stirred for 2h. The solvent was removed *in vacuo* and the oily residue washed with light petroleum to afford the product which was recrystallised from dichloromethane-diethyl ether, and the yellow-orange microcrystalline solid identified as [Rh(Etmalt)(Me)I(CO)PPh₃] (98), (0.20g, 77%). (Found: C, 41.3; H, 2.98. $C_{27}H_{25}IO_4PRh.2CH_2Cl_2$ requires C, 41.3; H, 3.46%), m.p. 155-7°C.

 u_{max} at 2060vs (u_{CO}), 1600s ($u_{C.-O}$), 1550m (u_{ring}) and 1460s (u_{PPh}) cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (300 MHz), δ 1.15 [t, 3H, CH₂CH₃, ³J(HH) 7.5], 1.90 [dd, 3H, ²J(RhH) 2.0, ³J(PH) 3.6], 2.70 [q, 2H, CH₂CH₃, ³J(HH) 7.5], 5.30 [s, 2H, CH₂Cl₂], 6.15 [d, 1H, H₅, ³J(H₆H₅) 5] and δ 7.3-7.9 p.p.m. [m, 16H, Ph+H₆]. ¹³C-{¹H} (75.47 MHz), δ 1.0 [dd, CH₃, ¹J(RhC) 18.6, ²J(PC) 3.4] and δ 184.7 p.p.m. [dd, CO, ¹J(RhC) 60, ²J(PC) 10].
³¹P-{¹H} (24 MHz), δ 29.8 p.p.m. [d, ¹J(RhP) 122].
Mass spectrum (FAB), [M-CO]⁺ 647 and [M-I]⁺ 547.

(ii) With I_2

A stoichiometric amount of iodine (0.1g, 0.39 mmol) was added to a stirred solution of (96) (0.2g, 0.38 mmol) in dichloromethane (25 cm³), and the resulting dark brown solution stirred for 2h. Removal of the solvent and addition of light petroleum afforded the product as a dark brown microcrystalline solid which was dried *in vacuo*, and identified as [Rh(Etmal)I₂(CO)PPh₃] (99), (0.22g, 75%).

(Found: C, 33.2; H, 2.53. C₂₆H₂₂I₂O₄PRh.CHCl₃ requires C, 32.8; H, 2.36%), m.p. 170-2°C.

υ_{max} at 2090vs (υ_{CO}), 1590s (υ_{C-O}), 1545s (υ_{ring}) and 1460m (υ_{PPh}) cm ⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (300.13 MHz), δ 1.40 [t, 3H, Me, ³J(HH) 7.5], 2.95 [q, 2H, C<u>H</u>₂CH₃, ³J(HH) 7.5], 6.75 [d, 1H, H₅, ³J(H₆H₅) 5], 7.25 [s, 1H, CHCl₃], 7.36-7.50 [m, 10H, Ph], 7.75 [d, 1H, H₆, ³J(H₅H₆) 5] and δ 8.04-8.31 p.p.m. [m, 5H, Ph]. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 30.5 p.p.m. [d, ¹J(RhP) 105]. Mass spectrum (FAB) [M]⁺787, [M-CO]⁺759 and [M-I]⁺ 659.

(iii) With TCNE

On addition of TCNE (0.05g, 0.37 mmol) to a stirred solution of (96) (0.2g, 0.37 mmol) in dichloromethane (20 cm³) a colour change from orange to yellow-green was observed. The solution was stirred for 3h, and after work-up as above, the product identified as [Rh(Etmal)(TCNE)(CO)PPh₃] (100) was obtained as a bright yellow-green microcrystalline solid (0.21g, 83%).

(Found: C, 53.0; H, 3.29; N, 7.88. C₃₂H₂₂N₄O₄PRh.CH₂Cl₂ requires C, 53.2; H, 3.25; N, 7.52%), m.p. 230-2°C.

 v_{max} at 2210s (v_{CN}), 2080vs (v_{CO}), 1590s (v_{C-O}), 1545m (v_{ring}) and 1465m (v_{PPh}) cm⁻¹

(KBr).

N.m.r.: ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 26.2 p.p.m. [d, ¹J(RhP) 124.5]. Complex too insoluble for ¹H and ¹³C-{¹H} n.m.r. spectra. Mass spectrum (FAB), [M-TCNE-CO]⁺ 504.

(iv) With Br₂

A slight excess of bromine $(0.08g, 0.026 \text{ cm}^3, 0.40 \text{ mmol})$ was added to a solution of (96) (0.2g, 0.38 mmol) in dichloromethane (20 cm³) with stirring. The colour immediately darkened to a blood-red colour and slight fuming was observed. The solution was stirred under a nitrogen atmosphere for 3h, during which time, after 0.25h a dark-red insoluble solid had precipitated from the reaction solution. This solid was removed by filtration and found to be insoluble in all solvents, and was dried *in vacuo* and identified as (101) (0.21g, 80%). Due to the insolubility, a ³¹P-{¹H} n.m.r. spectrum was only possible on the filtrate from the reaction mixture.

(Found: C, 33.3; H, 2.40. C₂₆H₂₃Br₃O₄PRh.2CHCl₃ requires C, 33.2; H, 2.49%), m.p. 150-2°C.

 v_{max} at 2090vs (v_{CO}), 1610s (v_{C-O}), 1470m (v_{PPh}) cm⁻¹ (KBr).

N.m.r.: ³¹P-{¹H} (36.2 MHz), Isomer A, δ 29.2 p.p.m. [d, PPh₃, ¹J(RhP) 105]; Isomer B, δ 28.3 p.p.m. [d, PPh₃, ¹J(RhP) 102]

Mass spectrum (FAB), [M]⁺ 771, [M-Br]⁺ 691, [M-2Br]⁺ 611.

4.15.5 Reactions of cis-[RhCl(CO){Ph2PN(Ph)P(O)Ph2}] (66)

(i) With Cl₂

Complex (66) (0.2g, 0.31 mmol) was dissolved in dichloromethane (20 cm³) and a slow stream of chlorine passed through the solution. The solution lightened in colour gradually to a pale yellow-green colour, and was stirred further for 2h under a nitrogen atmosphere. The volume of the solution was then concentrated and light petroleum added to afford an orange microcrystalline solid identified as $[RhCl_3(CO){Ph_2PN(Ph)P(O)Ph_2}]$ (102), (0.14g, 65%).
(Found: C, 48.0; H, 3.63; N, 1.96. C₃₁H₂₅Cl₃NO₂P₂Rh requires C, 48.1; H, 3.40; N, 1.75%), m.p. 280-2°C.

 v_{max} at 2090vs (v_{CO}), 1440s (v_{PPh}), 1140s and 1125s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), δ 59.3 [vd, P_X, ²J(P_AP_X) 41.5, ²J(RhP_X) 2.4], and δ 93.9 p.p.m. [dd, P_A, ¹J(RhP_A) 94, ²J(P_XP_A) 41.5].

Mass spectrum (FAB), [M-Cl]⁺ 674, [M-Cl-CO]⁺ 650, [M-Cl-CO-Cl]⁺ 615, and [M-Cl₃-CO] 580.

(ii) With Br₂

Similarly, the addition of bromine $(0.05g, 0.02 \text{ cm}^3, 0.31 \text{ mmol})$ to a solution of (66) (0.2g, 0.31 mmol) in dichloromethane (20 cm³) resulted in the formation of a dark red solution which was stirred for 2h. Concentration and the addition of light petroleum afforded a dark orange solid which was collected by filtration, recrystallised from chloroform-light petroleum and dried *in vacuo*. This solid was identified as [RhClBr₂(CO){Ph₂PN(Ph)P(O)Ph₂}] (103) (0.25g, 90%).

(Found: C, 37.8; H, 3.16; N, 1.75. C₃₁H₂₅Br₂ClNO₂P₂Rh.2CHCl₃ requires C, 38.0; H, 2.71; N, 1.35%), m.p. 205-7°C.

 v_{max} at 2090vs (v_{CO}), 1430s (v_{PPh}), 1140s ($v_{P=O}$), 1125s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CH₂Cl₂: ³¹P-{¹H} (36.2 MHz), Isomer A, δ 59.1 [vd, P_X, ²J(P_AP_X) 41.3], and δ 96.1 p.p.m. [dd, P_A, ¹J(RhP_A) 95, ²J(P_XP_A) 41.3]; Isomer B, δ 60.0 [vd, P_X, ²J(P_AP_X) 41.5], and δ 94.0 p.p.m. [dd, P_A, ¹J(RhP_A) 95.3, ²J(P_XP_A) 41.5].

Mass spectrum (FAB), [M-Cl]⁺ 768, [M-Cl-CO]⁺ 740, [M-Br]⁺ 724, [M-Br-CO]⁺ 696, and [M-Br-Cl-CO]⁺ 661.

(iii) With I2

Analogously, the addition of iodine (0.079g, 0.31 mmol) to a dichloromethane solution of (66) (0.2g, 0.31 mmol) followed by stirring for 2h and a work-up as above afforded a dark brown microcrystalline solid identified as $[RhCII_2(CO){Ph_2PN(Ph)P(O)Ph_2}]$ (104) which was dried *in vacuo*, (0.22g, 78%). (Found: C, 39.0; H, 2.74; N, 1.43. C₃₁H₂₅ClI₂NO₂P₂Rh.CH₂Cl₂ requires C, 39.1; H, 2.77; N, 1.43%), m.p. 217-9°C.

 v_{max} at 2095vs (v_{CO}), 1440s (v_{PPh}), 1140s ($v_{P=O}$), and 1120s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), Isomer A, δ 59.9 [vd, P_X, ²J(P_AP_X) 46.4], and δ 89.7 p.p.m. [dd, P_A, ¹J(RhP_A) 95.3, ²J(P_XP_A) 46.4]; Isomer B, δ 59.1 p.p.m. [vd, P_X, ²J(P_AP_X) 48.8]. Higher frequency resonance not discernable from those of Isomer A due to close spacing.

Mass spectrum (FAB), [M-Cl]⁺ 862, [M-Cl-CO]⁺ 834, [M-I-CO]⁺ 742, [M-I-Cl-CO]⁺ 707.

(iv) With TCNE

TCNE (0.04g, 0.31 mmol) was added to an orange solution of (66) (0.2g, 0.31 mmol) in dichloromethane (25 cm³) with stirring, whereupon the colour changed to yellow-brown. Further stirring for 3h, and work-up as previously afforded a bright yellow microcrystalline solid which was dried *in vacuo* and identified as $[RhCl{C_2(CN)_4}(CO){Ph_2PN(Ph)P(O)Ph_2}]$ (105) (0.21g, 88%).

(Found: C, 57.4; H, 3.23; N, 9.08. C₃₇H₂₅ClN₅O₂P₂Rh requires C, 57.6; H, 3.26; N, 9.07%), m.p. 225-7°C (decomp.).

 v_{max} at 2220m (v_{CN}), 2085vs (v_{CO}), 1440m (v_{PPh}), 1130s ($v_{P=O}$), and 1100s ($v_{P=O}$) cm⁻¹ (KBr).

N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), δ 65.3 [vd, P_X, ²J(P_AP_X) 51], and δ 91.5 p.p.m. [dd, P_A, ¹J(RhP_A) 120, ²J(P_XP_A) 51].

Mass spectrum (FAB), [M-TCNE]⁺ 643, [M-TCNE-Cl]⁺ 608, [M-TCNE-Cl-CO]⁺ 580.

(v) With SOCl₂

Thionyl chloride (0.06g, 0.03 cm³, 0.47 mmol) was added to a solution of (66) (0.2g, 0.31 mmol) in dichloromethane (20 cm³), and the resulting yellow-orange solution stirred for 1h. After removal of the solvent *in vacuo* the residue was washed with light petroleum and recrystallised from dichloromethane-diethyl ether to afford the complex

[RhCl(SOCl)(Cl)(CO){Ph₂PN(Ph)P(O)Ph₂}] (106) as a pale yellow microcrystalline solid (0.21g, 87%).

(Found: C, 46.8; H, 3.60; N, 1.82. C₃₁H₂₅Cl₃NO₃P₂SRh.0.5 CH₂Cl₂ requires C, 47.0; H, 3.25; N, 1.74%), m.p. 205-7°C (decomp.).

 v_{max} at 2085vs (v_{CO}), 1440s (v_{PPh}), 1140s ($v_{P=O}$), 1120s ($v_{P=O}$), and 1100s ($v_{S=O}$) cm⁻¹ (KBr).

N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), δ 51.3 [vd, P_X, ²J(P_AP_X) 34.2], and δ 74.2 p.p.m. [dd, P_A, ¹J(RhP_A) 128.2, ²J(P_XP_A) 34.2].

Mass spectrum (FAB), [M-SOCl]⁺ 678, [M-SOCl-CO]⁺ 650, [M-SOCl-CO-Cl] 615, [M-SOCl-CO-Cl₂]⁺ 580.

4.15.6 Reactions of [IrCl(CO){Ph2PN(Ph)P(O)Ph2}] (75)

(i) With TCNE

TCNE (0.035g, 0.27 mmol) was added to a pale yellow solution of (75) (0.2g, 0.27 mmol) in dichloromethane (20 cm³). The resulting orange/brown solution was stirred for 2h before work-up as above to afford the product identified as $[IrCl{C_2(CN)_4}(CO){Ph_2PN(Ph)P(O)Ph_2}]$ (107) as a yellow-green microcrystalline solid which was dried *in vacuo*, (0.18g, 75%).

(Found: C, 45.6; H, 2.98; N, 6.65. $C_{37}H_{25}ClN_5O_2P_2lr.2CH_2Cl_2$ requires C, 45.5; H, 2.84; N, 6.79%), m.p. 140-2°C (decomp.).

 υ_{max} at 2215s (υ_{CN}), 2060vs (υ_{CO}), 1440s (υ_{PPh}), 1080s (υ_{PO}), 1050s (υ_{PO}) cm⁻¹ (KBr). N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), δ 64.2 [d, P_X, ²J(P_AP_X) 44.9], and δ 68.1 p.p.m. [d, P_A, ²J(P_XP_A) 44.9]

¹³C-{¹H} (CDCl₃), δ 112-116 [m, <u>C</u>N], and δ 151.5 p.p.m. [d, CO, ²J(PC) 9.3]. Mass spectrum (FAB), [M-TCNE]⁺ 733, [M-TCNE-Cl]⁺ 698, [M-TCNE-Cl-CO]⁺ 668.

(ii) With I₂

Iodine (0.07g, 0.27 mmol) was added to a stirred orange solution of (75) (0.2g, 0.27 mmol) in dichloromethane (25 cm³), and the resulting dark orange-brown solution

stirred for a further 2h. Removal of the solvent *in vacuo* and the addition of light petroleum afforded an orange microcrystalline solid identified as $[IrCII_2(CO){Ph_2PN(Ph)P(O)Ph_2}]$ (108, (0.22g, 81%).

(Found: C, 35.0; H, 2.75; N, 1.37. C₃₁H₂₅Cll₂NO₂P₂Ir.1.5 CH₂Cl₂ requires C, 35.0; H, 2.53; N, 1.26%), m.p. 158-60°C (decomp.).

υ_{max} at 2080vs (υ_{CO}), 1460s (υ_{PPh}), 1145s (υ_{PO}), 1130s (υ_{PO}) cm⁻¹ (KBr).

N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), δ 58.4 [d, P_X, ²J(P_AP_X) 29.3], and δ 61.1 p.p.m. [d, P_A, ²J(P_XP_A) 29.3].

Mass spectrum (FAB), [M-Cl]⁺ 952, [M-I]⁺ 860, [M-Cl-I]⁺ 824, [M-Cl-I-CO]⁺ 797, [M-Cl-2I-CO]⁺ 668.

4.15.7 Miscellaneous reactions of complex (66)

(i) With MeI

The addition of excess MeI to a solution of (66) (0.2g, 0.31 mmol) in dichloromethane afforded after stirring for 3h, an orange oil which exhibited numerous signals in its ${}^{31}P$ -{ ${}^{1}H$ } n.m.r. spectrum.

(ii) With air

Similarly, stirring a solution of (66) (0.2g, 0.31 mmol) in dichloromethane-diethyl ether for several days in air afforded only unreacted starting material as shown by a $^{31}P-\{^{1}H\}$ n.m.r. spectrum.

(iii) With HCl gas

Treatment of (66) (0.2g, 0.31 mmol) in dichloromethane with a slow stream of HCl gas for 1h resulted in only unreacted starting material.

(iv) With HgCl₂ and HgBr₂

The addition of HgX₂ (X=Cl, Br) respectively to a solution of (66) (0.2g, 0.31 mmol) in acetone afforded only unreacted starting material as shown by a ${}^{31}P{}{}^{1}H{}$

n.m.r. spectrum.

(v) With DMAD

The addition of an excess of DMAD to a solution of (66) (0.1g, 0.16 mmol) in dichloromethane showed a slight colour change on stirring for 2h but a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum indicated only the presence of unreacted (66).

(vi) With tetraethylethylene tetracarboxylate

Similarly, the addition of a stoichiometric amount of tetraethylethylene tetracarboxylate to a solution of (66) (0.2g, 0.31 mmol) in dichloromethane afforded only unreacted starting complex.

(vii) With SO2

Treatment of a solution of (66) (0.2g, 0.31 mmol) with a slow stream of SO₂ for 1h caused a gradual lightening in colour of the reaction solution but a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum indicated the presence of unreacted starting complex.

(viii) With CO

Similarly, treatment of (66) (0.2g, 0.31 mmol) solution with a steady stream of CO for 2h caused no change in the ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum.

(ix) With CS₂

The addition of excess CS_2 to a solution of (66) (0.2g, 0.31 mmol) in dichloromethane caused a distinct colour change from pale yellow to dark orange but a ³¹P-{¹H} n.m.r. spectrum indicated the presence of unreacted (66).

(x) With p-toluidine

The addition of a stoichiometric amount of p-toluidine to a dichloromethane solution of (66) (0.2g, 0.31 mmol) afforded only unreacted (66).

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(xi) With Ph₃P

Treatment of (66) (0.2g, 0.31 mmol) with a two molar excesss of Ph_3P in dichloromethane indicated displacement of the ligand $Ph_2PN(Ph)P(O)Ph_2$ (2a) in a ³¹P-{¹H} n.m.r. spectrum.

(xii) With dppb

Similarly, the addition of a stoichiometric amount of dppb to a solution of (66) (0.2g, 0.31 mmol) in dichloromethane indicated the displacement of the ligand $Ph_2PN(Ph)P(O)Ph_2$ (2a).

4.15.8 Miscellaneous reactions of complex (50)

(i) With Ph₃P (1 mole)

Addition of a molar equivalent of Ph_3P to a solution of (50) (0.1g, 0.15 mmol) in dichloromethane, and stirring for 1h caused no change in the ${}^{31}P-{}^{1}H$ n.m.r. spectrum, showing unreacted starting complex.

(ii) With Ph₃P (2 mole)

The addition of a two molar equivalent of Ph_3P as above showed the presence of displaced ligand (2a) in the ${}^{31}P-{}^{1}H$ n.m.r. spectrum as well as a signal at 24 p.p.m. identified as $[PdCl_2(Ph_3P)_2]$ by comparison with an authentic sample.

(iii) With dppp

Similarly, the addition of a stoichiometric amount of dppp to a dichloromethane solution of (50) (0.1g, 0.15 mmol) indicated the presence of free (2a) and a single signal at 11.6 p.p.m. identified as [PdCl₂dppp] by comparison with an authentic sample.

(iv) With 2,2'-dipyridyl

Displacement of ligand (2a) was also observed from complex (50) on the addition

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of 2,2'-dipyridyl to a dichloromethane solution of (50) as indicated by a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum on the reaction mixture.

(v) With CO

The passage of CO through a dichloromethane solution of (50) (0.1g, 0.15 mmol) for 1h afforded only unreacted starting material.

(vi) With HCl in CH₂Cl₂

The passage of a slow stream of HCl through a dichloromethane solution of (50) (0.1g, 0.15 mmol) for 1h afforded only unreacted starting material as shown by a $^{31}P-\{^{1}H\}$ n.m.r. spectrum.

(vii) With HCl in MeOH

Similarly, the reaction of (50) with HCl in methanol afforded only unreacted starting material.

(viii) With KBr

The addition of a two molar equivalent of KBr to a .suspension of (50) (0.1g, 0.15 mmol) in acetone afforded after stirring overnight a solid with a FAB mass spectrum characteristic of $[PdBr_2(Ph_2PN(Ph)P(O)Ph_2)]$ (52)., Chapter 3.

(ix) With p-toluidine

The addition of *p*-toluidine to a solution of (50) in dichloromethane with stirring for 2h caused no change in the ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum, indicating unreacted starting material.

(x) With BuNC

A ${}^{31}P-{}^{1}H$ n.m.r. spectrum on the reaction mixture after the addition of ${}^{1}BuNC$ to a solution of (50) (0.1g, 0.15 mmol) in dichloromethane showed unreacted starting

material.

(xi) With AgOCOCH₃

Refluxing a suspension of (50) (0.1g, 0.15 mmol) and AgOCOCH₃ in dichloromethane for 3h showed only unreacted starting material in the ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum of the reaction filtrate.

(xii) N.m.r. tube reactions

(a) With MeCN

After the addition of excess MeCN to a small amount of (50) in an n.m.r. tube and shaking for 10 minutes, a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum indicated the presence of unreacted starting material.

(b) With pyridine

Similarly, the addition of dry pyridine to (50) in an n.m.r. tube afforded only unchanged starting material.

(c) <u>With DMSO</u>

The analogous reaction of (50) with DMSO showed, after 10 minutes numerous signals in the ${}^{31}P$ -{ ${}^{1}H$ } n.m.r. spectrum.

(xiii) With dimethyl 1,3-acetonedicarboxylate/Ag2O

A stoichiometric amount of dimethyl 1,3-acetonedicarboxylate was added to a dichloromethane solution of (50) (0.2g, 0.31 mmol), and excess Ag_2O added before refluxing the suspension for 3h. After filtration, a ³¹P-{¹H} n.m.r. spectrum indicated the presence of unreacted (50).

<u>4.15.9 Miscellaneous reactions of *cis*-[Mo(CO)₄{Ph₂PN(Ph)P(O)Ph₂}] (50)</u> (i) <u>With HCl gas</u>

The passage of HCl through both a dichloromethane solution, and a methanol suspension respectively for 0.5h afforded solutions on which ${}^{31}P-{}^{1}H$ n.m.r. spectra indicated the presence of unreacted starting material.

(ii) With [PdCl₂(COD)]

A molar equivalent of $[PdCl_2(COD)]$ was added to a solution of (54) in dichloromethane, and the solution stirred for 3h. Gradual darkening was seen, and after filtration to remove some insoluble residue a ³¹P-{¹H} n.m.r. spectrum indicated the presence of three sets of doublet of doublet signals.

(iii) With [PdCl₂(PhCN)₂]

Similarly, the reaction of (54) with $[PdCl_2(PhCN)_2]$ showed two sets of doublet of doublet signals in a ³¹P-{¹H} n.m.r. spectrum of the reaction mixture.

(iv) With HgCl₂

As above, reaction withh $HgCl_2$ showed a similar ³¹P-{¹H} n.m.r. spectrum exhibiting two sets of doublet of doublet signals.

(v) With BF3.Et2O

An excess of BF₃.Et₂O was added to a solution of (54) (0.1g, 0.09 mmol) in dichloromethane, but after 2h a ${}^{31}P$ -{ ${}^{1}H$ } n.m.r. spectrum indicated no reaction had occured.

4.15.10 Reaction of complex (58) with KPF₆

A molar equivalent of KPF₆ (0.05g, 0.25 mmol) was added to a stirred solution of (58) (0.2g, 0.25 mmol) in dichloromethane (20 cm³) and the resulting suspension stirred for 2h. After filtration of the reaction mixture, and removal of the solvent *in vacuo*, the addition of diethyl ether afforded an orange solid identified as $[RuCl(p-cym){Ph_2PN(Ph)P(O)Ph_2}][PF_6]$ (113) which was dried *in vacuo*, (0.2g, 90%).

(Found: C, 52.9; H, 4.54; N, 1.47; F, 8.43. $C_{41}H_{41}ClF_6NO_2P_3Ru$ requires C, 53.3; H, 4.48; N, 1.52; F, 12.4%).

N.m.r. (CH₂Cl₂): ³¹P-{¹H} (36.2 MHz), δ -143.0 [s, PF₆, ¹J(PF) 713], 59.2 [d, P_X, ²J(P_AP_X) 44], and δ 98.8 p.p.m. [d, P_A, ²J(P_XP_A) 44].

4.15.11 Miscellaneous reactions of complex (96)

(i) With DMAD

An excess of DMAD was added with stirring to a solution of (96) (0.2g, 0.38 mmol) in dichloromethane. A slight colour change was observed but a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum indicated the presence of unreacted (96).

(ii) With SO₂

A slow stream of SO₂ was passed through a solution of (96) (0.2g, 0.38 mmol) in dichloromethane for 2h but ${}^{31}P$ -{ ${}^{1}H$ } n.m.r. indicated no change.

(iii) With SOCl₂

An excess of $SOCl_2$ was added with stirring to a solution of (96) (0.2g, 0.38 mmol) in dichloromethane whereupon the colour darkened to blood-red. After stirring for 1h, a ³¹P-{¹H} n.m.r. spectrum showed numerous signals.

(iv) With HCl gas

A slow stream of HCl gas was passed through a solution of (96) (0.2g, 0.38 mmol) in dichloromethane for 2h. A ${}^{31}P{-}{^{1}H}$ n.m.r. spectrum showed numerous signals.

(v) With HgX2 (X=Cl, Br)

The addition of molar equivalents of the mercuric halides to a solution of (96) (0.2g, 0.38 mmol) in acetone also afforded solutions which exhibited numerous signals in their ${}^{31}P$ -{ ${}^{1}H$ } n.m.r. spectra.

(vi) With Cl₂

A slow stream of Cl_2 was passed through a solution of (96) (0.2g, 0.38 mmol) in dichloromethane for 1h. An orange solid gradually precipitated from the solution, and ³¹P-{¹H} n.m.r. and mass spectroscopic analysis showed many resonances.

4.15.12 Miscellaneous reactions of complex (94).

(i) With Ph₃As

After the passage for 0.5h of CO through a dichloromethane solution of (94) (0.2g, 0.57 mmol), a molar equivalent of Ph_3As was added and a darkening of colour observed. After further stirring for 2h, addition of light petroleum afforded a brown solid which exhibited numerous signals in its mass spectrum.

(ii) With Ph3Sb

Analogously, the reaction of (94) with Ph_3Sb afforded a solid which showed numerous signals in its mass spectrum, and a ¹H n.m.r. spectrum showing only signals in the aromatic region.

(iii) With ligand (2a)

A molar equivalent of (2a) (0.27g, 0.57 mmol) was added to a solution of (94) (0.2g, 0.57 mmol) in dichloromethane with accompanying darkening of the solution. After stirring for 2h, the volume was reduced *in vacuo*, and a ${}^{31}P{-}{}^{1}H$ n.m.r. spectrum indicated no complex formation.

(iv) With ligand (2a)/CO

Similarly, a molar equivalent of (2a) was added to a solution of (94) through which CO had been passed for 0.5h. Darkening was once again observed but ${}^{31}P-{}^{1}H$ n.m.r. analysis indicated once again no reaction.

(v) With Cl₂

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A slow stream of Cl_2 was passed through a dichloromethane solution of (94) (0.2g, 0.57 mmol) for 0.5h. The solvent was reduced *in vacuo* and light petroleum added to afford an orange solid which exhibited a single signal in its FAB mass spectrum at m/z 492 which was unassignable.

CHAPTER 5

Synthesis and Reactions of Some Metal Complexes of a Triphosphazane Monoxide

5.1 Introduction

The new ligand (41) whose synthesis and isolation were described earlier in Chapter 2 represents a new derivative of the previously investigated triphosphazanes, $\{Ph_2PN(R)\}_2PPh$ and several publications have appeared.¹⁸⁸⁻¹⁹⁰ More recently,



Schmutzler *et al.*¹⁹¹ extended this work by reacting N,N'-Dimethyl-N-N'-bis(trimethylsilyl)urea with *tert*-butyl(chloro)phenylphosphine. At room temperature the compound (114) was obtained but under more vigorous conditions the diphosphine (115) was formed. It was observed that treatment of the tetracarbonyl



norbornadiene derivatives of Cr, Mo and W with (115) gave the unusual complexes (116)-(118) in which the ligand was coordinated to the metal through only one of the phosphorus atoms and the oxygen atom of the carbonyl group, Scheme 1. In contrast,



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the reactions of (115) with $[Fe_2(CO)_9]$ and $[PtCl_2(COD)]$ afforded the complexes (119) and (120) with both phosphorus atoms coordinated, Scheme 2. It was therefore of interest to investigate the ligand properties of (41) to see whether P-P or P-O metal complexes were formed. Platinum(II), palladium(II), molybdenum(0) and tungsten(0) complexes have been prepared.





5.2 Preparation of cis-[PdX₂{(Ph₂PNPh)₂P(O)Ph}] (X=Cl, Br) complexes

The treatment of $[PdCl_2(COD)]$ or $[PdBr_2(COD)]$ with a molar equivalent of the ligand (41) in dichloromethane afforded the title complexes (121) and (122) in good yield, Scheme 3. The complexes were obtained as orange microcrystalline solids in 64 and 75% yields respectively. The ³¹P-{¹H} n.m.r. spectra of both complexes exhibited the expected A₂X type spin system with a triplet to low frequency due to the phosphine oxide at *ca*. 31 p.p.m. and a high frequency doublet at about 63-65 p.p.m. due to the diphenylphosphino moieties with a much lower $J(P_AP_X)$ coupling constant than observed for the free ligand. The FAB mass spectra of both complexes showed [M-X]⁺ and -107-

$$[PdX_{2}(COD)] \xrightarrow{\{Ph_{2}PN(Ph)\}_{2}P(O)Ph}_{CH_{2}Cl_{2}, 3h} \qquad \stackrel{O}{Ph} \stackrel{Ph}{Ph} \xrightarrow{Ph_{2}}_{Ph} Pd \xrightarrow{X}_{X}$$

$$(121): X=Cl$$

$$(122); X=Br$$

Scheme 3

 $[M-2X]^+$ as the highest species. In the infra-red spectrum of both complexes, the free phosphoryl moiety appeared at 1230cm⁻¹, this being about 100 cm⁻¹ higher than observed for the free phosphoryl bands in the ligands $Ph_2PN(Ph)P(O)Ph_2$ (2a) and $Ph_2PN(C_6H_4OMe-4)P(O)Ph_2$ (2b), Chapter 2. This change is presumably a consequence of the phosphoryl group of the metal complex being contained in a more strained cyclic system.

5.3 Preparation of cis-[PtX2{(Ph2PNPh)2P(O)Ph}] (X=Cl, I) complexes

The Pt(II) title complexes (123) and (124) were similarly prepared by treatment of $[PtCl_2(COD)]$ or $[PtI_2(COD)]$ with a stoichiometric amount of the diphosphine in dichloromethane. Complex (123) was obtained as a white solid and complex (124) as a bright yellow microcrystalline solid, Scheme 4. No attempt was made to synthesise

$$[PtX_{2}(COD)] \xrightarrow{\{Ph_{2}PN(Ph)\}_{2}P(O)Ph}_{CH_{2}Cl_{2}, 3h} \qquad \qquad \begin{array}{c} O = Ph_{2} & Ph_{2} \\ Ph_{2} & Ph_{2} & Ph_{2} \\ Ph_{3} & Ph_{2} & Ph_{3} \\ Ph_{3} & Ph_{3} & Ph_{3} \\ Ph_{3} & Ph_{3} & Ph_{3} \\ (123); X=Cl_{3} \\ (124); X=I \end{array}$$

Scheme 4

complex (124) by the reaction of complex (123) with sodium iodide in acetone, but this would be expected to lead to the same product. The spectroscopic properties of the complexes were in accord with the proposed structures. The room temperature ³¹P-{¹H} n.m.r. spectra exhibit characteristic A_2X patterns with associated satellites due to coupling with platinum-195 with ¹J(PtP) values of 3823 and 3607 Hz respectively. The

value for the dichloride complex is a little larger than those for other six-membered ring chelating diphosphine complexes of platinum dichloride.²⁰⁴ As expected, the palladium complexes (121) and (122) gave larger coordination shift values than the platinum complexes (123) and (124).²⁰⁶ The exchange of chloride with iodide made a slight change in the value of the chemical shift. The ¹⁹⁵Pt coupling constant ¹J(PPt) for the iodide complex (124) is significantly smaller than for the chloride derivative as expected due to the higher *trans* influence of iodide.¹⁹⁹ In contrast to the palladium complex, the FAB mass spectra of the platinum complexes exhibit characteristic [M]⁺ as the highest species as well as the [M-X]⁺ and [M-2X]⁺ species. The ¹⁹⁵Pt-{¹H} n.m.r. spectrum of complex (124) is shown in Figure 1. This shows a triplet of doublets due to coupling of the spin active platinum nuclei with two identical and one distinct phosphorus nuclei (I=1/2, 100%).



The ¹⁹⁵Pt-{¹H} n.m.r. spectrum of cis-[PtI₂{(Ph₂PNPh)₂P(O)Ph}] (124)

5.4 Preparation of [M(CO)₄{Ph₂PNPh)₂P(O)Ph}] (M=Mo, W) complexes

The reaction of the diphosphine (41) with $[M(CO)_4pip_2]$ (M=Mo,W)¹²¹ afforded the complexes (125) and (126), Scheme 5. The reaction to synthesise the tungsten complex requires more forcing conditions to displace the second piperidine. The complexes (125) and (126) were isolated as a grey and a yellow microcrystalline solid

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$$[Mo(CO)_4PIP_2] \xrightarrow{\{Ph_2PN(Ph)\}_2P(O)Ph}_{CH_2Cl_2, \Delta, 3h} \xrightarrow{OC} \xrightarrow{CO}_{Ph_2} \xrightarrow{Ph}_{Ph}_{Ph} \xrightarrow{P\in O}_{Ph}_{Ph}$$

$$[W(CO)_4PIP_2] \xrightarrow{\{Ph_2PN(Ph)\}_2P(O)Ph}_{CH_2Cl_2, \Delta, 2h} \xrightarrow{OC} \xrightarrow{Ph_2}_{OC} \xrightarrow{Ph}_{P-N} \xrightarrow{P \in O}_{Ph}_{Ph}$$

(126)

Scheme 5

respectively. The tungsten complex had poor solubility in common organic solvents. The ³¹P-{¹H} n.m.r. spectra of both complexes exhibit a low frequency 1:2:1 triplet and a high frequency doublet consistent with a P-P chelate complex. In the case of (126) satellites due to coupling of phosphorus to tungsten-183 (I= $\frac{1}{2}$, 14.3%) were too weak to be observed. The i.r. spectra of both complexes show absorptions in the v(CO) region indicative of approximately C_{2v} symmetry and *cis* geometry about the metal atom supporting chelate formation, Table 1.^{89,122} In the i.r. spectrum of (125) the band

Complex	v(CO) cm ⁻¹			
	a ₁	b ₁	b ₂	
(125)	2024	1920	1900	
(126)	2030	1909	1885	

Infrared data in the v(CO) stretching region of complexes (125) and (126)

<u>Table 1</u>

expected for the symmetry element a_2 was only observed as an unresolved shoulder. The ¹³C-{¹H} n.m.r. spectrum of the molybdenum complex contained two separate unresolved resonances in the carbonyl region at 208.5 and 214.2 p.p.m., attributed to equatorial and axial carbonyl groups respectively.

5.5 <u>Attempted preparation of cis-[MCl(CO){(Ph₂PNPh)₂P(O)Ph}] (M=Rh, Ir)</u> complexes

The reaction of the ligand (41) with $[RhCl(COD)]_2$ in the presence of CO in dichloromethane afforded an orange solution. The ³¹P-{¹H} n.m.r. spectrum of the solution contained the expected pattern for the desired complex (127), Figure 2. However, the addition of light petroleum to the solution afforded an orange microcrystalline solid whose ³¹P-{¹H} n.m.r spectrum exhibited many peaks and was clearly different to that of the reaction solution. The data indicate that the complex decomposed upon attempted isolation. The ³¹P-{¹H} n.m.r. spectrum of (127) exhibited

$$0 \underset{Ph}{\longrightarrow} P \underbrace{\stackrel{Ph}{\underset{N \to P}{\leftarrow}} P_{N} \underset{Ph}{\xrightarrow{P}} P_{Ph} \underbrace{\stackrel{Cl}{\underset{CO}{\leftarrow}} Rh \underset{CO}{\overset{Cl}{\underset{CO}{\leftarrow}} Ph} P_{Ph} \underbrace{\stackrel{Cl}{\underset{CO}{\leftarrow}} Ph \underbrace{\stackrel{Cl}{\underset{CO}{\leftarrow}} Ph \underbrace{\stackrel{Ph}{\underset{Ph}{\underset{Ph}{\rightarrow}} Ph_2} Ph \underbrace{\stackrel{Cl}{\underset{CO}{\leftarrow}} Ph \underbrace{\stackrel{Ph}{\underset{CO}{\leftarrow}} Ph \underbrace{\stackrel{Ph}{$$

(127)

an ABMX spin pattern due to the presence of three inequivalent phosphorus atoms with 103 Rh- 31 P coupling. The phosphorus atom *trans* to chloride in the complex (P_B) was downfield (higher frequency) and the value of 1 J(RhP) was larger than that of the phosphorus atom *trans* to carbonyl due to the smaller *trans* influence of the chloride.¹⁹⁹



The ³¹P-{¹H} n.m.r. spectrum of *cis*-[RhCl(CO){(Ph₂PNPh)₂P(O)Ph}] (127)

In a similar fashion, the reaction of the ligand (41) with $[IrCl(CO)_2p$ -tol] was carried out in dichloromethane with the solution darkening from yellow to orange on

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addition of the ligand. However, after work-up a ${}^{31}P-{}^{1}H$ n.m.r. spectrum on the solid obtained contained numerous resonances non pertaining to the expected product. A FAB mass spectrum on the same solid also contained numerous resonances but the presence of a small amount of the desired product (128) was indicated by the peaks corresponding to [M-CO]⁺ and [M-CO-Cl]⁺ at m/z 903 and 867 respectively. No single product could be separated from the reaction mixture or from the solid obtained, and oxidation and breakdown of the ligand must have occurred rapidly in the reaction mixture.

$$\overset{O}{\underset{Ph}{\Rightarrow}} \overset{Ph}{\underset{N}{\longrightarrow}} \overset{Ph}{\underset{N}{\longrightarrow}} \overset{Ph_{2}}{\underset{Ph}{\longrightarrow}} \overset{Ph}{\underset{Ph}{\longrightarrow}} \overset{Ph}{\underset{Ph}{\overset{Ph}{\underset{Ph}{\longrightarrow}} \overset{Ph}{\underset{Ph}{\longrightarrow}} \overset{Ph}{\underset{Ph}{\overset{Ph}{\underset{Ph}{\longrightarrow}} \overset{Ph}{\underset{Ph}{\overset{Ph}{\underset{Ph}{\longrightarrow}} \overset{Ph}{\underset{Ph}{\overset{Ph}{\underset{Ph}{\overset{Ph$$

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۰.	T	20)	1

The reaction of (41) with a system containing $[RhCl(COD)]_2$ and KPF_6 in dichloromethane afforded only an orange solid which exhibited numerous resonances in its ³¹P-{¹H} n.m.r. spectrum.

5.6 Preparation of metallalactam platinum complexes

The isolation of the platinum complexes $[PtX_2{(Ph_2PNPh)_2P(O)Ph}]$ (X=Cl, 123; X=I, 124) prompted us to explore the reactions of these systems with amides containing activated acidic hydrogen atoms (e.g. MeC(O)CH₂CONHPh, acetoacetanilide) and esters of acetone dicarboxylic acid, RCO₂CH₂COCH₂CO₂R, in the presence of silver(I) oxide. Such reactions have been shown to provide a powerful route to a range of metal-carbon bonded products.¹⁹²⁻¹⁹⁶ Treatment of the complex (123) with 4-acetoacetaniside in refluxing dichloromethane in the presence of silver(I) oxide however, afforded a complex mixture of products which could not be separated. However, the reactions of the platinum dichloride complexes *cis*-[PtCl₂L₂] (L= Ph₃P; L₂= dppp) with either acetoacetanilide, 2-acetoacetanisidide or 4-acetoacetaniside, in the presence of an excess of silver(I) oxide give high yields of the metallalactam complexes (129)-(134), Figure 3.¹⁹⁶ The complexes were isolated as white crystalline complexes, which are air-stable, both in solution and in the solid state. The complexes have been characterised by

$L \rightarrow Pt \stackrel{C}{\sim} C \stackrel{C}{\sim} C \stackrel{C}{=} O$					
Complex	L or L ₂	Ar			
(129)	PPh ₃	Ph			
(130)	PPh ₃	C ₆ H ₄ OMe-4			
(131)	PPh ₃	C ₆ H ₄ OMe-2			
(132)	dppp	Ph			
(133)	dppp	C ₆ H ₄ OMe-4			
(134)	dppp	C ₆ H ₄ OMe-2			

H (O)Me

Figure 3

multinuclear n.m.r., i.r. spectroscopies and FAB mass spectroscopy and elemental analysis. The ³¹P-{¹H} n.m.r. spectra of the complexes exhibit the expected AB spin system pattern with associated satellites due to coupling to platinum-195. The higher frequency resonance of the AB pattern is attributed to the phosphorus atom *trans* to carbon and the lower frequency resonance to that *trans* to nitrogen with respective ¹J(PtP) values of 2402 and 3709 Hz. The ¹³C-{¹H} n.m.r. spectra showed the resonance for the C(O)Me carbonyl groups appearing in the expected region of 205.2-206.7 p.p.m. The FAB mass spectra of these metallacyclic systems exhibited a molecular ion as a characteristic cluster of peaks, with the distribution of these closely matching the predicted isotopomer distribution. A ¹⁹⁵Pt-{¹H} n.m.r. spectrum of complex (132) exhibited the expected doublet of doublets centred at -4536 p.p.m. due to coupling to the two inequivalent phosphorus nuclei, Figure 4.



5.7 <u>Reactions of esters of acetone dicarboxylic acid with complexes of the type</u> [PtCl₂(P-P)]

Refluxing a dichloromethane solution of (123) with Dimethyl 1,3-acetone dicarboxylate in the presence of an excess of silver(I) oxide afforded a complex mixture, the ³¹P-{¹H} n.m.r. spectrum exhibiting a number of resonances including those attributable to the starting complex. A FAB mass spectrum on the solid obtained from the reaction mixture showed a peak at m/z 1044 which corresponded to [M]⁺ for the desired metallacyclobutanone complex but attempts to separate this complex from the mixture were unsuccessful. In view of the failure it was therefore decided to investigate similar reactions with dppp and dppb to see whether the size of the chelate ring had any effect upon the reaction and products. Treatment of [PtCl2dppp] and [PtCl2dppb] with RCO₂CH₂COCH₂CO₂R (R=CO₂Me and CO₂Et) in refluxing dichloromethane in the presence of silver(I) oxide gave white or grey air-stable microcrystalline solids, Scheme 5. The room temperature ³¹P-{¹H} n.m.r. spectra of complexes (136) and (137) exhibit a singlet with associated satellites due to coupling to platinum-195 with ¹J(PtP) values of 2939 and 2930 Hz respectively. The FAB mass spectra of both complexes exhibit the respective molecular ions at m/z 794 and 822. In the cases of complexes (134) and (135) the situation is a little more complex. The room temperature ${}^{31}P-{}^{1}H$ n.m.r. spectra of both complexes (134) and (135) indicate the presence of two singlet resonances each

$$[PtCl_2L_2] \xrightarrow{\text{RCO}_2\text{CHCOCHCO}_2\text{R}} Ag_2O, CH_2Cl_2, \Delta(5h) \xrightarrow{\text{L}} Pt \xrightarrow{\text{R}} R \xrightarrow{\text{R}} R$$

(134); $L_2 = dppp$, $R = CO_2Me$ (135); $L_2 = dppp$, $R = CO_2Et$ (136); $L_2 = dppb$, $R = CO_2Me$ (137): $L_2 = dppb$, $R = CO_2Et$

Scheme 5

with corresponding platinum-195 satellites. A room temperature ¹⁹⁵Pt-{¹H} n.m.r. spectrum of (134) also exhibited two sets of resonances. These phenomena have been attributed to the presence of both the equatorial-equatorial and the more favourable axial-equatorial isomers as shown, Figure 5.¹⁹³ In previous work, various low



axial-equatorial

equatorial-equatorial

Figure 5

temperature n.m.r. experiments have been performed to study the presence of axial-equatorial interconversion. In this work the presence of the more rigid chelating diphosphine seems to allow isolation of the equatorial-equatorial meso-isomer. An inverse-gated ¹⁹⁵Pt-{¹H} n.m.r. spectrum indicated the ratio of the isomers to be 2:1. This ¹⁹⁵Pt-{¹H} n.m.r. spectrum of (134) showing the two isomers is presented, Figure 6.



Figure 6 The inverse-gated ¹⁹⁵Pt-{¹H} n.m.r. spectrum of [Pt(CHRCOCHR)L₂] (R=CO₂Me, L=dppp) (134)

5.8 Miscellaneous reactions of complex (123)

(i) With SnCl₂

Complexes of the type [PtCl(SnCl₃)L₂] (where L₂=monodentate phosphine or L₂=chelating bisphosphine) have been known for sometime as effective hydroformylation catalysts.¹⁹⁷ Thus, the reaction of complex (123) with anhydrous tin dichloride in dichloromethane was carried out for 6h. The addition of light petroleum afforded a pale orange powder whose ³¹P-{¹H} n.m.r. spectrum indicated the presence of two species. The first was attributed to unreacted starting material by comparison with an authentic sample of (123). The other species was attributed to the complex (140) formed by insertion of SnCl₂ into one of the metal chlorine bonds. The ³¹P-{¹H} n.m.r. spectrum exhibits the expected ABMNX pattern indicative of (140).¹⁹⁸ The different

$$\begin{array}{c} O = Ph & Ph_2 \\ Ph & P & P \\ Ph & P & P \\ Ph & Ph_2 \end{array} Pt < \begin{array}{c} Cl \\ SnCl_3 \\ Ph & Ph_2 \end{array}$$

(140)

J(PtP) values observed are indicative of one phosphorus atom *trans* to chlorine (P_A), (the larger value), and the other opposite a ligand of stronger *trans* influence such as -SnCl₃ (P_X). The complex (140) could not be separated from the starting material (123) in the

mixture. The FAB mass spectrum of the mixture also indicated the prescence of both complexes, with complex (140) exhibiting $[M-SnCl_3]^+$ at m/z 907, which also corresponds to $[M-Cl]^+$ for (123).

(ii) With AgOCOCF₃

When a mixture of (123) and a two molar equivalent of $AgOCOCF_3$ was heated to reflux in dichloromethane the complex (139) was obtained. The ³¹P-{¹H} n.m.r.

spectrum of the complex exhibited the expected A_2X pattern with associated platinum-195 satellites. The value of ¹J(PtP) was 4033 Hz in comparison to a value of 3823 Hz for the starting complex. This larger value of ¹J(PtP) is consistent with the weaker *trans* influence of the oxygen atom, the ¹J(PtP) value being in agreement with similar values for phosphorus *trans* to oxygen.¹⁹⁹

(iii) With various other silver salts

Refluxing dichloromethane solutions of (123) with Ag_2CO_3 , $AgOSO_2CF_3$, $AgOCOCH_3$ and AgOCN all gave only unreacted starting material as shown by ³¹P-{¹H} n.m.r. spectra on the reaction residues.

(iv) With BuNC

The addition of a molar equivalent of 'BuNC to a dichloromethane solution of (123) followed by stirring for 3h gave only unreacted (123) as shown by a ${}^{31}P-{}^{1}H$ n.m.r. spectrum of the reaction mixture

(v) With diglycolic acid

Similarly, refluxing a solution of (123) with diglycolic acid in the presence of

Ag₂O afforded only unreacted (123) as indicated by $^{31}P-{^{1}H}$ n.m.r.

(vi) With 2-acetamidoacrylic acid

Treatment of complex (123) with a molar equivalent of 2-acetamidoacrylic acid in the presence of an excess of Ag_2O in refluxing CH_2Cl_2 afforded, after work-up as previously, the complex (138) as a light brown powder, Scheme 7. The complex (138)



Scheme 7

has been formulated as a five-membered platinacycle containing platinum-carbon and platinum-oxygen bonds. The complex was characterised by means of the ³¹P-{¹H} n.m.r. spectrum as well as its FAB mass spectrum. The ³¹P-{¹H} n.m.r spectrum of the complex indicated the presence of three inequivalent phosphorus nuclei as expected. Hence the spectrum exhibits a second order ABX spin-system pattern with corresponding platinum-195 satellites. It has been reported that the treatment of [PtCl₂(dppp)] with a one molar equivalent of 2-acetamidoacrylic acid forms the nitrogen-oxygen bonded complex.²⁰⁰ In fact other studies have shown that a mixture of both possible isomers is formed, but that with a two or three molar excess of the aminoacid only a carbon-oxygen bonded isomer was produced.²⁰¹ In complex (138) the phosphorus atom *trans* to carbon (P_B) exhibits a much smaller ¹⁹⁵Pt-³¹P coupling than the phosphorus atom *trans* to oxygen this being expected on the basis of the *trans* influence of the atoms. The value of J(PtP_B) is much less than for the N-bonded isomer

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[Pt(N-acry)dppp] which is 2869 Hz compared to 2091 Hz for complex (138), Table 4.^{202,203} Thus the less shielded signal (to higher frequency) in complex (138) has been

Complex	δ(P _a)	δ(P _b)	J(P _a P _b)	$J(PtP_a)$	J(PtPb)
[Pt(C-acry)(dcpam)] ²⁰¹	7.95	10.5	27	3721	1961
[Pt(C-acry)(dppp)] ²⁰¹	-0.51	1.85	27	3816	1899
[Pt(N-acry)(dppp)] ²⁰³	-7.65	-10.57	34	3731	2869
(138)	69.2	69.2	25.5	4265	2091

δ/ p.p.m.; J/Hz

<u>Table 4</u>

assigned to P_B (*trans* to carbon). In the infra-red spectrum the amide N-H stretching frequency was observed at 3330cm⁻¹, further evidencing the presence of the carbon bonded isomer. The molecular ion [M]⁺ was observed in the FAB mass spectrum of (138) at m/z 999.

5.9 Conclusion

Various metal complexes of the ligand (41) have been synthesised, and an investigation of the reactions of the novel platinum(II) complex (123) carried out to see if its behaviour is similar to other chelating diphosphine platinum dichloride metal complexes. Further work could entail attempts to isolate metal complexes of other metals with ligand (41), and a further attempt to isolate the rhodium(I) complex (127) and investigate its oxidative addition reactions in detail.

5.10 Experimental

General experimental techniques were as described in Chapter 2. The ${}^{195}Pt-{}^{1}H$ n.m.r. spectra were recorded on a Bruker AM300 spectrometer operating at 65.52 MHz with K₂[PtCl₄] as internal reference. The compounds acetoacetanilide, 2-acetoacetanisidide, 4-acetoacetanisidide, silver(I) oxide, 1,3-dimethylacetonedicarboxylate, 1,3-diethylacetonedicarboxylate, 1,3-bis(diphenylphosphino) propane, 1,4-bis(diphenylphosphino) butane, anhydrous tin dichloride, 'BuNC, silver(I) carbonate, silver(I) trifluoromethanesulphonate, 2-acetamidoacrylic acid, silver(I) acetate, silver(I) trifluoroacetate, silver(I) cyanate and diglycolic acid (Aldrich) were all used as supplied by commercial sources.

5.10.1 Preparation of [PdX₂{(Ph₂PNPh)₂P(O)Ph}] (X=Cl, Br) complexes

(i) X=Cl (121)

A solution of $\{Ph_2PNPh\}_2P(O)Ph$ (0.47g, 0.7 mmol) in dichloromethane (10 cm³) was added to a stirred solution of $[PdCl_2(COD)]$ (0.2g, 0.7 mmol) also in dichloromethane. The colour deepened immediately and the dark orange solution was stirred for 3h at room temperature. The volume of solvent was reduced *in vacuo* and the addition of light petroleum afforded the title product (121) as an orange microcrystalline solid which was recrystallised from dichloromethane-light petroleum, and dried *in vacuo* (0.38g, 64%).

(Found: C, 55.7: H, 4.49: N, 3.01. C₄₂H₃₅Cl₂N₂OP₃Pd.0.75 CH₂Cl₂ requires C, 55.9; H, 4.03; N, 3.05%), m.p. 250-52°C(decomp)

 v_{max} at 1420s (v_{P-Ph}), 1225s (v_{PO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 31.3 [t, P_X, ²J(P_AP_X) 26.8], and δ 64.7 p.p.m. [d, P_A, ²J(P_xP_A) 26.8].

Mass spectrum (FAB); [M-Cl]⁺ 817, [M-2Cl]⁺ 782.

(ii) <u>X=Br (122)</u>

As above, a solution of $\{Ph_2PNPh\}_2P(O)Ph$ (0.36g, 0.53 mmol) in dichloromethane (10 cm³) was added with stirring to one of $[PdBr_2(COD)]$ (0.2g, 0.53 mmol) also in dichloromethane. After stirring for 3h, and similar work-up the product (122) was obtained as a bright orange solid and dried *in vacuo* (0.38g, 75%).

(Found: C, 47.5; H, 3.67; N, 2.60. C₄₂H₃₅Br₂N₂OP₃Pd.2CH₂Cl₂ requires C, 47.5; H, 3.53; N, 2.52%), m.p. 253-55°C (decomp).

 v_{max} at 1420s ($v_{P.Ph}$) and 1230 (v_{PO}) cm⁻¹ (KBr). N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 31.2 [t, P_X, ²J(P_AP_X) 24.4] and δ 62.7 p.p.m. [d, P_A, ²J(P_XP_A) 24.4]. Mass spectrum (FAB); [M-Br]⁺ 864, [M-2Br]⁺ 782.

5.10.2 Preparation of [PtX2{(Ph2PNPh)2P(O)Ph}] (X=Cl, I) complexes

(i) X=Cl (123)

A solution of $\{Ph_2PNPh\}_2P(O)Ph$ (0.36g, 0.54 mmol) in dichloromethane (15 cm³) was added with stirring to one of $[PtCl_2(COD)]$ (0.2g, 0.54 mmol) also in CH₂Cl₂. The pale yellow solution was stirred for 3h, and after the removal of solvent *in vacuo* the addition of diethyl ether afforded the product identified as (123) as a white microcrystalline solid which was dried *in vacuo* (0.33g, 65%)

(Found: C, 53.2; H, 3.91; N, 2.98. $C_{42}H_{35}Cl_2N_2OP_3Pt$ requires C, 53.5; H, 3.74; N, 2.97%), m.p. 185-87°C(decomp).

 v_{max} at 1420s (v_{P-Ph}) and 1230s (v_{P-Ph}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz) δ 29.5 [t, P_X, ²J(P_AP_X) 19.5], and δ 44.4 p.p.m. [d, P_A, ¹J(PtP_A) 3823, ²J(P_XP_A) 19.5].

Mass spectrum (FAB); [M]⁺ 942, [M-Cl]⁺ 907, [M-2Cl]⁺ 871.

(ii) <u>X=I (124)</u>

As above, a solution $\{Ph_2PNPh\}_2P(O)Ph$ (0.24g, 0.36 mmol) in dichloromethane (10 cm³) was added to one of $[PtI_2(COD)]$ (0.2g, 0.36 mmol). After stirring for 3h, reduction of the solvent volume and the addition of light petroleum afforded the product (124) as a bright yellow microcrystalline solid which was dried *in vacuo* (0.29g, 71%). (Found: C, 39.3; H, 3.05; N, 2.18. C₄₂H₃₅I₂N₂OP₃Pt.3CH₂Cl₂ requires C, 39.2; H, 2.99; N, 2.03%), m.p. 182-84°C(decomp).

 v_{max} at 1425s (v_{PPh}) and 1235s (v_{PPh}) cm⁻¹(KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), δ 29.0 [t, P_X, ²J(P_AP_X) 19.5] and δ 38.4 p.p.m.

[d, P_A, ¹J(PtP_A) 3607, ²J(P_XP_A) 19.5]; ¹⁹⁵Pt-{¹H} (CH₂Cl₂, 64.5 MHz), δ -5145.9 p.p.m. [td, ¹J(PtP_A) 3607, ²J(PtP_X) 66.6]. Mass spectrum (FAB); [M]⁺ 1125, [M-I]⁺ 998, [M-2I]⁺ 871.

5.10.3 Preparation of [M(CO)₄{(Ph₂PNPh)₂P(O)Ph}] (M=Mo, W) complexes

(i) <u>M=Mo (125)</u>

A solution of $\{Ph_2PNPh\}_2P(O)Ph$ (0.37g, 0.54 mmol) in dichloromethane (10 cm³) was added with stirring to a suspension of $[Mo(CO)(pip)_2]$ (0.2g, 0.54 mmol). The suspension was heated to reflux for 3h, cooled, and the addition of methanol afforded a grey microcrystalline solid identified as (125) which was dried *in vacuo* (0.26g, 55%). (Found: C, 61.8; H, 3.90; N, 2.86. C₄₆H₃₅N₂O₅P₃Mo requires C, 62.4; H, 3.99; N, 3.17%), m.p. 170-72°C(decomp).

 v_{max} at 2025s (v_{CO}), 1920sbr (v_{CO}), 1430m (v_{PPh}), 1230s (v_{PO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 29.8 [t, P_X, ²J(P_AP_X) 31.7] and δ 95.9 p.p.m. [d, P_A, ²J(P_XP_A) 31.7]; ¹³C-{¹H} (CDCl₃, 75.47 MHz), δ 208.5 [m, CO_{eq}], and δ 214.2 p.p.m. [m, CO_{ax}].

Mass spectrum (FAB); [M-CO]⁺ 856, [M-2CO]⁺ 828.

(ii) <u>M=W (126)</u>

A molar equivalent of $\{Ph_2PNPh\}_2P(O)Ph$ (0.29g, 0.43 mmol) was added to a suspension of $[W(CO)_4(pip)_2]$ (0.2g, 0.43 mmol) in benzene (25 cm³). The resulting yellow suspension was brought to reflux for 2h, turning black after 0.5h. The reaction mixture was cooled and filtered to remove insoluble black residue before reduction of the solvent volume and the addition of methanol afforded the title product identified as (126) as a yellow microcrystalline solid (0.13g, 30%).

(Found: C, 49.5; H, 4.52; N, 4.55. C₄₆H₃₅N₂O₅P₃W.2CH₂Cl₂ requires C, 50.4; H, 3.44; N, 2.45%), m.p. 180-82°C (decomp).

 υ_{max} at 1930s ($\upsilon_{CO}),$ 1450 ($\upsilon_{PPh})$ and 1220s ($\upsilon_{PO})$ cm^{-1} (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 30.2 [t, P_X, ²J(P_AP_X) 28.3], δ 73.8 p.p.m. [d, P_A,

²J(P_XP_A) 28.3].

Mass spectrum (FAB); [M-CO]⁺ 944, [M-2CO]⁺ 916.

5.10.4 <u>Attempted preparation of cis-[MCl(CO){(Ph₂PNPh)₂P(O)Ph}] (M=Rh, Ir)</u> complexes

(i) <u>M-Rh (127)</u>

A solution in dichloromethane of $\{Ph_2NPh\}_2P(O)Ph$ (0.55g, 1.01 mmol) was added with stirring to one of $[RhCl(COD)]_2$ (0.25g, 0.52 mmol) after the passage of CO for 0.5h, and the resulting solution darkened immediately. After stirring for 3h, the volume of the solvent was reduced *in vacuo*, and a ³¹P-{¹H} n.m.r. spectrum showed the expected product, (127). The addition of light petroleum afforded an orange solid which showed many lines in its ³¹P-{¹H} n.m.r. spectrum.

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), δ 73.1 [m, P_X, ²J(P_BP_X) 24.4, ²J(P_AP_X) 36.6], 119.5 [m, P_A, ¹J(RhP_A) 137, ²J(P_BP_A) 50.3, ²J(P_AP_X) 36.6] and δ 130.6 p.p.m. [m, P_B, ¹J(RhP_B) 173, ²J(P_BP_X) 24.4, ²J(P_AP_B) 50.3]

(ii) <u>M= Ir</u>

Similarly, the reaction of (41) (0.35g, 0.51 mmol) with $[IrCl(CO)_2(p-tol)]$ afforded after work-up a pale yellow solid whose ³¹P-{¹H} n.m.r. spectrum exhibited numerous resonances.

Mass spectrum (FAB); [M-CO]⁺ 903, [M-Cl]⁺ 867 and numerous unassignable resonances.

5.10.5 Attempted preparation of [Rh(COD){(Ph2PNPh)2P(O)Ph}][PF6]

The reaction of ligand (41) with $[RhCl(COD)]_2$ (0.2g, 0.41 mmol) in the presence of KPF₆ in dichloromethane afforded an orange solid which exhibited numerous resonances in the ³¹P-{¹H} n.m.r. and FAB mass spectra.

5.10.6 Preparation of metallalactam derivatives

(i) $[Pt{CH(COCH_3)C(0)NPh}(PPh_3)_2](128)$

To a solution of $[PtCl_2(COD)]$ (0.2g, 0.54 mmol) in dichloromethane (30 cm³) was added in succession triphenylphosphine (0.28g, 1.07 mmol), acetoacetanilide (0.09g, 0.56 mmol), and silver(I) oxide (0.9g, excess), and the mixture refluxed for 6h. Filtration to remove silver salts afforded a pale yellow solution which was evaporated to dryness under reduced pressure to give a pale yellow oil. Dissolution of the oil in dichloromethane (5 cm³) followed by the addition of light petroleum gave an off white solid which was filtered off and dried *in vacuo* to give the title complex (0.44g, 92%). Slow recrystallisation from dichloromethane-light petroleum gave pale yellow needles. (Found C, 60.9; H, 4.24; N, 1.47. $C_{46}H_{39}NO_2P_2Pt$ requires C, 61.7; H, 4.39; N, 1.57%), m.p. 246-48°C (decomp).

 v_{max} at 1635vs (v_{CO}), 1590s (v_{CO}) and 1440m (v_{PPh}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (36.2 MHz), AB spin system at δ 10.8 [dd, P_{trans N}, ¹J(PtP) 3709], and δ 17.2 p.p.m. [dd, P_{trans C}, ¹J(PtP) 2402, ²J(PP) 17]

¹³C-{¹H} (75.47 MHz), δ 29.0 [s, CH₃], 50.4 [dd, Pt-<u>C</u>H, 123.4-144.0 [m, Ph], 174.8 [m, <u>C</u>(O)NPh], and δ 206.0 p.p.m. [d, <u>C</u>(O)CH₃, ³J(PC)_{trans} 4.8].

¹H (300.13 MHz), δ 2.09 [s, 3H, CH₃], 2.77 [dd, 1H, Pt-C<u>H</u>, ³J(PH)_{trans} 6.1, ³J(PH)_{cis} 4.1,

²J(PtH) 47.0], and δ 6.43-7.48 p.p.m. [m, 35H, Ph].

Mass spectrum (FAB); [M]+ 895.

(ii) [Pt{CH(COCH₃)C(O)N(C₆H₄OMe-4)}(PPh₃)₂] (129)

By an analogous procedure [PtCl₂(COD)] (0.2g, 0.54 mmol), triphenylphosphine (0.28g, 1.07 mmol), 4-acetoacetanisidide (0.11g, 0.54 mmol) and silver(I) oxide (0.6g, excess) afforded (129) as a white microcrystalline solid (0.39g, 78%).

(Found: C, 57.9; H, 4.20; N, 1.07. C₄₇H₄₁NO₃P₂Pt.CH₂Cl₂ requires C, 57.1; H, 4.29; N, 1.39%), m.p. 195°C.

 υ_{max} at 1650vs (υ_{CO}), 1590s (υ_{CO}) cm^{-1} (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), AB spin system, δ 11.0 [dd, P_{trans N}, ¹J(PtP) 3667], and δ 17.5 p.p.m. [dd, P_{trans C}, ¹J(PtP) 2402, ²J(PP) 17]. ¹³C-{¹H} (75.47 MHz), δ 29.0 [s, CH₃], 50.6 [m, PtCH], 56.0 [s, OMe], 128.0-136.0 [m, Ph], 175.0 [m, C(O)NC₆H₄OMe-4], and 206.0 p.p.m. [m, C(O)CH₃]. ¹H (300.13 MHz), δ 2.10 [s, CH₃], 2.77 [dd, 1H, PtC<u>H</u>, ³J(PH)_{trans} 6.2, ³J(PH)_{cis} 3.9, ²J(PtH) 45.2], 3.50 [s, 3H, OMe], 5.30 [s, 2H, CH₂Cl₂], 6.16 [d, 2H, ¹J_{a'b'} 8.9], 6.33 [d, 2H, ¹J_{a'b'} 8.9], and δ 6.90-7.80 p.p.m. [m, 30H, Ph]. Mass spectrum (FAB), [M]⁺ 925.

(iii) [Pt{CH(COCH₃)C(O)N(C₆H₄OMe-2)}(PPh₃)₂] (130)

[PtCl₂(COD)] (0.2g, 0.54 mmol), triphenylphosphine (0.28g, 1.07 mmol), 2-acetoacetanisidide (0.11g, 0.54 mmol) and silver(I) oxide (0.6g, excess) in dichloromethane afforded (130) as a creamy coloured microcrystalline solid (0.35g, 70%).

(Found: C, 58.7; H, 4.45; N, 1.44. C₄₇H₄₁NO₃P₂Pt.0.5CH₂Cl₂ requires C, 59.0; H, 4.38; N, 1.45%), m.p. 140-2°C.

 v_{max} at 1635vs (v_{CO}), 1595s (v_{CO}) cm⁻¹ (KBr).

N.m.r. ${}^{31}P-{}^{1}H$ (CH₂Cl₂, 36.2 MHz), AB spin system, δ 10.9 [dd, P_{trans N}, ${}^{1}J(PtP)$ 3669],

δ 17.3 p.p.m. [dd, P_{trans C}, ¹J(PtP) 2410, ²J(PP) 17].

¹³C-{¹H} (75.47 MHz), very broad and unassignable.

¹H (CDCl₃, 300.13 MHz), δ 2.10 [s, 3H, CH₃], 2.75 [m, Pt-C<u>H]</u>, 3.60 [s, 3H, OMe], 5.30 [s, 2H, CH₂Cl₂], and δ 6.30-7.60 p.p.m. [m, 34H, Ph+C₆H₄OMe-2]. Mass spectrum (FAB), [M]⁺ 925.

(iv) [Pt{CH(COCH₃)C(O)NPh}(dppp)] (131)

From [PtCl₂(COD)] (0.2g, 0.54 mmol), dppp (0.22g, 0.54 mmol), acetoacetanilide (0.09g, 0.54 mmol) and silver(I) oxide (0.6g, excess) in dichloromethane as a white-grey microcrystalline solid (0.28g, 66%).

(Found: C, 49.9: H, 4.10; N, 1.28. C₃₇H₃₅NO₂P₂Pt.2CH₂Cl₂ requires C, 49.3; H, 4.13; N, 1.47%), m.p. 133-5°C.

 v_{max} at 1710s (v_{CO}), 1635vs,br (v_{CO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), AB spin system, δ -6.9 [dd, P_{trans N}, ¹J(PtP) 3347], and δ -2.3 p.p.m. [dd, P_{trans C}, ¹J(PtP) 2339, ²J(PP) 27]. ¹³C-{¹H} (75.47 MHz), δ 25.0-28.0 [m, CH₂, dppp], 28.5 [s, CH₃], 51.0 [m, Pt-CH], 124.0-135.0 [m, Ph], 174.0 [m, C(O)NPh], and δ 205.0 p.p.m. [m, C(O)CH₃]. ¹H (300.13 MHz), δ 1.20-1.60 [m, 4H, CH₂ dppp], 2.00 [s, 3H, Me], 2.20-2.55 [m, 2H, CH₂, dppp], 2.65 [dd, 1H, Pt-CH, ³J(PH)_{trans} 7.7, ³J(PH)_{cis} 3.5, ²J(PtH) obscured by dppp], 5.30 [s, 2H, CH₂Cl₂], and δ 6.60-7.80 p.p.m. [m, 25H, Ph]. Mass spectrum (FAB), [M]⁺ 783.

(v) [Pt{CH(COCH₃)C(O)N(C₆H₄OMe-4)}(dppp)] (132)

From [PtCl₂(COD)] (0.2g, 0.54 mmol), dppp (0.22g, 0.54 mmol), 4-acetoacetanisidide (0.11g, 0.54 mmol) and silver(I) oxide (0.6g, excess) in dichloromethane afforded (132) as a white microcrystalline solid (0.31g, 70%).

(Found: C, 51.9; H, 4.26; N, 1.84. C₃₈H₃₇NO₃P₂Pt.CH₂Cl₂ requires C, 52.2; H, 4.38; N, 1.56%), m.p. 140-2°C.

 v_{max} at 1610m,sh (v_{CO}) and 1590vs,br (v_{CO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), AB spin system, δ -6.9 [dd, P_{trans N}, ¹J(PtP) 3291], δ -2.3 p.p.m. [dd, P_{trans C}, ¹J(PtP) 2349, ²J(PP) 27].

 $^{195}\text{Pt-}\{^1\text{H}\},\,\delta$ -4536 p.p.m. [dd, $^1\text{J}(\text{PtP})$ 3275, 2335].

¹³C-{¹H} (75.47 MHz), δ 19.5 [s, CH₂, dppp], 26.0-28.0 [m, <u>C</u>H₂, dppp], 29.0 [s, <u>C</u>H₃], 51.0 [m, Pt-<u>C</u>H], 55.5 [s, O<u>C</u>H₃, 126.0-135.0 [m, Ph], 175.0 [m, <u>C</u>(O)NC₆H₄OMe-4], and δ 205.0 p.p.m. [m, <u>C</u>(O)CH₃].

¹H (300.13 MHz), δ 1.20-1.60 [m, 4H, C<u>H</u>₂, dppp], 2.00 [s, 3H, Me], 2.20-2.55 [m, 2H, C<u>H</u>₂, dppp], 2.62 [dd, 1H, Pt-C<u>H</u>, ³J(PH)_{trans} 7.9, ³J(PH)_{cis} 3.1, ²J(PtH) obscured by dppp], 3.60 [s, 3H, OC<u>H</u>₃], 5.30 [s, 2H, CH₂Cl₂], 6.20 [d, 2H, ¹J_{a'b'} 8.8], 6.45 [d, 2H, ¹J_{a'b'} 8.8] and δ 7.10-7.80 p.p.m. [m, 20H, Ph].

Mass spectrum (FAB), [M]⁺ 813.

(vi) [Pt{CH(COCH₃)C(0)N(C₆H₄OMe-2)}(dppp)] (133)

From $[PtCl_2(COD)]$ (0.2g, 0.54 mmol, dppp (0.22g, 0.54 mmol), 2-acetoacetanisidide (0.11g, 0.54 mmol) and silver(I) oxide (0.6g, excess) in dichloromethane afforded (133) as a grey-white microcrystalline solid (0.25g, 58%). (Found: C, 54.2; H, 4.68; N, 1.41. $C_{38}H_{37}NO_3P_2Pt.0.5CH_2Cl_2$ requires C, 54.1; H, 4.48;

N, 1.64%), m.p. 148-50°C(decomp.).

 v_{max} at 1635vs,br (v_{CO}), 1595vs (v_{CO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 36.2 MHz), AB spin system, δ -7.2 [dd, P_{trans N}, ¹J(PtP) 3321], δ -2.9 p.p.m. [dd, P_{trans C}, ¹J(PtP) 2354, ²J(PP) 27].

¹³C-{¹H} 75.47 MHz), δ 19.5 [s, <u>C</u>H₂, dppp], 26.0-27.5 [m, <u>C</u>H₂, dppp], 28.5 [s, <u>C</u>H₃], 51.0 [m, Pt-<u>C</u>H], 55.0 [s, O<u>C</u>H₃] and 128.0-134.0 p.p.m. [m, Ph], carbonyl resonances not observed.

¹H (300.13 MHz), δ 1.20-2.30 [m.br, dppp], 2.40 [s, 3H, CH₃], 3.40 [s, 3H, OCH₃, 5.30 [s, 2H, CH₂Cl₂] and 6.40-7.80 p.p.m. [m,br, 24H, Ph+ring], resonance for Pt-C<u>H</u> not observed due to broad C<u>H₂</u> resonances of dppp moiety).

Mass spectrum (FAB), [M]⁺813.

5.10.7 Preparation of [Pt(CHRCOCHR)L₂] (R=CO₂Me, CO₂Et; L=dppp, dppb)

(i) <u>**R=CO₂Me, L=dppp (134)</u>**</u>

To a solution of $[PtCl_2(COD)]$ (0.2g, 0.54 mmol) in dichloromethane (25 cm³) was added in succession dppp (0.22g, 0.54 mmol), 1,3-dimethylacetonedicarboxylate (0.25g, 0.2 cm³, 1.45 mmol) and silver(I) oxide (0.7g, excess), and the mixture was refluxed for 5h. Filtration to remove silver salts afforded a pale yellow solution which was evaporated to dryness under reduced pressure to afford a pale yellow oil. The dissolution of this oil in dichloromethane (5 cm³) followed by the addition of light petroleum gave a white solid which was removed by filtration and dried *in vacuo* to afford the title complex (0.29g, 68%).

(Found: C, 50.7; H, 4.38. $C_{34}H_{34}O_5P_2Pt.0.5CH_2Cl_2$ requires C, 50.4; H, 4.29%), m.p. 128-30°C(decomp.).

 v_{max} at 1710vs (v_{CO}), 1695vs (v_{CO}), 1625vs (v_{CO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (36.2 MHz), Isomer A, δ -3.70 p.p.m. [s, ¹J(PtP) 2848]; Isomer B, δ -4.37 p.p.m. [s, ¹J(PtP) 2838].

¹H (300.13 MHz), δ 1.80-2.50 [m, CH₂, dppp], 2.90 [s, 6H, Me], 3.95 [d, second order, 2H, CH]²J(PH)_{trans}+ ³J(PH)_{cis}| 5.3, ²J(PtH) 52.5], 5.30 [s, 2H, CH₂Cl₂], and δ 7.20-7.80 p.p.m. [m, 20H, Ph].

¹⁹⁵Pt-{¹H} (64.52 MHz), Isomer A, δ -4884.6 p.p.m. [t, ¹J(PtP) 2848]; Isomer B, δ -4935.1 p.p.m. [t, ¹J(PtP) 2838].

Mass spectrum (FAB), [M]⁺ 780.

(ii) <u>R=CO₂Et, L=dppp (135)</u>

Similarly from $[PtCl_2(COD)]$ (0.2g, 0.54 mmol), dppp (0.22g, 0.54 mmol), 1,3-diethylacetonedicarboxylate (0.27g, 0.21 cm³, 1.45 mmol) and silver(I) oxide (0.7g, excess) afforded (135) as an off-white microcrystalline solid (0.28g, 62%).

(Found: C, 52.6; H, 4.74. $C_{36}H_{38}O_5P_2Pt.0.25CH_2Cl_2$ requires C, 52.5; H, 4.68%), m.p. 140-2°C(decomp.).

 v_{max} at 1710vs (v_{CO}), 1685vs (v_{CO}), 1625vs (v_{CO}), 1410s (v_{PPh}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (36.2 MHz), Isomer A, δ -3.30 p.p.m. [s, ¹J(PtP) 2829]; Isomer B, δ -4.17 p.p.m. [s, ¹J(PtP) 2817].

¹H (300.13 MHz), δ 1.0 [t, 6H, CH₂CH₃, ³J(HH) 7.1], 1.80-2.50 [m, CH₂, dppp], 3.0 [q, 4H, CH₂CH₃, ³J(HH) 7.1], 4.0 [d, second order, 2H, CH₁²J(PH)_{trans}+³J(PH)_{cis}] 5.4, ²J(PtH) 53.0], 5.30 [s, 2H, CH₂Cl₂], δ 7.20-7.80 p.p.m. [m, 20H, Ph]. Mass spectrum (FAB), [M]⁺ 808.

(iii) <u>R=CO₂Me, L=dppb (136)</u>

From [PtCl₂(COD)] (0.2g, 0.54 mmol), dppb (0.23g, 0.54 mmol), 1,3-dimethylacetonedicarboxylate (0.25g, 0.2 cm³, 1.45 mmol) and silver(I) oxide (0.6g, excess) in dichloromethane afforded (136) as a grey solid (0.23g, 53%). (Found: C, 51.8; H, 4.21. $C_{35}H_{36}O_5P_2Pt.0.5CH_2Cl_2$ requires C, 51.5; H, 4.46%), m.p. 240-2°C(decomp.).
υ_{max} at 1715vs (υ_{CO}), 1690vs (υ_{CO}), 1630vs (υ_{CO}) cm⁻¹ (KBr). N.m.r. ³¹P-{¹H} (36.2 MHz), δ 11.6 p.p.m. [s, ¹J(PtP) 2939]. ¹H (300.13 MHz), δ 1.5-1.65 [m, 2H, C<u>H</u>₂, dppb], 1.80-2.0 [m, 2H, C<u>H</u>₂, dppb], 2.40-2.65 [m, 4H, C<u>H</u>₂, dppb], 3.00 [s, 6H, Me], 3.75 [d, 2H, C<u>H</u>]²J(PH)_{trans}+³J(PH)_{cis}] 5.1, ²J(PtH) 53.1], 5.30 [s, 2H, CH₂Cl₂], δ 7.35-7.75 p.p.m. [m, 20H, Ph]. Mass spectrum (FAB), [M]⁺ 794.

(iv) <u>R=CO₂Et, L=dppb (137)</u>

From [PtCl₂(COD)] (0.2g, 0.54 mmol), dppb (0.23g, 0.54 mmol), 1,3-diethylacetonedicarboxylate (0.27g, 0.21 cm³, 1.45 mmol) and silver(I) oxide (0.6g, excess) afforded (137) as a fluffy white solid (0.32g, 72%).

(Found: C, 52.7; H, 4.83. C₃₇H₄₀O₅P₂Pt.0.5CH₂Cl₂ requires C, 52.2; H, 4.78%), m.p. 135-7°C(decomp.).

 v_{max} at 1675vs (v_{CO}), 1635vs (v_{CO}), 1575vs (v_{CO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (36.2 MHz), δ 11.7 p.p.m. [s, ¹J(PtP) 2930].

¹H (300.13 MHz), δ 1.0 [t, 6H, CH₂CH₃, ³J(HH) 7.1], 1.45-1.65 [m, 2H, CH₂, dppb], 1.75-2.05 [m, 2H, CH₂, dppb], 2.35-2.65 [m, 4H, CH₂, dppb], 3.20 [q, 4H, CH₂CH₃, ³J(HH) 7.1], 3.75 [d, 2H, CH²J(PH)_{trans}+³J(PH)_{cis}] 5.2, ²J(PtH) 53.0], 5.30 [s, 2H, CH₂Cl₂], δ 7.30-7.70 p.p.m. [m, 20H, Ph].

Mass spectrum (FAB), [M]⁺ 822.

5.10.8 Miscellaneous reactions of complex (123)

(i) With SnCl₂

Anhydrous stannous chloride (0.08g, 0.42 mmol) was added to a solution of $[PtCl_2{(Ph_2PNPh)_2P(O)Ph}]$ (0.2g, 0.21 mmol) (123) in dichloromethane (25 cm³). The mixture was stirred for 6h under a dry nitrogen atmosphere, then filtered to remove insoluble solids and the solvent reduced before addition of light petroleum to afford an orange solid (0.14g).

N.m.r. ³¹P-{¹H} (CH₂Cl₂, 121.5 MHz), Complex 1, δ 30.3 [t, P_X, ²J(P_AP_X) 18.2], δ 44.3

p.p.m. [d, P_A , ¹J(PtP_A) 3825, ²J(P_XP_A) 18.2]; Complex 2, δ 30.7 [dd, P_X , ²J(P_BP_X) 17.0, ²J(P_AP_X) 22.8], 44.2 [m, P_B , obscured by complex 1], δ 54.2 p.p.m. [dd, P_A , ¹J(PtP_A) 3154, ²J(P_XP_A) 22.7, ²J(P_BP_A) 16.5]. ¹⁹⁵Pt-{¹H} (64.52 MHz), Complex 2, δ -4572.5 p.p.m. [ddd, ¹J(PtP_B) 3781, ¹J(PtP_A) 3154, ³J(PtP_X) 66]; Complex 1, δ -4327 p.p.m. [td, ¹J(PtP_A) 3825, ²J(PtP_X) 67].

Mass spectrum (FAB), Complex 1, [M-Cl]⁺ 907, [M-2Cl]⁺ 871; Complex 2, [M-SnCl₃]⁺ 907.

(ii) With BuNC

The addition of a molar equivalent of 'BuNC to a solution of (123) (0.2g, 0.21 mmol) in dichloromethane (20 cm³) with stirring indicated only the presence of unreacted starting material in the ³¹P-{¹H} n.m.r. spectrum of the reaction mixture after 3h.

(iii) With 4-acetoacetanisidide/ Ag2O

Reflux of complex (123) (0.2g, 0.21 mmol) with 4-acetoacetanisidide and excess silver(I) oxide afforded only unreacted starting material after 5h as indicated by a $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the resulting mixture.

(iv) With various silver(I) salts

The reaction of complex (123) in refluxing dichloromethane with a molar equivalent of Ag_2CO_3 , or a two molar equivalent of $AgOSO_2CF_3$ afforded mixtures exhibiting numerous resonances in their ³¹P-{¹H} n.m.r. spectra.

(v) With 2-acetamidoacrylic acid(1 mole equivalent)/ Ag₂O

To a solution of complex (123) (0.2g, 0.21 mmol) was added in succession 2-acetamidoacrylic acid (0.3g, 0.21 mmol) and silver(I) oxide (0.6g, excess) and the resulting mixture refluxed for 6h in dichloromethane (25 cm³). Filtration to remove deposited silver salts afforded an orange solution which was evaporated to dryness under

reduced pressure to afford an orange oil. Dissolution of this oil in dichloromethane (5 cm³) followed by the addition of light petroleum afforded a pale brown solid which was removed by filtration, dried *in vacuo* and identified as $[Pt{(CH=C(NHCOMe)COO)}{(Ph_2PNPh)_2P(O)Ph}]$ (138), (0.12g, 55%).

(Found: C, 50.2; H, 3.86; N, 3.48. $C_{47}H_{40}N_3O_4P_3Pt.2CH_2Cl_2$ requires C, 50.4; H, 3.79; N, 3.60%), m.p. 185°C.

 v_{max} at 3330s (v_{NH}), 1685m (v_{N-CO}), 1600s (v_{COO}) cm⁻¹ (KBr).

N.m.r. ³¹P-{¹H} (121.5 MHz), δ 28.8 [dd, P_X, ²J(P_BP_X) 25.8, ²J(P_AP_X) 19], 49.2 [dd, P_{A(trans O)}, ¹J(PtP_A) 4265, ²J(P_XP_A) 19, ²J(P_BP_A) 25.5] δ 69.2 p.p.m. [vt, P_{B(trans C)}, ¹J(PtP_B) 2091, ²J(P_XP_B) 26, ²J(P_BP_A) not discernable].

Mass spectrum (FAB), [M]⁺ 999.

(vi) With 2-acetamidoacrylic acid(4 mole equivalent)/ Ag₂O

Similarly reaction of complex (123) (0.2g, 0.21 mmol), 2-acetamidoacrylic acid (0.11g, 0.84 mmol) and silver (I) oxide (0.6g, excess) was carried out but a $^{31}P-{^{1}H}$ n.m.r. spectrum of the resulting mixture indicated the presence of the previous product (138) by comparison of the data.

(vii) With other silver(I) salts

The reaction of complex (123) (0.2g, 0.21 mmol) with two molar equivalents of AgOCOCH₃ and AgOCN in refluxing dichloromethane (30 cm³) led only to unreacted starting material as indicated by ${}^{31}P$ -{ ${}^{1}H$ } n.m.r. spectra of the mixtures.

(ix) With AgOCOCF3

AgOCOCF₃ (0.09g, 0.42 mmol) was added to a stirred solution of (123) (0.2g, 0.21 mmol) in dichloromethane (25 cm³). After refluxing for 8h the mixture was filtered to remove deposited silver salts and light petroleum added slowly to afford the product $[Pt(OCOCF_3)_2\{(Ph_2PNPh)_2P(O)Ph\}]$ (139) as a grey solid (0.15g, 64%).

(Found: C, 46.2; H, 3.29; N, 1.70. C₄₆H₃₅F₆N₂O₅P₃Pt.1.5CH₂Cl₂ requires C, 46.5; H,

3.13; N, 2.29%), m.p. 200-2°C(decomp.).
υ_{max} at 1675s (υ_{CO}), 1450s (υ_{P.Ph}), 1230s (υ_{P=O}), 850s (υ_{C-F}) cm⁻¹ (KBr).
N.m.r. ³¹P-{¹H} (36.2 MHz), δ 28.6 [t, P_X, ²J(P_AP_X) 17.0], δ 37.0 p.p.m. [d, P_A, ¹J(PtP_A)
4033, ²J(P_XP_A) 17.0].
Mass spectrum (FAB), [M-2OCOCF₃]⁺ 870.

(ix) With 1,3-dimethylacetonedicarboxylate/ Ag₂O

Dimethyl 1,3-acetonedicarboxylate (0.04g, 0.21 mmol) was added to a solution of complex (123) (0.2g, 0.21 mmol) in dichloromethane with silver(I) oxide (0.6g, excess) and the mixture heated to reflux for 5h. After flitration and removal of the solvent *in vacuo*, a ^{31}P -{ ^{1}H } n.m.r. spectrum indicated the presence of numerous species Mass spectrum (FAB), [M]⁺ 1044.

(x) With diglycolic acid/ Ag₂O

Similarly, diglycolic acid (0.03g, 0.21 mmol), (123) (0.2g, 0.21 mmol) and silver(I) oxide in dichloromethane afforded after work-up as above unreacted starting material as indicated by a ${}^{31}P$ -{ $}^{1}H$ } n.m.r. spectrum of the reaction mixture. Mass spectrum (FAB), [M]⁺ 1037, 1004.

5.10.9 Reactions of {Ph2PNPh}2SO2 (45)

(i) With [PtCl2(COD)]

A solution of $\{Ph_2PNPh\}_2SO_2$ (0.22g, 0.36 mmol) in dichloromethane (10 cm³) was added with stirring to one of $[PtCl_2(COD)]$ (0.2g, 0.54 mmol). The pale yellow solution darkened slightly and was stirred for 3h whereupon removal of solvent and the addition of light petroleum afforded a white solid (0.21g).

N.m.r. ${}^{31}P-{}^{1}H$ (36.2 MHz), δ 53.8 p.p.m. [s, ${}^{1}J(PtP)$ 4018] plus numerous other unassigned resonances.

¹⁹⁵Pt-{¹H} (64.5 MHz), δ -4550 p.p.m. [d, ¹J(PtP) 3695].

(ii) With [Mo(CO)4pip2]

A solution of (45) (0.36g, 0.53 mmol) in dichloromethane (25 cm³) was added to one of [Mo(CO)₄pip₂]. After heating to reflux for 3h, and reduction of the solvent volume a ³¹P-{¹H} n.m.r. spectrum on the reaction residue.

N.m.r. ${}^{31}P{-}{^{1}H}$ (36.2 MHz), δ 100.3 p.p.m. [s, Mo complex] plus numerous other unassigned resonances.

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