STRUCTURAL AND SPECTRAL INVESTIGATION
OF PLATINUM-GROUP METAL COMPLEXES
CONTAINING WEAKLY BONDED LIGANDS

by

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ABSTRACT

This thesis describes the synthesis and characterisation of platinum-group metal complexes which model species believed to function as reaction intermediates or transition states. Thus, several complexes of the type $[ML_3S]^{n+}$ and $[RhL_5S]^{n+}$ (M = Rh, Pd, Pt or Ni, S = either a vacant site or a coordinated solvent molecule, n = 0 or 1) have been synthesised and characterised by spectroscopy and, where appropriate, by X-ray analysis.

The evidence for the existence of isolated three-coordinate complexes of d^8 transition metal ions is critically reviewed, and is related to experimental work on complexes of the type *trans*-$[Rh(CO)(PPh_3)_2S]^{n+}$ and $[Rh(PPh_3)_3S]^{n+}$. The crystal structures of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][ClO_4].CH_2Cl_2$ and *trans*-$[Rh(CO)(PPh_3)_2(OCMe_2)][ClO_4].OCMe_2$ are described. It is concluded that the evidence for the existence of three-coordinate d^8 metal complexes is less convincing than had previously been thought: the reported evidence of characterisation often does not exclude agostic interactions or expansion of the metal coordination polyhedron by addition of a solvent molecule or by dimer formation.

The synthesis of a related series of compounds, $[PdR(PPh_3)_2S]^{n+}$ (R = *o*-tolyl or mesityl) was undertaken but their instability precluded full characterisation. The crystal structure of *trans*-[PdBr(*o*-tolyl)$(PPh_3)_2$] is reported.

The terdentate ligands $[\textit{meta}\text{-}(PCy_2CH_2)_2(C_6H_3)]^-$ and $PhP(C_2H_4PCy_2)_2$ (PCP and PPP) have been prepared and used to obtain metal complexes. These ligands were designed to stabilise coordinatively-unsaturated species. Two series of complexes [MX(PCP)] (M = Pd, X = Cl, Br; M = Ni, X = Br) and $[RhCl_2(PCP)S]$ (S = OH_2, HOMe or HOEt) were prepared and all their crystal structures determined. Other complexes of PCP, and its protonated form PCHP, were also synthesised and characterised by spectroscopy and the relationships of these complexes to each other are discussed.

PCP has been shown to be at least partially successful in its designated role as a stabiliser of coordinatively-unsaturated species. It does prevent larger ligands (acetone and propan-2-ol) from binding to $[RhCl_2(PCP)]$ but a degree of conformational flexibility in the Rh(PCP) skeleton permits smaller ligands to bond to the metal centre. This conformational flexibility is largely due to the ability of the mutually *trans* PCy_2R groups of PCP to twist, in opposite directions, about the P-M-P axis. The range of ligand conformations found is discussed.

Also discussed are the factors influencing the M-S bond length. The lack of structural data on rhodium-alcohol complexes allows little to be said about them. A survey of structurally characterised rhodium-aqua complexes suggests that the most significant factor effecting the Rh-S bond length is *trans*-influence. Rh-OH_2 bond distances are found to show large variations which depend on the nature of the *trans* ligand but are

insensitive to other factors, such as steric effects or the charge on the complex.

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: EXPERIMENTAL

CHAPTER THREE: RESULTS AND DISCUSSION

ABBREVIATIONS

br	broad
BTFBD	bis(trifluoromethyl)bicyclodec-7-enediyl
Bu	butyl
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	doublet
dec.	decomposed
dmso	dimethylsulphoxide
dppe	bis(1,2-diphenylphosphino)ethane
dppp	bis(1,3-diphenylphosphino)propane
Et	ethyl
i	*iso*
L	ligand (general)
m	multiplet (n.m.r.)
m	medium (I.R.)
m	*meta*
M	metal
Me	methyl
MOXB	C,C'-tetrakis(methoxycarbonyl)butadiene
M.P.	melting point
NN	N,N'-dicyclohexyl-1,4-diazabuta-1,3-diene
NTHA	O,O'-nitroso-*p*-tolylhydroxylamido

o	*ortho*
OQ	N,O-8-oxyquinolato
p	*para*
Ph	phenyl
Pr	propyl
QCOX	N,O-quinolinecarboxylato
R	alkyl or aryl group
s	singlet (n.m.r.)
s	strong (I.R.)
S	solvent
sh	sharp
SNS	S,N,S-pentaoxaazadithiabicycloheptacosatriene
t	triplet
TACN	1,4,7-triazacyclononane
TTFB	tetrakis(trifluoromethyl)(C,C'-butadiene)
w	weak
X	anion
Y	ligand (general)

1, 1a INTRODUCTION.

Of the many areas of research which constitute organo-transition-metal chemistry one of the most important is that concerned with catalysis by organometallic intermediates. The realisation of the potential relevance of organometallic chemistry to large-scale, industrial, catalytic processes has fuelled the development of mechanistic studies of known systems.[1] The wider aims of these studies include the evolution of modified catalysts for desired reactions and the discovery of new organometallic catalysts which can be used in the synthesis of materials currently unobtainable by such routes. These aims are applicable to the work presented here which was undertaken with the objective of increasing understanding of the mechanisms of organometallic reactions through the synthesis and characterisation of compounds which could act as models for species which are currently believed to be intermediates or transition states in these reactions.

Examples of economically important catalytic reactions include Ziegler-Natta[2] polymerisation, in which polyolefins are produced from ethene or propene in a low-pressure process employing mixed-metal catalysts, and alkene metathesis which utilises a wide variety of Mo- and W-based catalysts. Both of these systems have generated much research.[3] As has been pointed out,[4] ideal catalysts are compounds in which changes in the coordination number of the metal can occur readily. The late transition metals, Ru, Co, Rh, Ir, Ni, Pd and Pt, are notable for their readiness to exist in coordinatively unsaturated states and thus most important homogeneous catalysts are complexes of these metals. It is appropriate here to declare an allegiance and the remainder of this work will deal largely with complexes of Rh, Pd and, to a lesser extent, Pt. Examples of complexes of these metals in catalysis are alkene hydrogenation by $[RhCl(PPh_3)_3]$ (Wilkinson's Catalyst),[5] alkene oxidation by $PdCl_2$ (the Wacker process)[6] and alkene hydroformylation by $[RhH(CO)(PPh_3)_3]$.[7] This last example is especially important since hydroformylation of olefins, the formal addition of H and HCO across a double bond, is the largest-scale industrial process to use homogeneous catalysts. The use of $[RhH(CO)(PPh_3)_3]$ in this process, known as the Union Carbide hydroformylation process, is a recent development, partially replacing the previously used OXO process which utilised $[HCo(CO)_4]$.[3]

The proposed mechanism of the Union Carbide hydroformylation process,[4, 7] will be discussed in order to illustrate how a series of simple organometallic reactions link together to form a catalytic cycle (Fig. 1, 1i).

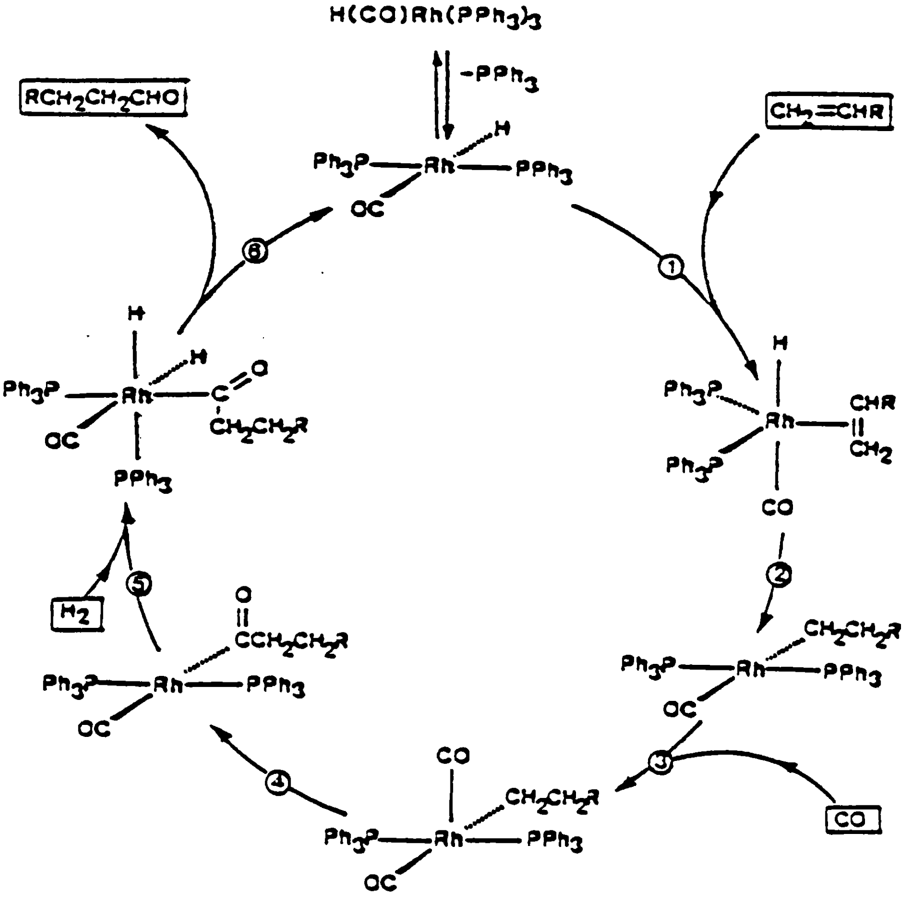


Fig. 1,1i The Union Carbide hydroformylation cycle (from Ref. 4).

It should be noted, however, that the actual conformations of the intermediates are not unambiguously known. The initial step is dissociation of PPh_3 from $[RhH(CO)(PPh_3)_3]$ to form the catalytically active species $[RhH(CO)(PPh_3)_2]$. Thus, strictly, $[RhH(CO)(PPh_3)_3]$ is not a catalyst but a precatalyst. Next (1) alkene adds to the four-coordinate species to give $[RhH(CO)(PPh_3)_2(\eta^2\text{-}C_2H_3R)]$ followed by alkene insertion into the Rh-H bond (2) to give $[Rh(CO)(PPh_3)_2(CH_2CH_2R)]$. Addition of a carbonyl ligand (3) and its subsequent migration (4) gives $[Rh(CO)(PPh_3)_2(COCH_2CH_2R)]$. Finally (5) oxidative addition of H_2 gives a dihydride species that reductively eliminates (6) the product aldehyde, RCH_2CH_2CHO, and leaves $[RhH(CO)(PPh_3)_2]$ to repeat the cycle. Thus a homogeneous catalyst operates by opening a lower activation energy pathway, which proceeds via stepwise reactions, to accelerate the rate of a thermodynamically feasible reaction. If alternative reaction paths exist a catalyst can enhance product selectivity by favouring just one of these routes. The low-energy nature of each step in a catalytic cycle is rationalised by the 16 and 18-electron rule.[8]

1, 1b THE 16 AND 18-ELECTRON RULE.

The 16 and 18-electron rule is a refinement of the 18-electron rule. The 18-electron rule is based on the observation that many transition metal complexes have valence shells which contain 18 electrons (a noble gas configuration). This has led to the view that transition metal complexes are most stable when all the valence orbitals of the transition metal atom are full as the five nd, the $(n + 1)s$ and the three $(n + 1)p$ orbitals can contain a maximum of 18 electrons. However, though most transition metal organometallics do indeed have 18 valence electrons several well-known groups of compounds contain metal atoms with fewer than 18 electrons. The most important of these exceptions to the 18-electron rule, as far as this work is concerned, are the square-planar d^8-

complexes which have 16 valence electrons. (Square-planar coordination is the most common state of complexes of Pd(II), Pt(II) and Rh(I)).[9] This observation is explained by the large energy differences between the *nd* and the $(n + 1)p$ orbitals of the late transition metals. This decreases the tendency of the metals to contain 18 valence electrons. An example of this is the empty $6p_z$ orbital of Pt(II) complexes. This trend continues so that complexes of later transition elements, such as [AuCl(PPh$_3$)], form stable 14-electron species. The d^6 ions of the platinum group metals (Pd(IV), Pt(IV) and Rh(III)) however, commonly form octahedral, 18-electron complexes.[9] The realisation that complexes of these metals are on the energy borderline between stable 18-electron and 16-electron molecules led to the proposal that organometallic reaction sequences proceed by elementary steps which involve intermediates having 16 or 18 valence electrons.[8] This proposal is one of the basic tenets of the 16 and 18-electron rule. Although not universally accepted[10] this rule has been widely applied and it is generally agreed that any proposed system that breaks the rule bears the burden of proof.

1, 1c SIMPLE SUBSTITUTION MECHANISMS.

The utility of the 16 and 18-electron rule can be illustrated by some simple examples. Ligand substitution reactions can be either associative, at one extreme, or dissociative at the other. If a coordinatively saturated, octahedral Rh(III) complex of type [RhX_3L_3] were to undergo ligand substitution by an associative mechanism then the intermediate [RhX_3L_3L'] would be a 20 electron species. These extra electrons would have to be accommodated in a high-energy metal atomic-orbital or in an antibonding molecular orbital and this is unfavourable. The preferred, low energy pathway would involve dissociation to form the coordinatively unsaturated 16-electron [RhX_3L_2]. This species will readily bind to other potential ligands. Although this scheme was originally proposed for reactions of Co(III) there is evidence to suggest that reactions of Rh(III) behave similarly.[8, 11] It can also be argued that a 16-electron d^8 metal complex of the type [MXL_3] will favour an associative route that involves an 18-electron [MXL_3L'] intermediate. Indeed, it is found that the vast majority of square-planar complexes do react via associative pathways.[12] It should not be overlooked that steric factors also favour association in square-planar complexes and dissociation in octahedral complexes.

The mechanisms outlined above are of the most general type. Actual reaction mechanisms are much more varied and complex, even for such an apparently simple procedure as replacing one ligand with another. To refine the given mechanisms only slightly it should be realised that as most organo-transition-metal reactions take place in solution, the most likely incoming ligand is a solvent molecule. Thus, in the case of an octahedral complex that has undergone dissociation to give coordinatively-unsaturated [MX_3L_2] the most likely next step is the binding of a solvent molecule S to give [MX_3L_2S]. To give the final product the solvent molecule must dissociate again to give the five-coordinate intermediate and allow attack by an incoming ligand.

The associative pathway similarly has a solvation route that competes with the desired reaction. The initial, associative, replacement of a ligand with a solvent molecule gives [ML_3S]. This solvated species must undergo a further, associative, replacement of S with the incoming, new ligand to give [ML_3Y].

Solvated complexes of the type [ML_3S] and [ML_5S] are therefore of interest for two related reasons: their reactive nature and their putative role as reactive intermediates in many reactions.

Although it is widely accepted that most square-planar d^8 complexes react by associative mechanisms there is a growing body of evidence that dissociative mechanisms, involving 3-coordinate 14-electron intermediates, operate in a number of systems.[13] Ligand exchange reactions for which there is strong evidence for a dissociative mechanism include the loss of SMe_2 or dmso from *cis*-[$PtR_2(SMe_2)_2$] or *cis*-[$PtR_2(dmso)_2$] (R = Me or Ph) prior to ligand replacement.[14, 15] Another recent example where ligand replacement possibly involves dissociative activation is provided by the anti-cancer drug *iproplatin*, *cis*-[$Pt(OH_2)_2(NH_2Pr^i)_2$]$^{2+}$.[16] It has also been suggested that some β-eliminations,[17] reductive eliminations[18] and carbonyl migratory insertions[19] of square-planar molecules proceed by 3-coordinate intermediates, but possibly the best documented dissociative reaction is the isomerisation of *cis*-[PtRX(PR'$_3$)$_2$] (X = halide) to the *trans*-form.[13]

1, 1d ISOMERISATION OF SQUARE-PLANAR SPECIES VIA A DISSOCIATIVE MECHANISM.

As early as 1961 the uncatalysed isomerisation of *cis*-[PtCl(*o*-tolyl)(PEt$_3$)$_2$] to its *trans*-form was found to be a first order reaction that was not accelerated by free PEt$_3$.[20] Later studies by Romeo and co-workers[13, 21, 22] established that this isomerisation reaction had a positive value of $\Delta S^{\ddagger}$ and showed rate retardation by excess [Cl$^-$]. The dissociative pathway of Figure 1, 1ii,

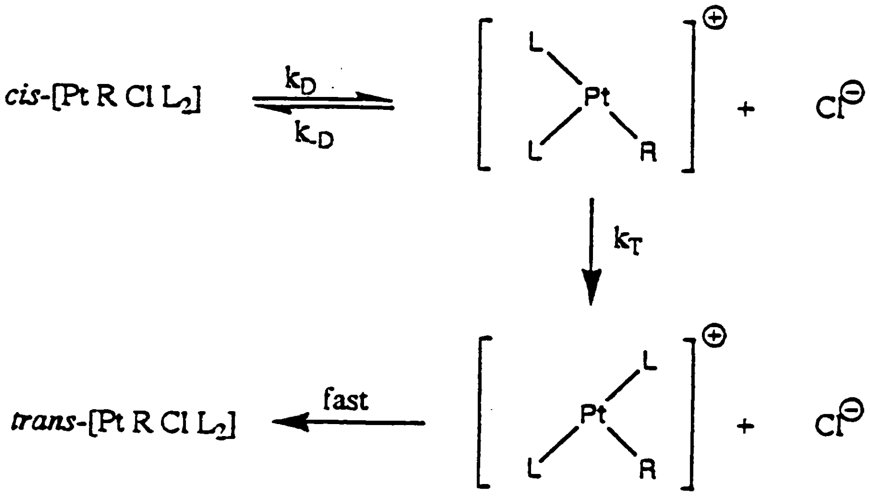


Fig. 1,1ii Romeo's proposed mechanism.

involving two T-shaped intermediates with different geometries, was proposed to account for these data. Similar studies on many related compounds fitted the same interpretation and came to the additional conclusion that very bulky R groups, such as mesityl, favoured dissociative reactions over associative reactions.[13]

There has been controversy over this reaction scheme. The major objection, based on experimental data and not merely on the breaking of the 16 and 18-electron rule, came from van Eldik *et al.*[23] who found a negative value for the volume of activation for the solvolysis of *cis*-$[Pt(PEt_3)_2(mesityl)Br]$. This would indicate an associative process for a reaction which Romeo and his co-workers had previously assigned to be dissociative. It can thus be seen that even in the case of the uncatalysed isomerisation of *cis*-$[Pt(PEt_3)_2(mesityl)Br]$ to its *trans*-form, which is one of the better characterised of the possible dissociative routes, there is some doubt as to the actual mechanism. This is due largely to the many different interpretations which can be made from the same kinetic data.

It should be noted that the reaction mechanism of Fig. 1, 1ii is a simplification. The isomerisations occur only in polar solvents (it is thought that these aid the dissociation of the M-Cl bond) and as such the most likely fate of a three coordinate species $[ML_2R]^+$ is solvation. It has been shown that the isomerisation of *cis*-$[Pt(PEt_3)_2(Me)(HOMe)]^+$ in diethyl ether/methanol is retarded by high concentrations of methanol, suggesting that a similar dissociative mechanism operates here.[13]

1, 1e THE NATURE OF A THREE COORDINATE INTERMEDIATE.

The rate law derived by Romeo and coworkers[13] for the uncatalysed isomerization of *cis*-$[Pd(PEt_3)_2RCl]$ to its *trans*-form (see Fig. 1, 1ii) is

$$k_I = \frac{k_D}{1 + \frac{k_{-D}}{k_T}[Cl^-]}$$

It was argued that this holds only if the 3-coordinate intermediate has T-shaped, as opposed to planar-trigonal, geometry. The rate of the isomerisation would not be retarded by high chloride ion concentrations if a symmetrical planar-trigonal species was the intermediate, as such a symmetrical intermediate would have the ability to recombine with the chloride ion to form either the *cis* or *trans* products. A T-shaped intermediate, however, has to first isomerise to a second T-shaped intermediate (with mutually *trans* phosphines) before addition of a chloride ion would produce a *trans* product. The operation of a dynamic isomerisation between T-shaped intermediates has been observed by variable temperature n.m.r. spectroscopy of $[Rh(PPh_3)_3][HC(SO_2CF_3)_2]$[24] and is supported by extended Hückel calculations.[25]

It appears that T-shaped geometry is favoured over trigonal-planarity because of the preference of those low-valent phosphine complexes for diamagnetism. A perfectly trigonal-planar complex would have *d* orbital energies split

$$d_{xz}, d_{yz} < d_{z^2} < d_{xy}, d_{x^2-y^2}.$$

A d^8 complex would thus be paramagnetic. A distortion to T-shaped geometry would split the d_{xy} and $d_{x^2-y^2}$ orbital energies and allow such d^8 complexes to be diamagnetic.[26]

A number of 3-coordinate d^8 transition metal complexes have been described as isolated complexes. However, no attempt has previously been made to review these species or to critically examine the evidence presented in support of their sterically unsaturated nature. An integral part of this work is thus the following discussion of the natures of these previously reported complexes. It should be noted that many of the doubts raised as to the true nature of these complexes are the result of experience in handling similar complexes and, perhaps more importantly, the result of drawing together all the literature available on this topic. Most of the papers discussed stand up to individual scrutiny but taken as a group inconsistencies appear.

Table 1, 1i shows the ten d^8 Rh, Pd and Pt species for which evidence of three coordination has been presented. Of these, compound 10, mentioned in Jardine's review of Wilkinson's catalyst,[35] is apparently a

TABLE 1, 1i

REPORTED d^8 METAL COMPLEXES THAT ARE THREE COORDINATE.

No.	COMPLEX	Ref.	CHARACTERISATION BY	AGAINST
1	$[Rh(PPh_3)_3][ClO_4]$	26	X-ray diffraction, ^{31}P n.m.r.	Agostic bonding present.
2	$[RhH(PR_3)_2]$	27	Mass spec., ^1H n.m.r., I.R.	R = i-Pr found to be polynuclear.
3	$[RhX(PCy_3)_2]$	28	^{31}P n.m.r.	Microanalysis poor. "Solvated in solution, polynuclear in solid."[36]
4	$[Rh\{N(SiMe_3)_2\}(PPh_3)_2]$	29	^{31}P n.m.r., microanalysis	
5	$[PtH(PBu^t_3)_2][X']$	30	^{31}P n.m.r., microanalysis, I.R.	υ(Pt-H) = 2860 cm^{-1}
6	$[Rh(BH_4)(PPh_3)_2]$	31	microanalysis, I.R.	Bidentate or bridging BH_4. EtOH present
7	$[Pd(PR'_2R'')_3][BF_4]_2$	32	^{31}P n.m.r. (poor)	Synth. + characterised in air / in acetone. Microanalysis poor.
8	$[RhH(PMe_3)_3][X'']$	33	^{31}P n.m.r., microanalysis	Reassigned $[Rh(PMe_3)_4][X'']$[37]
9	$[RhH(PPh_3)_2]$	34	Microanalysis, I.R.	Reassigned $[RhH(PPh_3)_3]$[38]
10	$[Rh\{NC(CF_3)_2\}(PPh_3)_2]$	35		Misquoted from $[Rh\{NC(CF_3)_2\}(PPh_3)_3]$[39]

R= Bu^t, Cy, *i*-Pr   R'= Ph, Et   R''= Ph
X= F, Cl,Br, I   X'= PF_6, BF_4, ClO_4, SO_3CF_3 X''= BPh_4, PF_6

misquotation. The reference given by Jardine (ref. 39) does not mention $[Rh\{NC(CF_3)_2\}(PPh_3)_2]$ and neither is this compound to be found in Chemical Abstracts. Compounds 8 and 9 were later formulated as four coordinate, as shown in Table 1, 1i, but are still sometimes described as being three coordinate.[35] Both compounds 6 and 7 have been tentatively suggested to be three coordinate (refs. 31 and 32). The available evidence, however, is very poor. Both were formed in the presence of donating solvents (ethanol and acetone) which are potential ligands and in addition compound 7 was formed in air. Alternative structures for 6 involving either a bridging BH_4^- group or a bidentate, chelated BH_4^- group have been suggested. There is thus little hard evidence that 6 - 9 contain three coordinate metal atoms.

Compounds 2 - 5 were assigned their three coordinate status largely on the basis of n.m.r. data. It was argued[28] that, as the $^1J_{M\text{-}P}$ coupling constant is directly related to the *s*-character of the metal orbital used in bonding to phosphorus, a low coordination number species should have an unusually high $^1J_{M\text{-}P}$ coupling constant. It is also well established that $^1J_{M\text{-}P}$ is a sensitive measure of the *trans*-influence on the M-P bond. Indeed, it is found that the $^1J_{M\text{-}P}$ coupling constants for 3 are very high. Compound 4 however, has $^1J_{Rh\text{-}P}$ = 180.67 Hz.[29] Although high for a phosphine group *trans* to another phosphine this compares well with the value of 189 Hz given for $^1J_{Rh\text{-}P}$ of the phosphorus atom *trans* to the chlorine atom in Wilkinson's catalyst or the similar value of 194 Hz given for the same coupling constant in the iodo-analogue of Wilkinson's catalyst.[40] Compound 5, [PtH(PBu$^t_3$)$_2$][X], has a normal value of $^1J_{Pt-P}$ (≈2625 Hz) but this value increases to 2664 Hz in the four coordinate complex [PtH(H$_2$O)(PBu$^t_3$)$_2$][BF$_4$] and to 2811 in [PtH(OCMe$_2$)(PBu$^t_3$)$_2$][BF$_4$].

Compound 1, [Rh(PPh$_3$)$_3$][ClO$_4$], has had its structure determined by X-ray analysis[26] (Fig 1, 1iii).

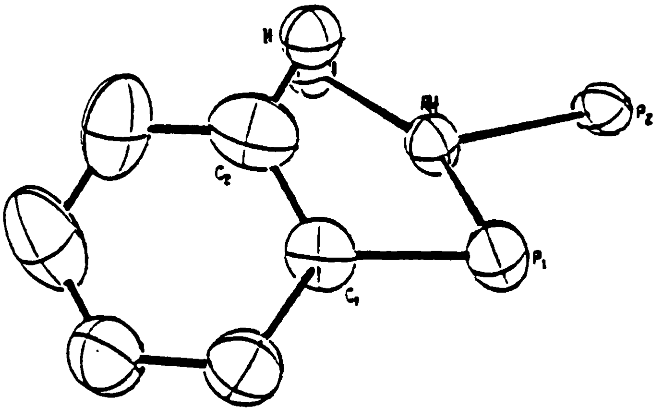


Fig. 1, 1iii Structure of [Rh(PPh$_3$)$_3$][ClO$_4$] (Ref. 26)

The P$_3$Rh unit adopts a distorted T-shaped geometry (P(1)-Rh-P(3) = 159.3(2)°). In addition, one phenyl ring is bent back towards the metal atom (Rh-P(1)-C(1) = 75.6(5)°) so that a C-H bond, and probably also a C-C bond, are unexpectedly close to the metal. The description of the metal atom in this species as three-coordinate thus depends on whether the proximity of the C-H bond to the metal implies, as was originally thought, merely a weak interaction or a genuine three-centre two-electron bond of the type now called agostic (Section 1, 1f). The ^{31}P n.m.r. spectra of the $[Rh(PPh_3)_3][HC(SO_2CF_3)_2]$ salt[24] yields an unusually high value of $J_{Rh\text{-}P}$ (244 Hz) for P *trans* to the proposed agostic site. Thus, it would appear that a high $^1J_{M\text{-}P}$ coupling constant may arise from an agostic interaction nor, considering compound 5 does it rule out the presence of solvent in the first coordination sphere.

There are other puzzling features present in the reports of compounds 2 to 5. For 5 ν(Pt-H) is reported as being 2860 cm^{-1}. This is ≈ 600 cm^{-1} higher than the normal range for metal-hydrides.[41] For 3 the microanalytical data are poor (±3% for carbon) and the complexes were prepared in acetone, a fairly good ligand. It was originally suggested that for 3 with X = Cl, that the complex exists in equilibrium with its dimer.[28] Further work carried out be Valentini *et al.*[36] came to the conclusion that 3 existed as polynuclear species in the solid state and a solvated species in solution. There is little evidence presented that this is not also the case for all the complexes 2 to 5.

In conclusion, five complexes (6 to 10) have been described as three coordinate with little or no evidence to support such a claim. For a further four complexes (2 to 5) the evidence of characterisation does not preclude the possibility that they are solvated, or dimers in the solid state or their stabilization by agostic bonds. $[Rh(PPh_3)_3][ClO_4]$, 1, is the only species to have been completely characterised; agostic bonding is present, and only by disregarding this feature can the metal atom be regarded as three coordinate.

1, 1f *trans*-INFLUENCE, AGOSTIC BONDING AND BULKY LIGANDS.

An understanding of the terms *trans*-influence, agostic bonding and bulky ligands is important to the interpretation of the results presented in subsequent chapters and a brief explanation of each of these therefore appears appropriate. The *trans*-influence of a ligand in a square-planar or octahedral complex was defined in 1966 by Pidcock *et al.*[42] as its ability to weaken the *trans* metal-ligand bond. The term has been widely adopted; it distinguishes the ground state, bond-weakening properties of a ligand from its *trans*-effect,[43] which is its effect on the rate of substitution of the group to which it is *trans*. Thus *trans*-influence is a thermodynamic phenomenon whereas *trans*-effect refers to reaction kinetics. The most widely accepted theoretical treatment is that of M^{c}Weeny, Mason and Towl[44] which states that the ability of a ligand L to weaken the M-X bond in a linear L-M-X system depends on the quantity $S^2/\Delta E$ (S is the L-M σ-overlap integral and ΔE is the energy separation between the L σ-donor and M σ-acceptor orbitals). Other theories, however, tend to contradict this and there is still disagreement as to the exact nature and effects of the hybrid orbitals involved.[45] What is clear, largely from crystallographic data, is the observed *trans*-influence series for square-planar complexes.[44, 46]

$$R_3Si > H > \sigma\text{-}C > R_3P > \pi\text{-}C > R_2N > Cl^- > O$$

(R = alkyl, aryl). In general it appears that strong σ-bonds from L to M weaken the *trans* M-X bond, possibly by using a disproportionate amount of the metal *s* orbital in the L-M bond. The observed *trans*-influence of ligands that have high π-accepting properties (e.g. CO) are not however adequately explained by current theories.

The term "agostic bonding" was coined by Green and coworkers[47] to describe complexes in which there is a close approach of a C-H bond to a metal atom. C-H bonds had usually been regarded as chemically inert and thus the suggestion of Green *et al.* that they could have a significant role in the coordination sphere of a metal involved a revision of previous views. However, these authors observed that there were many known examples of complexes with close C-H...M interactions although little significance had been attached to these observations. They proposed that many of these interactions were best explained in terms of two-electron three-centre bonds in which the σ-C-H bond formally donates two electrons to the metal. This proposal has been reviewed[48, 49] and it now seems fairly certain that in many systems σ-bond donation from a C-H group to a metal is a significant interaction, with parallels to be drawn with hydrogen atoms bridging between metal and boron atoms. It has been suggested that agostic bonding may be important in both Ziegler-Natta catalysis and in σ-bond metathesis. Of particular relevance to this work is the observation that coordinative unsaturation favours agostic bond formation.

The most widely used index of the steric requirements of a phosphine ligand is its cone angle, first proposed by Tolman.[50] These are, however, derived from hard-sphere models of fixed conformation. Despite their usefulness it should be remembered that they make no allowance for the conformational flexibility of real systems.[51] Other methods of measuring the steric requirements of ligands have been proposed and recently reviewed.[52] Although these methods give differing absolute values and size orders, what is clear is that phosphine ligands containing cyclohexyl, *tertiary*-butyl, *ortho*-tolyl or mesityl substituents are bulkier than, for example, PPh_3. Complexes containing bulky phosphines often show anomalous bond angles round the metal atom; more rarely they show unusually long metal-ligand bonds; there may even be changes in coordination geometry and even a decrease in coordination number of the metal.[53]

1, 2a GENERAL AIMS OF THE PROJECT.

The preceding sections show that there is much kinetic evidence to suggest a dissociative pathway exists for some reactions of square-planar, platinum-group metal complexes. Although apparently well documented it has been seen that a careful examination of all the data available casts some doubt on the true nature of some of the species previously presented as three coordinate complexes of d^8 transition metals. This project was undertaken in order to clarify the true nature of these species. This was to be done by synthesising and characterising, by crystallography and spectroscopy, possibly three coordinate complexes. The most successful routes previously used in attempts to form such complexes (Section 1, 1e) involved the loss of weakly bonding ligands such as solvents or N_2 from four coordinate species. (For example $[Rh(PPh_3)_3][ClO_4]$ is formed on recrystallising $[Rh(PPh_3)_3(OCMe_2)][ClO_4]$ from CH_2Cl_2[26] and $[RhH(PBu^t_3)_2]$[27] is formed by heating $[RhH(N_2)(PBu^t_3)_2]$). Thus it was decided to synthesise compounds of the type $[MRL_2S]$ in the hope that recrystallisation from hot, non-coordinating solvents would lead to three coordinate complexes. As there is some doubt as to whether such complexes actually exist as stable or isolable species it was decided that any coordinated solvent containing species isolated would also be investigated. This proposal has several merits. One possible identity of so-called three coordinate complexes is the solvated, four coordinated species. Thus, in investigating such solvent containing complexes we may actually be investigating the true nature of three coordinate complexes. Complexes of solvents are also interesting in their own right. As indicated in Sections 1, 1a to d they are cited as intermediates in many mechanistic studies and in many catalytic processes. Indeed in homogeneous catalysis the active species may well be a reactive, solvated species.[54] Also of relevance is the recent growth of interest in water-soluble homogeneous catalysts[55] and, in particular, those complexes whose organometallic chemistry is greatly influenced by the complex/water interaction.[56]

Despite this interest in solvents as hard donors to soft metals[57] and the applications of complexes of such species as homogeneous catalysts[57,58] very few complexes of rhodium or palladium with coordinated solvents have been studied crystallographically. Even for the "universal solvent", water, this is true. During the course of this work what were only the third and fourth crystal structures of aqua-palladium complexes were published ($[Pd(OH_2)(SC_4H_8)_2(C_6H_2(NO_2)_3)][ClO_4]$[59] and $[\overline{\mathrm{Pd}(\mathrm{OH}_2)(\mathrm{Bu}^t{}_2\mathrm{PC}_2\mathrm{H}_4\mathrm{CHC}_2\mathrm{H}_4\mathrm{P}}\mathrm{Bu}^t{}_2)]$)[60] and to date only three Rh^I-aqua complexes have had their structures determined. Further searching of the Cambridge Structural Database reveal only two organometallic Rh(I) or Rh(III) complexes of ethanol and one of methanol. No Rh(I) or Rh(III) complexes of acetone have previously had their structures determined. A review of crystallographic bond length data by Orpen *et al.*[61] in 1989 found no Pd or Pt compounds that contained simple alcohols, ketones or ethers as ligands.

In addition to their proposed role as reaction intermediates both three coordinate complexes and solvated complexes are of interest as reactive species. Of particular relevance is the general technique of producing unsaturated organometallic compounds in order to activate C-H bonds.[62] As saturated hydrocarbons are among the most abundant of petrochemicals but are also among the least responsive to chemical reagents any advances in introducing reactivity and/or selectivity to their chemistry are of great industrial importance.[3] Kaska and coworkers[63] have succeeded in activating C-H bonds in cyclohexane. The reactive species in this case was believed to be the 14-electron, 3-coordinate species $[Rh(PBu^t{}_2CH_2)_2(C_6H_3)]$. Similarly Pradella *et al.*[64] claim to have activated C-H bonds using $[RhCp^*(CO)]$, an unsaturated species formed by treatment of $[RhCp^*(CO)_2]$ with ultraviolet light. $[Rh(PPh_3)_3]^+$ has been used to hydrogenate cyclohexene[65] and is mentioned as a catalytic species in some recent patents.[66, 67] These uses of unsaturated complexes are in addition to useful reactions that are believed to involve three coordinate or solvent containing complexes as intermediates. Of these possibly the most important, catalytically, is the initial dissociation of PPh_3 from Wilkinson's catalyst to give $[RhCl(PPh_3)_2]$ in the proposed mechanism for this catalyst's hydrogenation of alkenes. There has been controversy over this step but it now seems likely that dissociation does indeed occur.[68, 69] Examples of other useful reactions, of relevance to both catalysis and anti-tumor activity, that are believed to proceed by a dissociative mechanism involving three coordinate intermediates are given in Section 1, 1e.

1, 2b THE $[Rh(CO)(PPh_3)_2L]^{n+}$ AND $[Rh(PPh_3)_3L]^{n+}$ SYSTEMS, n = 0, 1.

As discussed in Section 1, 1e the best characterised three coordinate d^8 transition metal complex is $[Rh(PPh_3)_3][ClO_4]$.[26] This was formed by the addition of $TlClO_4$ to Wilkinson's catalyst in a donating solvent S to give $[Rh(PPh_3)_3S][ClO_4]$. Recrystallisation of this solvated species from CH_2Cl_2 gave a product in which the metal was thought to be three coordinate. Characterisation by X-ray analysis showed that one phenyl group was bent around so as to place a C(1)-C(2)-H group close to the rhodium atom. (Fig 1, 1iii Rh...H = 2.56 Å, Rh...C(2) = 2.62 Å, Rh...C(1) = 2.48 Å). This work predates that of Green and coworkers who had not yet put forward their ideas on 3-centre, 2-electron, agostic bonds[47] and the apparent Rh...H interaction was originally dismissed as weak. The compound was therefore described as a three coordinate rhodium(1) species. $[Rh(PPh_3)_3][ClO_4]$ has been shown to contain an interaction with a ligand substituent and, given the absence of evidence to the contrary, it is not unreasonable to suggest that the other supposedly three coordinate species of Table 1, 1i may also involve similar interactions.

With the purpose of investigating the nature of the interaction (and possibly finding out if such interactions are necessary to stabilise three coordinate species) it was decided to travel the same synthetic route with analogues of Wilkinson's catalyst. It was also decided to prepare similar derivatives of Wilkinson's catalyst to see if these shed any light on the nature of $[Rh(PPh_3)_3][ClO_4]$. The complex *trans*-$[Rh(CO)Cl(PPh_3)_2]$ was used as a starting material for the preparation of a series of complexes analogous to those found in the synthesis of $[Rh(PPh_3)_3][ClO_4]$. This starting complex was chosen as it is readily accessible, has an easily removable Cl ligand and has mutually *trans* triphenylphosphine groups, similar to Wilkinson's catalyst. The nature of the phosphine groups is important. Although most of the complexes of Table 1, 1i rely on bulky phosphine substituents (Bu^t, Cy) to stabilise their coordinative unsaturation it is possible that phenyl groups may have a greater stabilising effect because of their electronic character and despite their smaller cone angles. Certainly, as has been pointed out, triphenylphosphine forms complexes where other phosphines will not and there is a prevalence of phenyl groups in cyclometallation reactions.[26]

An additional feature of *trans*-$[Rh(CO)Cl(PPh_3)_2]$ is that, in contrast to Wilkinson's catalyst, metallation of the Cl ligand reportedly leads to the coordinated perchlorato complex *trans*-$[Rh(CO)(OClO_3)(PPh_3)_2]$.[70] The results of this line of investigation are reported in Sections 3, 1a – i.

1, 2c THE $[PdR(PPh_3)_2L]^{n+}$ SYSTEM, n = 0,1.

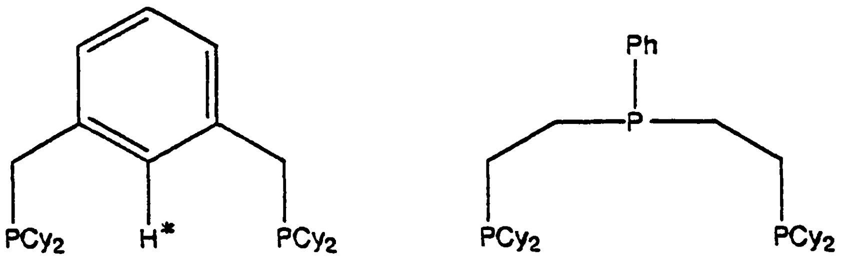
As was shown in Section 1, 1d there is a great deal of kinetic evidence that complexes of the type $[PtR(PEt_3)_2X]$ (X = halide) undergo isomerisation reactions by a dissociative mechanism. It was decided to attempt a preparation of $[PdR(PPh_3)_2]^+$ and $[PdR(PPh_3)_2S]^+$ as analogues to the platinum system. Palladium was preferred to platinum as it was felt that as a second row transition metal it was more analogous to the reportedly three-coordinate rhodium complexes, which make up the bulk of Table 1, 1i. Triphenylphosphine groups were used in order to stabilise any coordinatively unsaturated species formed (Section 1, 2b). R was chosen to be *o*-tolyl or mesityl. These were chosen as Romeo reported that bulky R groups favoured dissociation reactions.[13] Additionally, it was hoped that the strongly *trans*-influencing R groups would weaken any bond *trans* to them and thus perhaps facilitate the formation of a genuine three coordinate complex. The results of this line of investigation are reported in Sections 3, 2a to e.

1, 2d LIGANDS DESIGNED TO STABILISE COORDINATIVELY UNSATURATED SPECIES.

It should be apparent that three coordinate complexes of d^8 transition metals are inherently unstable. It was recognised that the routes outlined in Sections 1, 2b and c which use normal, unidentate ligands may well not yield any three coordinate species due to this instability. It was therefore decided to design ligands that would help to stabilise coordinatively unsaturated species and to characterise any compounds formed with these ligands in order to assess their suitability for this task.

Four main features were desirable for these ligands. They should be terdentate, have bulky substituents, contain a high *trans*-influencing group *trans* to the postulated vacant site and, if possible, should also carry a formal negative charge. A terdentate ligand should increase the stability of any complex containing it by blocking both ligand substitution reactions and possible reductive elimination pathways. It is also possible a catalytically reactive species such as [MLS] or[ML] (L = terdentate ligand) would be more selective than a comparable complex containing three unidentate ligands. The complexes of Table 1, 1i employ bulky ligands to stabilise their coordinatively unsaturated nature. This is a common property of bulky ligands[53] and seems to stem from two sources. These are their ability to provide groups that take part in agostic interactions and the steric hindrance or blocking of other coordination sites. The desirability of high *trans*-influencing groups has been discussed in Section 1, 2c. If the terdentate ligand is anionic the number of counterions present is reduced as is the likelihood of their interaction with the metal.

The two ligands chosen were *meta*-$(PCy_2CH_2)_2(C_6H_4)$ (PCHP) and $PPh(PCy_2C_2H_4)_2$ (PPP).



PCHP PPP

Fig. 1,2i The ligands PCHP and PPP.

By comparison with the known ligand *meta*-$(PBu^t{}_2CH_2)_2(C_6H_4)$, PCHP should be capable of terdentate complexation by metallation of H^* (see Fig 1, 2i). The resultant ligand, PCP, combines all four desired features. PPP, however, is a neutral ligand and its central phosphorus atom has a lower *trans*-influence than the σ-C of PCP. Despite this PPP has the advantage of having a n.m.r. active nuclei *trans* to the proposed vacant site. It was hoped that this would enable the formation of any coordinatively unsaturated species to be monitored by means of the $^1J_{M\text{-}P}$

coupling constant (Section 1, 1e). The experimental results of this line of investigation are discussed in Sections 3, 3a to g and in the crystallographic Sections 3, 4a to l.

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2, 1a INSTRUMENTATION.

N.m.r. spectra were measured on Bruker AM200 and WP200 (200 MHz F.T.N.M.R.) spectrometer and processed using the Bruker Aspect 3000 suite of programs. Spectra were referenced internally to solvent resonances. Deuterated solvents were stored under 4Å molecular sieves and, for air sensitive samples, degassed by freeze-thaw methods. Air sensitive samples were prepared on the vacuum line. Solid state n.m.r. spectra were measured by Dr. David Apperley of the S.E.R.C. service, University of Durham. The reference compound was 80 % H_3PO_4.

I.R. spectra were measured on a Phillips F.T.I.R. spectrophotometer in the range 4000 - 400 cm^{-1}. Frequencies in the 400 - 200 cm^{-1} range were measured on a Perkin-Elmer 983 continuous wave spectrophotometer. Except where stated, samples were in the form of 8 mm KBr discs made using 300 mg of KBr and a press force of 10 tons. Air sensitive samples were made up as nujol mulls in a nitrogen atmosphere dry-box using KBr plates and nujol dried over sodium. Silicone grease was smeared around the sides of the plates to help repel air. Solution samples were run in 0.1 mm KBr cells using solvents purified as in Section 2,1b.

Microanalyses were run in the University of Glasgow Chemistry Department by Mrs K. Wilson. Melting points were uncorrected and recorded in air using a Gallenkamp melting point apparatus.

2, 1b MATERIALS AND SOLVENTS.

Metal salts were used as purchased. The purities of phosphines (i.e. $HPCy_2$, PPh_3, $P(p\text{-}C_6H_4OMe)_3$ and $PPh(C_2H_3)_2$) were checked by ^1H and ^{31}P n.m.r. spectroscopy and the purities of the other organic compounds were checked by I.R. spectroscopy.

Oxygen-free nitrogen, as supplied by B.O.C., was further purified by passage through 4Å molecular sieves and a liquid nitrogen cold trap before use. Acetone, ethanol and methanol were analytical grade materials stored over 4Å molecular sieves. Solvents, as detailed in Table 2, 1i, were freshly distilled under nitrogen atmosphere. Other solvents were analytical grade materials used without further purification except, where noted, for degassing which was either by the freeze-thaw method or by passing nitrogen gas through the solvent for at least 2 hours.

Table 2, 1i

SOLVENT	DRYING AGENT
CH_2Cl_2	CaH_2
$CHCl_3$	CaH_2
ACETONITRILE	CaH_2
TOLUENE	SODIUM
CYCLOHEXANE	SODIUM/POTASSIUM AMALGAM
PETROLEUM ETHERS	SODIUM/POTASSIUM AMALGAM
Et_2O	SODIUM WITH BENZOPHENONE
T.H.F.	SODIUM WITH BENZOPHENONE

2, 1c APPARATUS.

Standard nitrogen/vacuum line techniques and apparatus were used for all reactions in Sections 2, 3a to 2, 6e and Sections 2, 2c and i. This included the flame drying of all apparatus prior to use, lengthy flushing of apparatus with nitrogen and the transfer of solvents from stills via oven-dried syringes. The "double Schlenk apparatus" referred to in the text consists of two off-vertical Schlenk-type arms connected via a medium porosity frit. A nitrogen atmosphere dry-box was used for the preparation of I.R. samples and for the weighing of air sensitive samples.

2, 2a PREPARATION OF *trans*-DICHLOROBIS(TRIPHENYLPHOSPHINE) PALLADIUM (II).[1]

10.64 g (40.61 mmol) of PPh_3 were dissolved in 350 ml of ethanol. To this solution were added, at room temperature, 6.02 g (20.46 mmol) of Na_2PdCl_4. On shaking a yellow precipitate immediately appeared.

This was filtered off and washed with water (30 ml), ethanol (50 ml) and ether (30 ml) to give 13.20 g (18.82 mmol, 92% yield) of *trans*-$[PdCl_2(PPh_3)_2]$ as a yellow powder. The I.R. spectrum of the product was identical to that of an authentic sample.

2, 2b PREPARATION OF *trans*-DICHLOROBIS(TRI(*para*-METHOXYPHENYL) PHOSPHINE) PALLADIUM (II).

5.06 g (14.38 mmol) of tri(*para*-methoxyphenyl)phosphine, $P(p\text{-}C_6H_4OMe)_3$, were added to 200 ml of ethanol to give a white suspension. Immediately upon addition of 2.51 g (7.20 mmol) of $Na_2PdCl_4.3H_2O$ a yellow colour appeared and on shaking a yellow precipitate formed. This was filtered off and washed with ethanol. The light yellow powder isolated was redissolved in chloroform and 0.64 g of NaCl were removed by filtration. The solvent was removed under reduced pressure and the light orange solid dried under vacuum to give 5.98 g (6.78 mmol, 95% yield) of *trans*-$[PdCl_2\{P(p\text{-}C_6H_4OMe)_3\}_2]$. M.P. 216 - 218 °C (dec.). $^{31}P\{H\}$ n.m.r. s 19.6 p.p.m. ^{1}H n.m.r. m 7.58 m 6.88 s 3.80 p.p.m. Integ. 2:2:3 I.R. ms 355 br 3070 br 3005 br 2960 sh 2920 cm^{-1}.

2, 2c PREPARATION OF TETRAKIS(TRIPHENYLPHOSPHINE) PALLADIUM (0).[2]

2.02 g (11.4 mmol) of $PdCl_2$ and 14.77 g (56.4 mmol) of PPh_3 were added, against a flow of nitrogen, to 140 ml of D.M.S.O. in a 3-necked flask. On heating to 140 °C an orange solution was obtained which was stirred as it cooled for 15 mins before 2.2 ml (45 mmol) of hydrazine hydrate were added. The reaction mixture turned brown and as it cooled a brown solid appeared. This was filtered off, under nitrogen, and dried under vacuum to give 12.81 g (11.1 mmol, 97% yield) of $[Pd(PPh_3)_4]$ as a crude yellow-brown powder, which was used in subsequent preparations with no further purification.

A second identical preparation gave 10.2 g (8.8 mmol, 78% yield) of $[Pd(PPh_3)_4]$. $[Pd(PPh_3)_4]$ was characterised by comparison of its I.R. spectrum with that given in the literature.

N.B. Ref. 2 states that, although it is air sensitive, [Pd(PPh_3)$_4$] can be handled briefly in air. Whilst weighing out a sample of [Pd(PPh_3)$_4$], with an exposure to air of less than 5 mins, the sample reacted vigorously leaving only a black tar.

2, 2d PREPARATION OF BIS(BENZONITRILE)DICHLORO PALLADIUM.[3]

2.00 g (11.3 mmol) of $PdCl_2$ and 50 ml of benzonitrile were placed in a conical flask and heated in a boiling water bath. After 20 mins the greater part of the $PdCl_2$ had dissolved. The red solution was filtered hot into 300 ml of distilled 40 - 60 ° petroleum ether. This precipitated a yellow solid which, after filtering, washing with petroleum ether and drying under vacuum, gave 1.98 g (5.2 mmol) of [Pd(NCPh)$_2$Cl$_2$].

All remaining portions were reheated, with an additional 40 ml of benzonitrile, and treated as above to give a further 1.46 g (3.8 mmol) of product. The product was characterised by comparison of its I.R. spectrum with that of a genuine sample. Total yield = 79%.

2, 2e PREPARATION OF BIS(BENZONITRILE)DICHLORO PLATINUM.[4]

1.50 g (5.64 mmol) of $PtCl_2$ and 100 ml of benzonitrile were placed in a conical flask and then heated in a water bath until the bath boiled. After 30 mins the greater part of the $PtCl_2$ had dissolved. The solution was filtered hot into 300 ml of distilled 40 - 60 ° petroleum ether. This precipitated a yellow powder which after filtering, washing with petroleum ether and drying under vacuum gave 2.18 g (4.62 mmol, 82% yield) of $[Pt(NCPh)_2Cl_2]$. The I.R. spectrum of the product was identical to that of an authentic sample.

2, 2f PREPARATION OF WILKINSON'S CATALYST.[5]

A solution of 0.25 g (0.95 mmol) of $RhCl_3.3H_2O$ in 25 ml of hot ethanol was added to a solution of 1.51 g (5.76 mmol) of PPh_3 in 75 ml of hot ethanol. This mixture was refluxed for 30 mins.

Purple crystals were filtered off hot and washed with ether to give 0.61 g (0.69 mmol) of $[RhCl(PPh_3)_3]$. The I.R. spectrum of the product was identical to that of an authentic sample.

Four such preparations of [RhCl(PPh_3)$_3$] were performed giving yields from 60 to 88%.

2, 2 g PREPARATION OF *trans*-CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM (I).[6]

2.00 g (7.59 mmol) of $RhCl_3.3H_2O$ as a suspension in 70 ml of absolute alcohol were slowly added to a boiling solution of 7.21 g (27.5 mmol) of PPh_3 in 300 ml of absolute alcohol. Once the solution was a clear red colour 20 ml of 37% formaldehyde solution were slowly added until the colour changed to clear yellow. On cooling yellow crystals precipitated out of solution and were collected on a filter and washed with ethanol and ether to give 4.37 g (6.32 mmol) of *trans*-[Rh(CO)Cl(PPh_3)$_2$]. On cooling to 5 °C, overnight, a second crop of orange crystals formed which on filtering and washing gave a further 0.16 g (0.23 mmol) of product. Total yield = 86%.

Before use, *trans*-[Rh(CO)Cl(PPh_3)$_2$] was recrystallised from the minimum of hot toluene to give large yellow crystals in approximately 75% recovery.

A second identical preparation was carried out and gave a total yield of 87%. *Trans*-[Rh(CO)Cl(PPh_3)$_2$] was characterised by comparison of its I.R. spectrum with that of a genuine sample and by ^{1}H and ^{31}P n.m.r. spectroscopy.

2, 2h PREPARATION OF THALLIUM PERCHLORATE.[7]

3.70 g (26.5 mmol) of 72% w/w perchloric acid solution were added dropwise, and with stirring, to a solution of 6.05 g (12.9 mmol) of Tl_2CO_3 in 110 ml of distilled water. After initial effervescence, the solution was stirred for 24 hrs. On being left to evaporate in a fume hood a white crystalline precipitate was formed. This was filtered off, washed with water and dried under vacuum. To ensure an anhydrous product the temperature was carefully raised to 90 °C and held there for 24 hrs. Once cool the anhydrous product weighed 7.60 g (15.0 mmol, 97% yield). I.R. spectroscopy (nujol mull made in dry-box) showed no H_2O and matched that given in the literature.

2, 2i PREPARATION OF LITHIUM BIS(TRIMETHYLSILYL) AMIDE.[8]

2.06 g (12.76 mmol) of $HN(SiMe_3)_2$ were placed in a Schlenk flask and 2 ml of distilled 30 - 40 ° petroleun ether added. The flask was placed in an ice-bath and after 5 mins 7.2 ml of 1.6 M (11.52 mmol) n-butyllithium were added by syringe, through a suba-seal. The cloudy mixture was stirred for 55 mins and then allowed to warm to room temperature. Still with stirring the solvent was removed, under vacuum, and the precipitated white solid dried by heating in an oil bath, under vacuum, to 50 °C.

2, 3a REACTIONS BETWEEN *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] AND AgClO$_4$ OR TlClO$_4$.

i) 1.00 g (1.45 mmol) of the title complex was added to 80 ml of distilled toluene in a 3-necked flask, under nitrogen, to give a yellow suspension. 0.29 g (1.42 mmol) of AgClO$_4$ were added, the flask was shielded from light with aluminium foil, and the mixture was stirred for 18 hrs. The reaction mixture was filtered, in air, into 250 ml of vigorously stirred distilled 30 - 40 ° petroleum ether. This gave white silver salts on the filter and a light yellow precipitate in solution. This precipitate was filtered off, washed with toluene and pentane and dried under vacuum to yield 1.01 g (1.31 mmol, 90% yield) of *trans*-[Rh(CO)(OH$_2$)(PPh$_3$)$_2$][ClO$_4$]. A second identical preparation gave a 91% yield.

An attempted anhydrous preparation, in benzene, using rigorously dried materials and the maintenance of a dry nitrogen atmosphere at all stages again gave the aqua complex as the product. It is believed that the water molecule was derived from the very hygroscopic AgClO$_4$ despite, in this case, drying a solution of AgClO$_4$ in benzene by Dean-Stark azeotropic distillation.

ii) Two anhydrous preparations using TlClO$_4$ in place of AgClO$_4$, one in toluene and one in CH$_2$Cl$_2$, gave no reaction over a period of three days.

2, 3b REACTION BETWEEN *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] AND AgClO$_4$, FOLLOWED BY TREATMENT WITH ACETONE.

A solution of 0.17 g (0.82 mmol) of AgClO$_4$ in 10 ml of distilled toluene was added slowly and with stirring to a slurry of 0.55 g (0.80 mmol) of *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] and 35 ml of distilled toluene in a double Schlenk flask. The apparatus was sealed and covered in aluminium foil before being left to stir for 18 hrs. The resulting solution was filtered through the internal frit of the apparatus to separate an off-white powder from the yellow solution. To this solution were added 1.5 ml of degassed acetone and immediately this gave a yellow precipitate. After seven days the solution was filtered, under nitrogen, to give, after washing carefully with portions of 1:1 toluene:petroleum ether and drying, 0.29 g (0.36 mmol) of yellow, crystalline *trans*-[Rh(CO)(OCMe$_2$)(PPh$_3$)$_2$][ClO$_4$].

The off-white powder collected earlier was extracted with 20 ml of distilled toluene at 60 °C to give, on filtering, a yellow solution. Addition of 0.5 ml of degassed acetone to this solution gave a second crop of *trans*-[Rh(CO)(OCMe$_2$)(PPh$_3$)$_2$][ClO$_4$] (15 mg). Total yield = 48%.

2, 3c CRYSTALLISATION OF *trans*-$[Rh(CO)(OH_2)(PPh_3)_2][ClO_4]$ FROM ACETONE.

Trans-$[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4]$ may also be prepared by dissolving, under nitrogen, the aqua complex in hot degassed acetone. Slow addition of 40 - 60 ° petroleum ether to the red solution precipitates yellow, crystalline *trans*-$[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4].x(OCMe_2)$, x = 1 to 2, in roughly 60% yield. It should be noted that if the volume of the acetone solution is reduced too much, or if excess petroleum ether is added, or if the solution is cooled too rapidly then a red oil is obtained rather than the desired crystalline compound. When stored under a nitrogen atmosphere acetone of crystallisation is lost within 2 weeks. On exposure to air coordinated acetone is replaced by water over a period of 3 days. Microanalysis (required) for $[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4].2(OCMe_2)$ C 58.29 (58.38)% H 5.16 (5.31)%.

2, 3d CRYSTALLISATION OF *trans*-$[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4].x(OCMe_2)$ FROM NON-COORDINATING SOLVENTS.

0.30 g (0.32 mmol) of *trans*-$[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4].2(OCMe_2)$ were dissolved in 4 ml of distilled CH_2Cl_2 in a double Schlenk flask. The yellow solution was stirred and heated to boiling for 5 mins before being allowed to cool. Once at room temperature distilled 30 - 40 ° petroleum ether was added dropwise until, after approximately 6 ml, the solution appeared cloudy. Gentle heating gave a clear solution.

A red oil appeared after standing overnight and the remaining yellow solution was carefully decanted through the internal frit of the apparatus to remove this. An ice bath was placed around the limb containing the solution and this gave large yellow crystals of *trans*-$[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4].CH_2Cl_2$ which were filtered off to give a yield of 0.12 g (0.13 mmol).

These crystals were redissolved in 5 ml of distilled $CHCl_3$ and the yellow solution heated at 55 °C for 15 mins, with nitrogen flowing freely through the apparatus. All volatiles were removed *in vacuo* and the solid redissolved in 5 ml of hot, distilled CH_2Cl_2. This solution was refluxed for 10 mins and then allowed to cool. Once at room temperature, distilled 30 - 40 ° petroleum ether was added dropwise ($\approx$ 10 ml) until the solution appeared cloudy. Gentle heating gave a clear solution and this was left overnight. A dark orange, microcrystalline product formed. This was filtered off and dried under vacuum to give 0.06 g (0.08 mmol) of *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$. Exposure of this product to air gives complete conversion to *trans*-$[Rh(CO)(OH_2)(PPh_3)_2][ClO_4]$ within 3 minutes. Total yield of *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$ = 25%.

2, 3e REACTION BETWEEN *trans*-[RhCl(CO)(PPh$_3$)$_2$] AND AgSO$_3$CF$_3$.

0.49 g (1.91 mmol) of silver trifluoromethanesulphonate were added, against a flow of nitrogen, to a suspension of 1.19 g (1.72 mmol) of the title complex and 100 ml of distilled toluene in a three-necked flask. The apparatus was covered in aluminium foil and the suspension was stirred for 17 hrs.

At the end of this time the reaction mixture contained a light yellow precipitate which was filtered off under nitrogen. This was extracted into 25 ml of hot, distilled CH_2Cl_2 and filtered to remove AgCl. The solvent was removed under vacuum to give 1.10 g (13.4 mmol, 78% yield) of *trans*-[Rh(OH$_2$)(CO)(PPh$_3$)$_2$][SO$_3$CF$_3$] as a light yellow powder. Microanalysis (required) C 55.31 (55.47)% H 4.00 (3.89)%.

2, 3f CRYSTALLISATION OF *trans*-[Rh(CO)(OH$_2$)(PPh$_3$)$_2$][SO$_3$CF$_3$] FROM ACETONE.

0.12 g (0.15 mmol) of *trans*-[Rh(CO)(OH$_2$)(PPh$_3$)$_2$][SO$_3$CF$_3$] were dissolved, under nitrogen, in 5 ml of dry acetone. This red solution was heated to boiling for 30 mins with nitrogen flowing through the apparatus to reduce the acetone volume to 2 ml. Distilled 30 - 40 ° petroleum ether was added to the hot solution, dropwise, until a cloudy precipitate first appeared. The apparatus was sealed and allowed to cool slowly to give 0.07 g (0.08 mmol, 50% yield) of yellow crystalline *trans*-$[Rh(CO)(OCMe_2)(PPh_3)_2][SO_3CF_3].(OCMe_2)$.

2, 3g REACTION BETWEEN WILKINSON'S CATALYST AND $TlClO_4$.

A suspension of 0.16 g (0.53 mmol) of $TlClO_4$ in 20 ml of degassed acetone was added to a suspension of 0.48 g (0.52 mmol) of $[RhCl(PPh_3)_3]$ in 120 ml of degassed acetone. The colour immediately lightened from red to orange. The apparatus was covered in aluminium foil to protect it from light and the reaction mix was stirred for 19½ hrs before being left to settle. This gave a light pink precipitate and an orange solution. The solution was filtered twice to remove the precipitate (a mixture of thallium salts and Wilkinson's catalyst). Only after reducing the solvent *in vacuo* to 40 ml and the addition of 35 ml of 30 - 40 ° petroleum ether followed by decanting of the solution to remove more precipitated Tl salts, was a completely clear orange solution obtained. This was layered with a further 35 ml of distilled 30 - 40 ° petroleum ether to give, after 48 hrs, a small quantity of air sensitive, crystalline $[Rh(OCMe_2)(PPh_3)_3][ClO_4].(OCMe_2)$.

These were filtered off and the mother-liquor reduced to dryness, *in vacuo*, to give 0.43 g (0.41 mmol) of $[Rh(OCMe_2)(PPh_3)_3][ClO_4]$ as an orange powder. Repeated attempts to crystallise this powder from acetone/cyclohexane and acetone/toluene mixtures gave only a small amount of poor quality crystals and a series of black-red oils. The hexagonal orange plates when stored under nitrogen for a period of months decomposed to a hygroscopic, green, unidentified compound. Total yield = 79%.

2, 3h REACTION BETWEEN WILKINSON'S CATALYST AND $AgNO_3$.

To a 3-necked flask covered with aluminium foil were added 70 ml of degassed methanol and 0.63 g (0.68 mmol) of $[Rh(PPh_3)_3Cl]$ to give, on heating, a clear red solution. A solution of 0.12 g (0.71 mmol) of $AgNO_3$ in 30 ml of warm, degassed methanol was added, resulting in an immediate colour change to green-grey and then progressive darkening, as the solution was stirred for 20 mins, to brown.

The reaction mixture was filtered, in air, to give a brown solid and a red solution. The brown solid was extracted with toluene to leave 0.15g of a black tar and, on work-up, 0.41 g of PPh_3O. The red solution was reduced to dryness under vacuum to leave a reddish solid. This was recrystallised from hot CH_2Cl_2/60 - 80 ° petroleum ether which on cooling gave 0.01 g of an orange powder. This has been formulated as the dimer $[(PPh_3)_2(HOMe)RhRh(HOMe)(PPh_3)_2][NO_3]_2$ (Section <u>3</u>, 1g) although other possibilities cannot be ruled out.

The CH_2Cl_2/60 - 80 ° petroleum ether solution was reduced under vacuum to precipitate firstly 0.23 g of PPh_3O and then 0.03 g of a brown powder formulated as $[Rh(PPh_3)_3(NO_3)]$.

<u>2</u>, 3i REACTION BETWEEN WILKINSON'S CATALYST AND $AgNO_3$ SUPPORTED ON KIESELGUHR-60.

1.86 g (10.95 mmol) of $AgNO_3$ were dissolved in 4 ml of distilled water and this solution was added dropwise, with hand stirring, to 16.66g of Kieselguhr in a round-bottomed flask covered in aluminium foil. After 40 mins of mechanical mixing the mixture was dried under vacuum for ½ hr and then placed in an oven, at 110 °C, for 20 mins, to form a 10% $AgNO_3$/Kieselguhr mix. 6.01 g of this mixture (containing 3.53 mmol of $AgNO_3$) were placed in a column (fitted with a side arm and a frit and covered in aluminium foil) and degassed by passing degassed ethyl acetate through it. Also under nitrogen 0.53 g (0.58 mmol) of $[RhCl(PPh_3)_3]$ were dissolved in 200 ml of a 1:8 hexane:ethyl acetate mixture and this solution was passed through the $AgNO_3$ impregnated column. This gave an orange solution which after reduction to dryness under vacuum and recrystallisation, in air, from CH_2Cl_2/60 - 80 ° petroleum ether gave 0.11 g of PPh_3O and 0.11 g of black decomposition products.

A further 300 ml of ethyl acetate were passed through the column. This again produced an orange solution which was reduced under vacuum until a brown precipitate appeared. This was filtered off (0.22 g) and recrystallised from CH_2Cl_2/60 - 80 ° petroleum ether to give 0.08 g of PPh_3O and 0.03 g of an unidentified, coordinated NO_3^- containing yellow powder. (Section 3, 1g)

2, 3j REACTION BETWEEN WILKINSON'S CATALYST AND $[Li\{N(SiMe_3)_2\}]$.

A solution of 0.91 g (0.98 mmol) of $[RhCl(PPh_3)_3]$ in 45 ml of distilled T.H.F. was cooled with an ice-bath. 0.19 g (1.14 mmol) of $[Li\{N(SiMe_3)_2\}]$ were added and stirring commenced. The solution gradually darkened to dark green and after 1 hr 35 mins of stirring the solvent was removed, under vacuum, to leave a green solid. The Schlenk tube was sealed and stored at 5 °C overnight. By the next morning the solid had largely turned orange.

An extraction into 100 ml of distilled cyclohexane gave, on filtering, an orange solution and 0.42 g of an unidentified yellow powder. The I.R. spectrum of this powder contained all the peaks expected for $[RhCl(PPh_3)_3]$ but interestingly also peaks at 746 and 327 cm^{-1} which may indicate the presence of $[Rh(PPh_3)_2(PPh_2C_6H_4)]$.[9] An attempt to crystallise this powder from toluene led to decomposition with only traces of $[RhCl(PPh_3)_3]$ isolated and identified.

The cyclohexane solution also decomposed over a period of weeks, to give only black tars and 0.33 g (0.36 mmol) of $[RhCl(PPh_3)_3]$.

2, 4a REACTION OF [Pd(PPh_3)$_4$] WITH *ortho*-BROMOTOLUENE.

3.98 g (3.45 mmol) of [Pd(PPh_3)$_4$] were added, against a flow of nitrogen, to a solution of 1.2 ml (10.0 mmol) of *o*-bromotoluene in 120 ml of distilled toluene to give a brown suspension. This was refluxed for 1 hr to give an orange solution with a small amount of black solid.

The orange solution was decanted off and the solvent removed under vacuum to give a yellow solid, which was washed, in air, with ether to remove PPh_3.

Dissolution of the solid in hot CH_2Cl_2 first gave, on cooling and addition of ether, 0.31 g (0.39 mmol) of golden orange *trans*-[$PdBr_2(PPh_3)_2$]. After removing this by filtration a second precipitate was obtained, 0.77g (0.96 mmol) of *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] as a white powder. A third, crystalline, crop was obtained by slow evaporation of the solution to yield a further 0.31 g (0.39 mmol) of *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$]. Total yield of *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] = 39%. M.P. = 202 - 206 °C. Microanalysis (required) C 64.38 (64.39)% H 4.53 (4.66)% Br 10.26 (9.96)%. Total yield of *trans*-[$PdBr_2(PPh_3)_2$] = 11%. Microanalysis (required) C 55.38 (54.63)% H 3.88 (3.83)%.

If not entirely pure, solutions of *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] in chlorinated solvents, T.H.F. or alcohols decomposed over several days to give palladium metal and triphenylphosphine-oxide-containing products.

2, 4b REACTION OF *trans*-[$PdCl_2(PPh_3)_2$] WITH *o*-TOLYL LITHIUM.

Ortho-tolyl lithium was formed from ≈ 1 g of lithium metal and 13.3g of *o*-bromotoluene in 45 ml of distilled ether.

A 1.2 ml portion containing approximately 1.9 mmol of *o*-tolyl lithium was syringed into a three-necked flask containing a suspension of 1.01 g (1.44 mmol) of *trans*-[$PdCl_2(PPh_3)_2$] in 12 ml of distilled T.H.F.

After stirring for 10 mins the reaction mixture turned deep red and was quenched with 20 ml of water. Extraction with 40 ml of ether gave a red ether solution floating on a colourless aqueous layer, which also contained an off-white solid. After separation from the ether layer the aqueous layer was filtered to remove 0.04 g (0.05 mmol) of *trans*-[PdBr(*o*-tolyl)$(PPh_3)_2$]. On removal of the solvent from the aqueous layer only lithium salts were obtained.

The red ether layer was dried with $MgSO_4$ and after filtration precipitated 0.21 g (0.26 mmol) of *trans*-[PdBr(*o*-tolyl)$(PPh_3)_2$] after standing for 30 mins and a further 0.15 g (0.19 mmol) of product on being reduced, under reduced pressure, to 30 ml. The remaining solution was left overnight and decomposed to give only a black powder (Pd metal) and triphenylphosphine oxide.

The $MgSO_4$ used for drying was extracted with 20 ml of CH_2Cl_2 to give, on evaporation, 0.07 g (0.09 mmol) of *trans*-[$PdBr_2(PPh_3)_2$]. Total yield of *trans*-[PdBr(*o*-tolyl)($PPh_3)_2$] = 35%. Total yield of *trans*-[$PdBr_2(PPh_3)_2$] = 6%.

2, 4c REACTION BETWEEN *trans*-[$PdCl_2(PPh_3)_2$] AND [Mg(*o*-TOLYL)Br].

The Grignard reagent was formed *in situ* from 0.28 g (11.5 mmol) of magnesium and 1.38 ml (11.5 mmol) of *ortho*-bromotoluene in 30 ml of distilled T.H.F. After the addition of an I_2 crystal a vigorous reaction gave a clear Grignard reagent.

To this were added 3.38 g (4.8 mmol) of *trans*-[$PdCl_2(PPh_3)_2$] as a slurry in 40 ml of distilled T.H.F. The solution immediately turned black and was stirred with gentle heating for 30 mins. The reaction mixture was quenched in water and a black precipitate was filtered off (2.83 g).

The solid was extracted into hot diethyl ether on three successive occasions giving three red-orange solutions. All these solutions decomposed to give a total of 1.64 g of unidentified black tars.

The filtrate was also extracted by diethyl ether. The ether layer was dried with $MgSO_4$ and then volatiles removed *in vacuo*. The orange solid left was redissolved in CH_2Cl_2 and left overnight at 5 °C. Such treatment yielded three crops of white crystals which proved to be PPh_3O (0.45 g) as characterised by I.R. spectroscopy and microanalysis. Also filtered off were 0.34 g of a black decomposition product which was not investigated further.

2, 4d REACTION BETWEEN *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] AND SILVER NITRATE.

0.10 g (0.56 mmol) of $AgNO_3$ were added, as a solution in 30 ml of hot methanol, to a suspension of 0.45 g (0.56 mmol) of the title palladium complex in 50 ml of methanol, under a nitrogen atmosphere.

The reaction flask was covered with aluminium foil and the reactants were stirred for 20 mins to give a milky solution. This was filtered, under nitrogen, to give 0.17 g of white powder and a clear solution. This white powder was shown, by I.R. spectroscopy (after extraction into CH_2Cl_2) to be a mixture of AgBr and the palladium starting complex.

Overnight the mother-liquor decomposed, despite being under nitrogen and shielded from light, to give a black tar and an orange solution.

The solution was decanted off and all solvent removed under vacuum to give a red film and colourless crystals. These were dissolved in 1:1 CH_2Cl_2:Et_2O and filtered, in air, to remove a small amount of $AgNO_3$ as a dark powder. This clear yellow solution yielded 0.11 g (0.14 mmol) of *trans*-[Pd(*o*-tolyl)(NO_3)(PPh_3)$_2$] as an off-white, crystalline solid. *Trans*-[Pd(*o*-tolyl)(NO_3)(PPh_3)$_2$] decomposes in solution (CH_2Cl_2, $CHCl_3$, EtOH and acetone) within 12 hrs to give Pd metal, triphenylphosphine oxide and a small amount of an unidentified yellowish complex. The I.R. spectrum of this complex is similar to that of *trans*-[Pd(*o*-tolyl)(NO_3)(PPh_3)$_2$] but contains strong bands in the region 2960 - 2860 cm^{-1}. Total yield of [Pd(*o*-tolyl)(NO_3)(PPh_3)$_2$] = 24%.

2, 4e REACTIONS BETWEEN *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] AND $AgClO_4$.

0.06 g (0.27 mmol) of $AgClO_4$ were added to a stirred suspension of 0.20 g (0.25 mmol) *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] in 5 ml of distilled toluene in a double Schlenk apparatus. The colour immediately darkened to black. This suspension was filtered, after 2 mins stirring, through the internal frit of the apparatus to remove a black solid and leave an orange solution. Volatiles were removed under vacuum to leave an off-white, crystalline solid which within one hour had darkened to a buff colour. The I.R. spectrum of this solid, run in air, showed the presence of free ClO_4^- and H_2O as well as the pattern observed for the title complex and on this basis we assign it the formula [Pd(OH_2)(*o*-tolyl)(PPh_3)$_2$][ClO_4]. 5 ml of degassed acetone were added to give, after filtering twice under nitrogen, a deep orange solution. Black material was being constantly deposited as this solution decomposed. An attempt to gain a precipitate quickly by addition of 4 ml of distilled 40 - 60 ° petroleum ether gave only a dark red oil and so all solvent was stripped off under vacuum to leave *trans*-[Pd(*o*-tolyl)($OCMe_2$)(PPh_3)$_2$][ClO_4] as a red solid. Evidence for these characterisations is presented in Section 3, 2c.

2, 4f REACTION OF [Pd(PPh_3)$_4$] WITH 2-BROMOMESITYLENE.

i) 1.70 g (8.50 mmol) of 2-bromomesitylene were added, against a flow of nitrogen, to 3.20 g (2.77 mmol) of [Pd(PPh_3)$_4$] in a suspension with 100 ml of distilled toluene. The reaction mixture was then refluxed for one hour.

After cooling all solvent was removed under vacuum and the remaining dark solid was extracted into a CH_2Cl_2/60 - 80 ° petroleum ether mixture, to give an orange solution and leave behind a dark green solid. Slow evaporation of the solution gave 1.39 g (1.76 mmol) of orange, crystalline *trans*-[$PdBr_2(PPh_3)_2$]. The I.R. spectrum of this sample was identical to that of an authentic sample. The dark green solid was again extracted with CH_2Cl_2/60 - 80 ° petroleum ether to give a yellow solution and leave behind 0.22 g of a black tar. The solution precipitated firstly 0.32 g of a light yellow, unidentified complex and secondly, after slow evaporation and repeated filtering to remove dark decomposition products, 0.19 g (0.24 mmol) of [PdBr(mesityl)(PPh_3)$_2$] as colourless crystals. These crystals were, however, contaminated with a black powder and thus accurate microanalysis was impossible. [PdBr(mesityl)(PPh_3)$_2$] is unstable in solution, decomposing within 24 hrs to PPh_3O and black tar. Total yield of [PdBr(mesityl)(PPh_3)$_2$] = 9% M.P. = 214 - 216 °C. Total yield of *trans*-[$PdBr_2(PPh_3)_2$] = 64%.

ii) A previous attempt at this reaction using 0.88 g of 2-bromomesitylene and 5.00 g of [Pd(PPh_3)$_4$], a 1:1 mole ratio, with similar conditions to (i) gave only PPh_3O, black tars and 0.10 g of *trans*-[PdBr_2(PPh_3)$_2$] as products.

2, 4g REACTION BETWEEN *trans*-[PdCl_2(PPh_3)$_2$] AND [Mg(mesityl)Br].

The Grignard reagent was formed *in situ* from 0.28 g (11.5 mmol) of magnesium and 2.28 g (11.5 mmol) of 2-bromomesitylene in 30 ml of distilled T.H.F. 3.98 g (5.7 mmol) of *trans*-[PdCl_2(PPh_3)$_2$] were added as a slurry in 25 ml of T.H.F. Heating for 15 mins turned the solution brown and this was then stirred for a further 16 hrs. The reaction mixture was then quenched in water and an extraction into ether was attempted. No product was present in the ether layer.

The aqueous layer contained a brown solid which was filtered off (3.65 g). This was extracted four times with ether to give four orange solutions which on evaporation gave only PPh_3O. A fifth extraction gave a dark red solution which on cooling gave 0.16 g (0.20 mmol) of orange, crystalline *trans*-[PdBr_2(PPh_3)$_2$] as characterised by I.R. spectroscopy and microanalysis.

2, 4h ATTEMPTED REACTION BETWEEN *trans*-$[PdCl_2(PPh_3)_2]$ AND $[Hg(MESITYL)_2]$.

A solution of 22 mg (3 x 10^{-2} mmol) of the title palladium complex in 50 ml of distilled CH_2Cl_2 was treated with 22 mg (5 x 10^{-2} mmol) of $[Hg(mesityl)_2]$. The solution was warmed to 30 °C and stirred for 3 days.

On evaporation of the solvent only starting materials were recovered, as shown by I.R. spectroscopy.

2, 4i ATTEMPTED REACTION BETWEEN *trans*-$[PdCl_2(P(p\text{-}C_6H_4OMe)_3)_2]$ AND *o*-TOLYL LITHIUM.

To a 3-necked flask containing 20 ml of distilled ether and ≈ 0.05 g (7.20 mmol) of lithium were added 0.64 g (3.76 mmol) of *o*-bromotoluene in 5 ml of distilled ether. After 1 hr a brown/orange solution was present containing some unreacted lithium.

To this was added a slurry of 2.72 g (3.08 mmol) of *trans*-$[PdCl_2(PR_3)_2]$ (R = *p*-C_6H_4OMe) in 80 ml of distilled ether. After stirring for 16 hrs a yellow precipitate was filtered off in air, and washed with ethanol. I.R. and ^1H n.m.r. spectroscopy identified this as unreacted palladium starting complex. Evaporation of the mother liquor gave only further starting material (92% recovered).

A second preparation using 2.90 g (3.28 mmol) of [$PdCl_2(PR_3)_2$] and a two-fold excess of *o*-tolyl lithium was stirred for 4 days. By the fourth day the colour of the suspension had darkened from yellow to mustard and on work-up gave 1.44 g (1.48 mmol, 45% yield) of orange *trans*-[$PdBr_2(PR_3)_2$] and a black tar. *Trans*-[$PdBr_2(PR_3)_2$] (R = *p*-C_6H_4OMe) gave an I.R. spectrum similar to that of *trans*-[$PdCl_2(PR_3)_2$] (Section 2, 2b) but lacks the peak at 355 cm^{-1}. $^{31}P\{H\}$ s 18.30 p.p.m.. ^1H m 7.60, m 6.88, s 3.80 p.p.m. (Intensity 2:2:3). M.P. = 223 - 225 °C (dec.).

2, 4j REACTION BETWEEN *trans*-[$PdBr_2(P(p\text{-}C_6H_4OMe)_3)_2$] AND *o*-TOLYL LITHIUM.

Ortho-tolyl lithium was prepared *in situ* from 0.04 g (5.76 mmol) of lithium metal in 10 ml of distilled diethyl ether to which was added dropwise and with stirring 0.52 g (3.04 mmol) of *o*-bromotoluene in 8 ml of distilled ether. After the vigorous reaction had subsided 2.59 g (2.67 mmol) of the title palladium complex was added in solution with 25 ml of distilled T.H.F. This solution was stirred for 1 hr at room temperature with no obvious reaction taking place. It was then refluxed for 10 mins.

This resulted in the colour darkening to black. The reaction mixture was quenched with water and the product extracted into ether. This gave a red ether solution, a yellow water solution and 0.46 g (0.48 mmol) of the starting palladium complex as a precipitate. The aqueous layer was reduced to dryness under reduced pressure to give 0.14 g of inorganic salts.

The red ether solution was also reduced to dryness to leave a brown solid. This was extracted firstly into toluene and secondly into acetonitrile to give two red solutions. Both these solutions decomposed with time to give unidentifiable black tars.

2, 4k REACTION OF *trans*-[PdCl$_2$(P(*p*-C$_6$H$_4$OMe)$_3$)$_2$] WITH [MgBr(*o*-tolyl).

An orange Grignard reagent was prepared from 0.18 g (7.29 mmol) of magnesium turnings and 1.24 g (7.28 mmol) of *ortho*-bromotoluene in 20 ml of distilled T.H.F.

3.02 g (3.43 mmol) of the title complex were added in a slurry with 40 ml of T.H.F. There was an immediate darkening of colour from orange through red to black as the solution was stirred for 50 mins.

The solvent was removed under vacuum to leave a mixture of clear and black solids. This was dissolved in 50 ml of chloroform and filtered, in air, to remove 0.26 g of magnesium salts. The solvent was removed under reduced pressure and a recrystallisation from ethanol was attempted but this gave a solution which darkened with time and so the ethanol was also taken off under reduced pressure.

Successful recrystallisation was achieved using a 1:1 mix of CH_2Cl_2 and 60 - 80 pet. ether, to give 1.93 g (1.99 mmol) of orange crystalline *trans*-$[PdBr_2(P(p\text{-}C_6H_4OMe)_3)_2]$. Total yield = 58%. M.P. = 223 - 225 °C (dec.).

2, 5a PREPARATION OF m-($Cy_2PCH_2)_2(C_6H_4)$ (PCHP).

4.87 g (18.4 mmol) of white, crystalline m-$(BrCH_2)_2(C_6H_4)$ were added to a clear solution of 7.30 g (36.8 mmol) $HPCy_2$ in 20 ml of degassed acetone. The solution was refluxed for 45 mins, during which time a white solid formed.

The reaction mix was allowed to cool slowly to room temperature and was then cooled further in an ice bath. The solvent was decanted off, leaving white, crystalline $[m\text{-}(HCy_2PCH_2)_2(C_6H_4)][Br]_2$.

To this was added a solution of 15.30 g (144 mmol) $Na_2(CO_3)$ in 65 ml of degassed water. The resulting gel was stirred, at 80 °C, for 6 hrs by which time complete dissolution had occured. The oil bath was removed and the cooling solution was stirred for a further 14 hrs.

This gave an aqueous layer with a sticky mass floating on top. The water was removed, with gentle heating, under vacuum to leave a white solid. This was extracted using 55 ml of warm, distilled Et_2O and filtered, under N_2, into a 3-necked flask. Removal of Et_2O under vacuum left 5.93g (11.9 mmol) of m-$(PCy_2CH_2)_2(C_6H_4)$ as a clear, sticky paste. A second Et_2O extraction yielded a further 1.70 g (3.4 mmol) of product. Total yield = 83%.

Two further preparations of PCHP were carried out, on ⅔ scale, these gave 75 and 78% yields respectively.

NOTE (i) $[m\text{-}(HPCy_2CH_2)_2(C_6H_4)][Br]_2$ does not react with sodium acetate.

(ii) Attempts to obtain the product as a crystalline solid by sublimation and by crystallisation, from a range of solvents, failed. The compound was thus used with no further purification.

2, 5b REACTION BETWEEN $[Pd(NCPh)_2Cl_2]$ AND PCHP.

0.50 g (1.30 mmol) of $[Pd(NCPh)_2Cl_2]$ were added, against a flow of nitrogen, to a suspension of 0.87 g (1.74 mmol) of PCHP in 6 ml of degassed 2-methoxyethanol.

The resulting light yellow slurry was refluxed for 25 mins and then allowed to cool slowly. All solvent was removed under vacuum to give a yellow powder. This was extracted into 50 ml of hot ethanol and filtered in air to leave 0.37 g (0.27 mmol) of $[PdCl_2(PCHP)]_2$ as a yellow powder. Reducing the solvent volume under reduced pressure gave a further 0.26g

(0.19 mmol) of $[PdCl_2(PCHP)]_2$. All the remaining solvent was removed and the solid left redissolved in 4 ml acetone. Cooling to 5 °C overnight gave 0.08 g (0.12 mmol) of [PdCl(PCP)] as a white powder. A further 0.06 g (0.10 mmol) of crystalline [PdCl(PCP)] was obtained by allowing the solvent to evaporate slowly over a period of one week. Total yield $[PdCl_2(PCHP)]_2$ = 71%. M.P. = 236 °C. Microanalysis (required) C 56.90 (56.85)% H 7.67 (7.77)% Cl 10.75 (10.49)%. Total yield of [PdCl(PCP)] = 17%. M.P. = 216 - 219 °C.

2, 5c REFLUX OF $[PdCl_2(PCHP)]_2$ IN 2-METHOXYETHANOL.

0.16 g (0.12 mmol) of $[PdCl_2(PCHP)]_2$ were added to 20 ml of degassed 2-methoxyethanol, in a 3-necked flask, to form a yellow suspension which was refluxed for 42 hrs. At the end of this time the yellow colour had faded and after cooling the suspension was filtered, in air, to give 0.08 g of a greenish solid and a light yellow solution.

Removing the solvent from this solution left a pale powder (0.06 g, 0.10 mmol, 43% yield) which ^{31}P n.m.r. and I.R. spectroscopy showed to be [PdCl(PCP)].

The greenish solid was dissolved in $CHCl_3$ and filtered to remove a small amount of grey material. This left a yellow solution which on work-up was shown to contain only *trans*-$[PdCl_2(PCHP)]_2$.

2, 5d REACTION BETWEEN *trans*-$[PdBr_2(PPh_3)_2]$ AND PCHP.

0.22 g (0.28 mmol) of orange, crystalline *trans*-$[PdBr_2(PPh_3)_2]$ were added, against a flow of nitrogen, to a clear solution of 0.30 g (0.60 mmol) of PCHP in 15 ml of degassed ethanol. Even with reflux and stirring the orange solid did not dissolve completely.

After 16 hrs a light yellow slurry was obtained, a further 20 ml of degassed ethanol were added and reflux continued for a further 3½ hrs.

On cooling slowly to R.T. a yellow precipitate separated out. This was filtered off, in air, to give 0.03 g of $[PdBr_2(PCHP)]_n$ and a clear solution, which, on sitting, yielded colourless crystals of [PdBr(PCP)] (0.13g, 0.19 mmol). Cooling the mother-liquor to 5 °C gave a second yield of 0.01 g (0.02 mmol) of [PdBr(PCP)]. Total yield of [PdBr(PCP)] = 72%. M.P. = 240 - 241 °C (dec.) (phase change = 148 - 151 °C). Microanalysis (required) C 56.00 (56.19)% H 7.40 (7.46)%. Total yield of $[PdBr_2(PCHP)]_n$ = 12%. M.P. = 204 - 208 °C (dec. 240 °C).

2, 5e ATTEMPTED REACTION OF $[Pd(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2][PF_6]$ WITH PCHP.

0.96 g (1.62 mmol) of $[PdCp(PMe_2Ph)_2][PF_6]$ were added as large purple crystals, against a flow of nitrogen, to 1.00 g (2.00 mmol) of PCHP dissolved in 40 ml of degassed ethanol. The resulting suspension was refluxed for 17½ hrs after which time it was allowed to cool to room temperature and a 4 ml portion removed. I.R. and ^{31}P n.m.r. spectroscopy showed this to contain only starting materials.

Reflux was restarted and continued for a further 55 hrs. The solvent was removed under vacuum, leaving a dark green tar. Work up in air using acetone, CH_2Cl_2 and petroleum as solvents yielded only small amounts of Pd metal and dark organometallic tars that were not investigated further.

2, 5f REACTION BETWEEN $NiBr_2$ AND PCHP.

0.20 g (0.61 mmol) of $NiBr_2.6H_2O$ were added, against a flow of nitrogen, to a suspension of 0.40 g (0.80 mmol) of PCHP in 8 ml of degassed ethanol and 2 ml of degassed water, at 60 °C. Within 30 s the milky suspension turned to a clear yellow solution which was refluxed for

2 hrs before being allowed to cool slowly back to room temperature.

The dark yellow powder which settled out was filtered off, in air, and washed with water and hexane before drying under vacuum to give 0.12 g (0.19 mmol, 31% yield) of [NiBr(PCP)]. This powder was recrystallised from hot ethanol to give dark, golden crystals.

The mother-liquor left after the filtration was lime green in colour and on removal of the solvent under reduced pressure an emerald green, crystalline solid was obtained. This was redissolved in a 50:50 hot chloroform:diethyl ether mix to give, on cooling, 0.09 g of an unidentified, mint green, crystalline compound. The remaining cloroform:ether solution was now yellow and gave as a second precipitate an unidentified, yellow powder (0.05 g). [NiBr(PCP)] M.P. 203 °C. Microanalysis (required) C 60.28 (60.39)% H 8.23 (8.09)% Br 12.82 (12.57)%.

2, 5g REACTION BETWEEN [Pt(NCPh)$_2$Cl$_2$] AND PCHP.

1.59 g (3.37 mmol) of *trans*-[Pt(NCPh)$_2$Cl$_2$] were added to a three-necked flask containing a solution of 1.97 g (3.95 mmol) of PCHP in 25 ml of degassed 2-methoxyethanol. The initial clear yellow solution rapidly changes to a light yellow slurry, which was refluxed for 18½ hrs.

After cooling to room temperature this slurry was filtered, in air, to give, after washing with ethanol and drying *in vacuo*, 2.13 g (1.39 mmol) of $[PtCl_2(PCHP)]_2$ as a white powder. The mother-liquor was reduced to dryness and the remainig solid washed with hot ethanol, to remove excess phosphines and leave behind a further 0.06 g (0.04 mmol) of $[PtCl_2(PCHP)]_2$. Total yield = 85%. M.P. 218 - 222 °C (dec.). Microanalysis (required) C 50.59 (50.25)% H 6.84 (6.87)% Cl 8.26 (9.27)%.

2, 5h REACTION BETWEEN *cis*-$[PtCl_2(dppp)]$ AND PCHP IN THE PRESENCE OF $AgNO_3$.

0.58 g (0.85 mmol) of *cis*-$[PtCl_2(dppp)]$ (dppp = $Ph_2P(CH_2)_3PPh_2$) were added to a solution of 0.63 g (1.26 mmol) of PCHP in 20 ml of degassed ethanol to give a milky slurry. [The solution was refluxed for 40 hrs after which time a 2 ml portion was removed. Addition of 30 - 40 ° petroleum ether, in air, to this portion gave crystals of the starting Pt complex and removal of the solvent gave only oxidised ligand.] 0.12 g (0.71 mmol) of $AgNO_3$ were added and a further 10 ml of degassed ethanol. The Schlenk flask was covered in aluminium foil and the reaction mixture was stirred for 48 hrs. The resulting white precipitate (0.13 g) was filtered off to leave a yellow solution. The yellow solution was reduced to dryness *in vacuo* to leave an off-white solid (0.56 g) the nature of which is discussed in Section 3, 2b together with that of the first white precipitate.

2, 5i REACTION BETWEEN $RhCl_3.3H_2O$ AND PCHP.

0.60 g (2.59 mmol) of $RhCl_3.3H_2O$ were added, against a flow of nitrogen, to a milky suspension of 1.42 g (2.85 mmol) of PCHP in 20 ml of degassed propan-2-ol and 2.5 ml of degassed water in a Schlenk flask. This gave a dark suspension which was refluxed for 9 hrs.

Hot filtration of this suspension gave 0.31 g of an insoluble, unidentified dark brown solid and an orange solution, which on cooling overnight yielded 0.22 g (0.29 mmol) of $[RhCl_2(PCP)(OH_2)]$.propan-2-ol as block-shaped, yellow crystals. These were filtered off, in air, and washed carefully with a small amount of propan-2-ol. The mother-liquor was reduced under vacuum to yield a further 0.71 g (0.95 mmol) of $[RhCl_2(PCP)(OH_2]$.propan-2-ol as an orange powder. Attempts to isolate further fractions from propan-2-ol gave only a sticky orange tar; however, on recrystallising this from hot ethanol, orange needle crystals formed. They were filtered off, washed carefully with ethanol and dried to give 0.06 g (0.08 mmol) of $[RhCl_2(PCP)(HOEt)]$.

Total yield of $[RhCl_2(PCP)(OH_2)]$.propan-2-ol = 55%. M.P. 262 -

266 °C (dec.). Microanalysis (required) C 54.92 (56.07)% H 8.28 (8.22)% Cl 9.13 (9.46)%.

Total yield of [RhCl$_2$(PCP)(HOEt)] = 4%. M.P. (changes to purple mass at approx. 205 °C) dec. 254 - 256 °C. Microanalysis (required) C 56.60 (56.90)% H 7.75 (8.02)% Cl 10.22 (9.88)%.

2, 5j REFLUX OF [RhCl$_2$(PCP)(OH$_2$)].CH$_3$CH(OH)CH$_3$ IN METHANOL.

0.22 g (0.29 mmol) of [RhCl$_2$(PCP)(OH$_2$)].CH$_3$CH(OH)CH$_3$ were dissolved, under nitrogen atmosphere, in 30 ml of degassed methanol. The yellow solution was refluxed for 24 hrs and then the solvent was slowly evaporated by a stream of nitrogen to leave a light brown powder.

This powder was redissolved in a mix of 20 ml of hot degassed methanol and 4 ml of distilled CH$_2$Cl$_2$ to give an orange solution which, after filtering, hot in air, and cooling to -5 °C overnight yielded 0.12 g (0.15 mmol, 51% yield) of orange needle crystals of [RhCl$_2$(PCP)(HOMe)].CH$_2$Cl$_2$. This product rapidly (≈ 20 mins) lost the CH$_2$Cl$_2$ of crystallisation to become an orange powder. M.P.[RhCl$_2$(PCP)(HOMe)] = 268 - 271 °C (dec.).

2, 5k RECRYSTALLISATION OF [$RhCl_2$(PCP)(HOMe)] FROM NON-COORDINATING SOLVENTS.

0.10 g (0.14 mmol) of orange [$RhCl_2$(PCP)(HOMe)] were dissolved in approximately 10 ml of distilled chloroform in a double Schlenk apparatus. The yellow solution was heated to boiling point for 1 hr under a constant flow of nitrogen. The solution was allowed to cool and then all solvent was rapidly removed under vacuum. This left a reddish powder which was redissolved in 5 ml of hot, distilled chloroform and then filtered hot through the internal frit of the apparatus. 15 ml of distilled 40 - 60 ° petroleum ether were added to the yellow solution in an attempt to precipitate a product but despite cooling none was obtained after one week. All solvent was removed under vacuum to leave 0.08 g (0.12 mmol) of a bright pink powder believed to be [$RhCl_2$(PCP)]. On exposure to air this complex immediately turned orange. The pink complex was reformed on flushing the apparatus with nitrogen for 90 mins. This change is completely reversible and has been carried out several times.

2, 5l HEATING [$RhCl_2$(PCP)(S)] UNDER VACUUM.

0.12 g (0.17 mmol) of orange crystalline [$RhCl_2$(PCP)(HOEt)] were placed in a Schlenk flask and exposed to vacuum. The flask was placed in an oil bath and the temperature raised, over a period of one hour, to 120 °C and held at this temperature for a further four hours. At the end of this time the colour of the compound had changed to a vivid pink, although the same crystalline shapes could still be seen.

Exposure of small samples to air quickly (10 s) gave an orange product, identified by I.R. spectroscopy as [$RhCl_2$(PCP)(OH_2)].

At room temperature both [$RhCl_2$(PCP)(HOEt)] and $RhCl_2$(PCP)(OH_2)].propan-2-ol are stable under vacuum but a sample of $RhCl_2$(PCP)(HOMe)] as very fine, fibrous crystals did alter, over a period of approximately 8 hrs to again give a vivid pink solid that on brief exposure to air turns into orange [$RhCl_2$(PCP)(OH_2)]. This colour change reverses under vacuum.

2, 5m REACTION BETWEEN WILKINSON'S CATALYST AND PCHP.

0.68 g (0.73 mmol) of [$RhCl(PPh_3)_3$] was added to a warm (40 °C) solution of 0.61 g (1.22 mmol) of PCHP in 40 ml of degassed ethanol. After 20 mins of reflux all the purple Wilkinson's catalyst had dissolved to leave an orange suspension. This was refluxed for 18 hrs before being allowed to cool. A pink solid was filtered off under nitrogen and was shown, by I.R., ^1H n.m.r. and ^{31}P n.m.r. spectroscopy, to be a mixture of $[RhCl(PPh_3)_3]$ and oxidised ligand (0.46 g).

The remaining orange solution gave a few orange needles of an unknown complex, before the solvent was reduced, *in vacuo*, to 15 ml precipitating 0.08 g(0.11 mmol, 12% yield) of $[RhCl_2(PCP)(HOEt)]$ as an orange powder. Microanalysis (required) C 56.57 (56.90)% H 7.55 (8.02)%.

2, 5n REACTION BETWEEN *trans*-$[Rh(CO)Cl(PPh_3)_2]$ AND PCHP.

To a hot solution of 1.15 g (2.31 mmol) PCHP in 45 ml of degassed ethanol, in one limb of a double Schlenk apparatus, were added, against a nitrogen flow, 1.20 g (1.74 mmol) of yellow crystalline *trans*-$[Rh(CO)Cl(PPh_3)_2]$ to form a suspension.

After refluxing for 14½ hrs a light yellow slurry had formed. This was filtered hot, through the internal frit of the apparatus to yield, after washing with toluene, 1.06 g (0.80 mmol, 92% yield) of the light yellow powder $[RhCl(CO)(PCHP)]_2$. On work up of the mother-liquor only phosphines were isolated.

A second, similar preparation using 0.61 g (1.22 mmol) PCHP and 0.62 g (0.90 mmol) *trans*-[Rh(CO)Cl$(PPh_3)_2$] with a 9 hr reflux gave 0.485 g (0.36 mmol, 60% yield) of [RhCl(CO)(PCHP)]$_2$. M.P. = 256 - 258 °C (dec.). Microanalysis (required) C 59.82 (59.59)% H 8.09 (7.90)% Cl 5.16 (5.33)%.

2, 5o ATTEMPTED REACTION BETWEEN *trans*-[Rh(CO)Cl(PCHP)]$_2$ AND LiBr.

0.22 g (2.53 mmol) of LiBr were added to a slurry of 0.24 g (0.40 mmol) of *trans*-[Rh(CO)Cl(PCHP)]$_2$ in 40 ml of degassed 2-methoxyethanol. The reaction mixture was refluxed for 50 hrs. Filtering hot gave the starting material back unchanged, as shown by I.R. spectroscopy.

2, 5p ATTEMPTED REACTION OF *trans*-[PtCl$_2$(PCHP)]$_2$ WITH LiBr.

0.30 g (3.45 mmol) of LiBr were added to a slurry of 0.26 g (0.37 mmol) of *trans*-[PtCl$_2$(PCHP)]$_2$ in 40 ml of degassed 2-methoxyethanol. The reaction mixture was refluxed for 50 hrs and then filtered hot to remove a small amount of white material. The volume of the solution was reduced, under reduced pressure, to give only the platinum starting material as a product, as ws shown by I.R. spectroscopy.

2, 5q REACTION BETWEEN $Rh(NO_3)_3$ AND PCHP.

A solution of 0.32 g (1.11 mmol) of $Rh(NO_3)_3$ in 5 ml of water was added to a solution of 0.63 g (1.26 mmol) of PCHP in 40 ml of degassed ethanol at 60 °C via a pressure-equilibrated dropping funnel. The orange solution gradually turned black over 16 hrs under reflux. It was then cooled and filtered to remove a small amount of black powder. The volume of the solution was reduced, *in vacuo*, to 30 ml to precipitate an orange-brown solid, which after filtering and drying *in vacuo* weighed 0.20g.

The mother-liquor was reduced to dryness, *in vacuo*, to leave a black-red solid. This was extracted, in air, into 60 ml of 1:1 CH_2Cl_2:30 - 40° petroleum ether to give a red solution. The remaining red-brown solid was extracted twice into acetone to give two dark-red solutions and leave 0.23 g of a brown solid which was shown by I.R. spectroscopy to contain only traces of organic ligands.

The orange-brown solid has been characterised by I.R., ^1H and ^{31}P

n.m.r. spectroscopy and is currently formulated as [$Rh(NO_3)_2$(PCP)] (Section 3, 3e). Total yield based on [$Rh(NO_3)_2$(PCP)] = 25%. To date no solid product has been isolated from the three extractions, evaporation or addition of petroleum yielding only red tars.

2, 6a PREPARATION OF $PPh(PCy_2(C_2H_4))_2$[10] PPP.

1.96 g (12.08 mmol) of $PPh(CHCH_2)_2$ and 5.15 g (25.97 mmol) of $HPCy_2$ were syringed into a 2-necked flask against a flow of nitrogen. The flask was then immersed in an oil bath at 110 °C and after 2 mins 0.02 g of 2,2'-azobis(2-methylpropionitrile) (AIBN) were added. More 0.02 g portions of AIBN were added every 30 mins until 2 hrs had passed. Then a 0.04 g portion was added as was a second 0.04 g portion after a total of 2½ hrs. Finally after a total of 3 hrs a 0.05 g portion of AIBN was added and the mixture heated for a further hour. The mixture was allowed to cool slowly to give a yellow oil.

The oil was pumped under vacuum and the temperature slowly raised, over 90 mins to 150 °C to remove unreacted starting materials. Once the reaction mixture had cooled it was extracted into acetone and filtered under nitrogen to remove a small amount of brown material. On removing acetone under vacuum 5.39 g (9.65 mmol) of $PPh(PCy_2(C_2H_4))_2$ was obtained as a yellowish oil. Yield = 79%.

2, 6b REACTION BETWEEN $PdCl_2$ AND PPP.

A solution of 1.97 g (3.53 mmol) PPP in 25 ml of degassed ethanol was added to a solution of 0.40 g (2.25 mmol) $PdCl_2$ and 0.24 g (4.10 mmol) NaCl in 16 ml of degassed, distilled water. There was an immediate colour change from orange/brown to yellow. The solution was stirred for 24 hrs and the solvent was then removed under vacuum, with gentle heating. This left a yellow solid, [PdCl(PPP)][Cl], which was redissolved in 25 ml of acetone and undissolved NaCl removed by filtration. Despite volume reduction of the acetone and cooling no solid was isolated. 0.75 g (4.60 mmol) NH_4PF_6 in 2 ml of degassed water was added to the acetone solution and this precipitated a yellow oil. The oil was redissolved by warming and addition of more acetone and then left to cool. This gave 0.11 g of an off-white powder which was filtered off, in air, and washed with water and petroleum ether. Further crops of white powder were obtained on work up from propan-2-ol solutions to give a total yield of 0.59 g (0.81 mmol, 36% yield) of $[PdCl(PPP)][PF_6].2H_2O$. M.P. = 157 - 161 °C. Microanalysis (required) C 48.48 (48.00)% H 7.13 (7.24)%.

2, 6c REACTION BETWEEN $[PdCl(PPP)][PF_6]$ AND $AgPF_6$.

To one arm of a double Schlenk apparatus were added 0.43 g (0.51 mmol) of the title palladium salt and 0.18 g (0.71 mmol) of $AgPF_6$. 12 ml of degassed acetone were added and the resulting milky slurry was stirred for 14 hrs by which time the reaction mixture contained a buff suspension.

All solvent was removed under vacuum to give a reddish/buff powder that was redissolved in distilled CH_2Cl_2 and filtered to remove a dark inorganic material and leave an orange solution. Further filtration through a membrane filter was required before the orange solution was free of suspended particles.

The solvent volume was reduced to 5 ml and distilled 30 - 40 ° petroleum ether added dropwise until a dark oil was precipitated. This was redissolved by heating and addition of CH_2Cl_2 but cooling and/or addition of petroleum ether did not give a solid product so all solvent was removed, *in vacuo*, to leave a buff powder. On storing overnight in a sealed Schlenk flask at 5 °C this had decomposed to a brown tar which on vigorous pumping to vacuum gave a brown, insoluble powder.

2, 6d REACTION BETWEEN [RhCl(PPh$_3$)$_3$] AND PPP.

0.47 g (0.51 mmol) of [RhCl(PPh$_3$)$_3$] were added against a flow of nitrogen to a solution of 0.50 g (0.89 mmol) of PPP in 60 ml of distilled toluene. The clear yellow/orange solution was stirred at 40 °C for 30 mins.

After being cooled to -5 °C overnight a yellow precipitate formed which was filtered off, in air, and dried *in vacuo* to give 0.15 g of a mix of

[RhCl(PPP)] and oxidised ligand. [RhCl(PPP)] was isolated from this buff mixture by recrystallisation from 5 ml of ethanol, to give 0.06 g (0.09 mmol) of [RhCl(PPP)] as a yellow powder.

The mother-liquor was dried *in vacuo* and recrystallisation from the minimum of hot ethanol gave a further 0.03 g (0.05 mmol) of [RhCl(PPP)] and an impure red oil. This oil could not be solidified despite successive treatments with ether, ethanol, acetone, petroleum ether and CH_2Cl_2. Total yield = 17%.

2, 6e REACTION BETWEEN $RhCl_3.3H_2O$ AND PPP.

0.45 g (1.71 mmol) of $RhCl_3.3H_2O$ were added, against a countercurrent of nitrogen, to 1.24 g (2.22 mmol) of PPP dissolved in 20 ml of degassed ethanol. The mixture was stirred for 24 hrs and then filtered through the internal frit of the apparatus to separate an orange powder from the orange solution. The solution was decanted into a nitrogen-filled 2-necked flask.

The orange powder was dried under vacuum and then recrystallised, in air, from chloroform to give 0.26 g (0.34 mmol) of [$RhCl_3$(PPP)] as an orange powder.

The mother-liquor was reduced to dryness under vacuum to leave a pale yellow solid. This was recrystallised from a 2:1 chloroform:ether mixture to yield 0.05 g (0.07 mmol) of [$RhCl_3$(PPP)] as a yellow crystalline product. Total yield = 24%. M.P. = 269 - 271 °C (dec.). Microanalysis (required) C 52.40 (53.16)% H 7.26 (7.50)% Cl 14.70 (13.90)%.

2, 7a CRYSTALLOGRAPHIC MEASUREMENTS.

The following general experimental and computational methods were used for all structures. Measurements were made at ambient temperatures (22 - 28 °C) with Mo K_α X-rays, $\lambda = 0.71073$ Å (except for 2, 71 Cu K_α, $\lambda = 1.5418$ Å) on an Enraf-Nonius CAD4 diffractometer fitted with a graphite monochromator. Intensities, I, and their standard deviations, $\sigma(I) = (s^2 + p^2I^2)^{½}$ where s is based on counting statistics and p = 0.03, were derived from $\omega/2\Theta$ scans. Corrections were applied for Lp effects, for absorption by the empirical method of Walker and Stuart[11], and for crystal decomposition if the variation in intensities of the standard reflections warranted it. Equivalent intensities were then averaged and unobserved reflections with $I < 3\sigma(I)$ excluded from further consideration.

The heavy atoms were located from the Patterson function and the remaining non-hydrogen atoms from subsequent difference syntheses. In the final calculations anisotropic displacement parameters were usually refined for all non-hydrogen atoms.

Final least-squares refinements were on F with $w = 1/\sigma^2(F)$. If possible, full-matrix refinement was used and refinement was only terminated when the maximum shift/esd (Δ/σ) ratio was less than 0.1. Neutral atom scattering factors and anomalous dispersion corrections were taken from Ref. 12 and the calculations were performed on a VAX3600 with the GX package.[13] Details of the individual analyses and divergences from the procedures described here are presented in Sections 2, 7b - l and Tables 2, 7i - xxvi.

2, 7b CRYSTAL STRUCTURE OF [PdCl{(PCy$_2$CH$_2$)$_2$(C$_6$H$_3$)}].

Colourless prismatic crystals were obtained by slow evaporation of an acetone solution. The selected crystal of dimensions 0.10 x 0.10 x 0.10 mm was mounted on a glass fibre. Cell dimensions were obtained from the least-squares treatment of 24 reflections with $2° < \Theta < 14°$.

Hydrogen atoms, although located in difference syntheses, were positioned according to expected stereochemistry and constrained to ride on the parent carbon atoms with C-H = 1.00 Å and $U(H) = 1.2\ U_{eq}(C)$. For further details see Tables 2, 7i - iii.

2, 7c CRYSTAL STRUCTURE OF [PdBr{(PCy$_2$CH$_2$)$_2$(C$_6$H$_3$)}]

A colourless, tabular crystal obtained directly from the ethanol reaction mixture (Section 2, 5d) and of dimensions 0.25 x 0.08 x 0.08 mm, was mounted on a glass fibre. Cell dimensions were obtained from the least-squares treatment of 22 reflections with $9.6° \leq \Theta \leq 23.4°$.

H atoms, although located in difference syntheses, were positioned according to expected stereochemistry and constrained to ride on their parent carbon atoms with C-H = 0.96 Å and $U(H) = 1.2\ U_{eq}(C)$. For further details see Tables 2, 7i and 2, 7iv - v.

2, 7d CRYSTAL STRUCTURE OF $[NiBr\{(PCy_2CH_2)_2(C_6H_3)\}]$.

Golden, prismatic crystals were obtained on cooling a hot ethanol solution. The selected crystal of dimensions 0.35 x 0.20 x 0.20 mm was mounted on a glass fibre. Cell dimensions were obtained from the least-squares treatment of 22 reflections with $10.3° \leq \Theta \leq 20.8°$.

H atoms, although located in difference syntheses, were placed according to stereochemical expectations and constrained to ride on their parent carbon atoms with C-H = 0.96 Å and $U(H) = 1.2\ U_{eq}(C)$. For further details see Tables 2, 7i and 2, 7vi - vii.

2, 7e CRYSTAL STRUCTURE OF $[RhCl_2\{(PCy_2CH_2)_2(C_6H_3)\}(HOEt)].H_2O$.

A yellow diamond-shaped plate obtained by slow evaporation of an ethanol-hexane solution and of dimensions 0.45 x 0.30 x 0.05 mm, was mounted on a glass fibre. Cell dimensions were obtained from the least-squares treatment of 25 reflections with $15.4° \leq \Theta \leq 22.0°$.

Hydrogen atoms were located in a low angle difference synthesis with the exception of the solvent water hydrogens which were not found and were not included in the final refinement. HOEt was placed as found and constrained to ride on its parent oxygen atom with refinement of U(H). Hydrogen atoms on carbon atoms were placed in calculated positions and were then constrained to ride on their parent carbon atoms with C-H = 0.96 Å and U(H) = 1.2 U_{eq}(C). For further details see Tables 2, 7viii - x.

2, 7f CRYSTAL STRUCTURE OF $[RhCl_2\{(PCy_2CH_2)_2(C_6H_3)\}(HOEt)]$.

Orange needle crystals were obtained from cooling a hot ethanolic solution. The selected crystal, of dimensions 0.20 x 0.05 x 0.05 mm, was mounted on a glass fibre. Cell dimensions of the weakly diffracting crystal were calculated from the least-squares treatment of 15 reflections with 1.8° ≤ Θ ≤ 10.7°. Rh, Cl and P atoms were refined with anisotropic displacement parameters. All H atoms were located in a low angle difference synthesis. HOEt was placed as found and constrained to ride on its parent oxygen atom with $U(H) = 1.2\ U_{iso}(O)$. All other H atoms were placed in calculated positions and constrained to ride on their parent C atoms with C-H = 0.96 Å and $U(H) = 1.2\ U_{iso}(C)$. For further details see Tables 2, 7viii and 2, 7xi - xii.

2, 7g CRYSTAL STRUCTURE OF $[RhCl_2\{(PCy_2CH_2)_2(C_6H_3)\}(OH_2)]$.PROPAN-2-OL.

A yellow, tabular crystal obtained directly from the propan-2-ol reaction mixture (Section 2, 5i) and of dimensions 0.25 x 0.12 x 0.08 mm was mounted on a glass fibre. Cell dimensions were obtained from the least-squares treatment of 25 reflections with 20° < Θ < 25°. A correction was made for a linear decay of 3% over the last 4894 of the 11894 reflections processed. Final refinement was by the method of block-diagonal least-squares.

All H atoms were located in difference syntheses. The position of O-bonded H atoms were derived from difference syntheses but all other H atoms were placed in calculated positions with C-H = 0.96 Å and all H atoms were constrained to ride on their parent C or O atoms with U(H) = 1.2 U_{eq}(C) or 1.2 U_{eq}(O). For further details see Tables 2, 7xiii - xv.

2, 7h CRYSTAL STRUCTURE OF $[RhCl_2\{(PCy_2CH_2)_2(C_6H_3)\}(HOMe)].0.41(CH_2Cl_2)$.

Orange, prismatic crystals were grown on cooling a 5:1 methanol:CH_2Cl_2 solution to -5 °C. An air-sensitive crystal of dimensions 0.40 x 0.35 x 0.32 mm was mounted in a Lindemann capillary. Cell dimensions were obtained from the least-squares treatment of 22 reflections with $11.7° \leq \Theta \leq 22.8°$.

Hydrogen atoms attached to carbon atoms of the MeOH and CH_2Cl_2 molecules were not found in difference syntheses and were not included in the final model. Other hydrogen atoms were located in difference syntheses but were placed in calculated positions and constrained to ride on their parent carbon atoms with C-H = 0.96 Å and U(H) = 1.2 U_{eq}(C), with the exception of <u>H</u>OMe which was positioned as found and set to ride on O(1) with refinement of U_{iso}.

The CH_2Cl_2 solvent molecule site was found to be only partially occupied and in addition disordered so as to give two separate positions - with a 2:1 occupancy ratio - for each Cl atom and a common C atom position. The atoms of the CH_2Cl_2 molecule were placed as found in a difference synthesis, with no positional refinement, and refined with isotropic displacement parameters. It was found impossible to refine both the occupancy of the solvent sites and the isotropic displacement parameters simultaneously due to the high degree of correlation between these parameters. Thus after a series of trial calculations the isotropic displacement parameters were set to the values given in Table 2, 7xvi and only overall occupancy of the solvent was refined, to 0.414(6), in the final model. For further details see Tables 2, 7xiii and 2, 7xvi - xvii.

2, 7i CRYSTAL STRUCTURE OF *trans*-$[Rh(CO)(OH_2)(PPh_3)_2][ClO_4].CH_2Cl_2$.

Large yellow crystals were grown from a CH_2Cl_2/petroleum ether mixture. A fragment of dimensions 0.63 x 0.45 x 0.40 mm was cut from a larger crystal and mounted in a Lindemann capillary. Cell dimensions were obtained from the least-squares treatment of 22 reflections with 12° $< \Theta <$ 14°.

Final refinement was by the method of block-diagonal least-squares.

All hydrogen atoms, except for those in the CH_2Cl_2 molecule, were observed in a low angle difference synthesis. Coordinates of H_2O hydrogens were determined from this synthesis, while those of remaining hydrogens were geometrically calculated (C-H = 1.00 Å). All H atoms were constrained to ride on the atoms to which they were attached with U(H) = 1.2 U_{eq}, where U_{eq} is the equivalent isotropic displacement parameter of the parent O or C atom. For further details see Tables 2, 7 xviii- xx.

2, 7j CRYSTAL STRUCTURE OF *trans*-[Rh(CO)(OCMe$_2$)(PPh$_3$)$_2$][ClO$_4$].(OCMe$_2$).

Air-sensitive, yellow, needle crystals were obtained by slow addition of petroleum ether to an acetone solution. A crystal of dimensions 0.40 x 0.10 x 0.10 mm was mounted in a Lindemann capillary. Cell dimensions of the poorly diffracting crystal were obtained from the least-squares treatment of 25 reflections with $15° < \Theta < 19°$.

Rh, Cl and P atoms were refined with anisotropic displacement parameters. All O atoms and the C atoms of the two acetone groups and the carbonyl group were refined with isotropic displacement parameters. The phenyl rings were refined as rigid groups with C-C = 1.38 Å and C-H = 1.08 Å and all angles set at 120°. A single isotropic displacement parameter was refined for each C atom in the phenyl rings and U(H) set to equal 1.2 U(C) where U(C) is the isotropic displacement parameter of the parent C atom prior to final refinement. H atoms of the acetone groups were not included in the final refinement. For further details see Tables 2, 7xviii and 2, 7xxi - xxii.

2, 7k CRYSTAL STRUCTURE OF *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$].

Cooling a hot CH_2Cl_2/Et_2O solution gave colourless, prismatic crystals. The selected crystal, of dimensions 0.23 x 0.15 x 0.08 mm, was mounted on a glass fibre. Cell dimensions were obtained from the least-squares treatment of 25 reflections with $20.8° \leq \Theta \leq 22.9°$.

It was discovered that of the 4912 reflections with $I > 3\sigma(I)$ 4352 reflections could be indexed using a unit cell one third the volume of the true cell. The transformation matrix used was (3 x 3) 1, 0, 0, -⅓, ⅓, -⅓, 0, 0, 1. Details of both the original cell used in data collection and the sub-cell are given in Table 2, 7xxiii. Structural refinement was continued as normal using this smaller unit cell. H atoms, although located in difference syntheses, were placed according to stereochemical expectations and constrained to ride on their parent carbon atoms with C-H = 0.96 Å and U(H) = 0.05. To reduce the number of parameters in the final refinement the positions of the phenyl rings were refined by group methods although each carbon atom in the rings had individual anisotropic temperature factors refined.

The evidence at present available suggests that the true structure is a superstructure of the basic structure with pseudo translational symmetry relating the independent molecules of this displacively modulated commensurate structure.

2, 71 CRYSTAL DATA COLLECTION FOR THE REACTION PRODUCT FROM THE ADDITION OF WILKINSON'S CATALYST TO $TlClO_4$.

Small, orange, hexagonal plates were grown by layering an acetone solution with petroleum ether as described in Section 2, 3g. The selected, air-sensitive crystal was of dimensions 0.10 x 0.10 x 0.02 mm, and was mounted in a Lindemann capillary. Cell dimensions of this small, weakly diffracting crystal were obtained by the least-squares treatment of 21 reflections with $10° < \Theta < 20°$.

The Rh atom position was located from the Patterson synthesis but other atoms were not located in refinable positions. For further details see

Table 2, 7xxvi.

Table 2, 7i	PdCl(PCP)	PdBr(PCP)	NiBr(PCP)
FORMULA	$C_{32}H_{51}ClP_2Pd$	$C_{32}H_{51}BrP_2Pd$	$C_{32}H_{51}BrNiP_2$
F. Wt.	639.64	684.09	636.36
CRYSTAL SYSTEM	MONOCLINIC	MONOCLINIC	MONOCLINIC
SPACE GROUP	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	10.4956 (6)	10.4780 (10)	10.407 (1)
b, Å	18.7996 (18)	18.8889 (18)	18.900 (1)
c, Å	16.1232 (12)	16.2454 (11)	16.142 (1)
β, deg.	91.5683 (52)	91.0773 (68)	92.496 (9)
U, $Å^3$	3180.1 (4)	3214.7 (5)	3172.0 (4)
Z	4	4	4
D_{CALC}, g cm^{-3}	1.336	1.413	1.333
F(000)	1344	1416	1344
μ, cm^{-1}	7.78	19.17	19.79
crystal, mm	0.10x0.10x0.10	0.25x0.08x0.08	0.20x0.35x0.20
kV	50	55	55
mA	20	32	32
COLLIMATOR, mm	0.40	0.40	0.40
Θ_{RANGE}, deg.	2 - 25	2 - 25	2 - 31
h	0 - 12	$\overline{12}$ - 12	0 - 12
k	$\overline{22}$ - 22	0 - 22	0 - 23
l	$\overline{19}$ - 19	19 - 0	$\overline{20}$ - 20
reflns. measured	7032	5619	6739
unique reflns.	5615	5410	6381
observed reflns.	3272	2520	2997
R_{int}	0.023	0.033	0.028
R	0.0358	0.0370	0.0358
R_w	0.0476	0.0359	0.0354
S	1.99	1.11	1.19
Parameters	325	325	325
$\Delta\rho_{max}$, e/$Å^3$	0.98	0.42	0.33
$\Delta\rho_{min}$, e/$Å^3$	-0.24	-0.43	-0.30

Table 2,7ii Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For [PdCl(PCP)]

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^* a_j^*(\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Pd	0.19908(4)	0.22156(2)	0.21558(3)	0.030
Cl	0.08040(13)	0.28800(8)	0.31688(8)	0.039
P(1)	0.39576(13)	0.22614(9)	0.28100(8)	0.031
P(2)	0.02373(14)	0.19047(9)	0.13887(9)	0.034
C(1)	0.2893(5)	0.1665(3)	0.1277(3)	0.034
C(2)	0.4221(5)	0.1511(3)	0.1362(3)	0.036
C(3)	0.4806(6)	0.1085(3)	0.0788(4)	0.046
C(4)	0.4135(7)	0.0804(3)	0.0109(4)	0.052
C(5)	0.2857(7)	0.0973(3)	0.0001(4)	0.049
C(6)	0.2241(6)	0.1395(3)	0.0560(3)	0.037
C(7)	0.4987(6)	0.1850(3)	0.2052(4)	0.042
C(8)	0.0874(6)	0.1585(4)	0.0416(3)	0.046
C(A1)	0.4724(6)	0.3100(3)	0.3109(3)	0.037
C(A2)	0.4448(6)	0.3673(3)	0.2462(4)	0.047
C(A3)	0.5034(7)	0.4390(4)	0.2713(4)	0.059
C(A4)	0.6464(7)	0.4324(4)	0.2903(5)	0.067
C(A5)	0.6773(6)	0.3751(4)	0.3530(4)	0.059
C(A6)	0.6169(6)	0.3035(4)	0.3288(4)	0.050
C(B1)	0.4075(5)	0.1677(3)	0.3721(3)	0.035
C(B2)	0.3548(7)	0.0941(3)	0.3513(4)	0.053
C(B3)	0.3645(8)	0.0445(4)	0.4237(5)	0.066
C(B4)	0.2963(8)	0.0734(4)	0.4968(4)	0.067
C(B5)	0.3454(6)	0.1469(4)	0.5195(4)	0.054
C(B6)	0.3401(6)	0.1983(3)	0.4470(4)	0.046
C(C1)	-0.0940(6)	0.2590(3)	0.1144(3)	0.040
C(C2)	-0.2060(6)	0.2338(4)	0.0593(4)	0.050
C(C3)	-0.2991(6)	0.2947(4)	0.0430(4)	0.059
C(C4)	-0.2362(8)	0.3572(4)	0.0036(4)	0.067
C(C5)	-0.1249(8)	0.3830(4)	0.0567(5)	0.072
C(C6)	-0.0298(7)	0.3234(4)	0.0773(4)	0.058
C(D1)	-0.0623(6)	0.1128(3)	0.1774(4)	0.041
C(D2)	-0.1360(7)	0.1279(4)	0.2552(4)	0.056
C(D3)	-0.2078(7)	0.0620(4)	0.2839(5)	0.069
C(D4)	-0.1190(8)	0.0000(4)	0.2992(5)	0.076
C(D5)	-0.0418(9)	-0.0165(4)	0.2222(6)	0.081
C(D6)	0.0288(7)	0.0503(4)	0.1921(5)	0.058

Table 2,7iii Anisotropic Displacement Parameters For [PdCl(PCP)].

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}h_ih_ja_i^*a_j^*]$$

	U11	U22	U33	U12	U13	U23
Pd	0.0288(2)	0.0302(2)	0.0300(2)	0.0036(3)	0.0006(2)	-.0018(3)
Cl	0.0412(8)	0.0449(10)	0.0295(7)	0.0185(8)	0.0007(6)	-.0167(7)
P(1)	0.0293(7)	0.0331(8)	0.0308(7)	0.0002(8)	0.0003(6)	0.0005(8)
P(2)	0.0319(8)	0.0360(9)	0.0347(8)	0.0011(8)	-.0022(7)	0.0006(7)
C(1)	0.040(3)	0.029(3)	0.033(3)	0.004(3)	0.009(3)	0.001(3)
C(2)	0.039(3)	0.034(4)	0.035(3)	0.004(3)	0.002(3)	0.004(3)
C(3)	0.044(4)	0.051(4)	0.042(4)	0.015(3)	0.012(3)	-0.002(3)
C(4)	0.066(5)	0.048(4)	0.043(4)	0.015(4)	0.013(3)	-0.010(3)
C(5)	0.066(5)	0.044(4)	0.037(4)	0.006(4)	-0.001(3)	-0.008(3)
C(6)	0.042(4)	0.039(4)	0.029(3)	0.001(3)	0.001(3)	0.000(3)
C(7)	0.034(3)	0.049(4)	0.044(4)	0.005(3)	0.006(3)	-0.001(3)
C(8)	0.056(4)	0.047(4)	0.034(3)	0.000(4)	-0.005(3)	-0.003(3)
C(A1)	0.040(3)	0.032(3)	0.038(3)	-0.001(3)	0.000(3)	0.003(3)
C(A2)	0.048(4)	0.044(4)	0.049(4)	-0.003(3)	-0.005(3)	0.011(3)
C(A3)	0.066(5)	0.039(4)	0.071(5)	-0.008(4)	-0.005(4)	0.011(4)
C(A4)	0.069(5)	0.051(5)	0.083(6)	-0.028(4)	-0.004(4)	0.015(4)
C(A5)	0.044(4)	0.066(5)	0.068(5)	-0.020(4)	-0.006(4)	0.001(4)
C(A6)	0.046(4)	0.047(4)	0.056(4)	-0.003(3)	-0.013(3)	0.005(3)
C(B1)	0.032(3)	0.035(3)	0.038(3)	0.001(3)	0.001(3)	0.001(3)
C(B2)	0.075(5)	0.034(4)	0.049(4)	-0.001(4)	-0.005(4)	-0.003(3)
C(B3)	0.102(6)	0.037(4)	0.060(5)	-0.010(4)	0.000(5)	0.011(4)
C(B4)	0.084(6)	0.059(5)	0.057(5)	-0.017(5)	0.006(4)	0.025(4)
C(B5)	0.062(5)	0.059(5)	0.041(4)	-0.001(4)	0.002(3)	0.007(4)
C(B6)	0.053(4)	0.043(4)	0.042(4)	-0.001(3)	0.000(3)	0.004(3)
C(C1)	0.036(3)	0.041(4)	0.044(3)	0.004(3)	-0.001(3)	0.000(3)
C(C2)	0.041(3)	0.062(5)	0.047(4)	0.005(4)	-0.011(3)	0.001(3)
C(C3)	0.045(4)	0.081(6)	0.051(4)	0.020(4)	-0.011(3)	0.000(4)
C(C4)	0.079(5)	0.068(5)	0.053(5)	0.036(5)	-0.008(4)	0.011(4)
C(C5)	0.075(5)	0.048(5)	0.093(6)	0.018(4)	0.005(5)	0.017(4)
C(C6)	0.053(4)	0.047(5)	0.075(5)	0.006(4)	-0.002(4)	0.012(4)
C(D1)	0.035(3)	0.041(4)	0.047(4)	-0.003(3)	-0.007(3)	-0.002(3)
C(D2)	0.059(4)	0.054(4)	0.056(4)	-0.003(4)	0.016(4)	0.007(4)
C(D3)	0.068(5)	0.070(5)	0.070(5)	-0.018(5)	0.016(4)	0.003(5)
C(D4)	0.092(6)	0.060(5)	0.077(6)	-0.020(5)	0.003(5)	0.019(5)
C(D5)	0.082(6)	0.047(5)	0.115(8)	0.004(5)	-0.002(5)	0.013(5)
C(D6)	0.056(4)	0.043(4)	0.076(5)	0.003(4)	0.004(4)	0.006(4)

Table 2,7iv Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For [PdBr(PCP)]

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j^* (\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Pd	0.20004(5)	0.22071(3)	0.21688(3)	0.031
Br	0.07584(8)	0.28924(5)	0.32109(5)	0.056
P(1)	0.39680(17)	0.22527(11)	0.28136(11)	0.035
P(2)	0.02499(18)	0.19025(10)	0.14062(12)	0.036
C(1)	0.2922(7)	0.1670(3)	0.1293(4)	0.035
C(2)	0.4228(7)	0.1513(4)	0.1367(4)	0.040
C(3)	0.4841(7)	0.1087(4)	0.0798(5)	0.046
C(4)	0.4164(9)	0.0815(4)	0.0139(5)	0.055
C(5)	0.2897(9)	0.0976(4)	0.0027(5)	0.052
C(6)	0.2276(7)	0.1398(4)	0.0592(5)	0.040
C(7)	0.5009(7)	0.1842(4)	0.2049(5)	0.045
C(8)	0.0891(7)	0.1594(4)	0.0441(4)	0.045
C(A1)	0.4736(7)	0.3098(3)	0.3107(4)	0.036
C(A2)	0.4457(7)	0.3657(4)	0.2461(5)	0.052
C(A3)	0.5031(9)	0.4373(4)	0.2725(5)	0.063
C(A4)	0.6469(9)	0.4308(5)	0.2901(6)	0.070
C(A5)	0.6768(8)	0.3742(5)	0.3529(5)	0.062
C(A6)	0.6158(7)	0.3036(4)	0.3287(5)	0.050
C(B1)	0.4093(6)	0.1676(4)	0.3722(4)	0.039
C(B2)	0.3431(8)	0.1975(4)	0.4478(5)	0.051
C(B3)	0.3493(8)	0.1462(5)	0.5200(5)	0.061
C(B4)	0.3003(8)	0.0731(5)	0.4969(6)	0.065
C(B5)	0.3671(9)	0.0441(4)	0.4239(6)	0.073
C(B6)	0.3564(8)	0.0944(4)	0.3507(5)	0.056
C(C1)	-0.0626(7)	0.1133(4)	0.1794(4)	0.041
C(C2)	-0.1392(8)	0.1291(4)	0.2562(5)	0.054
C(C3)	-0.2095(9)	0.0626(5)	0.2839(6)	0.072
C(C4)	-0.1192(10)	0.0016(5)	0.3001(7)	0.087
C(C5)	-0.0416(9)	-0.0145(5)	0.2255(7)	0.084
C(C6)	0.0293(8)	0.0516(4)	0.1957(6)	0.061
C(D1)	-0.0926(6)	0.2592(4)	0.1154(4)	0.038
C(D2)	-0.2028(7)	0.2343(4)	0.0595(5)	0.053
C(D3)	-0.2957(8)	0.2946(5)	0.0415(5)	0.069
C(D4)	-0.2293(9)	0.3566(5)	0.0030(6)	0.076
C(D5)	-0.1194(9)	0.3821(4)	0.0573(6)	0.073
C(D6)	-0.0257(7)	0.3237(4)	0.0792(5)	0.056

Table 2,7v Anisotropic Displacement Parameters For [PdBr(PCP)].

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}h_ih_ja_i^*a_j^*]$$

	U11	U22	U33	U12	U13	U23
Pd	0.0310(3)	0.0312(3)	0.0322(3)	0.0034(3)	0.0005(3)	-.0021(3)
Br	0.0556(6)	0.0628(6)	0.0497(6)	0.0172(5)	0.0001(5)	-.0163(5)
P(1)	0.033(1)	0.035(1)	0.036(1)	0.001(1)	0.000(1)	0.002(1)
P(2)	0.034(1)	0.035(1)	0.039(1)	0.001(1)	-0.003(1)	-0.002(1)
C(1)	0.039(5)	0.027(4)	0.039(5)	0.001(4)	0.016(4)	0.002(4)
C(2)	0.042(5)	0.039(5)	0.037(5)	0.002(4)	0.013(4)	-0.001(4)
C(3)	0.048(5)	0.040(5)	0.050(5)	0.007(4)	0.010(5)	-0.001(4)
C(4)	0.059(6)	0.048(6)	0.058(6)	0.019(5)	0.022(5)	-0.017(5)
C(5)	0.072(7)	0.044(5)	0.041(5)	0.003(5)	0.000(5)	-0.007(4)
C(6)	0.049(5)	0.031(5)	0.040(5)	0.003(4)	0.004(4)	-0.002(4)
C(7)	0.031(5)	0.050(5)	0.055(5)	0.001(4)	0.018(4)	-0.003(4)
C(8)	0.056(5)	0.043(5)	0.036(5)	0.003(4)	0.002(4)	-0.003(4)
C(A1)	0.039(5)	0.040(5)	0.029(4)	0.001(4)	-0.003(4)	0.005(4)
C(A2)	0.047(5)	0.052(6)	0.057(6)	-0.001(4)	-0.008(4)	0.008(5)
C(A3)	0.074(7)	0.039(5)	0.076(7)	-0.004(5)	0.002(6)	0.012(5)
C(A4)	0.063(7)	0.063(6)	0.084(7)	-0.030(5)	0.005(6)	0.008(6)
C(A5)	0.045(6)	0.073(6)	0.068(6)	-0.012(5)	-0.013(5)	0.005(5)
C(A6)	0.045(5)	0.046(5)	0.060(6)	-0.010(4)	-0.014(4)	0.010(4)
C(B1)	0.036(5)	0.042(5)	0.038(5)	0.006(4)	-0.006(4)	0.007(4)
C(B2)	0.062(6)	0.045(5)	0.045(5)	-0.006(4)	0.006(5)	0.006(4)
C(B3)	0.064(7)	0.072(7)	0.047(6)	0.003(5)	0.003(5)	0.003(5)
C(B4)	0.068(7)	0.060(7)	0.066(7)	-0.006(5)	0.004(5)	0.027(5)
C(B5)	0.103(8)	0.048(6)	0.068(7)	-0.009(5)	0.006(6)	0.022(6)
C(B6)	0.078(7)	0.034(5)	0.056(6)	0.000(5)	-0.003(5)	-0.005(5)
C(C1)	0.040(5)	0.039(5)	0.043(5)	-0.005(4)	-0.007(4)	-0.001(4)
C(C2)	0.054(6)	0.054(6)	0.055(5)	-0.010(5)	0.002(5)	0.005(5)
C(C3)	0.080(7)	0.069(6)	0.067(6)	-0.020(6)	0.021(5)	0.004(6)
C(C4)	0.088(8)	0.070(8)	0.103(9)	-0.023(6)	-0.006(7)	0.037(7)
C(C5)	0.087(8)	0.051(7)	0.115(10)	0.008(6)	0.007(7)	0.024(6)
C(C6)	0.058(6)	0.040(5)	0.086(7)	0.000(4)	0.011(5)	0.012(5)
C(D1)	0.027(4)	0.044(5)	0.044(5)	0.007(4)	-0.003(4)	0.000(4)
C(D2)	0.045(5)	0.055(6)	0.058(5)	0.005(4)	-0.012(4)	-0.005(5)
C(D3)	0.059(6)	0.084(7)	0.063(6)	0.029(6)	-0.020(5)	-0.005(6)
C(D4)	0.083(8)	0.075(7)	0.069(7)	0.048(6)	-0.016(6)	0.008(6)
C(D5)	0.075(7)	0.053(6)	0.091(8)	0.014(5)	0.001(6)	0.024(6)
C(D6)	0.043(5)	0.045(5)	0.081(7)	-0.003(4)	0.000(5)	0.018(5)

Table 2,7vi Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For [NiBr(PCP)].

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*(\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Ni	0.20445(5)	0.21973(3)	-0.28975(3)	0.030
Br	0.09611(5)	0.28952(3)	-0.19367(3)	0.051
P(1)	0.39120(11)	0.22398(6)	-0.22257(7)	0.032
P(2)	0.02999(12)	0.19170(6)	-0.36046(7)	0.034
C(1)	0.2891(5)	0.1662(2)	-0.3715(3)	0.035
C(2)	0.4208(5)	0.1498(2)	-0.3638(3)	0.036
C(3)	0.4806(5)	0.1071(3)	-0.4204(3)	0.049
C(4)	0.4110(6)	0.0804(3)	-0.4884(3)	0.054
C(5)	0.2838(6)	0.0976(3)	-0.5007(3)	0.050
C(6)	0.2229(5)	0.1398(2)	-0.4439(3)	0.039
C(7)	0.5002(5)	0.1829(3)	-0.2939(3)	0.044
C(8)	0.0840(5)	0.1601(3)	-0.4594(3)	0.045
C(A1)	0.4035(4)	0.1671(2)	-0.1303(3)	0.034
C(A2)	0.3494(5)	0.0940(2)	-0.1521(3)	0.051
C(A3)	0.3615(7)	0.0438(3)	-0.0783(4)	0.073
C(A4)	0.2938(6)	0.0730(3)	-0.0049(3)	0.069
C(A5)	0.3446(5)	0.1460(3)	0.0176(3)	0.053
C(A6)	0.3365(5)	0.1970(3)	-0.0561(3)	0.046
C(B1)	0.4663(4)	0.3080(2)	-0.1908(3)	0.036
C(B2)	0.6110(5)	0.3025(3)	-0.1682(3)	0.050
C(B3)	0.6692(5)	0.3736(3)	-0.1431(3)	0.060
C(B4)	0.6425(6)	0.4300(3)	-0.2090(3)	0.066
C(B5)	0.4992(6)	0.4355(3)	-0.2312(3)	0.063
C(B6)	0.4413(5)	0.3645(2)	-0.2578(3)	0.046
C(C1)	-0.0904(4)	0.2602(2)	-0.3842(3)	0.036
C(C2)	-0.0272(5)	0.3239(3)	-0.4238(3)	0.053
C(C3)	-0.1236(6)	0.3834(3)	-0.4430(3)	0.064
C(C4)	-0.2385(6)	0.3562(3)	-0.4947(3)	0.066
C(C5)	-0.3014(5)	0.2949(3)	-0.4532(3)	0.058
C(C6)	-0.2068(5)	0.2346(2)	-0.4372(3)	0.047
C(D1)	-0.0568(5)	0.1148(2)	-0.3203(3)	0.041
C(D2)	0.0323(6)	0.0516(3)	-0.3078(3)	0.059
C(D3)	-0.0384(6)	-0.0136(3)	-0.2777(4)	0.077
C(D4)	-0.1094(7)	0.0017(3)	-0.2011(4)	0.081
C(D5)	-0.1999(6)	0.0643(3)	-0.2150(3)	0.070
C(D6)	-0.1281(5)	0.1296(3)	-0.2415(3)	0.053

Table 2,7vii Anisotropic Displacement Parameters For [NiBr(PCP)].

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}h_ih_ja_i^*a_j^*]$$

	U11	U22	U33	U12	U13	U23
Ni	0.0300(3)	0.0302(3)	0.0310(3)	0.0037(3)	0.0013(3)	-.0026(3)
Br	0.0496(3)	0.0565(4)	0.0470(3)	0.0159(3)	-.0007(3)	-.0178(3)
P(1)	0.0310(7)	0.0327(7)	0.0331(7)	0.0012(6)	0.0017(5)	-.0002(6)
P(2)	0.0335(7)	0.0344(7)	0.0342(7)	0.0020(6)	-.0019(6)	-.0007(6)
C(1)	0.037(3)	0.031(3)	0.037(3)	0.001(2)	0.007(2)	0.007(2)
C(2)	0.043(3)	0.031(3)	0.035(3)	0.002(2)	0.007(2)	0.000(2)
C(3)	0.048(3)	0.050(3)	0.048(3)	0.006(3)	0.010(3)	-0.004(3)
C(4)	0.065(4)	0.047(3)	0.050(3)	0.015(3)	0.018(3)	-0.013(3)
C(5)	0.059(4)	0.051(3)	0.038(3)	0.003(3)	0.002(3)	-0.010(3)
C(6)	0.046(3)	0.036(3)	0.035(3)	0.004(3)	0.000(3)	0.004(2)
C(7)	0.035(3)	0.046(3)	0.050(3)	-0.001(3)	0.010(2)	-0.003(3)
C(8)	0.050(3)	0.050(3)	0.036(3)	0.001(3)	-0.004(3)	-0.007(2)
C(A1)	0.030(3)	0.036(3)	0.035(3)	0.002(2)	-0.006(2)	0.002(2)
C(A2)	0.069(4)	0.037(3)	0.046(3)	-0.003(3)	-0.003(3)	0.005(2)
C(A3)	0.117(6)	0.040(3)	0.063(4)	-0.012(3)	-0.002(4)	0.010(3)
C(A4)	0.081(5)	0.071(4)	0.055(4)	-0.020(4)	0.003(4)	0.026(3)
C(A5)	0.055(4)	0.064(4)	0.041(3)	0.003(3)	0.005(3)	0.011(3)
C(A6)	0.055(3)	0.041(3)	0.041(3)	-0.002(3)	0.000(3)	0.004(2)
C(B1)	0.037(3)	0.036(3)	0.035(3)	0.000(2)	0.006(2)	0.001(2)
C(B2)	0.047(3)	0.048(3)	0.055(3)	-0.007(3)	-0.012(3)	0.007(2)
C(B3)	0.043(3)	0.069(4)	0.066(4)	-0.018(3)	-0.006(3)	-0.001(3)
C(B4)	0.066(4)	0.053(4)	0.077(4)	-0.026(3)	-0.003(3)	0.010(3)
C(B5)	0.069(4)	0.045(3)	0.075(4)	-0.006(3)	-0.008(3)	0.015(3)
C(B6)	0.044(3)	0.039(3)	0.054(3)	-0.002(3)	-0.002(3)	0.007(3)
C(C1)	0.032(3)	0.039(3)	0.036(3)	0.004(2)	-0.001(2)	0.000(2)
C(C2)	0.046(3)	0.042(3)	0.072(4)	0.003(3)	-0.003(3)	0.012(3)
C(C3)	0.065(4)	0.041(3)	0.084(4)	0.009(3)	-0.004(4)	0.017(3)
C(C4)	0.072(4)	0.065(4)	0.062(4)	0.032(4)	-0.009(3)	0.014(3)
C(C5)	0.050(3)	0.073(4)	0.052(3)	0.014(3)	-0.013(3)	-0.004(3)
C(C6)	0.039(3)	0.053(3)	0.048(3)	0.002(3)	-0.007(2)	0.003(3)
C(D1)	0.037(3)	0.040(3)	0.046(3)	-0.007(2)	-0.006(2)	0.002(2)
C(D2)	0.060(4)	0.033(3)	0.085(4)	0.002(3)	-0.003(3)	0.006(3)
C(D3)	0.079(5)	0.039(3)	0.113(6)	-0.003(3)	0.005(4)	0.009(4)
C(D4)	0.094(5)	0.056(4)	0.092(5)	-0.018(4)	0.001(4)	0.025(4)
C(D5)	0.073(5)	0.067(4)	0.072(4)	-0.018(4)	0.027(3)	0.008(3)
C(D6)	0.056(4)	0.049(3)	0.053(3)	-0.009(3)	0.007(3)	0.004(3)

Table 2, 7viii	$[RhCl_2(PCP)(HOEt)].H_2O$	$[RhCl_2(PCP)(HOEt)]$
FORMULA	$C_{34}H_{59}Cl_2O_2P_2Rh$	$C_{34}H_{57}Cl_2OP_2Rh$
F. Wt.	735.67	717.65
CRYSTAL SYSTEM	MONOCLINIC	MONOCLINIC
SPACE GROUP	$P2_1/a$	$P2_1/a$
a, Å	12.3894 (12)	14.4845 (41)
b, Å	22.5745 (18)	10.7917 (34)
c, Å	12.9366 (17)	22.962 (12)
β, deg.	93.273 (9)	103.177 (31)
U, $Å^3$	3612.3 (7)	3494.8 (24)
Z	4	4
D_{CALC}, g cm^{-3}	1.353	1.364
F(000)	1552	1512
μ, cm^{-1}	7.28	7.46
crystal, mm	0.45 x 0.30 x 0.05	0.20 x 0.05 x 0.05
kV	55	55
mA	32	32
COLLIMATOR, mm	0.80	0.40
Θ_{RANGE}, deg.	2 - 28	1.8 - 23
h	$\overline{16}$ - 16	0 - 15
k	0 - 29	$\overline{11}$ - 0
l	$\overline{16}$ - 0	$\overline{25}$ - 25
reflns. measured	8859	4931
unique reflns.	8498	4705
observed reflns.	3089	1186
R_{int}	0.032	0.031
R	0.0552	0.0701
R_w	0.0539	0.0680
S	1.65	1.95
Parameters	371	186
$\Delta\rho_{max}$, e/$Å^3$	0.98	0.82
$\Delta\rho_{min}$, e/$Å^3$	-0.77	-0.59

Table 2,7ix Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For [RhCl$_2$(PCP)(EtOH)].H$_2$O

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j^* (\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Rh	0.20396(5)	0.11546(3)	-0.12004(6)	0.029
Cl(1)	0.20464(18)	0.01278(9)	-0.08808(18)	0.035
Cl(2)	0.21108(17)	0.21950(9)	-0.14632(18)	0.036
P(1)	0.15107(18)	0.12396(11)	0.05195(20)	0.035
P(2)	0.20607(19)	0.10772(11)	-0.30163(20)	0.036
O(1)	0.3839(4)	0.1202(3)	-0.0791(5)	0.041
O(2)	0.4703(5)	0.2287(3)	-0.1195(6)	0.072
C(1)	0.0437(6)	0.1192(4)	-0.1525(7)	0.029
C(2)	-0.0282(7)	0.1095(4)	-0.0717(7)	0.035
C(3)	-0.1381(7)	0.1202(5)	-0.0926(9)	0.050
C(4)	-0.1790(8)	0.1360(4)	-0.1883(10)	0.053
C(5)	-0.1105(8)	0.1427(4)	-0.2677(8)	0.045
C(6)	0.0017(7)	0.1341(3)	-0.2487(8)	0.033
C(7)	0.0179(7)	0.0905(4)	0.0338(8)	0.043
C(8)	0.0773(7)	0.1448(4)	-0.3354(8)	0.042
C(9)	0.4608(8)	0.0732(4)	-0.0877(8)	0.045
C(10)	0.5672(8)	0.0881(5)	-0.0347(10)	0.073
C(A1)	0.2191(8)	0.0882(4)	0.1659(8)	0.046
C(A2)	0.3389(8)	0.0814(5)	0.1578(9)	0.057
C(A3)	0.3979(9)	0.0594(5)	0.2563(10)	0.069
C(A4)	0.3440(11)	0.0061(6)	0.3002(10)	0.095
C(A5)	0.2237(10)	0.0118(5)	0.3077(9)	0.065
C(A6)	0.1683(9)	0.0341(5)	0.2053(10)	0.073
C(B1)	0.1278(7)	0.1998(4)	0.0948(7)	0.040
C(B2)	0.0478(7)	0.2072(5)	0.1807(8)	0.056
C(B3)	0.0290(8)	0.2731(5)	0.2004(9)	0.065
C(B4)	0.1330(9)	0.3049(5)	0.2297(9)	0.068
C(B5)	0.2161(8)	0.2971(4)	0.1477(9)	0.060
C(B6)	0.2342(7)	0.2316(4)	0.1261(8)	0.044
C(C1)	0.1954(8)	0.0369(4)	-0.3694(7)	0.041
C(C2)	0.2951(8)	-0.0041(4)	-0.3507(8)	0.051
C(C3)	0.2809(10)	-0.0619(5)	-0.4078(9)	0.065
C(C4)	0.1774(10)	-0.0946(5)	-0.3809(9)	0.070
C(C5)	0.0808(9)	-0.0554(4)	-0.4027(9)	0.066
C(C6)	0.0918(8)	0.0035(4)	-0.3457(8)	0.049
C(D1)	0.3018(8)	0.1554(4)	-0.3713(9)	0.050
C(D2)	0.4196(9)	0.1417(5)	-0.3528(9)	0.066
C(D3)	0.4925(10)	0.1891(6)	-0.3970(11)	0.092
C(D4)	0.4665(11)	0.1993(6)	-0.5080(11)	0.090
C(D5)	0.3475(12)	0.2103(6)	-0.5299(10)	0.099
C(D6)	0.2756(9)	0.1631(6)	-0.4857(9)	0.075
H(O1)	0.41376	0.16724	-0.09418	0.12(4)

Table 2,7x Anisotropic Displacement Parameters For [$RhCl_2$(PCP)(EtOH)] .H_2O

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$$

	U11	U22	U33	U12	U13	U23
Rh	0.0292(4)	0.0292(4)	0.0300(5)	-.0030(4)	0.0017(3)	-.0004(5)
Cl(1)	0.0453(15)	0.0308(13)	0.0299(16)	-.0058(11)	-.0009(13)	0.0024(12)
Cl(2)	0.0368(14)	0.0319(12)	0.0388(18)	-.0013(11)	0.0053(12)	0.0007(12)
P(1)	0.0336(13)	0.0393(16)	0.0326(17)	-.0073(13)	0.0080(12)	-.0057(14)
P(2)	0.0406(14)	0.0370(15)	0.0311(17)	0.0050(13)	0.0055(12)	0.0009(14)
O(1)	0.030(3)	0.038(4)	0.053(5)	0.002(3)	-0.004(3)	0.005(4)
O(2)	0.054(5)	0.043(4)	0.119(7)	-0.017(4)	-0.004(5)	0.016(5)
C(1)	0.035(5)	0.026(5)	0.025(6)	-0.004(5)	-0.005(4)	-0.006(5)
C(2)	0.034(5)	0.033(5)	0.037(6)	-0.009(5)	0.002(5)	-0.011(5)
C(3)	0.041(6)	0.048(6)	0.063(8)	-0.007(6)	0.011(6)	-0.021(7)
C(4)	0.036(6)	0.051(7)	0.073(9)	0.001(5)	-0.005(6)	-0.005(7)
C(5)	0.046(6)	0.036(6)	0.053(8)	0.001(5)	-0.014(6)	-0.002(6)
C(6)	0.032(5)	0.023(5)	0.043(7)	0.005(4)	-0.003(5)	-0.009(5)
C(7)	0.043(6)	0.049(6)	0.036(7)	-0.017(5)	0.010(5)	-0.012(5)
C(8)	0.048(6)	0.037(5)	0.042(7)	0.014(5)	-0.004(5)	-0.004(5)
C(9)	0.038(6)	0.048(6)	0.050(8)	0.008(5)	0.007(5)	-0.002(6)
C(10)	0.048(7)	0.061(7)	0.108(11)	0.016(6)	-0.008(7)	-0.008(8)
C(A1)	0.046(6)	0.044(6)	0.047(8)	-0.011(5)	0.001(6)	0.005(6)
C(A2)	0.050(7)	0.066(8)	0.054(9)	-0.006(6)	0.012(6)	0.015(7)
C(A3)	0.065(8)	0.072(8)	0.071(10)	-0.010(7)	-0.001(7)	0.013(8)
C(A4)	0.097(11)	0.114(12)	0.072(11)	0.014(9)	-0.012(9)	0.037(9)
C(A5)	0.089(10)	0.059(8)	0.047(9)	-0.023(7)	0.006(7)	0.009(7)
C(A6)	0.074(9)	0.068(8)	0.076(10)	-0.003(7)	0.014(8)	0.011(8)
C(B1)	0.032(5)	0.051(6)	0.035(7)	0.001(5)	0.002(5)	-0.009(5)
C(B2)	0.035(6)	0.072(8)	0.060(8)	-0.009(5)	0.012(6)	-0.029(7)
C(B3)	0.050(7)	0.081(8)	0.064(9)	0.012(6)	0.012(6)	-0.028(7)
C(B4)	0.059(8)	0.062(7)	0.082(10)	0.008(6)	-0.006(7)	-0.045(7)
C(B5)	0.055(7)	0.050(7)	0.073(9)	-0.005(6)	-0.008(6)	-0.020(7)
C(B6)	0.037(6)	0.042(6)	0.054(8)	-0.005(5)	0.005(5)	-0.016(6)
C(C1)	0.049(6)	0.052(6)	0.021(6)	0.001(5)	0.002(5)	-0.002(5)
C(C2)	0.060(7)	0.047(6)	0.048(8)	0.012(6)	0.014(6)	0.010(6)
C(C3)	0.094(9)	0.046(6)	0.053(9)	0.033(7)	0.003(7)	0.000(6)
C(C4)	0.084(9)	0.042(7)	0.083(11)	0.003(6)	-0.012(8)	0.000(7)
C(C5)	0.085(9)	0.039(6)	0.074(10)	-0.003(6)	-0.017(7)	-0.003(7)
C(C6)	0.048(6)	0.045(6)	0.052(8)	-0.002(5)	-0.015(6)	-0.011(6)
C(D1)	0.056(7)	0.048(6)	0.045(8)	-0.001(6)	0.011(5)	0.014(6)
C(D2)	0.052(7)	0.081(8)	0.064(9)	-0.018(6)	-0.004(6)	0.013(7)
C(D3)	0.078(9)	0.130(12)	0.067(11)	-0.054(8)	0.009(8)	0.010(9)
C(D4)	0.096(11)	0.111(11)	0.062(11)	-0.049(9)	0.026(9)	0.006(9)
C(D5)	0.124(13)	0.123(13)	0.050(10)	-0.027(10)	0.020(9)	0.031(9)
C(D6)	0.074(8)	0.112(11)	0.041(9)	-0.018(7)	0.013(7)	0.026(8)

Table 2,7xi [$RhCl_2(PCP)(EtOH)$] Fractional Coordinates and Isotropic Displacement Parameters ($Å^2$).

For isotropic atoms U is the isotropic displacement parameter and for other atoms

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j^* (\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Rh	0.18706(16)	0.13995(23)	0.24698(9)	0.046
Cl(1)	0.0833(5)	0.2587(7)	0.2893(3)	0.056
Cl(2)	0.3024(5)	0.0306(7)	0.2089(3)	0.059
P(1)	0.1072(5)	0.2278(7)	0.1566(3)	0.045
P(2)	0.2341(5)	0.0084(7)	0.3309(3)	0.044
O(1)	0.3106(12)	0.2834(16)	0.2718(7)	0.056(6)
C(1)	0.0848(17)	0.0151(24)	0.2229(10)	0.033(8)
C(2)	0.0011(19)	0.0395(26)	0.1823(11)	0.044(9)
C(3)	-0.0676(19)	-0.0477(28)	0.1673(11)	0.050(9)
C(4)	-0.0600(19)	-0.1587(29)	0.1959(12)	0.066(9)
C(5)	0.0190(18)	-0.1926(22)	0.2389(10)	0.039(8)
C(6)	0.0912(17)	-0.1028(22)	0.2524(9)	0.032(7)
C(7)	-0.0117(16)	0.1680(25)	0.1528(10)	0.045(8)
C(8)	0.1831(16)	-0.1353(27)	0.2946(9)	0.046(8)
C(9)	0.310(3)	0.375(4)	0.318(2)	0.153(16)
C(10)	0.379(3)	0.466(4)	0.318(2)	0.157(17)
C(A1)	0.0865(19)	0.3925(26)	0.1520(11)	0.057(9)
C(A2)	0.0132(18)	0.4394(27)	0.0952(11)	0.064(10)
C(A3)	-0.007(2)	0.577(3)	0.100(1)	0.088(11)
C(A4)	0.079(2)	0.656(3)	0.108(1)	0.094(11)
C(A5)	0.156(2)	0.613(3)	0.161(1)	0.082(10)
C(A6)	0.172(2)	0.472(3)	0.158(1)	0.079(11)
C(B1)	0.1305(18)	0.1806(24)	0.0831(11)	0.049(9)
C(B2)	0.233(2)	0.216(3)	0.077(1)	0.093(11)
C(B3)	0.248(2)	0.176(3)	0.014(1)	0.101(13)
C(B4)	0.232(2)	0.042(3)	0.006(1)	0.099(13)
C(B5)	0.137(2)	0.001(3)	0.012(1)	0.098(12)
C(B6)	0.123(2)	0.039(3)	0.075(1)	0.080(11)
C(C1)	0.3582(19)	-0.0306(29)	0.3680(11)	0.058(9)
C(C2)	0.391(2)	-0.153(3)	0.361(1)	0.091(11)
C(C3)	0.493(3)	-0.188(3)	0.396(1)	0.117(14)
C(C4)	0.560(3)	-0.081(4)	0.393(2)	0.169(19)
C(C5)	0.529(2)	0.033(3)	0.407(1)	0.100(13)
C(C6)	0.433(2)	0.068(3)	0.370(1)	0.102(13)
C(D1)	0.1751(17)	0.0311(26)	0.3938(11)	0.044(8)
C(D2)	0.2060(17)	0.1475(29)	0.4287(11)	0.065(9)
C(D3)	0.1475(18)	0.1696(27)	0.4757(12)	0.067(10)
C(D4)	0.1557(18)	0.0640(30)	0.5179(12)	0.073(10)
C(D5)	0.1249(18)	-0.0571(27)	0.4829(12)	0.070(10)
C(D6)	0.1832(19)	-0.0799(27)	0.4348(12)	0.074(10)

Table 2,7xii Anisotropic Displacement Parameters for [$RhCl_2(PCP)(EtOH)$].

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$$

	U11	U22	U33	U12	U13	U23
Rh	0.0430(15)	0.0464(18)	0.0465(15)	-.0014(21)	0.0109(12)	-.0127(19)
Cl(1)	0.070(6)	0.056(6)	0.042(5)	0.012(5)	0.019(4)	0.002(5)
Cl(2)	0.054(5)	0.064(7)	0.056(6)	0.024(5)	0.012(5)	-0.003(5)
P(1)	0.041(5)	0.047(7)	0.044(5)	0.002(5)	0.005(4)	-0.008(5)
P(2)	0.040(5)	0.040(7)	0.048(6)	0.002(5)	0.003(5)	-0.002(5)

Table 2, 7xiii	$[RhCl_2(PCP)(OH_2)]$. propan-2-ol	$[RhCl_2(PCP)(HOMe)]$. 0.41 CH_2Cl_2
FORMULA	$C_{35}H_{61}Cl_2O_2P_2Rh$	$C_{33.41}H_{55.82}Cl_{2.82}OP_2Rh^*$
F. Wt.	749.70	738.44
CRYSTAL SYSTEM	MONOCLINIC	MONOCLINIC
SPACE GROUP	$P2_1/a$	$P2_1/a$
a, Å	11.5131 (10)	11.0025 (10)
b, Å	25.8744 (20)	27.322 (11)
c, Å	13.5759 (8)	13.3909 (22)
β, deg.	113.468 (57)	113.546 (12)
U, $Å^3$	3709.7 (2)	3690.2 (18)
Z	4	4
D_{CALC}, g cm^{-3}	1.342	1.329
F(000)	1584	1548.88
μ, cm^{-1}	7.11	7.08
crystal, mm	0.25 x 0.12 x 0.08	0.40 x 0.35 x 0.32
kV	55	55
mA	32	32
COLLIMATOR, mm	0.40	0.80
Θ_{RANGE}, deg.	2 - 31	2 - 31
h	$\overline{16}$ - 16	$\overline{15}$ - 15
k	0 - 36	0 - 39
l	0 - 19	0 - 19
reflns. measured	11643	11720
unique reflns.	11228	11295
observed reflns.	5197	3971
R_{int}	0.027	0.042
R	0.0391	0.0620
R_w	0.0397	0.0660
S	1.26	2.17
Parameters	379	354
$\Delta\rho_{max}$, e/$Å^3$	0.39	0.88
$\Delta\rho_{min}$, e/$Å^3$	-0.50	-0.73

* All further calculations are based on this non-empirical formula.

Table 2,7xiv Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For [$RhCl_2(PCP)(OH_2)$].propan-2-ol.

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^* a_j^* (\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Rh	-0.04141(3)	0.13083(1)	0.13892(2)	0.030
Cl(1)	0.10653(9)	0.07229(4)	0.12453(8)	0.044
Cl(2)	-0.18395(9)	0.19341(4)	0.15394(8)	0.043
P(1)	-0.16930(9)	0.10455(4)	-0.03688(7)	0.034
P(2)	0.06550(9)	0.13884(4)	0.32644(8)	0.036
O(1)	0.0516(3)	0.1979(1)	0.0898(2)	0.052
O(S)	0.0235(3)	0.3037(1)	0.0930(3)	0.087
C(1)	-0.1317(3)	0.0735(1)	0.1785(3)	0.035
C(2)	-0.2028(4)	0.0368(2)	0.1020(3)	0.041
C(3)	-0.2670(5)	-0.0020(2)	0.1304(4)	0.060
C(4)	-0.2599(5)	-0.0058(2)	0.2341(4)	0.072
C(5)	-0.1889(4)	0.0299(2)	0.3103(3)	0.061
C(6)	-0.1261(4)	0.0690(2)	0.2834(3)	0.042
C(7)	-0.2049(4)	0.0388(2)	-0.0092(3)	0.043
C(8)	-0.0540(4)	0.1090(2)	0.3660(3)	0.049
C(A1)	-0.0980(4)	0.0940(2)	-0.1361(3)	0.040
C(A2)	-0.1836(4)	0.0677(2)	-0.2406(3)	0.053
C(A3)	-0.1063(5)	0.0515(2)	-0.3040(3)	0.064
C(A4)	-0.0362(5)	0.0963(2)	-0.3257(4)	0.068
C(A5)	0.0457(5)	0.1236(2)	-0.2224(4)	0.072
C(A6)	-0.0320(4)	0.1409(2)	-0.1589(3)	0.059
C(B1)	-0.3207(4)	0.1392(2)	-0.0952(3)	0.043
C(B2)	-0.4364(4)	0.1110(2)	-0.1750(4)	0.060
C(B3)	-0.5560(4)	0.1440(2)	-0.1989(4)	0.065
C(B4)	-0.5414(5)	0.1964(2)	-0.2404(4)	0.077
C(B5)	-0.4250(5)	0.2242(2)	-0.1649(4)	0.080
C(B6)	-0.3058(4)	0.1919(2)	-0.1375(3)	0.053
C(C1)	0.2089(3)	0.0988(2)	0.3867(3)	0.039
C(C2)	0.3195(4)	0.1204(2)	0.3632(3)	0.051
C(C3)	0.4295(4)	0.0827(2)	0.3986(4)	0.061
C(C4)	0.4730(4)	0.0708(2)	0.5175(4)	0.060
C(C5)	0.3661(5)	0.0491(2)	0.5426(3)	0.062
C(C6)	0.2537(4)	0.0858(2)	0.5066(3)	0.059
C(D1)	0.0909(5)	0.2024(2)	0.3931(3)	0.060
C(D2)	0.1027(7)	0.2051(2)	0.5042(5)	0.117
C(D3)	0.1017(6)	0.2592(2)	0.5451(4)	0.095
C(D4)	0.1834(6)	0.2956(2)	0.5197(6)	0.120
C(D5)	0.1741(7)	0.2934(2)	0.4099(5)	0.107
C(D6)	0.1715(5)	0.2395(2)	0.3634(4)	0.082
C(S1)	-0.0530(5)	0.3396(2)	0.1196(4)	0.072
C(S2)	-0.1842(5)	0.3340(2)	0.0420(5)	0.095
C(S3)	-0.0028(6)	0.3933(2)	0.1295(6)	0.111

Table 2,7xv Anisotropic Displacement Parameters For [RhCl$_2$(PCP)(OH$_2$)].propan-2-ol.

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$$

	U11	U22	U33	U12	U13	U23
Rh	0.0287(1)	0.0282(1)	0.0289(1)	-.0011(2)	0.0116(1)	-.0029(2)
Cl(1)	0.0401(6)	0.0463(6)	0.0390(5)	0.0092(5)	0.0145(5)	-.0051(5)
Cl(2)	0.0326(5)	0.0432(6)	0.0460(6)	0.0033(5)	0.0149(5)	-.0071(5)
P(1)	0.0359(6)	0.0300(6)	0.0292(5)	-.0017(5)	0.0101(4)	-.0022(4)
P(2)	0.0343(5)	0.0372(6)	0.0297(5)	-.0023(5)	0.0117(4)	-.0049(4)
O(1)	0.0437(17)	0.0360(17)	0.0691(20)	-.0058(14)	0.0312(16)	-.0032(14)
O(S)	0.047(2)	0.057(2)	0.144(4)	0.002(2)	0.045(2)	-0.005(2)
C(1)	0.031(2)	0.032(2)	0.036(2)	0.004(2)	0.011(2)	0.004(2)
C(2)	0.042(2)	0.034(2)	0.039(2)	-0.001(2)	0.015(2)	0.001(2)
C(3)	0.064(3)	0.042(3)	0.061(3)	-0.018(2)	0.021(3)	-0.005(2)
C(4)	0.084(4)	0.053(3)	0.070(3)	-0.025(3)	0.043(3)	0.001(3)
C(5)	0.065(3)	0.060(3)	0.049(3)	-0.012(3)	0.031(2)	0.008(2)
C(6)	0.041(2)	0.039(2)	0.040(2)	-0.002(2)	0.020(2)	-0.003(2)
C(7)	0.048(3)	0.029(2)	0.040(2)	-0.004(2)	0.011(2)	-0.001(2)
C(8)	0.043(2)	0.062(3)	0.037(2)	-0.003(2)	0.021(2)	-0.004(2)
C(A1)	0.039(2)	0.041(2)	0.034(2)	0.000(2)	0.015(2)	-0.007(2)
C(A2)	0.056(3)	0.056(3)	0.036(2)	-0.007(2)	0.016(2)	-0.012(2)
C(A3)	0.079(4)	0.060(3)	0.045(3)	-0.006(3)	0.028(3)	-0.018(2)
C(A4)	0.083(4)	0.064(3)	0.049(3)	0.006(3)	0.036(3)	0.001(2)
C(A5)	0.076(3)	0.064(4)	0.071(3)	-0.011(3)	0.049(3)	-0.015(3)
C(A6)	0.067(3)	0.052(3)	0.055(3)	-0.014(2)	0.037(2)	-0.015(2)
C(B1)	0.041(2)	0.040(3)	0.039(2)	0.003(2)	0.012(2)	0.000(2)
C(B2)	0.050(3)	0.059(3)	0.054(3)	-0.003(2)	0.005(2)	-0.003(2)
C(B3)	0.036(2)	0.092(4)	0.053(3)	0.003(3)	0.005(2)	-0.004(3)
C(B4)	0.057(3)	0.085(4)	0.067(3)	0.025(3)	0.003(3)	0.010(3)
C(B5)	0.079(4)	0.057(3)	0.085(4)	0.025(3)	0.027(3)	0.016(3)
C(B6)	0.052(3)	0.047(3)	0.050(3)	0.009(2)	0.017(2)	0.008(2)
C(C1)	0.036(2)	0.037(2)	0.035(2)	-0.001(2)	0.011(2)	0.001(2)
C(C2)	0.040(2)	0.055(3)	0.047(2)	0.002(2)	0.013(2)	0.004(2)
C(C3)	0.043(3)	0.062(3)	0.069(3)	0.007(2)	0.023(2)	0.004(2)
C(C4)	0.050(3)	0.058(3)	0.057(3)	0.012(2)	0.007(2)	-0.003(2)
C(C5)	0.063(3)	0.063(3)	0.044(3)	0.020(3)	0.012(2)	0.009(2)
C(C6)	0.058(3)	0.070(3)	0.038(2)	0.018(3)	0.018(2)	0.008(2)
C(D1)	0.083(4)	0.041(3)	0.045(3)	-0.006(2)	0.025(2)	-0.013(2)
C(D2)	0.173(7)	0.081(5)	0.089(4)	-0.038(4)	0.086(5)	-0.046(4)
C(D3)	0.109(5)	0.083(4)	0.071(4)	-0.006(4)	0.030(3)	-0.047(3)
C(D4)	0.117(6)	0.079(5)	0.133(6)	-0.011(4)	0.037(5)	-0.068(4)
C(D5)	0.147(6)	0.052(4)	0.088(4)	-0.038(4)	0.025(4)	-0.023(3)
C(D6)	0.086(4)	0.049(3)	0.100(4)	-0.019(3)	0.052(3)	-0.021(3)
C(S1)	0.063(3)	0.066(3)	0.075(4)	0.007(3)	0.031(3)	0.000(3)
C(S2)	0.048(3)	0.097(5)	0.122(5)	0.002(3)	0.030(3)	0.008(4)
C(S3)	0.088(5)	0.063(4)	0.156(7)	-0.003(3)	0.043(5)	-0.022(4)

Table 2,7xvi Fractional Coordinates and Isotropic Displacement Parameters (Å^2) For [RhCl$_2$(PCP)(MeOH)].0.41CH$_2$Cl$_2$. For solvent atoms U is the isotropic displacement parameter and for other atoms

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*(\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Rh	0.17869(6)	0.12697(3)	0.13067(5)	0.038
Cl(1)	0.0136(2)	0.0720(1)	0.1269(2)	0.051
Cl(2)	0.3407(3)	0.1842(1)	0.1370(2)	0.068
P(1)	0.2652(2)	0.1363(1)	0.3206(2)	0.045
P(2)	0.1257(2)	0.1008(1)	-0.0500(2)	0.043
O(1)	0.0275(6)	0.1868(3)	0.0910(5)	0.075
C(1)	0.3095(7)	0.0729(3)	0.1675(6)	0.041
C(2)	0.4135(8)	0.0689(3)	0.2693(7)	0.053
C(3)	0.5029(10)	0.0313(4)	0.2925(9)	0.077
C(4)	0.4943(11)	-0.0026(4)	0.2177(10)	0.097
C(5)	0.3942(10)	0.0002(4)	0.1147(9)	0.074
C(6)	0.3030(8)	0.0370(3)	0.0894(7)	0.049
C(7)	0.4271(8)	0.1079(3)	0.3538(7)	0.055
C(8)	0.1873(8)	0.0375(3)	-0.0207(7)	0.053
C(9)	0.0267(17)	0.2323(5)	0.0416(13)	0.174
C(A1)	0.3071(9)	0.1966(3)	0.3824(7)	0.062
C(A2)	0.3941(13)	0.1992(4)	0.5018(9)	0.101
C(A3)	0.4402(13)	0.2512(5)	0.5393(10)	0.105
C(A4)	0.3331(17)	0.2860(5)	0.5133(13)	0.131
C(A5)	0.2403(16)	0.2853(4)	0.3958(14)	0.143
C(A6)	0.1916(11)	0.2337(4)	0.3503(9)	0.094
C(B1)	0.1843(8)	0.0990(3)	0.3909(7)	0.050
C(B2)	0.0502(9)	0.1204(4)	0.3756(8)	0.069
C(B3)	-0.0269(10)	0.0837(4)	0.4137(9)	0.086
C(B4)	0.0519(12)	0.0692(4)	0.5284(9)	0.086
C(B5)	0.1852(11)	0.0467(4)	0.5432(8)	0.084
C(B6)	0.2649(10)	0.0829(5)	0.5076(8)	0.084
C(C1)	0.2109(8)	0.1256(3)	-0.1330(7)	0.057
C(C2)	0.1826(10)	0.1799(4)	-0.1578(8)	0.076
C(C3)	0.2535(11)	0.1988(5)	-0.2307(10)	0.101
C(C4)	0.3906(13)	0.1859(6)	-0.1919(11)	0.124
C(C5)	0.4157(11)	0.1324(5)	-0.1664(10)	0.098
C(C6)	0.3536(11)	0.1139(4)	-0.0917(9)	0.083
C(D1)	-0.0494(8)	0.0918(3)	-0.1428(7)	0.054
C(D2)	-0.0712(9)	0.0636(4)	-0.2448(8)	0.069
C(D3)	-0.2175(11)	0.0524(5)	-0.3079(9)	0.091
C(D4)	-0.3041(10)	0.0967(5)	-0.3314(9)	0.091
C(D5)	-0.2769(10)	0.1257(5)	-0.2318(10)	0.091
C(D6)	-0.1310(10)	0.1384(4)	-0.1692(9)	0.077
Cl(3)	-0.18031	0.19371	0.14224	0.151
Cl(4)	-0.32663	0.09954	0.14704	0.269
Cl(5)	-0.33855	0.13195	0.16728	0.143
Cl(6)	-0.22462	0.19717	0.03372	0.243
C(S)	-0.24393	0.13333	0.07899	0.086

Table 2.7xvii Anisotropic Displacement Parameters For [RhCl$_2$(PCP)(MeOH)].0.41CH$_2$Cl$_2$.

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$$

	U11	U22	U33	U12	U13	U23
Rh	0.0364(3)	0.0354(4)	0.0368(3)	0.0000(4)	0.0153(3)	-.0024(4)
Cl(1)	0.0422(12)	0.0622(16)	0.0418(13)	-.0178(11)	0.0169(11)	-.0077(11)
Cl(2)	0.0745(17)	0.0584(17)	0.0610(16)	-.0308(13)	0.0356(14)	-.0122(13)
P(1)	0.0401(12)	0.0498(16)	0.0362(12)	-.0026(11)	0.0123(10)	-.0050(11)
P(2)	0.0398(13)	0.0462(15)	0.0346(12)	0.0008(11)	0.0148(11)	-.0028(11)
O(1)	0.082(5)	0.064(5)	0.065(5)	0.037(4)	0.025(4)	0.000(4)
C(1)	0.036(5)	0.039(5)	0.042(5)	0.005(4)	0.020(4)	-0.005(4)
C(2)	0.048(5)	0.048(6)	0.052(6)	0.002(5)	0.018(5)	-0.014(5)
C(3)	0.069(7)	0.069(8)	0.068(7)	0.030(6)	0.005(6)	-0.006(6)
C(4)	0.079(8)	0.084(9)	0.096(10)	0.050(7)	0.003(7)	-0.016(8)
C(5)	0.072(7)	0.054(7)	0.078(8)	0.020(6)	0.020(6)	-0.019(6)
C(6)	0.047(5)	0.037(5)	0.052(6)	0.007(4)	0.016(5)	0.000(5)
C(7)	0.042(5)	0.055(6)	0.054(6)	0.002(4)	0.010(5)	0.001(5)
C(8)	0.062(6)	0.043(6)	0.045(5)	0.004(5)	0.022(5)	-0.002(4)
C(9)	0.223(17)	0.097(12)	0.176(16)	0.087(12)	0.106(15)	0.064(11)
C(A1)	0.076(7)	0.047(6)	0.050(6)	-0.005(5)	0.022(5)	-0.013(5)
C(A2)	0.127(10)	0.071(9)	0.072(8)	-0.022(8)	0.010(8)	-0.022(7)
C(A3)	0.127(11)	0.077(10)	0.085(9)	-0.041(8)	0.030(9)	-0.029(8)
C(A4)	0.174(16)	0.078(11)	0.119(12)	-0.062(10)	0.069(12)	-0.063(10)
C(A5)	0.188(15)	0.037(8)	0.169(15)	0.011(8)	0.071(14)	-0.034(9)
C(A6)	0.083(8)	0.073(9)	0.105(10)	0.001(6)	0.035(7)	-0.035(7)
C(B1)	0.055(5)	0.040(5)	0.049(5)	0.000(4)	0.030(5)	0.000(5)
C(B2)	0.064(6)	0.072(8)	0.066(6)	-0.001(6)	0.043(5)	0.013(6)
C(B3)	0.066(7)	0.103(10)	0.080(8)	0.003(7)	0.036(7)	0.002(7)
C(B4)	0.103(9)	0.075(8)	0.072(8)	-0.034(7)	0.052(7)	-0.014(6)
C(B5)	0.083(8)	0.094(9)	0.058(7)	-0.011(7)	0.022(6)	0.024(6)
C(B6)	0.072(7)	0.114(11)	0.049(6)	-0.009(7)	0.012(6)	0.024(6)
C(C1)	0.050(5)	0.055(6)	0.056(6)	0.012(5)	0.024(4)	0.013(5)
C(C2)	0.074(7)	0.077(8)	0.072(7)	0.009(6)	0.046(6)	0.020(6)
C(C3)	0.071(8)	0.108(10)	0.108(10)	0.002(7)	0.037(8)	0.051(8)
C(C4)	0.107(10)	0.137(13)	0.123(12)	-0.037(10)	0.083(10)	0.003(10)
C(C5)	0.093(8)	0.088(9)	0.112(9)	-0.011(7)	0.080(8)	0.001(8)
C(C6)	0.075(7)	0.088(9)	0.079(8)	-0.001(6)	0.046(6)	-0.006(6)
C(D1)	0.049(5)	0.063(7)	0.044(5)	-0.003(5)	0.023(5)	-0.002(5)
C(D2)	0.058(6)	0.083(8)	0.051(6)	-0.002(6)	0.011(5)	-0.011(6)
C(D3)	0.070(8)	0.126(11)	0.060(7)	-0.026(8)	0.015(6)	-0.027(7)
C(D4)	0.051(7)	0.134(12)	0.063(8)	-0.003(7)	-0.007(6)	0.006(8)
C(D5)	0.052(6)	0.109(10)	0.093(9)	0.022(7)	0.014(6)	-0.018(8)
C(D6)	0.058(6)	0.077(9)	0.077(7)	0.018(6)	0.011(6)	-0.017(6)

Table 2, 7xviii	$[Rh(CO)(OH_2)(PPh_3)_2]$ $[ClO_4].CH_2Cl_2$	$[Rh(CO)(OCMe_2)(PPh_3)_2]$ $[ClO_4].OCMe_2$
FORMULA	$C_{38}H_{34}Cl_3O_6P_2Rh$	$C_{43}H_{42}ClO_7P_2Rh$
F. Wt.	857.91	880.10
CRYSTAL SYSTEM	TRICLINIC	MONOCLINIC
SPACE GROUP	$P\bar{1}$	$P2_1/n$
a, Å	12.158 (2)	12.8299 (11)
b, Å	12.689 (2)	25.1452 (17)
c, Å	13.822 (1)	12.9121 (10)
α, deg.	86.67 (1)	-
β, deg.	65.15 (1)	96.6329 (68)
γ, deg.	78.65 (1)	-
U, $Å^3$	1896.4 (4)	4137.7 (6)
Z	2	4
D_{CALC}, g cm^{-3}	1.502	1.413
F(000)	872	1792
μ, cm^{-1}	7.82	5.93
crystal, mm	0.63 x 0.45 x 0.40	0.10 x 0.10 x 0.40
kV	50	50
mA	20	20
COLLIMATOR, mm	0.80	0.40
Θ_{RANGE}, deg.	2 - 25	2 - 22
h	$\overline{14}$ - 1	$\overline{11}$ - 11
k	$\overline{15}$ - 15	$\overline{23}$ - 0
l	$\overline{16}$ - 16	$\overline{11}$ - 0
reflns. measured	7245	5327
unique reflns.	6635	5062
observed reflns.	4826	1974
R_{int}	0.069	0.032
R	0.0481	0.1578
R_w	0.0617	0.2414
S	2.91	21.26
Parameters	451	165
$\Delta\rho_{max}$, e/$Å^3$	0.88	1.90
$\Delta\rho_{min}$, e/$Å^3$	-0.96	-3.71

Table 2,7xix Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For $[Rh(OH_2)(CO)(PPh_3)_2][ClO_4]$. CH_2Cl_2.

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j^* (\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Rh	0.00332(3)	0.24250(3)	-0.23925(3)	0.042
P(1)	-0.18982(12)	0.35217(10)	-0.14247(9)	0.046
P(2)	0.20138(11)	0.14181(9)	-0.33841(9)	0.042
O(1)	-0.0373(3)	0.1355(3)	-0.1098(3)	0.061
O(2)	0.0401(4)	0.3781(3)	-0.4259(3)	0.077
C(1)	0.0254(5)	0.3271(4)	-0.3511(4)	0.057
C(A1)	-0.2514(5)	0.4548(4)	-0.2145(4)	0.053
C(A2)	-0.1897(6)	0.5388(5)	-0.2597(5)	0.075
C(A3)	-0.2359(6)	0.6173(5)	-0.3144(5)	0.083
C(A4)	-0.3442(7)	0.6137(5)	-0.3222(5)	0.090
C(A5)	-0.4061(7)	0.5319(5)	-0.2778(5)	0.089
C(A6)	-0.3607(6)	0.4525(4)	-0.2246(4)	0.070
C(B1)	-0.1926(5)	0.4279(4)	-0.0333(4)	0.058
C(B2)	-0.2639(7)	0.5295(5)	0.0011(5)	0.096
C(B3)	-0.2613(9)	0.5834(6)	0.0815(6)	0.120
C(B4)	-0.1887(8)	0.5384(6)	0.1328(6)	0.116
C(B5)	-0.1193(9)	0.4368(6)	0.1018(6)	0.129
C(B6)	-0.1200(7)	0.3830(5)	0.0177(5)	0.097
C(C1)	-0.3134(4)	0.2769(3)	-0.0815(3)	0.047
C(C2)	-0.4149(5)	0.3098(4)	0.0118(4)	0.060
C(C3)	-0.5118(5)	0.2547(5)	0.0504(5)	0.075
C(C4)	-0.5092(6)	0.1685(5)	-0.0022(5)	0.083
C(C5)	-0.4101(6)	0.1340(5)	-0.0958(5)	0.087
C(C6)	-0.3103(5)	0.1874(4)	-0.1355(4)	0.067

Table 2,7xix cont.

C(D1)	0.3253(4)	0.2114(4)	-0.3548(3)	0.048
C(D2)	0.3238(6)	0.3137(4)	-0.3983(5)	0.075
C(D3)	0.4201(6)	0.3661(5)	-0.4174(6)	0.090
C(D4)	0.5157(6)	0.3220(5)	-0.3930(5)	0.084
C(D5)	0.5180(6)	0.2227(6)	-0.3512(6)	0.106
C(D6)	0.4238(6)	0.1678(5)	-0.3322(6)	0.088
C(E1)	0.2288(4)	0.1138(3)	-0.4752(3)	0.045
C(E2)	0.3425(5)	0.1091(4)	-0.5604(4)	0.056
C(E3)	0.3574(6)	0.0908(5)	-0.6629(4)	0.070
C(E4)	0.2584(6)	0.0732(5)	-0.6808(4)	0.081
C(E5)	0.1475(6)	0.0758(5)	-0.5971(5)	0.080
C(E6)	0.1308(5)	0.0954(4)	-0.4945(4)	0.064
C(F1)	0.2438(4)	0.0107(3)	-0.2892(4)	0.048
C(F2)	0.2432(5)	0.0045(4)	-0.1878(4)	0.059
C(F3)	0.2777(6)	-0.0953(5)	-0.1508(4)	0.076
C(F4)	0.3104(6)	-0.1861(4)	-0.2103(5)	0.086
C(F5)	0.3129(7)	-0.1796(4)	-0.3109(5)	0.088
C(F6)	0.2782(6)	-0.0823(4)	-0.3509(4)	0.069
Cl(1)	0.09734(15)	0.13293(12)	0.11615(12)	0.081
O(3)	0.0375(7)	0.1377(7)	0.0510(5)	0.223
O(4)	0.0604(8)	0.0514(5)	0.1892(5)	0.190
O(5)	0.0717(9)	0.2235(5)	0.1757(5)	0.218
O(6)	0.2196(6)	0.0963(8)	0.0597(6)	0.214
Cl(2)	0.16464(19)	0.77017(20)	-0.53069(20)	0.134
Cl(3)	0.1790(3)	0.5907(2)	-0.3964(2)	0.165
C(2)	0.0926(8)	0.7027(10)	-0.4175(7)	0.156

Table 2,7xx

Anisotropic Displacement Parameters for $[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$.

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$$

	U11	U22	U33	U12	U13	U23
Rh	0.0371(2)	0.0417(2)	0.0370(2)	-.0068(2)	-.0124(2)	0.0013(1)
P(1)	0.0418(7)	0.0426(7)	0.0400(6)	-.0035(6)	-.0121(6)	0.0000(5)
P(2)	0.0370(7)	0.0404(6)	0.0383(6)	-.0083(5)	-.0145(5)	-.0007(5)
O(1)	0.064(2)	0.053(2)	0.049(2)	-0.011(2)	-0.017(2)	0.011(2)
O(2)	0.068(3)	0.081(3)	0.057(2)	-0.005(2)	-0.013(2)	0.024(2)
C(1)	0.045(3)	0.056(3)	0.049(3)	-0.004(2)	-0.010(2)	-0.001(2)
C(A1)	0.055(3)	0.041(2)	0.044(2)	-0.004(2)	-0.011(2)	0.004(2)
C(A2)	0.058(4)	0.059(3)	0.079(4)	-0.004(3)	-0.011(3)	0.012(3)
C(A3)	0.082(5)	0.055(3)	0.073(4)	-0.004(3)	-0.003(4)	0.015(3)
C(A4)	0.109(6)	0.070(4)	0.061(3)	0.007(4)	-0.033(4)	0.008(3)
C(A5)	0.106(6)	0.060(3)	0.084(4)	0.000(3)	-0.061(4)	-0.003(3)
C(A6)	0.079(4)	0.052(3)	0.065(3)	-0.006(3)	-0.040(3)	-0.001(3)
C(B1)	0.058(3)	0.054(3)	0.047(3)	-0.013(3)	-0.018(3)	-0.005(2)
C(B2)	0.101(6)	0.073(4)	0.091(5)	0.018(4)	-0.051(4)	-0.035(4)
C(B3)	0.142(8)	0.078(5)	0.109(5)	0.011(5)	-0.059(6)	-0.043(4)
C(B4)	0.135(7)	0.103(5)	0.086(5)	-0.026(5)	-0.052(5)	-0.022(4)
C(B5)	0.169(9)	0.094(5)	0.105(5)	-0.010(6)	-0.092(6)	-0.014(4)
C(B6)	0.123(6)	0.066(4)	0.082(4)	0.000(4)	-0.064(4)	-0.010(3)
C(C1)	0.043(3)	0.041(2)	0.043(2)	-0.003(2)	-0.015(2)	0.002(2)
C(C2)	0.052(3)	0.064(3)	0.047(3)	-0.006(3)	-0.014(3)	0.002(2)
C(C3)	0.046(3)	0.089(4)	0.066(3)	-0.010(3)	-0.007(3)	0.010(3)
C(C4)	0.058(4)	0.074(4)	0.095(4)	-0.026(3)	-0.021(4)	0.014(3)
C(C5)	0.077(5)	0.065(4)	0.094(5)	-0.024(3)	-0.023(4)	-0.010(3)
C(C6)	0.055(3)	0.060(3)	0.063(3)	-0.013(3)	-0.011(3)	-0.002(3)

Table 2,7xx cont.

C(D1)	0.043(3)	0.046(3)	0.044(2)	-0.009(2)	-0.017(2)	-0.008(2)
C(D2)	0.060(4)	0.055(3)	0.096(4)	-0.021(3)	-0.038(3)	0.006(3)
C(D3)	0.070(4)	0.056(3)	0.124(5)	-0.033(3)	-0.037(4)	0.010(3)
C(D4)	0.063(4)	0.078(4)	0.095(4)	-0.032(3)	-0.031(4)	-0.011(3)
C(D5)	0.070(5)	0.109(5)	0.130(6)	-0.040(4)	-0.064(5)	0.027(5)
C(D6)	0.060(4)	0.084(4)	0.108(5)	-0.031(3)	-0.047(4)	0.031(4)
C(E1)	0.049(3)	0.032(2)	0.043(2)	-0.006(2)	-0.022(2)	-0.004(2)
C(E2)	0.050(3)	0.053(3)	0.050(3)	-0.009(2)	-0.018(2)	-0.006(2)
C(E3)	0.074(4)	0.068(3)	0.044(3)	-0.003(3)	-0.015(3)	-0.004(2)
C(E4)	0.097(5)	0.067(4)	0.062(3)	0.000(3)	-0.045(4)	-0.014(3)
C(E5)	0.086(5)	0.069(4)	0.074(4)	-0.009(3)	-0.051(4)	-0.016(3)
C(E6)	0.057(3)	0.060(3)	0.063(3)	-0.016(3)	-0.029(3)	-0.004(3)
C(F1)	0.043(3)	0.043(2)	0.048(3)	-0.011(2)	-0.019(2)	0.005(2)
C(F2)	0.052(3)	0.063(3)	0.048(3)	-0.006(3)	-0.019(3)	0.006(2)
C(F3)	0.062(4)	0.091(4)	0.056(3)	-0.011(3)	-0.023(3)	0.020(3)
C(F4)	0.086(5)	0.053(3)	0.097(5)	-0.011(3)	-0.042(4)	0.023(3)
C(F5)	0.105(5)	0.043(3)	0.095(4)	-0.009(3)	-0.052(4)	0.004(3)
C(F6)	0.074(4)	0.053(3)	0.068(3)	-0.012(3)	-0.038(3)	0.003(3)
Cl(1)	0.0794(11)	0.0726(9)	0.0781(10)	-.0117(8)	-.0478(9)	-.0016(8)
O(3)	0.183(7)	0.308(10)	0.143(5)	0.085(7)	-0.134(6)	-0.074(6)
O(4)	0.250(9)	0.141(5)	0.156(5)	-0.112(6)	-0.114(6)	0.029(4)
O(5)	0.364(13)	0.092(4)	0.142(5)	-0.010(6)	-0.131(7)	-0.022(4)
O(6)	0.077(4)	0.342(11)	0.184(7)	-0.036(6)	-0.044(5)	-0.044(7)
Cl(2)	0.0712(13)	0.1511(20)	0.1494(20)	-.0188(13)	-.0459(14)	0.0414(16)
Cl(3)	0.172(3)	0.085(1)	0.186(3)	-0.024(2)	-0.065(2)	0.019(2)
C(2)	0.074(6)	0.228(11)	0.123(7)	0.002(7)	-0.027(6)	0.036(7)

Table 2,7xxi Fractional Coordinates and Isotropic Displacement Parameters (Å^2) For $[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].OCMe_2$. For O and C atoms U is the isotropic displacement parameter and for other atoms

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*(\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Rh	0.0696(3)	0.0808(2)	-0.2199(4)	0.012
P(1)	-0.1046(10)	0.0779(7)	-0.2970(12)	0.018
P(2)	0.2448(10)	0.0778(7)	-0.1427(14)	0.025
O(1)	0.0041(28)	0.0632(14)	-0.0116(32)	0.024(10)
O(2)	0.1162(26)	0.0934(14)	-0.3621(29)	0.022(9)
C(1)	0.034(3)	0.067(2)	-0.100(4)	0.002(11)
C(2)	0.142(5)	0.133(3)	-0.410(5)	0.033(16)
C(3)	0.129(6)	0.186(3)	-0.347(7)	0.064(23)
C(4)	0.165(8)	0.131(4)	-0.516(9)	0.10(3)
C(A1)	-0.188(5)	0.133(1)	-0.256(5)	0.002(11)
C(A2)	-0.1477(23)	0.1624(26)	-0.1703(49)	0.022(14)
C(A3)	-0.204(4)	0.204(2)	-0.136(2)	0.034(16)
C(A4)	-0.301(4)	0.217(1)	-0.188(4)	0.046(19)
C(A5)	-0.3415(29)	0.1882(25)	-0.2737(39)	0.029(15)
C(A6)	-0.285(5)	0.146(2)	-0.308(3)	0.029(16)
C(B1)	-0.118(4)	0.084(2)	-0.437(2)	0.025(13)
C(B2)	-0.1118(26)	0.0406(15)	-0.5005(38)	0.020(14)
C(B3)	-0.110(5)	0.048(1)	-0.606(4)	0.019(13)
C(B4)	-0.113(3)	0.098(2)	-0.648(2)	0.045(19)
C(B5)	-0.119(3)	0.142(1)	-0.584(4)	0.028(15)
C(B6)	-0.122(5)	0.135(2)	-0.479(4)	0.029(16)
C(C1)	-0.171(5)	0.012(2)	-0.284(4)	0.038(17)
C(C2)	-0.114(4)	-0.028(3)	-0.230(5)	0.046(19)
C(C3)	-0.162(3)	-0.075(3)	-0.209(7)	0.069(23)
C(C4)	-0.267(4)	-0.083(2)	-0.243(4)	0.079(25)
C(C5)	-0.324(4)	-0.043(3)	-0.297(6)	0.062(23)
C(C6)	-0.276(4)	0.005(3)	-0.317(7)	0.068(25)
C(D1)	0.289(8)	0.127(3)	-0.039(5)	0.057(22)
C(D2)	0.216(5)	0.156(3)	0.008(5)	0.09(3)
C(D3)	0.248(5)	0.199(2)	0.069(7)	0.056(22)
C(D4)	0.352(6)	0.214(2)	0.083(4)	0.050(20)
C(D5)	0.425(3)	0.185(3)	0.036(5)	0.053(20)
C(D6)	0.394(6)	0.141(2)	-0.025(7)	0.061(23)

Table 2,7xxi cont.

C(E1)	0.331(4)	0.071(1)	-0.238(4)	0.019(13)
C(E2)	0.368(6)	0.116(1)	-0.285(5)	0.037(17)
C(E3)	0.423(3)	0.110(1)	-0.371(4)	0.043(18)
C(E4)	0.440(4)	0.060(1)	-0.409(4)	0.052(21)
C(E5)	0.403(5)	0.016(1)	-0.363(5)	0.065(24)
C(E6)	0.3489(28)	0.0215(13)	-0.2770(32)	0.039(17)
C(F1)	0.2779(28)	0.0193(25)	-0.0574(57)	0.026(15)
C(F2)	0.355(5)	0.022(2)	0.026(4)	0.028(15)
C(F3)	0.376(5)	-0.022(3)	0.090(4)	0.16(5)
C(F4)	0.3190(27)	-0.0685(21)	0.0691(48)	0.047(19)
C(F5)	0.242(5)	-0.071(2)	-0.015(3)	0.09(3)
C(F6)	0.221(5)	-0.027(3)	-0.078(5)	0.050(20)
Cl	0.0856(17)	-0.2197(8)	-0.1487(16)	0.061
O(3)	0.068(6)	-0.258(3)	-0.075(7)	0.129(28)
O(4)	0.033(8)	-0.180(4)	-0.078(9)	0.19(4)
O(5)	-0.081(8)	0.237(4)	0.290(9)	0.18(4)
O(6)	-0.194(9)	0.202(4)	0.130(9)	0.20(5)
O(S)	0.430(7)	-0.120(4)	-0.434(8)	0.16(4)
C(S1)	0.415(6)	-0.145(3)	-0.341(7)	0.062(23)
C(S2)	0.370(10)	-0.137(5)	-0.212(11)	0.14(5)
C(S3)	0.416(12)	-0.199(7)	-0.407(14)	0.18(6)

Table 2,7xxii
Anisotropic Displacement Parameters For $[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].OCMe_2$.
The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$$

	U11	U22	U33	U12	U13	U23
Rh	0.0077(21)	0.0118(24)	0.0161(25)	0.0034(28)	-.0022(16)	0.0023(33)
P(1)	0.024(9)	0.012(8)	0.018(9)	0.005(8)	0.003(7)	0.001(9)
P(2)	0.013(7)	0.013(9)	0.049(12)	-0.004(8)	0.001(7)	-0.021(11)
Cl	0.084(16)	0.048(12)	0.050(14)	-0.044(11)	0.005(11)	0.014(11)

Table 2, 7xxiii	***trans*-[PdBr(otolyl)(PPh_3)$_2$]**	**CELL USED IN REFINEMENT**
FORMULA	**$C_{43}H_{37}BrP_2Pd$**	**$C_{43}H_{37}BrP_2Pd$**
F. wt.	**802.06**	**802.06**
CRYSTAL SYSTEM	**TRICLINIC**	**TRICLINIC**
SPACE GROUP	**$P\bar{1}$**	**$P\bar{1}$**
a, Å	**12.1779 (11)**	**12.1779 (1)**
b, Å	**18.4277 (7)**	**11.0691 (4)**
c, Å	**25.4606 (15)**	**25.4606 (15)**
α, deg.	**93.1250 (39)**	**136.65 (4)**
β, deg.	**101.5182 (59)**	**101.518 (6)**
γ, deg.	**95.0191 (51)**	**105.199 (5)**
U, Å^3	**5561.9 (6)**	**1854.0 (4)**
Z	**6**	**2**
D_{CALC}, g cm^{-3}	**1.437**	**1.437**
F(000)	**2436**	**812**
μ, cm^{-1}	**16.74**	**16.74**
crystal, mm	**0.23 x 0.15 x 0.08**	**0.23 x 0.15 x 0.08**
KV	**55**	**55**
mA	**32**	**32**
COLLIMATOR, mm	**0.40**	**0.40**
Θ_{RANGE}, deg.	**2 - 25**	**2 - 25**
h	**0 - 14**	
k	**$\bar{21}$ - 21**	
l	**$\bar{29}$ - 29**	
reflns. measured	**19684**	
unique reflns.	**18706**	
observed reflns.	**4912**	**4352**
R_{int}	**0.030**	
R		**0.0579**
R_w		**0.0777**
S		**3.08**
Parameters		**352**
$\Delta\rho_{max}$, e/Å^3		**0.89**
$\Delta\rho_{min}$, e/Å^3		**-1.15**

Table 2,7xxiv Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) For [PdBr(o-tolyl)(PPh$_3$)$_2$].

$$U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^* a_j^*(\vec{a_i}.\vec{a_j}).$$

	x	y	z	U
Pd	0.18255(8)	0.13505(13)	0.22481(6)	0.063
Br	0.12675(15)	-0.16235(25)	0.18902(12)	0.160
P(1)	0.4007(3)	0.2243(4)	0.2533(2)	0.065
P(2)	-0.0281(3)	0.0730(4)	0.2069(2)	0.063
C(1)	0.2122(10)	0.3333(17)	0.2315(8)	0.080
C(2)	0.2753(12)	0.5570(19)	0.3128(9)	0.094
C(3)	0.2838(14)	0.6751(22)	0.3063(11)	0.144
C(4)	0.2354(19)	0.5713(33)	0.2222(15)	0.203
C(5)	0.1773(18)	0.3559(38)	0.1420(15)	0.233
C(6)	0.1646(13)	0.2333(22)	0.1449(9)	0.127
C(7)	0.3264(13)	0.6615(20)	0.4004(9)	0.105
C(A1)	0.4904(12)	0.2064(22)	0.3121(10)	0.069
C(A2)	0.4663(11)	0.2434(21)	0.3714(10)	0.108
C(A3)	0.5393(7)	0.2454(9)	0.4209(4)	0.152
C(A4)	0.6306(10)	0.2042(18)	0.4102(8)	0.114
C(A5)	0.6577(10)	0.1616(18)	0.3500(8)	0.113
C(A6)	0.5878(7)	0.1639(11)	0.3001(5)	0.082
C(B1)	0.5360(14)	0.4989(16)	0.3271(7)	0.076
C(B2)	0.6421(11)	0.6576(17)	0.4219(9)	0.100
C(B3)	0.7397(9)	0.8720(15)	0.4795(6)	0.105
C(B4)	0.7349(12)	0.9255(13)	0.4448(6)	0.103
C(B5)	0.6344(9)	0.7742(16)	0.3550(8)	0.151
C(B6)	0.5300(11)	0.5593(16)	0.2959(6)	0.094
C(C1)	0.3841(9)	0.0435(12)	0.1444(5)	0.071
C(C2)	0.2564(8)	-0.1619(13)	0.0602(5)	0.086
C(C3)	0.2428(11)	-0.3012(15)	-0.0237(4)	0.079
C(C4)	0.3484(8)	-0.2411(11)	-0.0272(4)	0.127
C(C5)	0.4794(9)	-0.0381(14)	0.0559(5)	0.115
C(C6)	0.4957(12)	0.1011(16)	0.1393(3)	0.089

Table 2,7xxiv cont.

C(D1)	-0.0476(9)	0.0516(14)	0.2690(6)	0.069
C(D2)	-0.1619(11)	-0.1254(16)	0.2285(6)	0.078
C(D3)	-0.1677(12)	-0.1348(14)	0.2780(4)	0.115
C(D4)	-0.0588(8)	0.0361(12)	0.3724(6)	0.137
C(D5)	0.0530(11)	0.2112(15)	0.4129(5)	0.121
C(D6)	0.0591(12)	0.2129(14)	0.3604(5)	0.100
C(E1)	-0.0597(13)	0.2740(21)	0.2499(11)	0.065
C(E2)	-0.0812(10)	0.3849(17)	0.3211(9)	0.097
C(E3)	-0.1079(7)	0.5269(10)	0.3485(5)	0.098
C(E4)	-0.1096(11)	0.5702(17)	0.3107(9)	0.112
C(E5)	-0.0907(8)	0.4658(14)	0.2419(7)	0.127
C(E6)	-0.0649(9)	0.3220(13)	0.2127(7)	0.118
C(F1)	-0.1830(12)	-0.1805(18)	0.0877(4)	0.071
C(F2)	-0.1755(10)	-0.3440(21)	0.0192(8)	0.101
C(F3)	-0.2926(11)	-0.5429(16)	-0.0745(8)	0.106
C(F4)	-0.4182(10)	-0.5743(15)	-0.0994(4)	0.102
C(F5)	-0.4269(10)	-0.4128(19)	-0.0323(8)	0.109
C(F6)	-0.3106(12)	-0.2182(15)	0.0608(7)	0.091

Table 2,7xxv Anisotropic Displacement Parameters for [PdBr(o-tolyl)($PPh_3)_2$].

The form of the anisotropic temperature factor is:

$$\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}h_ih_ja_i^*a_j^*]$$

	U11	U22	U33	U12	U13	U23
Pd	0.0261(4)	0.0329(4)	0.0410(5)	0.0177(3)	0.0189(3)	0.0308(4)
Br	0.0604(9)	0.0751(10)	0.1196(13)	0.0450(8)	0.0526(9)	0.0843(11)
P(1)	0.0267(13)	0.0337(14)	0.0397(16)	0.0161(12)	0.0162(12)	0.0299(14)
P(2)	0.0251(13)	0.0334(14)	0.0392(15)	0.0174(12)	0.0188(12)	0.0287(14)
C(1)	0.033(5)	0.043(6)	0.050(7)	0.022(5)	0.023(5)	0.039(6)
C(2)	0.044(6)	0.045(7)	0.059(8)	0.022(6)	0.031(6)	0.041(7)
C(3)	0.063(8)	0.068(9)	0.103(12)	0.042(7)	0.050(9)	0.075(10)
C(4)	0.096(12)	0.114(14)	0.132(16)	0.069(12)	0.075(13)	0.115(15)
C(5)	0.084(12)	0.161(19)	0.134(16)	0.072(13)	0.066(12)	0.137(17)
C(6)	0.057(7)	0.075(9)	0.074(9)	0.034(7)	0.035(7)	0.067(8)
C(7)	0.062(8)	0.044(7)	0.058(8)	0.035(7)	0.034(7)	0.035(7)
C(A1)	0.039(6)	0.032(5)	0.039(6)	0.018(5)	0.019(5)	0.028(5)
C(A2)	0.054(7)	0.063(8)	0.055(8)	0.034(7)	0.029(6)	0.048(7)
C(A3)	0.087(10)	0.095(11)	0.070(10)	0.054(10)	0.045(9)	0.072(10)
C(A4)	0.082(10)	0.054(8)	0.049(8)	0.036(8)	0.020(7)	0.040(7)
C(A5)	0.066(8)	0.051(8)	0.059(8)	0.042(7)	0.019(7)	0.038(7)
C(A6)	0.051(7)	0.035(6)	0.041(6)	0.027(6)	0.016(6)	0.024(6)
C(B1)	0.031(5)	0.037(6)	0.051(6)	0.022(5)	0.028(5)	0.036(6)
C(B2)	0.045(7)	0.047(7)	0.061(8)	0.023(6)	0.026(6)	0.042(7)
C(B3)	0.038(7)	0.035(7)	0.067(9)	0.015(6)	0.021(7)	0.025(7)
C(B4)	0.050(8)	0.030(7)	0.066(9)	0.011(6)	0.027(7)	0.027(7)
C(B5)	0.074(9)	0.066(9)	0.112(12)	0.051(8)	0.072(10)	0.076(10)
C(B6)	0.055(7)	0.038(6)	0.057(8)	0.025(6)	0.026(6)	0.036(6)
C(C1)	0.045(6)	0.030(5)	0.041(6)	0.022(5)	0.020(5)	0.029(5)
C(C2)	0.037(6)	0.042(6)	0.055(7)	0.021(5)	0.026(6)	0.039(6)
C(C3)	0.054(7)	0.034(6)	0.029(6)	0.018(6)	0.013(6)	0.017(6)
C(C4)	0.093(10)	0.070(9)	0.057(8)	0.059(9)	0.055(8)	0.052(8)
C(C5)	0.056(7)	0.069(8)	0.062(8)	0.038(7)	0.043(7)	0.055(8)
C(C6)	0.044(6)	0.053(7)	0.046(7)	0.029(6)	0.026(5)	0.041(6)

Table 2,7xxv cont.

C(D1)	0.027(5)	0.037(6)	0.042(6)	0.019(5)	0.022(5)	0.030(5)
C(D2)	0.043(6)	0.037(6)	0.044(6)	0.021(5)	0.027(5)	0.031(6)
C(D3)	0.074(9)	0.046(7)	0.069(8)	0.027(7)	0.045(8)	0.048(7)
C(D4)	0.089(10)	0.073(9)	0.077(9)	0.055(8)	0.058(9)	0.068(9)
C(D5)	0.077(9)	0.071(9)	0.052(8)	0.039(8)	0.032(7)	0.054(8)
C(D6)	0.041(6)	0.058(7)	0.054(7)	0.017(6)	0.021(6)	0.047(7)
C(E1)	0.023(5)	0.034(5)	0.040(6)	0.012(4)	0.013(4)	0.029(5)
C(E2)	0.047(6)	0.052(7)	0.055(7)	0.032(6)	0.028(6)	0.043(7)
C(E3)	0.058(7)	0.041(7)	0.057(8)	0.031(6)	0.036(7)	0.034(7)
C(E4)	0.052(8)	0.040(7)	0.074(10)	0.028(6)	0.020(7)	0.038(8)
C(E5)	0.059(8)	0.064(8)	0.082(10)	0.041(7)	0.036(8)	0.062(9)
C(E6)	0.048(7)	0.074(8)	0.067(8)	0.043(7)	0.034(6)	0.060(8)
C(F1)	0.036(5)	0.034(6)	0.039(6)	0.015(5)	0.015(5)	0.029(5)
C(F2)	0.049(7)	0.058(7)	0.059(8)	0.036(6)	0.039(6)	0.050(7)
C(F3)	0.072(9)	0.049(7)	0.051(8)	0.038(7)	0.034(7)	0.037(7)
C(F4)	0.068(9)	0.042(7)	0.042(7)	0.026(7)	0.010(7)	0.024(7)
C(F5)	0.036(7)	0.048(8)	0.051(8)	0.020(6)	-0.002(6)	0.017(7)
C(F6)	0.042(7)	0.044(7)	0.042(7)	0.027(6)	0.014(6)	0.021(6)

Table 2, 7xxvi	REACTION PRODUCT OF 2, 3g
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	$P2_1/m$
a, Å	12.8282 (10)
b, Å	10.5280 (7)
c, Å	20.5523 (28)
β, deg.	102.266 (9)
U, $Å^3$	2712.3 (5)
crystal, mm	0.10 x 0.10 x 0.02
KV	50
mA	20
COLLIMATOR, mm	0.40
Θ_{RANGE}, deg.	2 - 60
h	0 - 14
k	0 - 11
l	$\overline{23}$ - 23
reflns. measured	4486
unique reflns.	4272
observed reflns.	1153
R_{int}	0.045

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3, 1a SYNTHESIS AND CHARACTERISATION OF *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][X]$. X = ClO_4^-, $CF_3SO_3^-$.

As stated in Section 1, 2b it was decided to prepare *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$, as described by Vaska and coworkers,[1] in order to compare its structure with that of the formally three coordinate species $[Rh(PPh_3)_3][ClO_4]$.[2] To this end $AgClO_4$ was added to a slurry of *trans*-$[RhCl(CO)(PPh_3)_2]$ in toluene and the resulting light yellow powder was isolated as described; without taking precautions to exclude air. Both I.R. and ^1H n.m.r. spectroscopy suggested the presence of water in the product (Tables 3, 1i and 3, 1ii) and as the ^{31}P n.m.r. spectrum showed only a doublet (δ = 30.21 p.p.m., $J_{Rh\text{-}P}$ = 124.2 Hz), indicative of mutually *trans* phosphine groups, it was suspected that the product was in fact *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4]$. This was later confirmed when recrystallisation from CH_2Cl_2 gave crystals of *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$ suitable for X-ray diffraction (Section 3, 4m). Definite characterisation of the product as the aqua complex prior to the solution of the crystal structure was hindered by several factors. The water signal in the ^1H n.m.r. spectrum was small and broad and, additionally, it moved around in the range 3.25 to 2.62 p.p.m. with no obvious correlation to concentration or to the presence or lack of solvents of crystallisation in the solid product. Also, the appearance of the I.R. spectrum of the product is very dependent on the medium in which it is run as can be seen in Table 3, 1i. The I.R. spectrum run as a nujol mull

TABLE 3, 1i

I.R. DATA FOR COMPOUNDS $[Rh(CO)(S)(PPh_3)_2]^{n+}$, n = 0 or 1

COMPLEX	METHOD[a]	WATER	CARBONYL	ACETONE CO	ClO_4^-	$CF_3SO_4^-$
trans-$[Rh(OH_2)(CO)(PPh_3)_2]$ $[ClO_4]$	nujol	3400vbr	2000vs + 1980s	-	1125s, 1160sh,1070sh	-
"	KBr	3400vbr	2004vs + 1985s	-	1121s, 1165w, 1080w	-
"	CH_2Cl_2	not obs.	1980 vs	-	1110s	-
trans-$[Rh(OCMe_2)(CO)(PPh_3)_2]$ $[ClO_4]$	nujol	-	2004br,vs	1655m	1087br,s	-
"	KBr	-	2006vs +1987s	1655m	1095br,s	-
trans-$[Rh(CO)(ClO_4)(PPh_3)_2]$	nujol	-	1993vs	-	1150s + 1015s	-
trans-$[Rh(OH_2)(CO)(PPh_3)_2]$ $[CF_3SO_3]$	nujol	3280vbr	2010vs	-	-	1246ms, 1172m,1163m,1030 ms
"	KBr	3300vbr	2020vs	-	-	1250ms, 1180m,1170m,1035 ms
trans- $[Rh(OCMe_2)(CO)(PPh_3)_2]$ $[CF_3SO_3]$	nujol	-	1981vs	1655m	-	1246ms, 1162m,1030ms

a/ All spectra run as KBr discs were prepared in air and showed a peak at 1967cm^{-1} due to $[RhBr(CO)(PPh_3)_2]$.

and made up under a nitrogen atmosphere shows only a weak, broad signal in the O-H stretch region. Additionally there are 3 peaks in the 1000 - 1200 cm^{-1} region which are attributable to a non-tetrahedral ClO_4^- group (although the peaks at 1160 and 1070 cm^{-1} appear as shoulders on the main peak). This is identical to the I.R. spectrum described by Vaska[1] and constitutes the evidence on which he based his formulation of the product as a coordinated perchlorate complex.

Perchlorate as a counterion should be tetrahedral and give only one I.R. ν(Cl-O) peak, in the 1000 - 1200 cm^{-1} region. Unidentate coordination of ClO_4^- leads to loss of symmetry and two peaks are expected in this region whilst bridging ClO_4^- will show three peaks.[3]

If the I.R. spectrum of *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4]$ is run as a KBr disc then the water peak sharpens and the shoulders on the main perchlorate peak at 1121 cm^{-1} become weaker and less distinct. This was initially thought to be due to a reaction between the product and excess water present in the KBr. Running the spectrum as a solution in CH_2Cl_2 gives only one broad peak, indicative of free, tetrahedral ClO_4^-, at 1110 cm^{-1}.

The apparent asymmetric nature of the perchlorate anion in the solid state, which led to its initial assignment as coordinated to Rh(I), is explained by the crystal structure (Section 3, 4m). It can be seen that

TABLE 3, 1ii

N.M.R. SPECTROSCOPIC DATA FOR $[Rh(CO)S(PPh_3)_2]^{n+}$, n = 0 or 1

COMPLEX	^{31}P		^{1}H	
	δ (ppm)	$J_{Rh\text{-}P}$ (Hz)	δ phenyl (ppm)	δ $OH_2/OCMe_2$ (ppm)
$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4]$	30.21	124.2	7.55m	3.25 → 2.62 broad s
$[Rh(OH_2)(CO)(PPh_3)_2][CF_3SO_3]$	28.89	124.4	7.52m	2.20 → 2.40 broad s
$[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4]$	30.38	133.7	7.53m	1.74s
$[Rh(OCMe_2)(CO)(PPh_3)_2][CF_3SO_3]$	29.88	133.6	7.52m	1.81s
$[Rh(CO)(ClO_4)(PPh_3)_2]$	30.29	116.4	7.53m	-

there is extensive hydrogen bonding present in the solid state, leading to the presence of $[Rh(OH_2)(CO)(PPh_3)_2]_2[ClO_4]_2$ dimers linked by a twelve membered $Cl_2O_6H_4$ ring. This hydrogen bonding distorts the ClO_4^- anions away from tetrahedral geometry and explains the nature of the ClO_4^- region in the nujol and KBr I.R. spectra. In CH_2Cl_2 solution the dimeric units cease to exist and the ClO_4^- anion is tetrahedral. Further complications in using I.R. spectroscopy to identify this, and the following, similar complexes are reactions between the complexes and KBr forming $[RhBr(CO)(PPh_3)_2]$ and the observance of two peaks in the carbonyl region of the spectra run in the solid state. The presence of two peaks could be due to the existence of two conformations of the complexes, as is the case with *trans*-$[RhCl(CO)(PPh_3)_2]$ which is known in two conformational forms, one with staggered PPh_3 ligands and one with eclipsed PPh_3 ligands.[4]

A similar reaction was performed by treating *trans*-$[Rh(CO)Cl(PPh_3)_2]$ with $AgCF_3SO_3$ instead of $AgClO_4$, and this also gives an aqua complex, *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][CF_3SO_3]$, as the sole product. This was shown by I.R. spectroscopy, ^1H and ^{31}P n.m.r. spectroscopy and microanalysis. That the $CF_3SO_3^-$ anion is not coordinated to rhodium is shown by the good match of the 1000 - 1300 cm^{-1} region of the I.R. spectrum with that of other non-coordinating triflates (e.g. $[Mn(CO)_5(PBu_3)][SO_3CF_3]$).[5,6]

Several attempts to form a genuine sample of *trans*-

$[Rh(CO)(ClO_4)(PPh_3)_2]$ from the chloro complex by addition of silver salts, using rigorously dry conditions, failed. The aqua complex was always formed despite measures such as drying the nitrogen used and drying a $AgClO_4$ solution in benzene by azeotropic distillation. It is thought that the most likely source of water is the extremely hygroscopic $AgClO_4$. Attempts to use the more easily dried $TlClO_4$ failed as no suitable solvent was found in which both $TlClO_4$ and $[RhCl(CO)(PPh_3)_2]$ were sufficiently soluble to react together.

3, 1b THE CASE AGAINST VASKA'S FORMULATION OF $[Rh(CO)(ClO_4)(PPh_3)_2]$.

Vaska and coworkers assigned the formulation *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$ to their product mainly on the basis of I.R. spectroscopy which showed what appeared to be bound, non-T_d geometry for the ClO_4^- species. It is shown above that low symmetry in the ClO_4^- anion does not necessarily mean coordination to the metal and indeed the nujol I.R. spectrum of *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4]$ matches that described for Vaska's *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$, which was also run in nujol and which also gave a spectrum containing free ClO_4^- when run as a solution in $CHCl_3$. This indicates that the compound Vaska and coworkers formed was in fact the aqua complex and not the coordinated perchlorate complex. That this is so is supported by the following. Vaska describes an air stable compound that in our hands is very susceptible to moisture. In fact Vaska recovers his perchlorato complex unchanged after attempting to dissolve it in water[1, 7] and uses it as a catalyst to form water.[8] Also the microanalytical and molecular weight data presented by Vaska are equally well fitted to both the aqua and perchlorato complexes. As final proof that Vaska's rhodium compound is in fact the aqua complex a genuine sample of *trans*-[Rh(CO)(ClO_4)(PPh_3)$_2$] was eventually synthesised (Section 3, 1d), via the acetone complex, and this has different properties to those described by Vaska for his coordinated perchlorate complex.

3, 1c SYNTHESIS AND CHARACTERISATION OF *trans*-[Rh($OCMe_2$)(CO)(PPh_3)$_2$][X].nS WHERE X = ClO_4^-, $CF_3SO_3^-$, S = $OCMe_2$, CH_2Cl_2, n = 0 → 2.

Recrystallisation, under nitrogen atmosphere, of *trans*-[Rh(OH_2)(CO)(PPh_3)$_2$][X] from hot acetone, by the addition of petroleum ether, gave the species *trans*-[Rh($OCMe_2$)(CO)(PPh_3)$_2$][ClO_4].2$OCMe_2$ and *trans*-[Rh($OCMe_2$)(CO)(PPh_3)$_2$][CF_3SO_3].$OCMe_2$. Both species showed I.R. absorbances at 1711 cm^{-1} due to uncoordinated acetone and at 1655 cm^{-1} for coordinated acetone.[2] A second recrystallisation, from hot CH_2Cl_2, with precipitation by petroleum ether, gave the crystalline species *trans*-$[Rh(OCMe_2)(CO)(PPh_3)_2][X].CH_2Cl_2$. These rapidly lost CH_2Cl_2, both under nitrogen and in air, to give the non-solvated complexes whose spectroscopic details are given in Tables 3, 1i and 3, 1ii.*

The loss of solvent of crystallisation made these species unsuitable for X-ray diffraction. Exposure to air for brief periods did not displace the coordinated acetone ligand but over a period of 12 - 72 hrs, depending on crystal size and the nature of solvents of crystallisation, the aqua complex was reformed.

The coordinated acetone complex *trans*-$[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].OCMe_2$ was also prepared by the addition of a little acetone to a mixture of $[RhCl(CO)(PPh_3)_2]$ and $AgClO_4$ in toluene. The crystalline product was of sufficient quality to give the crystal structure reported in Section 3, 4n which despite its poor resolution confirmed the monomeric nature of the product and its formulation.

* N.B. The proton n.m.r. spectra of compounds containing acetone of solvation, which were run in $CDCl_3$, show only one singlet due to the methyl groups of acetone. The chemical shift of this singlet varied from 2.00 p.p.m. to 1.80 p.p.m. for the different samples run. This compares with a value found of 2.20 p.p.m. for free acetone in $CDCl_3$ and that of 1.74 p.p.m. found for the species *trans*-$[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4]$

which contains no acetone of crystallisation. This indicates that in solution coordinated acetone is rapidly exchanged for free acetone and that the resulting methyl signal is an average of the two forms.

3, 1d SYNTHESIS AND CHARACTERISATION OF *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$.

Having formed *trans*-$[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4]$ it was hoped that further recrystallisation from non-coordinating solvents would follow a path similar to that in ref. 2 where recrystallisation of $[Rh(OCMe_2)(PPh_3)_3][ClO_4]$ from CH_2Cl_2 gave the formally three coordinate species $[Rh(PPh_3)_3][ClO_4]$. On recrystallising *trans*-$[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$, however, the orange, microcrystalline product proved to be *trans*-$[Rh(CO)(ClO_4)(PPh_3)_2]$.

The product was given this formula on the basis of its I.R. spectrum, which showed no trace of water and the ClO_4^- region of which was separated into distinct bands, the ^1H n.m.r. spectrum also showed no trace of water and additionally the ^{31}P n.m.r. spectrum indicated mutually *trans* phosphine ligands. Also the product was very air sensitive converting completely to the aqua complex within 3 minutes of exposure to air, even in the crystalline state. Attempts to grow crystals suitable for X-ray analysis gave only very small crystals that were made even less suitable by their inclusion of easily lost solvents of crystallisation. Full spectroscopic details are given in Tables 3, 1i and 3,1ii.

3, 1e OTHER LITERATURE ON THE $[Rh(CO)(ClO_4)(PPh_3)_2]$ SYSTEM - A DIVERSION.

Two compounds *trans*-$[Rh(CO)(ClO_4)(AsPh_3)_2]$[9] and *trans*-$[Rh(CO)(ClO_4)(PCy_3)_2]$[10] are reported in the literature as being prepared by similar methods to Vaska's $[Rh(CO)(ClO_4)(PPh_3)_2]$ and are characterised as air-stable and containing coordinated perchlorates by analogy with Vaska's conclusions. In the light of the realisation that Vaska's coordinated perchlorate complex is in fact *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4]$ it seems that the two analogues are probably aqua complexes as well, especially since the $AsPh_3$ complex is prepared in air and the PCy_3 complex is precipitated by plunging the reaction mixture into water.

Since Vaska first prepared his rhodium complex and used it in oxidative addition reactions[11] a large number of papers have been published which use the complex prepared by his method as a reagent. For example C. S. Chin and his coworkers have published 20 papers using

Vaska's so-called coordinated perchlorate compound as a catalyst for hydrogenation and isomerisation of unsaturated aldehydes, ketones, nitriles and alcohols. (Selected refs. 12, 13, 14 and 15). The knowledge that this group were in fact using the aqua complex does not greatly affect their results but does account for there being no alteration to the rate of reaction on the addition of small amounts of water. Also the proposed intermediate $[Rh(ClO_4)(NCR)(CO)(PPh_3)_2]$ from their kinetic study of the reaction of Vaska's perchlorate complex with nitriles[16] is probably incorrect.

During the course of this work two papers were published with the first reported syntheses of *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][X]$. P. J. Stang and his coworkers claimed to have formed the aqua complex[17] by reaction of $[Rh(CO)(CF_3SO_3)(PPh_3)_2]$, made by Vaska's method, with a 1:10 water:benzene mixture under nitrogen atmosphere. It seems likely that they did not actually ever isolate the species $[Rh(CO)(CF_3SO_3)(PPh_3)_2]$. In a later publication D. M. Branan and coworkers[6] stated that whilst trying to purify the species $[Rh(CO)X(PPh_3)_2]$, X = $SO_3CF_3^-$, ClO_4^- and BF_4^-, which they had previously used as starting materials for a series of substitution reactions,[18, 19] and which they had prepared using Vaska's method, they obtained instead the $CF_3SO_3^-$, ClO_4^- and BF_4^- salts of the aqua complex. Again it appears that in their earlier papers (Refs. 18 and 19) this group had not actually isolated the species containing coordinated anions. This conclusion is based on the reportedly air stable nature of the species used, the reported lack of effect of adding small amounts of water to their substitution reactions and the groups subsequent failure to use rigorously water free methods.

3, 1f SYNTHESIS AND CHARACTERISATION OF $[Rh(OCMe_2)(PPh_3)_3][ClO_4]$.

It has been shown, in Section 3, 1d, that treatment of $[Rh(CO)Cl(PPh_3)_2]$ with $AgClO_4$ leads to the formation of the coordinated perchlorate species $[Rh(CO)(ClO_4)(PPh_3)_2]$ via intermediates containing coordinated solvents. The similar treatment of Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, with $TlClO_4$ gave firstly similar complexes containing coordinated solvents, acetone, alcohols and ethers, but on recrystallisation from CH_2Cl_2 gave the complex $[Rh(PPh_3)_3][ClO_4]$ which, as discussed in Section 1, 1e, has one phenyl group bent round to occupy the fourth coordination position.[2]

There is no convincing electronic explanation for the carbonyl species $[Rh(CO)(PPh_3)_2]^+$ filling its coordination sphere with a ClO_4^- ligand but $[Rh(PPh_3)_3]^+$ preferring an interaction with an aryl system. Despite being electronically similar, however, study of the published crystal structures of $[RhCl(CO)(PPh_3)_2]$[4] and $[RhCl(PPh_3)_3]$[20] show them to have marked steric differences. [RhCl(PPh_3)$_3$], in both its orange and red crystalline forms, shows a large distortion towards tetrahedral geometry. (The angle P-Rh-P for the mutually *trans* phosphine ligands is 159.1(2)° in the orange form and 152.8(1)° in the red form.) This is presumably due to the steric strains caused by accommodating three large triphenylphosphine ligands around the metal. Also in both the orange and red forms of [RhCl(PPh_3)$_3$] a hydrogen atom on a phenyl ring approaches closely to the metal, forming an agostic bond. In the orange form this agostic interaction is from a phenyl group on the ligand *trans* to the chlorine (Rh...H = 2.84 Å) and in the red form it is on the phenyl group on the ligand *cis* to chlorine (Rh...H = 2.77 Å). Neither a large tetrahedral distortion nor any agostic interactions are observed in the published crystal structures of *trans*-[RhCl(CO)(PPh_3)$_2$] or in the structures of *trans*-[Rh(OH_2)(CO)(PPh_3)$_2$][ClO_4].CH_2Cl_2 and *trans*-[Rh($OCMe_2$)(CO)(PPh_3)$_2$][ClO_4].$OCMe_2$ presented in Sections 3, 4m and 3,4n. It is interesting to speculate that the agostic interaction between phenyl ring and metal centre seen in Wilkinson's catalyst, and caused by steric crowding, persists throughout the synthesis of [Rh($OCMe_2$)(PPh_3)$_3$][ClO_4] and its subsequent recrystallisation to give the species [Rh(PPh_3)$_3$][ClO_4] where the agostic interaction now completes the square-planar coordination shell. In this theory the interaction with the phenyl ring is preferred to bonding to ClO_4^- as it is already present. Bonding to ClO_4^- is thus not necessary to complete the coordination sphere.

In order to test this theory $TlClO_4$ was added to $[RhCl(PPh_3)_3]$ in acetone to give an orange material which matched the brief description of $[Rh(OCMe_2)(PPh_3)_3][ClO_4]$ given by Yared *et al.* in ref. 2. I.R. and n.m.r. spectroscopic data are given in Tables 3, 1iii and 3, 1iv. Repeated attempts to grow good quality crystals using petroleum ether or toluene as poor solvents failed. The orange crystals produced were always hexagonal plates with a mica-like appearance. A crystallographic data set was collected from the best of the available crystals (Section 2, 71) but the poverty of the data from the very small, platey crystal meant that structural solution was impossible. What was interesting however was that a Patterson function showed a vector of 3.01 Å between two heavy atoms. Furthermore on leaving a crystalline sample stored under nitrogen for several months the crystal lost coordinated acetone, as seen by I.R. spectroscopy, and turned green. A green colour is common in Rh_2^{4+} dimers when an oxygen donor is present.[22] A possible interpretation of this is that the complex $[Rh(OCMe_2)(PPh_3)_3][ClO_4]$ exists, in the solid state, as a dimer with a Rh-Rh distance of 3.01 Å. The ^{31}P n.m.r. spectrum, in $CDCl_3$ solution shows only one singlet peak indicating fluxionality, as in Wilkinson's catalyst. The ^1H n.m.r. shows only phenyl protons and a singlet for the methyl protons. Thus it seems likely that if a dimeric compound is present in the solid state then it does not persist in solution.

In conclusion it would seem that the actual nature of the solvated species $[Rh(S)(PPh_3)_3][ClO_4]$ reported as precursors to $[Rh(PPh_3)_3][ClO_4]$

TABLE 3, 1iii

I.R. DATA (cm^{-1}) FOR WILKINSON'S CATALYST AND ITS DERIVATIVES.

COMPLEX	UNSAT.C-H	SAT.C-H	NO_3^- or ClO_4^-	FINGERPRINT
$[RhCl(PPh_3)_3]$ (red)[a]	3060m	-	-	520s, 695s, 740m, 1095m, 1435s, 1480m
$[Rh(OCMe_2)(PPh_3)_3][ClO_4]$ $.OCMe_2$	3058w	2926br,m	1091br,s	542s, 623m, 695s, 723s, 1120s, 1437s, 1665w, 1728br,m
GREEN COMPLEX	3055m	-	1092br,s	542s,623m, 693s, 724s, 1120s, 1437s, 1483m, 1590m
$[Rh(NO_3)(PPh_3)_3]$	3060m	-	1000br,m 1270br,s 1500br,s	520s, 535s, 695s, 750m, 1095m, 1435s, 1480s
$[(PPh_3)_2(HOMe)Rh]_2[NO_3]_2$	3060m	2930w	1385br,s (840br,m)	520s, 695s, 740m, 1095m, 1435s, 1480s, 1490s
UNKNOWN FROM $AgNO_3$ IMPREGNATED COLUMN	3060m	-	1180br,s 1320br,s (1440br,s + 830m)	540s, 695s, 730s, 1120s, 1440br,s
$[Rh(PPh_3)_2(PPh_2(C_6H_4))]$	3060m	-	-	327m, 520s, 695s, 740s, 746m, 1095m, 1435s, 1480m

a/ ν(Rh-Cl) = 295w

TABLE 3, 1iv

N.M.R. SPECTROSCOPIC DATA FOR WILKINSON'S CATALYST AND ITS DERIVATIVES.

COMPLEX	^{31}P n.m.r.		^1H n.m.r. (δ p.p.m.)
	δ (p.p.m.)	J (Hz)	
$[RhCl(PPh_3)_3]$	s 29.10	-	m 7.68 → 7.25
$[RhCl(PPh_3)_3]^a$	Ref.21	$J(Rh\text{-}P_A) = 192$ $J(Rh\text{-}P_B) = 146$ $J(P\text{-}P) = 37.5$	
$[Rh(OCMe_2)(PPh_3)_3][ClO_4].(OCMe_2)$	s 30.73	-	m 7.64 → 7.35 s 1.24
$[Rh(NO_3)(PPh_3)_3]$	s 29.91	-	m 7.70 → 7.30
$[(PPh_3)_2(HOMe)Rh]_2^{2+}$	d.d.t. 33.64 d.d.d. 24.29	$J(Rh\text{-}P_A) = 173.6$ $J(P_A\text{-}P_B) = 31.2$ $J(P_A\text{-}X) = 6.2$ $J(Rh\text{-}P_B) = 124.8$ $J(P_A\text{-}P_B) = 31.2$ $J(P_B\text{-}X) = 6.2$	m 6.50 → 7.60 s 1.55
UNKNOWN FROM $AgNO_3$ IMPREGNATED COLUMN	s 30.42	-	m 6.67 → 6.28

a/ Run in CD_2Cl_2

may be more complicated than previously supposed.

3, 1g THE REACTIONS OF WILKINSON'S CATALYST WITH $AgNO_3$.

On adding a methanolic solution of $AgNO_3$ to a hot methanolic solution of $[RhCl(PPh_3)_3]$ only small amounts of characterisable products were formed (Section 2, 3h). The larger fraction of these was the expected product $[Rh(NO_3)(PPh_3)_3]$ as identified by I.R. and ^1H and ^{31}P spectroscopy (Tables 3,1iii and 3,1iv). This formulation is based largely on peaks at 1500, 1270 and 1000 cm^{-1} in the I.R. spectrum which are characteristic of a coordinated nitrate group[23] and the lack of either a Rh-Cl stretch in the I.R. spectrum or any signal in the ^1H n.m.r. spectrum other than those attributable to phenyl groups.

Of more interest is the minor product. The I.R. spectrum of this orange powder shows[23] (Table 3, 1iii) free NO_3^- and saturated C-H groups but lacks the Rh-Cl stretch seen in $[RhCl(PPh_3)_3]$ at 295 cm^{-1}. The ^1H n.m.r. spectrum shows a broad multiplet due to phenyl group protons and a singlet at 1.55 p.p.m.. Thus far the evidence points to the other expected product $[Rh(HOMe)(PPh_3)_3][NO_3]$. The ^{31}P n.m.r. spectrum, however, consists of two distinct signals of equal size. These are, as shown in Table

3, liv, a doublet of doublets of triplets and a doublet of doublets of doublets. The largest coupling constants for both signals are of the correct amplitudes for Rh-P coupling over a single bond.[24] The middle coupling constant of 31.2 Hz is indicative of *cis* P-P coupling. The smallest coupling constants are approximately 6 Hz (resolution here is poor) and are probably due to coupling over several bonds.[25, 26] This pattern is obviously that of a dimeric structure[25] and the formulation $[(PPh_3)_2(HOMe)RhRh(HOMe)(PPh_3)_2][NO_3]_2$ is tentatively suggested as best fitting the available evidence. What is clear is that in a reaction very similar to the addition of $TlClO_4$ to $[RhCl(PPh_3)_3]$, as discussed in the previous section, a dimeric species has been formed which incorporates a non-coordinating counterion and a coordinated solvent. It is felt that this evidence strengthens the suggestion of section 3, 1f that $[Rh(OCMe_2)(PPh_3)_3][ClO_4]$ is in fact a dimeric species.

A second reaction between $AgNO_3$ and $[RhCl(PPh_3)_3]$ was carried out using a column impregnated with $AgNO_3$ and a solution of Wilkinson's catalyst in ethyl acetate. This was undertaken largely to see if columns impregnated with silver salts were useful synthetic tools for this type of metallation reaction. The sole isolable product was a rather impure yellow powder which contained coordinated nitrate and which was different from the previously described $[Rh(NO_3)(PPh_3)_3]$. Spectroscopic details of this compound are given in Tables 3, liii and 3, liv but its identity remains unknown.

3, 1h ATTEMPTED PREPARATION OF [Rh{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$] AND ITS DECOMPOSITION.

In a brief communication[27] Lappert and his coworkers reported the synthesis of the title compound as a green solid from the addition of [LiN(SiMe$_3$)$_2$] to [RhCl(PPh$_3$)$_3$] in T.H.F. solution. The characterisation of this product was by microanalysis and by n.m.r. spectroscopy of a T.H.F. solution. The evidence presented does not rule out the possibility of a dimeric configuration or, in solution, a coordinated solvent containing species. The reaction was repeated (section 2, 3j) in an effort to determine crystallographically whether the product was indeed a three coordinate compound as claimed by Lappert and coworkers.

The initial product was indeed a green solid but after storing overnight, under nitrogen atmosphere and at 5 °C, only an orange powder was left. Working this solid up gave only Wilkinson's catalyst as an isolatable product and traces of a compound which fits the description of [Rh(PPh$_3$)$_2$(PPh$_2$(C$_6$H$_4$))] formed by Keim[28], in 1968, by reductive elimination of CH$_4$ from [Rh(Me)(PPh$_3$)$_3$]. The I.R. spectrum of our complex is reported in Table 3, 1iii. It is interesting to note that reductive elimination of volatile, HN(SiMe$_3$)$_2$ from a species such as [Rh{N(SiMe$_3$)$_2$}(PPh$_3$)$_3$] would give cyclometallated [Rh(PPh$_3$)$_2$(PPh$_2$(C$_6$H$_4$))] and would also account for the absence of the N(SiMe$_3$)$_2$ group from any of the solid fractions isolated.

3, 1i CONCLUSIONS AND COMMENTS.

The proceeding Sections 3, 1a - 1h have dealt with derivatives of the complexes *trans*-[RhCl(CO)(PPh_3)$_2$] and Wilkinson's catalyst, [RhCl(PPh_3)$_3$]. In conclusion, the complex [Rh(CO)(ClO_4)(PPh_3)] was not previously known despite its widespread occurrence in the literature. It can however be formed from the solvated species *trans*-[Rh($OCMe_2$)(CO)(PPh_3)$_2$][ClO_4] and is a highly air sensitive, microcrystalline, orange complex. As seen from the literature the analogous recrystallisation of [Rh($OCMe_2$)(PPh_3)$_3$][ClO_4] forms not a coordinated perchlorate complex but a formally three coordinate complex [Rh(PPh_3)$_3$][ClO_4] in which one phenyl ring of a phosphine ligand is bent around to interact, agostically, with the fourth coordination site. Sections 3, 1f and 3, 1g indicate that this reaction may not be as simple as it appears, as the precursor [Rh($OCMe_2$)(PPh_3)$_3$][ClO_4] may in fact be a dimeric species.

One of the more interesting features of this section is that the complex [Rh(OH_2)(PPh_3)$_3$][ClO_4] was at no time isolated, despite many recrystallisations of [Rh($OCMe_2$)(PPh_3)$_3$][ClO_4] from a variety of solvents over a period of months. This aqua complex is also unknown in the literature despite much work being present which deals with [Rh(PPh_3)$_3$][ClO_4].[29, 30, 31] This seems unusual as [Rh(OH_2)(CO)(PPh_3)$_2$][ClO_4] is very easily formed and is also the product of exposing complexes of stronger ligands, such as acetone, to air.

Exposure of [$Rh(CO)(ClO_4)(PPh_3)_2$] to air gives, almost instantly, complete conversion to the aqua complex but by comparison exposure of solutions of [$Rh(PPh_3)_3$][ClO_4] reportedly leads to complete decomposition, but only slowly.[31] This indicates that the Rh to phenyl interaction in [$Rh(PPh_3)_3$][ClO_4] is stabler than an Rh to OH_2 bond would be for the same substrate.

In the absence of stronger ligands both water and perchlorate groups are able to bond to Rh^I as is evinced by the synthesis of *trans*-[$Rh(OH_2)(CO)(PPh_3)_2$][ClO_4] and *trans*-[$Rh(CO)(ClO_4)(PPh_3)_2$] as well as by the compounds in Table 3, 4xi. It thus seems strange that the phenyl to rhodium interaction was dismissed by Yared *et al.* as a weak interaction that does not contribute to the formal coordination number. It seems more likely that the interaction is in fact a fairly strong three-centre, two-electron bond as described in Crabtree's recent review on "Transition Metal Complexation of σ Bonds".[32] This would explain why the supposedly weak interaction is capable of preventing both OH_2 and ClO_4^- (and also H_2)[2] from binding to the Rh metal and also why it is capable of closing, and holding, the Rh-P-C angle to 75.6(5)°, a configuration which is clearly strained. Yared *et al.*'s argument that the lack of internal changes in the phenyl ring's geometry indicates a weak C-H to rhodium interaction is flawed. C-H to metal sigma bonds do not require lengthening of an attached C-C framework.[32] Crabtree in fact also demonstrates that in practice neither C-H nor H-H bonds are observed to be stretched when involved in σ donation to a metal centre. If it is accepted that the agostic interaction is strong enough to place it below acetone but above water, H_2 and perchlorate in a ligand strength series then the compound $[Rh(PPh_3)_3][ClO_4]$ cannot be described as a three-coordinate, 14-electron complex but must be seen formally as a four-coordinate, 16-electron complex.

The Rh^{III} complex $[Rh(mesityl)_3]$ was recently prepared and its crystal structure published.[33] In this structure each of the mesityl groups are tilted so as to bring a C-H group from an *ortho* methyl substituent into contact with the metal. If these interactions were to be ignored as weak interactions, as Yared *et al.* designated in their complex, then we have a three-coordinate, 12-electron complex. If, however, the interactions are classified as σ bonds coordinated to the metal then the structure is that of a classical octahedral 18 electron complex.

3, 2a GENERAL COMMENTS ON THE SYSTEM *trans*-[$Pd(PPh_3)_2(R)L]^{n+}$.

As stated in the introduction (Section 1, 2c) there is strong kinetic evidence for species of the type *trans*-[$Pt(PEt_3)_2(R)Cl$] (R = H, CH_3, C_2H_5, C_6H_5, *o*-tolyl or mesityl) undergoing nucleophilic substitution by dissociative processes. In theory the strong σ-donor nature of the R group promotes labilization of the halide ligand. In order to probe the nature of the intermediates in these nucleophilic substitutions (such as solvated species) attempts were made to form *trans*-[$Pd(PPh_3)_2(R)L]^{n+}$. R is *o*-tolyl or mesityl and L is Br^-, donating solvents, NO_3^- or ClO_4^- (n = 0 or 1).

PPh_3 was preferred over PEt_3 as it was hoped that the bulkier phenyl groups would help stabilise any 3-coordinate transition states and palladium was preferred over platinum on grounds of cost and of chemical novelty, the palladium complexes being previously unknown. Additionally palladium complexes offer a better comparison with the known unsaturated rhodium complexes.[2]

It soon became apparent that the synthesis of *trans*-[$Pd(PPh_3)_2(R)Br$] was not trivial as the complexes are not stable in solution if impurities are present. Furthermore, replacement of the bromine ligand with more weakly bonding ligands exacerbates decomposition to such a level that isolation of any pure materials was problematic. This section thus describes the various methods that were used in attempting to synthesise *trans*-[Pd(PPh_3)$_2$(R)Br] and compares their relative effectiveness. Also described are the reactions of *trans*-[Pd(PPh_3)$_2$(*o*-tolyl)Br] with $AgNO_3$ and $AgClO_4$ and a discussion of the likely products.

3, 2b SYNTHESIS AND CHARACTERISATION OF *trans*-[Pd(PPh_3)$_2$(R)Br].

As shown in Table 3, 2i a variety of methods were used in attempting the synthesis of *trans*-[Pd(PPh_3)$_2$(R)Br] (R = *o*-tolyl or mesityl). The most successful methods for forming the *o*-tolyl complex were reaction of [Pd(PPh_3)$_4$] with *o*-bromotoluene and treatment of *trans*-[$PdCl_2$(PPh_3)$_2$] with Li(*o*-tolyl) in the presence of LiBr. Of these two methods the preparation from the Pd^0 species is the route of choice as it gives a cleaner reaction with easier separation of products and hence a product of greater purity. The importance of quick and complete isolation of the *o*-tolyl complex is that impure solutions of the complex, in chlorinated solvents, T.H.F. or alcohols, decompose over a period of 12 - 48 hrs to give only palladium metal and triphenylphosphine (or triphenylphosphine oxide if in air). Once pure a CH_2Cl_2 solution of *trans*-[Pd(PPh_3)$_2$(*o*-tolyl)Br] will stand, in air, for several weeks without decomposing. This lack of stability of the complex with respect to other species in solution helps to explain why the yield values in Table 3, 2i are maximum values and that when the preparations were repeated smaller yields were often found. Treating *trans*-$[PdCl_2(PPh_3)_2]$ with a Grignard type reagent (Section 2, 4e) resulted in only palladium metal, PPh_3O and black tars being isolated.

Table 3, 2i SHOWING MAXIMUM % YIELDS OF *trans*-$[Pd(PPh_3)_2(R)Br]$		
METHOD	R = *o*-tolyl	R = mesityl
$[Pd(PPh_3)_4]$ + BrR	39%	9%
$[PdCl_2(PPh_3)_2]$ + Li(*o*-tolyl)	35%	n/a
$[PdCl_2(PPh_3)_2]$ + MgRBr	no tolyl complex	no mesityl complex
$[PdCl_2(PPh_3)_2]$ + $Hg(mesityl)_2$	n/a	no reaction

Trans-$[Pd(PPh_3)_2(o\text{-tolyl})Br]$ was characterised by I.R. spectroscopy, ^1H and ^{31}P n.m.r. spectroscopy, microanalysis and single crystal X-ray diffraction. These confirmed the identity of the product and confirm that it adopts the *trans* configuration in both the solid state and in solution. I.R. and n.m.r. spectroscopic data (which are unexceptional) are reported in Tables 3, 2ii to 3, 2iv and the crystal structure is discussed in Section 3, 4d.

The synthesis of $[Pd(PPh_3)_2(mesityl)Br]$ was also attempted in three different ways. The reaction between $[PdCl_2(PPh_3)_2]$ and [Mg(mesityl)Br] gave only *trans*-$[PdBr_2(PPh_3)_2]$ and PPh_3O as identifiable products.

TABLE 3, 2ii

^{31}P N.M.R. DATA FOR $[Pd(PPh_3)_2(R)L]$ SPECIES.

COMPLEX	^{31}P n.m.r. Spectra	
	δ (p.p.m.)	Intensity
$[Pd(PPh_3)_2$(o-tolyl)Br]	s 23.45	
$[Pd(PPh_3)_2$(o-tolyl)$(NO_3)]$	s 19.42	
$[Pd(PPh_3)_2$(o-tolyl)$(OCMe_2)]$ $[ClO_4]$	s 22.09	
M.P.	s 22.33 s 22.12	4 : 5
$[Pd(PPh_3)_2$(mesityl)Br] MR1	s 28.37 d^a 29.45 d^a 27.30	4.6 : 1 : 1

a/ $J_{(P-P)}$ = 3.80 Hz

TABLE 3, 2iii

^{1}H N.M.R. DATA FOR [Pd(PPh_3)$_2$(R)L] SPECIES

COMPLEX	^{1}H n.m.r.				
	Me	Subst. Aryl	Phenyls	$OCMe_2$	INTEGRATION
[Pd(PPh_3)$_2$(o-tolyl)Br]	s 1.79	4t 6.82, 6.40, 6.24, 6.08	m 7.21 → 7.71		3:4:30
[Pd(PPh_3)$_2$(o-tolyl)(NO_3)]	s 2.25	4t 6.73, 6.61, 6.49, 6.25	m 7.25 → 7.66		3:4:30
[Pd(PPh_3)$_2$(o-tolyl)($OCMe_2$)][ClO_4]	s 2.05	4t 6.88, 6.77, 6.56, 6.38	m 7.09 → 7.87	s 2.17	poor
MP	3s 1.95, 1.93, 1.90	s 5.90	m 7.15 → 7.69		9:2:31
[Pd(PPh_3)$_2$(mesityl)Br] MR1	4s 2.51, 2.48, 2.03, 1.53	s 6.26	m 7.05 → 7.50		9:2:28

Chemical shifts in p.p.m.

TABLE 3, 2iv
I.R. SPECTRA OF [Pd(PPh$_3$)$_2$(R)L] SPECIES

PEAK	[Pd(PPh$_3$)$_2$ (o-tolyl) Br]	[Pd(PPh$_3$)$_2$ (o-tolyl) (NO$_3$)]	[Pd(PPh$_3$)$_2$ (o-tolyl) (OH$_2$)] [ClO$_4$]	[Pd(PPh$_3$)$_2$ (o-tolyl) (OCMe$_2$)] [ClO$_4$]	MP	MR1
O-H (OH$_2$)	-	-	3405mbr	3430mbr	-	-
Aryl C-H	3055w	3055m	3055s	3055m	3050m	3055m
"	-	-	-	-	3005w	3010w
Alkyl C-H	2990w	-	-	2925m	2960mbr	2960mbr
"	2910w	2920w	2940vw	2910w	2910w	2910m
Pd-Br	285w	-	-	-	285vw	-
NO$_3^-$ or ClO$_4^-$		1450sbr 1280sbr 1030mbr	1120sbr 1100s 1020mbr	1095sbr		
C=O	-	-	-	1675, 1655br	-	-
Finger print	1480m	1480m	1480m	1480m	1480m	1480m
"	1435s	1435s	1435s	1435s	1435s	1435s
"	1190mw	1160m			1185m	1180mw
"		1120m				
"	1100s	1095m	1100s	1095sbr	1095s	1095s
"					1040m	
"	1030m	1000m	1020mbr	1025m	1030m	1020m
"					845m	845m
"	745s	745s	740s	745m	740s	745m
"		730m				
"	695s	695s	695s	695s	695s	695s
"		540m	620m	625m		
"	520s br	520m	520m	520m		530s
"		510m	510m	510m	515s	510s
"		495w	495w	500m	500s	500m
"		455w			460m	455w
"		440w			445m	
"	430w br				430w	435br

Treatment of the same starting material with [Hg(mesityl)$_2$] gave no reaction at all. However the reaction between the Pd^0 species [Pd(PPh$_3$)$_4$] and bromomesitylene does give two mesityl-containing complexes. The first (MP) is a yellowish micro-crystalline solid and the second (MRI) a colourless crystalline solid. Neither was stable in solution, with both decomposing quickly to give Pd metal and PPh$_3$O. Neither product was isolated in sufficient purity to enable accurate microanalysis and recrystallisation proved impossible due to the unstable nature of the products in solution. The I.R. spectra of the two products are similar (Table 3, 2iv), differences being restricted to small changes in wavenumber and the splitting of single peaks into two.

The n.m.r. spectra of the two products are very different. Both products show complicated multiplets in their ^{1}H n.m.r. spectra corresponding to the triphenylphosphine groups and both show singlets due to the two aryl hydrogens of the mesityl group (at 5.90 p.p.m. for MP and 6.26 p.p.m. for MRI). The methyl group signals in MP are also at higher field than those in MRI (Table 3, 2iii).

The ^{31}P n.m.r. spectrum of MRI (Table 3, 2ii) consists of two doublets (J = 3.80 Hz) and a larger singlet. The doublets are interpreted as being indicative of mutually *cis* phosphine groups, which are unequivalent due to different groups being placed *trans* to them. This would indicate a species of the type *cis*-[Pd(PPh$_3$)$_2$XY] and thus these signals are assigned to *cis*-[Pd(PPh_3)$_2$(mesityl)Br]. If the larger singlet is assigned to *trans*-[Pd(PPh_3)$_2$(mesityl)Br], indicating a mixture of isomers in solution, then this explains the four methyl signals in the ^1H n.m.r. spectrum. The singlet at 2.51 p.p.m. is due to the two methyl groups in the mesityl *ortho*-positions of the *trans*-isomer, the singlet at 2.03 p.p.m. is half the size and is attributed to the *para*-methyl group of the same *trans* isomer. The peaks at 2.48 and 1.53 p.p.m. are in the same 4.6:2 ratio to the peaks at 2.51 and 2.03 p.p.m. as exists between the *trans* and *cis* isomers in the ^{31}P spectrum. Thus they are attributed to the *ortho* and *para* methyl groups of the mesityl ligand in the *cis* isomer. The peak due to the two aryl hydrogens of the mesityl ligand is broader than the other peaks in the ^1H n.m.r. spectrum and this may be due to two slightly different signals from the two isomers overlapping to give the appearance of one signal.

Thus product MRI is assigned the formulation [Pd(PPh_3)$_2$(mesityl)Br]. It is acknowledged that detecting the presence of both *cis* and *trans* isomers of a palladium bis (triphenylphosphine) complex is unusual but it is not unique. Some examples exist in the literature[35] especially where the bulk of the phosphine group does not dominate the stereochemistry. A recent related example of this is in the presence of both *cis* and *trans* isomers of [Pd(PPh_3)$_2$(CH_2COR)Cl] in $CDCl_3$ solution (R = Me or CH_2Cl).[36]

The identity of product MP is problematical. The ^{31}P spectrum shows two peaks at 22.33 and 22.12 p.p.m. in a ratio of 4:5. If these peaks are not related then they must be due to either two separate complexes or, taking into account the similarity of their chemical shifts, two separate conformations of the same complex. As Shaw has pointed out[37, 38] it is possible for different conformations of complexes containing bulky ligands to be detected in solution. The three signals in the ^{1}H n.m.r. spectrum due to the methyl groups of the mesitylene ligand are in the ratio 2:2:1 and have very similar chemical shifts. The proton n.m.r. spectrum and the I.R. data are consistent with this product, MP, also being $[Pd(PPh_3)_2(mesityl)Br]$ but this does not explain the existence of two peaks in the ^{31}P n.m.r. spectrum.

Whilst this work was being carried out the first synthesis of the platinum analogue, $[Pt(PPh_3)_2(mesityl)Br]$, was reported by Anderson *et al.*[39] The ^{31}P and ^{1}H spectra of both the *cis* and *trans* isomers were reported and are shown here in table 3, 2v. It can be seen that the ^{1}H n.m.r. spectrum of the *trans* Pt complex shows a remarkable correlation with the ^{1}H n.m.r. spectrum of MP. Also the spectrum of the *cis* Pt analogue is similar to parts of the ^{1}H n.m.r. spectrum of MRI. However simply assigning MP as the *trans* Pd complex and MRI as the *cis* isomer does not explain the ^{31}P n.m.r. spectra.

A final point to note from reference 39 is that $CDCl_3$ solutions of

TABLE 3, 2v

^1H AND ^{31}P N.M.R. SPECTRA OF $[Pt(PPh_3)_2(mesityl)Br]$

ISOMER	δP	J_{PtP}	J_{PP}	o-CH_3	p-CH_3	m-CH
CIS	16.5d 18.9d	4530 1575	15	2.49	2.01	6.24
TRANS	21.5s	3138	-	1.93	1.90	5.88

$[Pt(PPh_3)_2(mesityl)Br]$ decompose to Pt metal and phosphine oxides on warming. This corresponds with the observation that $[PdBr(mesityl)(PPh_3)_2]$ is unstable in solution.

3, 2c REACTIONS OF *trans*-$[Pd(PPh_3)_2(o\text{-tolyl})Br]$ WITH SILVER SALTS.

The reaction between *trans*-$[Pd(PPh_3)_2(o\text{-tolyl})Br]$ and $AgNO_3$ in methanol gave a white powder as the product, which has been identified by I.R. and ^1H and ^{31}P n.m.r. spectroscopy as *trans*-$[Pd(PPh_3)_2(o\text{-tolyl})(NO_3)]$. That this is indeed a coordinated nitrate containing complex is shown by the I.R. spectrum which shows three broad bands, at 1450, 1280 and 1030 cm^{-1}, which are characteristic of such nitrato compounds.[23] The *trans* configuration is confirmed by the ^{31}P n.m.r. spectrum which shows only a singlet (at 19.42 p.p.m.) and the presence of the *o*-tolyl group is confirmed by a methyl peak at 2.25 p.p.m. in the ^1H n.m.r. spectrum of the complex and by the characteristic 4 triplets in the range 6.25 → 6.73 p.p.m. due to the 4 aryl hydrogens of the *o*-tolyl ligand. It should be noted that in all the ^1H spectra of *o*-tolyl complexes reported here, the term triplet is used loosely to describe the aryl hydrogen signals. These signals are not first order and are sometimes considerably distorted. The presence of these signals is however the most useful way of confirming the presence of the *o*-tolyl ligand. Despite being stable in air as a solid [Pd(PPh_3)$_2$(*o*-tolyl)(NO_3)] decomposed within hours in solution.

Trans-[Pd(PPh_3)$_2$(*o*-tolyl)Br] was treated, in toluene, with $AgClO_4$ and palladium metal was deposited immediately. Rapid filtration gave an orange solution which also started to rapidly deposit dark material believed to be palladium. Removal of the solvent gave an off-white crystalline material which even under a nitrogen atmosphere continues to darken and decompose. An I.R. spectrum was measured as a KBr disc in air, this being the quickest method available. This appears to confirm that the product is [Pd(PPh_3)$_2$(*o*-tolyl)(OH_2)][ClO_4] as would be expected from the comparable reaction between *trans*-[Rh(PPh_3)$_2$(CO)Cl] and $AgClO_4$ (Section 3, 1a). The I.R. spectrum is detailed in Table 3, 2iv and clearly shows peaks compatible with this structure, including a peak at 1120 cm^{-1} assigned to the presence of ClO_4^- as a free anion.

In an attempt to halt the rapid decomposition of [Pd(PPh_3)$_2$(*o*-tolyl)(OH_2)][ClO_4], acetone was added. It was hoped that acetone, being a stronger ligand than water, would stabilize the complex. The rate of deposition of palladium metal did indeed slow but not enough to enable crystal growth from the orange solution. Evaporation, under reduced pressure, of the solvent left a red solid which was characterised by I.R., ^{1}H n.m.r. and ^{31}P n.m.r. spectroscopy (Tables 3, 2ii → iv). The broad I.R. peak at 1095 cm^{-1} indicates an anionic perchlorate grouping and the ^{1}H n.m.r. spectrum confirms the presence of the *o*-tolyl group whilst the ^{31}P n.m.r. shows one main peak, indicating mutually *trans* phosphine groups. Thus the red product has been tentatively given the formula *trans*-$[Pd(PPh_3)_2(o\text{-tolyl})(OCMe_2)][ClO_4]$. There are, however, two objections to this formulation. The first is the deep red colour of the complex. Complexes of the type *trans*-$[PdP_2RX]$ are usually colourless or nearly so. Secondly the carbonyl region of the I.R. spectrum shows, in addition to free acetone at 1710 cm^{-1}, two broad peaks due to coordinated acetone. The peak at 1655 cm^{-1} matches those found in *trans*-$[Rh(PPh_3)_2(CO)(OCMe_2)][X]$, X = ClO_4^- or $CF_3SO_3^-$, but there is also a second peak at 1675 cm^{-1}. This peak falls at a higher wavenumber than that of any of the previously discussed acetone complexes but is sufficiently similar to probably also be attributable to unidentate bound acetone. It should be noted that, due to the instability of *trans*-$[Pd(PPh_3)_2(o\text{-tolyl})(OCMe_2)][ClO_4]$ in $CDCl_3$ solution, a number of small impurity peaks exist in the ^{31}P n.m.r. spectrum at 23.13, 20.92, 20.67 and 19.98 p.p.m., and in the ^1H n.m.r. spectrum at 2.06 and 1.18 p.p.m. These peaks grow with time but have not been assigned any identity.

3, 2d SUBSTITUTION OF $P(p\text{-}C_6H_4OMe)_3$ FOR PPh_3.

In order to circumvent problems with decomposition of aryl-palladium complexes $[PdCl_2(P(p\text{-}C_6H_4OMe)_3)_2]$ was prepared and treated with lithium and Grignard type reagents (Sections 2, 4i - k) in an attempt to form $[Pd(P(p\text{-}C_6H_4OMe)_3)_2(o\text{-tolyl})Br]$. It was hoped that the more strongly electron donating nature of the methoxy-substituted phosphine would lead to stabilisation of the product. However no reaction occurred between the dichloro starting material and [Li(*o*-tolyl)] or [Mg(*o*-tolyl)Br] until conditions were so severe as to result in reduction to palladium metal, phosphines and unidentified tars.

3, 2e CONCLUSIONS.

As a main aim of this project was to study complexes of weak ligands, such as solvents, it was desirable that such complexes as were formed were sufficiently stable to allow isolation, purification and hopefully crystallisation. As has been seen the aryl-palladium complexes formed are not stable in solution, indeed $[Pd(PPh_3)_2(o\text{-tolyl})(OH_2)][ClO_4]$ is unstable as a solid stored under nitrogen. (It is noticeable that as the bromine ligand is replaced by successively weaker ligands, NO_3^-, $OCMe_2$ and OH_2, the stability of the complexes decreases.) It was thus decided that the substrates $[Pd(PPh_3)_2(o\text{-tolyl})L]$ and $[Pd(PPh_3)_2(\text{mesityl})L]$ were not suitable for the purpose of studying complexes of weak ligands.

3, 3a SYNTHESIS AND CHARACTERISATION OF TERDENTATE LIGANDS.

The unstable nature of the aryl-palladium complexes discussed in Sections 3, 2a to 3, 2e led to the decision to synthesise terdentate ligands, the complexes of which should be more stable than complexes containing only monodentate ligands. It was therefore decided to attempt the synthesis of two ligands. PCHP is the bisphosphine *meta*-$(PCy_2CH_2)_2(C_6H_4)$ which, by comparison with the known *meta*-$(PBu^t{}_2CH_2)(C_6H_4)$,[40] should be able to complex in a terdentate fashion by the metallation of the carbon atom mutually *ortho* to both phosphine-containing substituents. The resulting deprotonated ligand is PCP, *meta*-$[(PCy_2CH_2)_2(C_6H_3)]^-$. PPP is $PPh(C_2H_4PCy_2)$ which has three phosphorus atoms available for complex formation.

PCHP was formed via the crystalline, air-stable salt [*m*-$(HPCy_2CH_2)_2(C_6H_4)][Br]_2$ by reaction of *meta*-$(BrCH_2)_2(C_6H_4)$ with $HPCy_2$. Treatment of the salt with $Na_2(CO_3)$ gives PCHP as a colourless paste which, on exposure to air, slowly gives a white solid. PPP was formed on heating $HPCy_2$ and $PPh(CHCH_2)_2$ in the presence of the radical initiator 2,2'-azobis(2-methylpropionitrile). PPP exists as a colourless, air-sensitive oil.

^{31}P n.m.r. spectroscopy was found to be the best method for

TABLE 3, 3i

^{1}H AND ^{31}P N.M.R. DATA FOR THE FREE LIGANDS.

COMPOUND	^{31}P	δ ^{1}H p.p.m.		
	δ p.p.m.	Aryl	Cy	$(CH_2)_n$
PPP	- 16.22 (t, 1P, J_{PP} 26.7Hz) 1.11 (d, 2P, J_{PP} 26.7 Hz)	m 7.12 → 7.47	m 0.74 → 2.08	overlain by Cy signal ?
PCHP	s 2.89	m 7.01 → 7.25	m 0.81 → 2.17	q 3.66 J = 6.98 Hz
$[HPCHPH][Br]_2$	s 18.48	m 7.15 → 7.29	m 0.75 → 2.12	dd 4.05 J = 14.98 Hz J = 6.72 Hz

determining the purity of both PCHP and PPP. ^1H and ^{31}P n.m.r. data for these two ligands and for [m-$(HPCy_2CH_2)_2(C_6H_4)$][Br]$_2$ are given in Table 3, 3i. An additional diagnostic feature of the salt is the presence of a strong P-H stretch at 2310 cm^{-1} in its I.R. spectrum,[41] measured as a KBr disc.

Both PCHP and PPP were used as prepared as it was felt that further purification by vacuum distillation would lead to a significant loss of ligand whilst working on a small scale.

3, 3b FORMATION OF d^8 TRANSITION METAL COMPLEXES CONTAINING PCHP OR PCP.

When $[PdCl_2(NCPh)_2]$ was refluxed with PCHP in 2-methoxyethanol two separate complexes were formed. The major product was a yellow powder identified as *trans*-$[PdCl_2(PCHP)]_2$. In this complex each PCHP ligand acts in a bidentate fashion, bridging two Pd atoms. The minor, more soluble, product was a colourless, crystalline complex characterised as [PdCl(PCP)]. In this monomeric product the ligand is terdentate and metallated.

These and related PCHP/PCP containing complexes were

TABLE 3, 3ii

REACTIONS OF d^8 COMPLEXES INVOLVING PCHP.

REACTANTS	SOLVENT	REFLUX TIME (hrs)	% YIELD $[MX(PCP)]$	% YIELD $[MX_2(PCHP)]_n$
$[PdBr_2(PPh_3)_2]$ + PCHP	EtOH	19.5	72	12
$[PdCl_2(PCHP)]_2$	2-methoxyethanol	42	43	57
$NiBr_2$ + PCHP	$EtOH/H_2O$	2	31	-
$[PdCl_2(NCPh)_2]$ + PCHP	2-methoxyethanol	0.5	17	71
$[PtCl_2(NCPh)_2]$ + PCHP	2-methoxyethanol	18.5	-	85
$[Rh(CO)Cl(PPh_3)_2]$ + PCHP	EtOH	14.5	-	92
$[RhCl(PPh_3)_3]$ + PCHP	EtOH	18	-	-
$[PdCp(PMe_2Ph)_2][PF_6]$ + PCHP	EtOH	72	-	-
$[PtCl_2(dppp)]$ + PCHP	EtOH	40	-	-

X = Cl, Br, CO X_2 = Cl_2, Br_2, ClCO characterised by I.R. spectroscopy and ^1H and ^{31}P n.m.r. spectroscopy (Tables 3, 3iii and iv). Appropriate microanalysis results are reported in the experimental chapter. Crystal structures of the cyclometallated products are detailed in Sections 3, 4a - c.

Table 3, 3iii shows the products of the reactions between d^8 transition metal species and PCHP. As can be seen three reactions give a mixture of monomeric and polymeric products, one reaction (with $NiBr_2$) gave only a metallated, monomeric species as an isolatable product, two reactions (those of $[PtCl_2(NCPh)_2]$ and $[Rh(CO)Cl(PPh_3)_2]$) gave only polymeric products and three reactions gave no isolatable products of either type. The mechanism of all the reactions and the factors governing whether a monomeric, metallated product, [MX(PCP)], or a bridging bisphosphine containing species, $[MX_2(PCHP)]_n$, is formed are unclear.

When$[PdCl_2(PCHP)]_2$ was refluxed for 42 hrs in 2-methoxyethanol a 43% yield of the metallated complex [PdCl(PCP)] was obtained. This seems to indicate that the dimeric species is a precursor to the metallated species. The lack of any metallated products from the reactions of *trans*-$[Rh(CO)Cl(PPh_3)_2]$ and $[PtCl_2(NCPh)_2]$ with PCHP might then be attributed to the insoluble nature of $[Rh(CO)Cl(PCHP)]_2$ and $[PtCl_2(PCHP)]_2$ which effectively removes them from the reaction mixture. This is however a simplification. Neither $[Rh(CO)Cl(PCHP)]_2$ nor $[PtCl_2(PCHP)]_2$ underwent any change when refluxed with LiBr in 2-

methoxyethanol for prolonged periods (Sections 2, 5o and p) but much of the Pt complex did dissolve under these conditions so the lack of any metallated product cannot be attributed solely to the insoluble nature of the dimer. That this Pt dimer dissolves without metallating is also puzzling as similar Pt(II) complexes in general undergo metallation more easily than Pd(II) complexes. This is a trend which Shaw and coworkers partially explain, in their work on internal metallation in $[MX_2(PR_3)_2]$ (M = Pt, Pd X = halide) complexes,[37] by reference to the observation that Pd(II) complexes are less likely to undergo oxidative addition to give Pd(IV) intermediates than the Pt(II) complexes are to give Pt(IV) intermediates.

Rimml and Venanzi[42, 43] have prepared complexes of an analogous ligand to PCHP. This compound PPCHPP, *meta*-$(PPh_2CH_2)_2(C_6H_4)$, has also recently been used by Bennett and coworkers[44] to form complexes with platinum(II). A second analogous ligand (BPCHPB), *meta*-$(PBu^t{}_2CH_2)_2(C_6H_4)$, and its complexes were investigated by Moulton and Shaw and their work on Rh complexes was expanded by Kaska and coworkers.[45, 46] These four groups used a wide variety of starting materials but throughout their work and the work presented here there appears to be no obvious pattern as to why monomeric products are preferred in some reactions but not in others.

Both Rimml *et al.*[42] and Bennett *et al.*[44] suggested that the cyclometallation reactions proceed by the bidentate complexation of the bisphosphine ligand to the metal centre to form *trans*-[MX_2(PCHP)]. This would place the central C-H bond above the metal centre to facilitate oxidative addition to form cyclometallated [MX_2H(PCP)]. Reductive elimination of HX would give the final product [MX(PCP)]. It would seem that our formation of [PdCl(PCP)] by heating [$PdCl_2$(PCHP)]$_2$ argues against the involvement of a *trans*-[$PdCl_2$(PCHP)] intermediate but this is not so. In solution, and especially in a hot solution, it is reasonable to assume some break-up of the dimer species. The monomeric species resulting from this can easily be envisaged rearranging to form *trans*-[$PdCl_2$(PCHP)]. As will be seen in Section 3, 3e PCHP complexes with one phosphine group of the ligand coordinated and one phosphine group non-coordinated have been detected by ^{31}P n.m.r. spectroscopy.

Thus two methods for the formation of the proposed transition state *trans*-[MX_2(PCHP)] are available. It can either be formed directly by reaction between the starting materials [MX_2L_2] and PCHP or by the decomposition of the polymeric species *trans*-[MX_2(PCHP)]$_n$. (It seems reasonable to assume that the formation of the polymeric species is faster than the formation of the monomeric, cyclometallated species [MX(PCP)] as the high energy step involving cleavage of a C-H bond is absent.)

Here we have a possible explanation why the reaction between [$PdCl_2(NCPh)_2$] and PCHP leads to the formation of [PdCl(PCP)] but the analogous reaction involving Pt species gives only $[PtCl_2(PCHP)]_2$. If the first, kinetic product is $[MCl_2(PCHP)]_n$ then the platinum species will be more inert in solution than the palladium species. It is a general observation that platinum complexes are kinetically more inert to substitution than analogous palladium complexes.[47] This reluctance of $[PtCl_2(PCHP)]_2$ to dissociate in solution, combined with its low solubility, could explain why [PtCl(PCP)] is not formed.

It was found that when *trans*-$[PdBr_2(PPh_3)_2]$ was used as a starting material that a high yield of monomeric, cyclometallated [PdBr(PCP)] was formed with $[PdBr_2(PCHP)]_n$ occurring only as a minor product (Table 3, 3iii). Shaw and coworkers[37] demonstrated that bromine containing complexes undergo cyclometallation more easily than their chlorine containing counterparts as greater electron density at the metal centre favours oxidative-addition of the C-H bond. It may also be that the presence of PPh_3 in solution destabilises $[PdBr_2(PCHP)]_n$ as nucleophilic substitution, by attack of a PPh_3 group, could lead to the breaking of a Pd-PCHP bond. It is also interesting to theorise that the bulky PPh_3 groups may even disfavour the initial formation of the polymeric species. In ref. 44, which was published after this work was carried out, the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and PPCHPP gave the cyclometallated $[Pt(PPh_3)(PPCPP)]^+$. The PPh_3 group was only removed by treatment with sulphur. It may be that with larger cyclohexyl substituents, as compared with phenyl groups, the cyclometallated ligand PCP cannot coexist with a PPh_3 ligand. From examination of the crystal structures [MX(PCP)] (M = Pd X = Cl, Br; M = Ni X = Br) discussed in Sections 3, 4a - c it is difficult to see how a PPh_3 group could be accommodated.

The hypothesis that bulky PPh_3 groups help prevent the formation of polymeric species fails in the case of the reaction between *trans*-[Rh(CO)Cl$(PPh_3)_2$] and PCHP. This gave, in 92% yield, only $[Rh(CO)Cl(PCHP)]_2$ as a product. The reason for this may be the complete insolubility of the product in all common chlorinated, donating, aromatic and alkane solvents. It is difficult to know how significant the failure of this starting material to give a cyclometallated product is as the only other reaction between PCHP and a Rh(I) species, $[RhCl(PPh_3)_3]$, gave neither any cyclometallated product nor any dimeric product. The only product isolated from this reaction was a small amount of $[RhCl_2(PCP)(HOEt)]$ but this could conceivably have come from some $RhCl_3$ impurity in the sample of Wilkinson's catalyst used (Section 2, 5i).

What is of interest is that the carbonyl ligand was retained in the product in preference to a PPh_3 group. Again this may be due to steric factors as the smaller carbonyl group should not cause as much steric strain in conjunction with the bulky PCHP ligands as a large PPh_3 group.

The reaction of $NiBr_2$ with PCHP in refluxing aqueous ethanol gave a 31% yield of [NiBr(PCP)] as dark golden crystals. No other nickel-containing fraction was unambiguously characterised.

Two further reactions between d^8 complexes and PCHP were attempted. Refluxing PCHP with $[Pd(Cp)(PMe_2Ph)_2][PF_6]$ in ethanol gave no reaction after 17 hrs and after 72½ hrs only Pd metal and organometallic tars were present. Similarly, addition of PCHP to *cis*-$[PtCl_2(dppp)]$ in refluxing ethanol gave no reaction after 40 hrs. When $AgNO_3$ was added to the reaction mixture two separate white powders were obtained. ^1H n.m.r. and I.R. spectroscopy showed signals indicating the presence of PCHP in the second fraction and PCP in the first fraction. (For assignment of characteristic spectral features of PCHP and PCP see Section 3, 3c.) The I.R. spectra additionally showed the presence of uncoordinated NO_3^- in the first fraction (1341 cm^{-1} br + s, 830 cm^{-1} w) and in the second fraction (1337 cm^{-1} br + s, 829 cm^{-1} w).[23] The ^{31}P n.m.r. spectra however showed that both powders contained several different compounds and as further separation proved impossible no further characterisation of the products has been undertaken.

3, 3c CHARACTERISATION OF PCHP AND PCP CONTAINING d^8 T.M. COMPLEXES.

The general methods used to characterise the reaction products

TABLE 3, 3iii

N.M.R. DATA FOR d^8 T.M. COMPLEXES OF PCHP AND PCP.

COMPLEX	^{31}P	^1H			
	δ p.p.m.	aryl δ p.p.m.	Cy δ p.p.m.	CH_2 δp.p.m.	'J' (Hz)[b]
[PdCl(PCP)]	s 52.4	m 6.95	br 2.13, br 1.70, br 1.24	t 3.17	8.52
[PdBr(PCP)]	s 52.7	m 6.97	br 2.15, br 1.68, br 1.23	t 3.21	8.49
[NiBr(PCP)]	s 51.9	brs 6.86	m 2.18, m 1.72, m 1.24	t 3.08	7.91
$[PdCl_2(PCHP)]_2$	s 25.0	m 7.91, m 7.59, m 7.23	br 2.21, br 1.82, br 1.70, br 1.18	br s 3.48	
$[PdBr_2(PCHP)]_n$	br m 22.6	m 7.72, m 7.45, m 7.15	br 1.77, s 1.54, m 1.24, br 1.20	br s 3.51	
$[PtCl_2(PCHP)]_2$	s 16.8[a]	m 7.93, m 7.63, m 7.18	br 2.30, br 1.83, br 1.69, br 1.16	br s 3.52	

a/ $J_{Pt\text{-}P} = 2407.2$ Hz
b/ $'J' = |{}^2J_{(P\text{-}H)} + {}^4J_{(P\text{-}H)}|$

TABLE 3, 3iv

I.R. SPECTROSCOPIC DATA FOR d^8 T.M. COMPOUNDS OF PCHP/PCP (cm^{-1})

COMPLEX	ARYL C-H	ALKYL C-H	ARYL C=C	M-Cl	SELECTED FINGERPRINT
[PdCl(PCP)]	3038w 3020w	2930s 2849s			1443s, 1412m, 1397m, 1183m, 1003m, 853m, 833m, 395w
[PdBr(PCP)]	3038w 3020w	2930s 2849s			1443s, 1412m, 1397m, 1182m, 1003m, 852s, 833m, 395w
[NiBr(PCP)]	3038w 3020w	2930s 2950s			1443s, 1412m, 1397m, 1182m, 1003m, 853m, 833m, 395w
$[PdCl_2(PCHP)]_2$	3040w	2928s 2851s	1601m 1585w 1487m	342m	1449s, 1400mw, 1269m, 1179m, 1005m, 851m, 824m, 400w
$[PdBr_2(PCHP)]_n$	3040w	2926s 2851s	1601m 1585w 1487m		1447s, 1400mw, 1269m, 1179m, 1005m, 851m, 824m, 400w
$[PtCl_2(PCHP)]_2$	3050w	2928s 2851s	1601m 1585w 1487m	335m	1447s, 1406m, 1269m, 1179m, 1005m, 851m, 824m, 400w
$[Rh(CO)Cl(PCHP)]_2^a$	3020w	2928s 2851s	1601m 1585m 1487m		1447s, 1398m, 1269m, 1005m, 851s, 824m, 795s, 365w

a/ υ_{CO} = 1945s

discussed in this section were I.R. spectroscopy and ^{1}H and ^{31}P n.m.r. spectroscopy. Details are given in Tables 3, 3iii and 3, 3iv. Microanalysis was also used where appropriate and crystal structures of [PdCl(PCP)], [PdBr(PCP)] and [NiBr(PCP)] have been determined (Sections 3, 4a → c).

Examination of the spectral data reveals six key differences which can be used to determine whether the complex contains bidentate PCHP or terdentate PCP. In the ^{1}H n.m.r. spectra of [MX(PCP)] the signal due to the CH_2 arms appears as a 1:2:1 triplet whereas in the polymeric PCHP species this signal appears, at lower field, as a broad singlet. (Shaw and coworkers[37, 48] have used the presence of similar triplets to show that complexes have mutually *trans* phosphine groups and as an extension of this and Harris' work[49] the distance between the two outer peaks of the triplet is assigned to $|^2J_{(P\text{-}H)} + {^4J_{(P\text{-}H)}}|$.) In the ^{1}H n.m.r. spectra of [MX(PCP)] the aryl hydrogens of the metallated ring appear as one complicated multiplet but for the non-metallated aryl rings of the polymeric species three distinct multiplets are observed, again at lower field. The ^{1}H n.m.r. signals due to the hydrogens of the cyclohexyl rings of both types of complexes are very broad but again a difference is notable as the [MX(PCP)] species give three broad signals and the $[MX_2(PCHP)]_n$ species give four broad signals. The ^{31}P n.m.r. spectra of all the compounds presented in Table 3, 3iii consists of singlets but again there is an appreciable difference between monomeric and polymeric species. The monomeric, metallated species all have chemical shifts in the range

52 (±1) p.p.m. whilst the polymeric species chemical shifts lie in the range 16 to 25 p.p.m. The I.R. spectra also exhibit diagnostic features. The I.R. spectra of polymeric species all contain three peaks at 1601, 1585 and 1487 cm^{-1} due to C-C stretch in the six-membered aromatic ring.[50] These absorptions are not observed for the monomeric, metallated species. Another useful feature of the I.R. spectra of the chlorinated polymeric species is the presence of the M-Cl stretch which for mutually *trans* Cl ligands is observed at 342 cm^{-1} for $[PdCl_2(PCHP)]_2$ and at 335 cm^{-1} for $[PtCl_2(PCHP)]_2$. For the metallated species the M-Cl stretches should be at lower wavenumber due to the high *trans*-influence of the σ-bonded carbon atom. These were, however, not detected due to interference from the absorption edge of the KBr used as a medium.

The ^{31}P n.m.r. spectrum of $[PdBr_2(PCHP)]_n$ contains several broad, overlapping peaks centred about 22.6 p.p.m. This is interpreted as indicating the presence of several different values for n. That the ^{31}P n.m.r. spectra of the $[PdCl_2(PCHP)]_n$ and $[PtCl_2(PCHP)]_n$ species consist of single peaks is taken as an indication that only one polymeric species is present. Throughout Shaw and coworker's work[38] and in Seligson *et al.*'s work[51] on large ring chelate systems involving bridging diphosphines in platinum group metal complexes, if a single polymeric species is isolated it is usually a dimeric species. Thus for the species $[PdCl_2(PCHP)]_n$ and $[PtCl_2(PCHP)]_n$ n has been tentatively assigned to be two.

As $[Rh(CO)Cl(PCHP)]_2$ proved to be insoluble in all common solvents it was necessary to measure its ^{31}P n.m.r. spectrum in the solid state. This spectrum contained four doublets at 45.56, 43.00, 32.46 and 29.86 p.p.m. Rh-P coupling is 110.5, 110.5, 120.2 and 117.8 Hz respectively. Resolution was not good enough to observe smaller coupling constants. This spectrum is interpreted as showing one signal for each of the four P atoms in $[Rh(CO)Cl(PCHP)]_2$. It is reasonable for all four phosphines to be inequivalent in the solid state as is illustrated by the inequivalent nature of the phosphines in the crystal structures of [MX(PCP)] (Sections 3, 4a - c). It is appropriate to note here that the inequivalent nature of the phosphine atoms detected in the crystal structures of [MX(PCP)] and of $[RhCl_2(PCP)S]$ does not persist in solution as the ^{31}P n.m.r. of all these species show the presence of equivalent phosphine groups. Whether this is due to the presence of a fast equilibrium between two inequivalent phosphine conformations or whether the phosphine groups actually have the same conformation in solution is unknown.

The I.R. spectrum of $[Rh(CO)Cl(PCHP)]_2$ shows only one peak in the carbonyl region (at 1945 cm^{-1}) in the solid state. Of the possible conformations of $[Rh(CO)Cl(PCHP)]_2$ only one has sufficiently high symmetry for theory to predict only one carbonyl peak. *Trans*-$[Rh(CO)Cl(PCHP)]_2$ with the two carbonyl groups on opposite sides of the chelate ring has C_2h symmetry and as such only one carbonyl peak is predicted, as is seen in the spectrum. This assumes that the two carbonyl groups can couple over such a large distance. In M-M bonded dimers, such as dimanganese decacarbonyl,[52] the carbonyl groups do couple but it is not known whether or not this holds for large ring chelates.

3, 3d SYNTHESIS AND CHARACTERISATION OF Rh(III) PCP COMPLEXES.

When PCHP was added to a hot slurry of $RhCl_3.3H_2O$ in aqueous propan-2-ol the yellow, crystalline product was shown to be $[RhCl_2(PCP)(OH_2)]$.propan-2-ol by I.R. spectroscopy, ^1H and ^{31}P n.m.r. spectroscopy, microanalysis and X-ray diffraction studies. Recrystallising this complex from ethanol or methanol/CH_2Cl_2 solutions gave $[RhCl_2(PCP)(HOEt)]$ and $[RhCl_2(PCP)(HOMe)].CH_2Cl_2$ respectively. These orange crystalline complexes were also characterised by the methods outlined above. I.R. spectroscopic data for the complexes is presented in Table 3, 3v and ^1H and ^{31}P n.m.r. spectroscopic data is presented in Table 3, 3vi.

$[RhCl_2(PCP)(HOMe)].CH_2Cl_2$ rapidly loses CH_2Cl_2 on exposure to air and over a period of days absorbs water to give $[RhCl_2(PCP)(HOMe)].H_2O$. Crystalline $[RhCl_2(PCP)(HOEt)]$ is not hygroscopic but as a powder this complex will also absorb water to give $[RhCl_2(PCP)(HOEt)].H_2O$. It is the

TABLE 3, 3v

I.R. SPECTROSCOPIC DATA FOR Rh(III) PCP COMPLEXES (cm^{-1}).

COMPLEX	SOLVENT O-H	ARYL C-H	ALKY C-H	Rh-Cl	FINGERPRINT
$[RhCl_2(PCP)(OH_2)]$.propan-2-ol	3640m sh 3420s br 3180m (1540m)	3020w 3060w	2930s 2850s	340m	1445m,1120ms, 1005ms,850ms,725m
$[RhCl_2(PCP)(HOEt)].H_2O$	3560m 3450ms 3250m br (1580m)	3050w	2920s 2845s	340m	1445m,1050ms, 1005m,855ms,735m
$[RhCl_2(PCP)(HOMe)].H_2O$	3580m 3430s 3240m br (1580m)	3050w	2920s 2845s	340m	1445s,1030ms, 1005m,855ms,735m
$[RhCl_2(PCP)]$	-	3040w	2925s 2850s	330m	1445m,1260s,1100s br, 1020s br,800s br

TABLE 3, 3vi

N.M.R. SPECTROSCOPIC DATA FOR Rh(III) PCP COMPLEXES.

COMPLEX	SOLVENT	^{31}P		^{1}H				
		δ (p.p.m.)	$J_{(P\text{-}M)}$ (Hz)	δ Alcohol	δ Aryl	δ Cy	CH_2 δ(p.p.m.) +	"J" (Hz)
$[RhCl_2(PCP)(OH_2)]$ .propan-2-ol	$CDCl_3$	d 39.8	95.2	sept 4.02	m 6.77	br 2.55-1.20	t 3.31	8.32
$[RhCl_2(PCP)(OH_2)]$ .propan-2-ol	$OC(CD_3)_2$	d 38.0	96.8	sept 3.88	m 6.76	br 2.56-1.18	t 3.43	8.63
$[RhCl_2(PCP)(HOEt)].H_2O$	$CDCl_3$	d 39.9	95.3	q 3.76	m 6.78	br 2.55-1.20	t 3.31	8.32
$[RhCl_2(PCP)(HOMe)]$	$CDCl_3$	d 39.5	95.1	s 3.52	m 6.79	br 2.56-1.20	t 3.31	8.32
$[RhCl_2(PCP)]$	$CDCl_3$	d 40.4	95.5	-	m 6.78	br 2.56-1.20	t 3.30	8.36

$"J" = \left|{}^{2}J_{(P\text{-}H)} + {}^{4}J_{(P\text{-}H)}\right|$

I.R. spectra of these hydrated species that are reported in Table 3, 3v. The anhydrous species lack the O-H stretch seen at 3250 or 3240 cm^{-1} in the I.R. spectra of the hydrated species.

The main difference in the I.R. spectra of the three complexes (aqua, EtOH and MeOH containing) is that the aqua complex's spectrum contains a sharp peak at 3640 cm^{-1} whilst the alcohol complexes show broader peaks at 3560 and 3580 cm^{-1}. The peak at 3640 cm^{-1}, for the aqua complex, is indicative of a terminal hydroxyl group.[53] The peak positions for the alcohol complexes indicate that their hydroxyl groups are involved in fairly extensive bonding, as is confirmed by X-ray crystallography.[53]

As for the metallated Ni(II) and Pd(II) species, [MX(PCP)], no peaks are observed in the 1600 - 1450 cm^{-1} range,of the I.R. spectra, due to carbon-carbon stretch in the aromatic ring. The ^{1}H n.m.r. spectra of the three cyclometallated Rh(III) complexes also resemble those of the cyclometallated M(II) complexes in that the signal due to the aromatic protons consists of one multiplet at a higher field than in the non-cyclometallated d^8 complexes [MX$_2$(PCHP)]$_n$. Also the signals due to the cyclohexyl rings form three broad signals, not four as in the non-cyclometallated species, and the CH$_2$ signals are apparent triplets with similar couplings as in the complexes [MX(PCP)].

The ^{31}P n.m.r. spectra of the three [RhCl$_2$(PCP)S].S' species all consist of one doublet, which is consistent with the mutually *trans*-phosphine ligands found in their crystal structures (Sections 3, 4e - h). The ^1H and ^{31}P n.m.r. spectroscopy signals due to the PCP ligand are practically identical for the three [$RhCl_2$(PCP)S] complexes. Additionally the observed $HOC\underline{H}_xR_{3-x}$ signals are similar to the signals obtained for the free alcohols in $CDCl_3$ solution. This would appear to indicate that dissolving any of the complexes [$RhCl_2$(PCP)S] in $CDCl_3$ gives the same species. This is discussed later in this section.

Shaw and coworkers treated $RhCl_3.3H_2O$ with *m*-$(PBu^t_2CH_2)_2(C_6H_4)$[40], BPCHPB, and other diphosphines with alkyl backbones such as $PBu^t_2(CH_2)_5PBu^t_2$ [54] and $PBu^t_2(CH_2)_2(CHMe)(CH_2)_2PBu^t_2$.[55, 56] Despite using reaction conditions similar to those used to prepare [$RhCl_2$(PCP)(OH_2)] the products from the reactions of Shaw and coworkers were always 5-coordinate hydride species of the type [RhHCl(BPCPB)].

It would seem likely from our isolation of a dichloro species that Shaw and coworkers' hydride complexes are formed via similar dichloro complexes. A possible mechanism for this reaction is the elimination of the elements of HCl to give an alkoxy species, [RhCl(BPCPB)($OCHMe_2$)], followed by β-elimination to give the hydride [RhClH(BPCPB)($OCMe_2$)], which contains coordinated acetone. Loss of the acetone ligand would give the reported final product. It is interesting to note that if formation of our

[$RhCl_2$(PCP)(OH_2)] proceeds via the likely transition state [$RhCl_3$(PCHP)], where the PCHP ligand is bidentate i.e has not yet undergone metallation, then simple oxidative addition would give a seven coordinate, Rh(V) species. This seems unlikely. It is possible that the formation of the Rh-C bond and the elimination of HCl may thus be a concerted process and involve a four membered Rh-C-H-Cl ring.

In an attempt to form a hydride species analagous to those described, [$RhCl_2$(PCP)(OH_2)].propan-2-ol was refluxed for 24 hrs in methanol but neither this nor its recrystallisation from hot ethanol gave any hydride containing species. X-ray crystallography showed, Sections 3, 4e - g, that despite the bulky cyclohexyl rings of PCP both ethanol and methanol are small enough to coordinate. Thus the reason for the lack of hydride formation is presumably not steric hindrance preventing coordination of alcohol and thus preventing β-elimination. It may be that the very bulky tertiary-butyl groups used by Shaw and coworkers favours hydride formation. It is known that sterically large groups do favour hydride formation[38, 57] but usually cyclohexyl substituents on phosphine groups are just as effective as tertiary butyl substituents.[58, 59, 60]

Heating [$RhCl_2$(PCP)(HOEt)] under vacuum gave a bright pink compound (Section 2, 51). The I.R. spectrum of this air-sensitive species is very different to those of the three yellow/orange complexes [$RhCl_2$(PCP)S] (Table 3, 3v), but a peak is present at 330 cm^{-1}, indicating mutually *trans* chlorine ligands, and the PCP ligand is also clearly still present. The ^1H and ^{31}P n.m.r. spectra are practically identical to those measured for the species [$RhCl_2$(PCP)S] although the alcohol signals are missing from the ^1H n.m.r. spectra. The pink solid is thus characterised as [$RhCl_2$(PCP)] a five-coordinate complex with mutually *trans* chloride ligands. given the geometry of the PCP chelate, as found in the crystal structures of Sections 3, 4a - c and e - h, it is assumed that the phosphine groups are also mutually *trans* and that the coordination geometry about rhodium is square-pyramidal with the sigma-bonded carbon in the apical position. [$RhCl_2(PPh_3)_2Ph$] has a similar structure, as shown by X-ray diffraction[61] and is red in colour. Solutions of [$RhCl_2$(PCP)] are orange and it is assumed that in solution a solvent molecule returns the complex to octahedral geometry. In $CDCl_3$ solution the complex thus probably exists as [$RhCl_2$(PCP)($CDCl_3$)]. As has been noted above the ^1H and ^{31}P n.m.r. spectra, in $CDCl_3$ solution, of [$RhCl_2$(PCP)] and the three [$RhCl_2$(PCP)S] species isolated as solids are all practically identical. It is proposed that in $CDCl_3$ solution OH_2, MeOH and EtOH ligands are displaced by coordinating $CDCl_3$. Examples of chlorinated solvents coordinating to phosphine complexes of rhodium are known.[62]

[$RhCl_2$(PCP)] is very air sensitive, forming orange [$RhCl_2$(PCP)(OH_2)] within 2 minutes of exposure to air. The aqua product was identified by its I.R. spectrum which is similar to that of [$RhCl_2$(PCP)(OH_2)].propan-2-ol but lacks the O-H adsorptions at 3640 and

3180 cm^{-1} indicating the lack of any hydrogen bonding in the complex. A lack of hydrogen bonding may explain why [$RhCl_2$(PCP)(OH_2)], formed by exposure of the five coordinate species to air, returns to the pink five coordinate species when flushed with nitrogen gas but crystalline [$RhCl_2$(PCP)(OH_2)].propan-2-ol is stable under nitrogen atmosphere, and also under vacuum.

[$RhCl_2$(PCP)] may also be formed by repeatedly heating [$RhCl_2$(PCP)(HOMe)] in $CHCl_3$ and petroleum ether and then removing the solvent under reduced pressure (Section 2, 5k). The ^{31}P n.m.r. spectrum of this product shows a small impurity signal (δ = 56.0 p.p.m. (d), $J_{(Rh-P)}$ = 85.1 Hz). The I.R. spectrum also shows an impurity, a sharp peak occurring at 2068 cm^{-1}. This peak is characteristic of a M-H stretch[63] and thus the impurity is tentatively characterised as [RhClH(PCP)].

3, 3e CHARACTERISATION OF THE PRODUCTS FROM THE REACTION BETWEEN PCHP AND $Rh(NO_3)_3$.

Two fractions were isolated, from the above reaction, which contained PCHP or PCP (Section 2, 5q). Fraction 1 was a light coloured semi-crystalline powder. The I.R. spectrum of this showed the presence of both coordinated (1500, 1275 and 1005 cm^{-1}) and free NO_3^- (1385 and

TABLE 3, 3vii

^{31}P N.M.R. SPECTRA OF PRODUCTS FROM PCHP + $Rh(NO_3)_3$

	SOLVENT	δ ^{31}P (p.p.m.)	$J_{(Rh-P)}$(Hz)	$^6J_{(P-P)}$(Hz)	INTEGRATION
FRACTION 1	$CDCl_3$	A d 52.5 B dd 79.4 C d 61.9	98.9 138.6 -	- 2.4 2.4	A:B:C 0.6:1:1
FRACTION 1	$OC(CD_3)_2$	A d 51.4 B dd 77.7 C d 60.4	99.2 139.1 -	- 2.2 2.2	A:B:C 1.4:1:1
FRACTION 2*	$CDCl_3$	A,B,C as above D d 51.1 E dd 81.6 F d 62.3	102.4 143.1 -	- 2.3 2.3	D:E:F 0.7:1:1

* (A,B,C):(D,E,F) = 10:7

825 cm^{-1})[23] as well as very strong C-H stretch absorptions (2925 and 2850 cm^{-1}), characteristic of the PCHP/PCP ligand. There is also evidence of the presence of water. The ^{31}P n.m.r. spectrum (Table 3, 3vii) shows two species are present. Signal A is a doublet typical of mutually *trans* phosphine groups. The signal has been interpreted as pertaining to a cyclometallated complex, possibly [Rh(NO$_3$)$_2$(PCP)(HOEt)], by dint of its ^{31}P chemical shift, which is similar to those of the metallated [RhCl$_2$(PCP)S] and [MX(PCP)] species (M = Pd, Ni), and its coupling constant, which is also similar to those found in the [RhCl$_2$(PCP)S] species. Also the ^{1}H n.m.r. spectra contains a triplet at δ = 3.26 p.p.m. (J = 7.8 Hz) which has previously (Sections 3, 3c and 3, 3d) been found to be characteristic of cyclometallated systems.

Signal B in the ^{31}P n.m.r. (a doublet of doublets) is in a 1:1 ratio with signal C (a doublet). The smaller coupling constant of signal B matches that of signal C and the larger coupling constant is consistent with a one bond rhodium to phosphorus coupling. These two signals are thus interpreted as belonging to a PCHP ligand where only one phosphine group is coordinated to the Rh metal, a one on, one off situation. This interpretation is strengthened by the presence of two doublets in the CH$_2$ arm region of the ^{1}H n.m.r. spectrum (δ 3.41 p.p.m., $J_{(P-H)}$ = 11.75 Hz and δ 3.21 p.p.m., $J_{(P-H)}$ = 12.34 Hz).

^{1}H and ^{31}P n.m.r. spectra measured in d^6-acetone showed the same species present but changed the relative intensity of signal A to signals B and C (Table 3, 3vii). It is uncertain whether this indicates that the two species present are in equilibrium in solution or whether this merely reflects differences in solubility between the two species.

The I.R. spectrum of fraction 2, a brown powder, was similar to that of fraction 1. The ^{31}P n.m.r. spectrum however contained not only those signals present in fraction 1 but a second set of similar signals with offset chemical shift values (Table 3, 3vii). The signals D, E and F may be due to isomeric forms of those species which cause the signals A, B and C.

3, 3f FUTURE WORK ON THE CHEMISTRY OF THE PCHP LIGAND AND ITS DERIVATIVES.

It has been shown that PCHP can react to become a terdentate ligand (with Pd(II), Ni(II) and Rh(III)) in its deprotonated form PCP, or remain as a bidentate P ,P-ligand (with Pd(II), Pt(II) and Rh(I)). It also can probably act as a monodentate ligand (with Rh(III)).

The octahedral Rh(III) complexes [$RhCl_2$(PCP)S] (S = OH_2, EtOH, MeOH) have been isolated and studied as has the coordinatively unsaturated species [$RhCl_2$(PCP)]. Sections 3, 4e - k deal with the molecular structure of the $[RhCl_2(PCP)S]$ complexes and it is hoped that this series of crystal structures can be extended by reacting $[RhCl_2(PCP)]$ with a variety of small ligands (e.g. H_2, C_2H_4, C_2H_2, CO, CO_2, NH_3, PH_3, SH_2, SO_2, NO_2 and NCMe). The isolation of the coordinatively unsaturated $[RhCl_2(PCP)]$ and the failure to isolate complexes containing coordinated acetone or propan-2-ol indicates that the steric bulk of the cyclohexyl groups does discriminate against coordination of larger potential ligands as originally planned (Ref. 38 and Section 3, 4j).

The isolation of the square-planar complexes [MX(PCP)], and in particular the discovery of a high yield route to [PdBr(PCP)] via $[PdBr_2(PPh_3)_2]$, should enable future work to be carried out on solvated complexes of the type [Pd(PCP)S][X] by reacting the metallated halide-containing complexes with silver salts AgX (S = OH_2, MeOH, EtOH, $OCMe_2$ or vacant site, X = ClO_4^- or $CF_3SO_3^-$).

It is hoped that in future [Rh(CO)(PCP)] and [PtCl(PCP)] may also be prepared from the dimeric species $[Rh(CO)Cl(PCHP)]_2$ and $[PtCl_2(PCHP)]_2$ by treatment with CF_3COOH.[56] The rhodium carbonyl complex is of particular interest as treatment of this with u.v. light may give [Rh(PCP)], a neutral 3-coordinate species, or [Rh(PCP)S] where S is a coordinated solvent molecule. A second route to these complexes may be available via the reduction of the $[RhCl_2(PCP)S]$ species.

3, 3g SYNTHESIS AND CHARACTERISATION OF PPP CONTAINING COMPLEXES.

Complexes were formed by direct reaction of PPP, $(Cy_2PC_2H_4)_2PPh$, with $PdCl_2$, $RhCl_3$ and $[RhCl(PPh_3)_3]$ as described in Sections 2, 6a - e. The products of these reactions were $[PdCl(PPP)][PF_6]$, $[RhCl_3(PPP)]$ and [RhCl(PPP)] respectively. I.R. spectroscopy and ^1H and ^{31}P n.m.r. spectroscopy were used to characterise the products and details of these are given in Tables 3, 3viii and 3, 3ix. The intermediate in the formation of $[PdCl(PPP)][PF_6]$ was [PdCl(PPP)][Cl], characterised by its I.R. spectrum which was identical to that of the PF_6^- salt, though lacking the broad peak at 841 cm^{-1}* due to the uncoordinated PF_6^- anion.

$[PdCl(PPP)][PF_6]$ was treated with $AgPF_6$ in an attempt to remove the second coordinated chlorine but work-up produced only unidentified tars. Work on the complexes of this ligand, PPP, was discontinued as a result of the unpromising outcome of this experiment and because of the relatively low yields found for formation of the simple metal-halide PPP complexes. Also these compounds were difficult to purify as they often existed in a tacky, semi-solid state and thus work on the ligand PCHP and its complexes was preferred.

* Identified by comparison with the I.R. spectrum of $AgPF_6$.

TABLE 3, 3viii

^{31}P N.M.R. SPECTRA OF PPP CONTAINING COMPLEXES.

COMPLEX	CHEMICAL SHIFTS (p.p.m.)	INTEGRATION	COUPLING CONSTANTS (Hz)			
			$J(Rh-P_a)$	$J(Rh-P_b)$	$J(P_a-P_b)$	J(P-F)
$[PdCl(PPP)][PF_6]$	66.9 s, 111.5 s, -144.2 sept	2:1:1	-	-	-	714.2
[RhCl(PPP)]	59.8 dd, 69.7 d.t.	2:1	137.9	177.8	28.2	-
$[RhCl_3(PPP)]$	34.7 dd, 88.9 d.t.	2:1	83.0	108.7	7.9	-

P_a = Terminal Phosphine
P_b = Central Phosphine

TABLE 3, 3ix

^{1}H N.M.R. AND I.R. SPECTRA OF PPP CONTAINING COMPLEXES.

COMPLEX	^{1}H n.m.r. δ(p.p.m.)			I.R. ADSORPTIONS (cm^{-1})					
	Ph	C_2H_4	Cy	O-H	Phenyl C-H	Alkyl C-H	P-F	M-Cl	OTHERS
[PdCl(PPP)][PF_6]. $2H_2O$	br.m. 7.63	br.m. 2.51	br.m. 2.20→1.15	3476m.br	3055w	2928s 2851s	841s.br 557s 1448m	305m	1448m 1435m
[RhCl(PPP)]	br.m. 7.51	br.m. 2.63	br.m. 2.20→1.10	-	3056m	2926s 2851s	-	-	1445m 1439s 750m 721s 542s
[$RhCl_3$(PPP)]	br.m. 7.48	br.m. 2.75	br.m. 2.20→1.10	-	3056w	2924s 2851s	-	-	1445m 1435m 735m 714m 687m 538m

3, 4a STRUCTURE OF [PdCl{$(PCy_2CH_2)_2(C_6H_3)$}].

The coordination geometry about the palladium atom is essentially *trans* square-planar with a distortion of the P(1)-Pd-P(2) bond angle which has closed to 165.5(1)°. It can be seen from Table 3, 4xxi that this distortion, which is due to the intrinsically small bite angle of the chelate ligand, is a common feature of all complexes of the PCP ligand. A small tetrahedral distortion is also apparent in [PdCl(PCP)] as is shown by the displacements of the P(1), P(2), Cl and C(1) atoms by 0.088(2), 0.092(2), -0.047(1) and -0.078(6) Å, respectively, from the coordination plane PdP(1)P(2)ClC(1). Here, and throughout this section, least-squares planes have been calculated with unit weights.

ORTEP drawings of [PdCl(PCP)] are presented in Fig. 3, 4i and Fig. 3, 4ii. Except where otherwise noted, all such drawings show non-hydrogen atoms with 50% probability ellipsoids and hydrogen atoms, for reasons of clarity, are either omitted or are shown as small spheres of arbitrary size. Bond lengths and bond angles are presented in Tables 3, 4i and 3, 4ii. Selected torsion angles are compared with those of other PCP-containing complexes in Table 3, 4iii.

The Pd-Cl distance of 2.427(2) Å is extremely long, as can be seen from the average value of 2.326 Å derived from 224 such distances in square-planar palladium(II) complexes.[64] The lengthening by 0.1 Å could

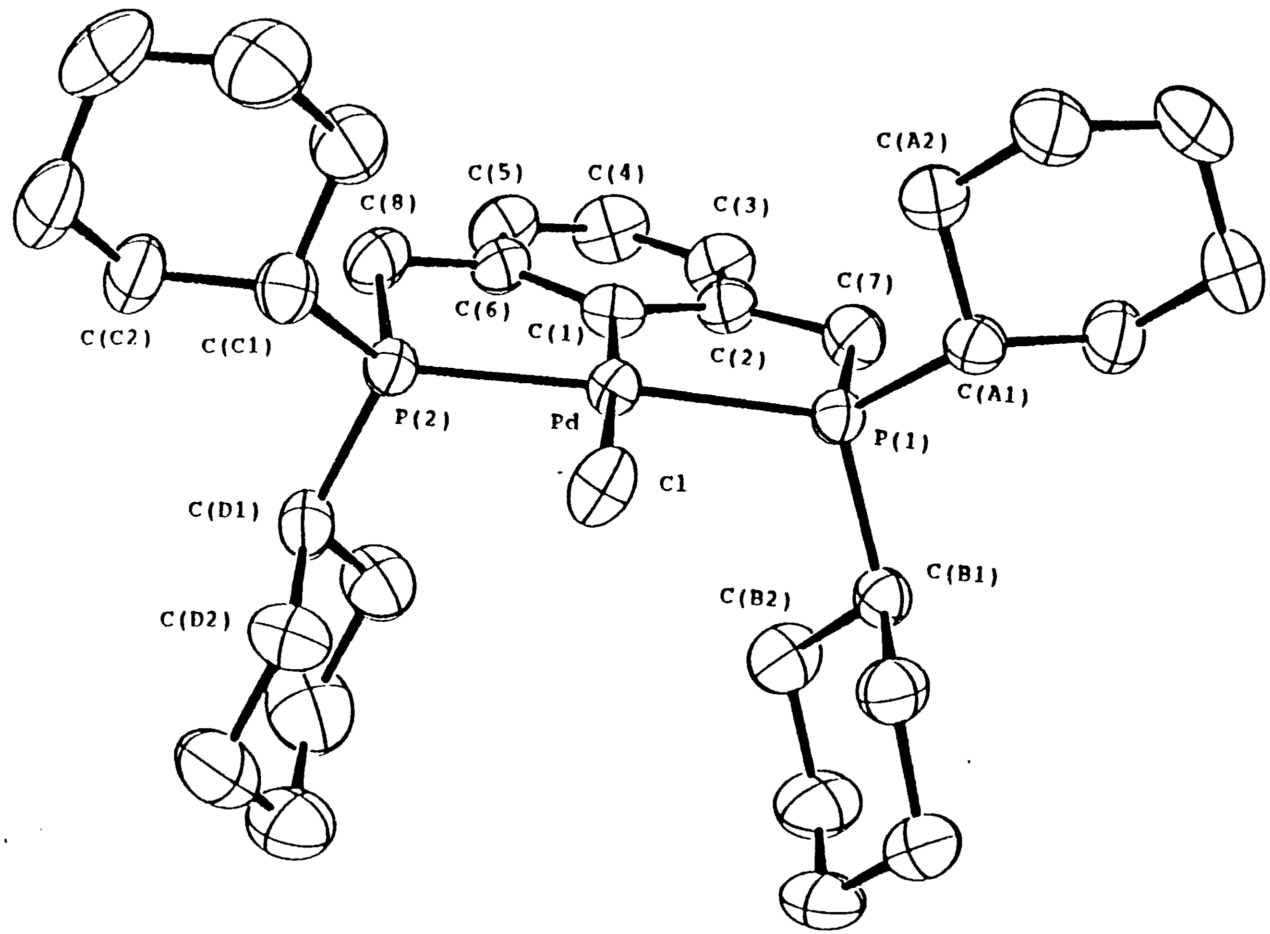

Fig.3,4i Structure of [PdCl(PCP)].

arise from a combination of two factors: the presence of the strongly *trans*-influencing σ-bonded carbon *trans* to the chlorine ligand and the deliberately-introduced steric crowding, caused by the four cyclohexyl rings, which may prevent even small ligands from gaining an optimal binding position. Indeed the Pd-Cl bond distance in the compound $[\overline{\mathrm{PdCl\{Bu^t_2PCH_2CHMeCHCH_2CH_2P}}\mathrm{Bu^t_2\}}]$, where both the above conditions also apply,[56] is identical to within experimental error to that in [PdCl(PCP)]. The Pd-C(1) bond length of 2.012(6) Å is identical, to within experimental error, to those in [PdBr(PCP)] and *trans*-[PdBr(*o*-tolyl)$(PPh_3)_2$] (Sections 3, 4b and 3, 4d) but is shorter than that given for the saturated species described in ref. 56 (*vide supra*). The Pd-P(1) and Pd-P(2) distances (2.294(2) and 2.266(2) Å respectively) are identical to those found in [PdBr(PCP)] and are in fair agreement with the average Pd-P bond lengths found in ref. 64 (2.315 Å for 18 Pd-PEt_3 bonds, 2.308 Å for 51 Pd-PPh_3 bonds and 2.287 Å for 6 Pd-PMe_3 bonds). The angles Pd-P(1)-C(7) and Pd-P(2)-C(8) (102.6(2) and 104.1(3)° respectively) are both smaller than would be expected for similar angles in non-chelating phosphines. (For example in *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$, Section 3, 4m, the six Rh-P-C angles range from 112.8(2) to 117.9(2)°). This indicates that the chelate nature of PCP imposes ring strain.

The two five-membered rings Pd, P(1), C(7), C(2), C(1) and Pd, P(2), C(8), C(6), C(1) are unsymmetrical, as is shown by the difference in the Pd-P(1) and Pd-P(2) bond lengths and the torsion angles given in Table 3,

Table 3,4i Bond lengths (Å) for [PdCl(PCP)].

Pd - Cl	2.427(2)	Pd - P(1)	2.294(2)
Pd - P(2)	2.266(2)	Pd - C(1)	2.012(6)
P(1) - C(7)	1.826(7)	P(1) - C(A1)	1.828(7)
P(1) - C(B1)	1.836(6)	P(2) - C(8)	1.824(7)
P(2) - C(C1)	1.821(7)	P(2) - C(D1)	1.834(7)
C(1) - C(2)	1.426(9)	C(1) - C(6)	1.421(8)
C(2) - C(3)	1.380(9)	C(2) - C(7)	1.497(9)
C(3) - C(4)	1.389(9)	C(4) - C(5)	1.385(10)
C(5) - C(6)	1.375(9)	C(6) - C(8)	1.490(9)
C(A1) - C(A2)	1.522(9)	C(A1) - C(A6)	1.541(9)
C(A2) - C(A3)	1.531(10)	C(A3) - C(A4)	1.529(11)
C(A4) - C(A5)	1.507(11)	C(A5) - C(A6)	1.533(11)
C(B1) - C(B2)	1.523(9)	C(B1) - C(B6)	1.529(9)
C(B2) - C(B3)	1.497(10)	C(B3) - C(B4)	1.498(11)
C(B4) - C(B5)	1.515(11)	C(B5) - C(B6)	1.517(10)
C(C1) - C(C2)	1.529(9)	C(C1) - C(C6)	1.517(10)
C(C2) - C(C3)	1.524(10)	C(C3) - C(C4)	1.497(11)
C(C4) - C(C5)	1.510(11)	C(C5) - C(C6)	1.532(11)
C(D1) - C(D2)	1.519(10)	C(D1) - C(D6)	1.530(10)
C(D2) - C(D3)	1.527(11)	C(D3) - C(D4)	1.509(12)
C(D4) - C(D5)	1.533(13)	C(D5) - C(D6)	1.542(11)

Table 3,4ii Bond angles (°) for [PdCl(PCP)].

Cl-Pd-P(1)	98.2(1)	Cl-Pd-P(2)	94.4(1)
Cl-Pd-C(1)	177.0(2)	P(1)-Pd-P(2)	165.5(1)
P(1)-Pd-C(1)	84.7(2)	P(2)-Pd-C(1)	82.8(2)
Pd-P(1)-C(7)	102.6(2)	Pd-P(1)-C(A1)	122.5(2)
Pd-P(1)-C(B1)	112.7(2)	C(7)-P(1)-C(A1)	106.1(3)
C(7)-P(1)-C(B1)	104.7(3)	C(A1)-P(1)-C(B1)	106.6(3)
Pd-P(2)-C(8)	104.1(3)	Pd-P(2)-C(C1)	118.2(3)
Pd-P(2)-C(D1)	114.9(2)	C(8)-P(2)-C(C1)	108.0(3)
C(8)-P(2)-C(D1)	103.0(3)	C(C1)-P(2)-C(D1)	107.4(3)
Pd-C(1)-C(2)	121.0(4)	Pd-C(1)-C(6)	122.1(5)
C(2)-C(1)-C(6)	116.9(5)	C(1)-C(2)-C(3)	120.4(6)
C(1)-C(2)-C(7)	119.2(5)	C(3)-C(2)-C(7)	120.3(6)
C(2)-C(3)-C(4)	121.5(6)	C(3)-C(4)-C(5)	118.7(6)
C(4)-C(5)-C(6)	121.4(6)	C(1)-C(6)-C(5)	120.9(6)
C(1)-C(6)-C(8)	118.8(6)	C(5)-C(6)-C(8)	120.3(6)
P(1)-C(7)-C(2)	111.2(4)	P(2)-C(8)-C(6)	108.6(4)
P(1)-C(A1)-C(A2)	110.8(5)	P(1)-C(A1)-C(A6)	113.9(5)
C(A2)-C(A1)-C(A6)	110.6(5)	C(A1)-C(A2)-C(A3)	112.0(6)
C(A2)-C(A3)-C(A4)	111.5(6)	C(A3)-C(A4)-C(A5)	112.6(6)
C(A4)-C(A5)-C(A6)	112.1(6)	C(A1)-C(A6)-C(A5)	112.1(6)
P(1)-C(B1)-C(B2)	110.5(4)	P(1)-C(B1)-C(B6)	112.6(5)
C(B2)-C(B1)-C(B6)	110.1(5)	C(B1)-C(B2)-C(B3)	112.2(6)
C(B2)-C(B3)-C(B4)	111.3(6)	C(B3)-C(B4)-C(B5)	110.8(7)
C(B4)-C(B5)-C(B6)	113.0(6)	C(B1)-C(B6)-C(B5)	111.1(6)
P(2)-C(C1)-C(C2)	114.4(5)	P(2)-C(C1)-C(C6)	110.1(5)
C(C2)-C(C1)-C(C6)	111.1(6)	C(C1)-C(C2)-C(C3)	110.3(6)
C(C2)-C(C3)-C(C4)	112.0(6)	C(C3)-C(C4)-C(C5)	110.8(6)
C(C4)-C(C5)-C(C6)	112.2(7)	C(C1)-C(C6)-C(C5)	112.1(6)
P(2)-C(D1)-C(D2)	113.5(5)	P(2)-C(D1)-C(D6)	110.7(5)
C(D2)-C(D1)-C(D6)	110.2(6)	C(D1)-C(D2)-C(D3)	111.5(6)
C(D2)-C(D3)-C(D4)	111.6(7)	C(D3)-C(D4)-C(D5)	111.2(7)
C(D4)-C(D5)-C(D6)	111.1(7)	C(D1)-C(D6)-C(D5)	111.7(6)

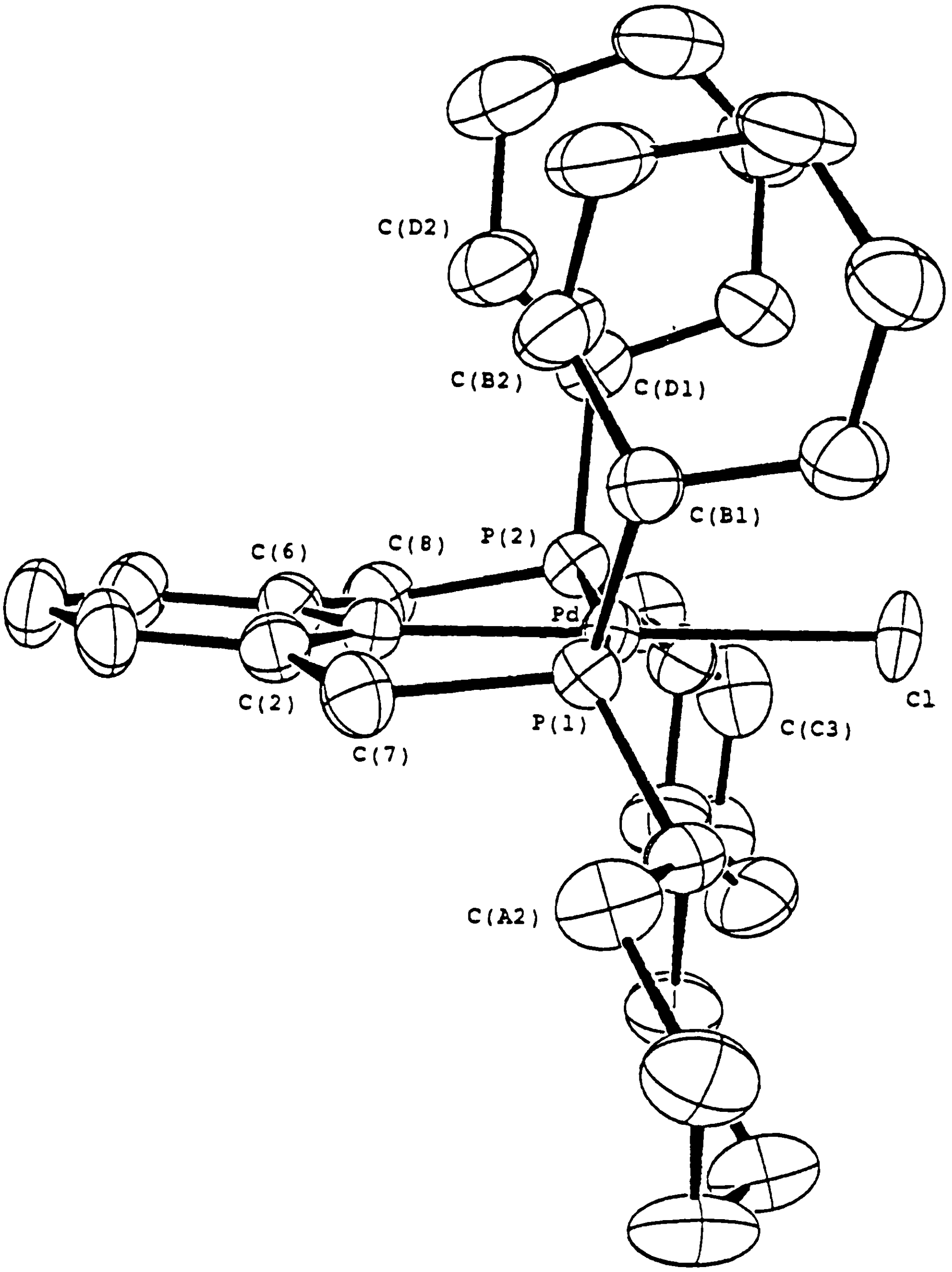

Fig.3,4ii [PdCl(PCP)] viewed along the P(1)-Pd-P(2) axis.

4iii. These indicate that the Pd, P(2), C(8), C(6), C(1) ring is more puckered than its counterpart. The non-planar nature of these rings leads to the plane of the aromatic ring being at an angle of 5.0° to the coordination plane of the metal centre.

The aromatic ring has two C-C bonds (C(1)-C(2) = 1.426(9) Å and C(1)-C(6) = 1.421(8) Å) which are larger than the average of the other four C-C distances (1.382 Å). Additionally, the C(2)-C(1)-C(6) angle is smaller than the expected Csp^2 angle of 120°. This distortion of the aromatic ring is noticeable in the structures of all the PCP-containing complexes presented here and, indeed, is a general feature of aromatic rings σ-bonded to metals. Domenicano *et al.*[65] argue that the presence of extra *p* character in the C(1)-C(2) and C(1)-C(6) bonds causes them to lengthen and the C(2)-C(1)-C(6) angle to close. In turn, the C-M bond is thought to contain less *p* and hence more *s* character than a C-X bond, where X is more electronegative than M.

Viewed along the P-Pd-P axis (see Fig. 3, 4ii) the P-C bonds are approximately eclipsed. Ignoring the cyclohexyl rings the complex thus nearly has a,non-crystallographic, mirror plane running at right angles to the coordination plane and containing the Pd-C(1) axis. The internal geometries of the cyclohexyl rings, in this and in all the other structures described in this chapter, adopt chair conformations with equatorial P-C bonds and have unexceptional bond lengths and angles. Also, in the

TABLE 3, 4iii

SELECTED TORSION ANGLES (°) FOR PCP-CONTAINING COMPLEXES

TORSION ANGLE	[NiBr(PCP)]	[PdBr(PCP)]	[PdCl(PCP)]	[$RhCl_2$(PCP)(OH_2)] .propanol	[$RHCl_2$(PCP)(HOMe)] .xCH_2Cl_2	[$RhCl_2$(PCP)(HOEt)]. OH_2
C(1)-C(2)-C(7)-P(1)	11.5(4)	12.8(6)	12.7(5)	24.4(3)	23.8(7)	32.0(7)
C(1)-C(6)-C(8)-P(2)	-17.4(4)	-19.2(6)	-17.7(5)	24.2(4)	27.0(7)	21.4(7)
M-P(1)-C(7)-C(2)	-10.0(3)	-10.0(5)	-10.4(4)	-29.0(3)	-30.2(6)	-36.8(6)
M-P(2)-C(8)-C(6)	20.6(3)	20.2(5)	19.8(4)	-30.1(3)	-30.8(6)	-30.2(6)
C(1)-M-P(1)-C(7)	5.7(3)	4.6(4)	5.1(3)	21.8(2)	23.7(4)	27.5(4)
C(1)-M-P(2)-C(8)	-15.2(3)	-13.6(4)	-13.7(3)	23.3(2)	22.9(4)	25.2(4)
P(1)-M-C(1)-C(2)	-0.2(4)	1.5(6)	0.9(5)	-13.6(3)	-16.5(7)	-15.9(7)
P(2)-M-C(1)-C(6)	7.9(4)	5.3(6)	6.6(5)	-15.6(3)	-13.4(7)	-20.0(7)
M-C(1)-C(2)-C(7)	-7.3(4)	-9.4(6)	-8.7(5)	-3.6(3)	-0.9(6)	-6.3(7)
M-C(1)-C(6)-C(8)	5.1(4)	7.8(6)	5.8(5)	-1.8(3)	-5.5(6)	3.6(7)

structure described here and in those discussed later in the chapter careful examination of intermolecular contacts reveals none which are significantly shorter than the sum of the appropriate van der Waals radii except when hydrogen bonding occurs.

3, 4b STRUCTURE OF [$PdBr\{(PCy_2CH_2)_2(C_6H_3)\}$].

[PdBr(PCP)] was found to be both isomorphous and isostructural with [PdCl(PCP)]. Thus the coordination geometry about the palladium atom is square-planar with an in-plane distortion of the P(1)-Pd-P(2) angle (to 165.6(1)°) and a small out-of-plane distortion towards tetrahedral geometry of similar magnitude to that in [PdCl(PCP)].

Fig. 3, 4iii shows the structure and numbering scheme of the complex and Tables 3, 4iv and 3, 4v contain bond lengths and bond angles, respectively. Bond lengths and angles, with the obvious exception of the Pd-Br bond length, are all similar to those in [PdCl(PCP)]. The Pd-Br distance of 2.514(2) Å is very long, compared to the average of 2.424 Å found for 8 similar bond lengths,[64] but is in good agreement with other Pd-Br distances *trans* to σ-bonded carbon, such as 2.523(3) Å in *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] (Sect. 3, 4d) and 2.512(2) Å in *trans*-[PdBr(PMe_3)$_2$(RC≡C-C=CR-C≡CR)] (R = Bu^t).[66]

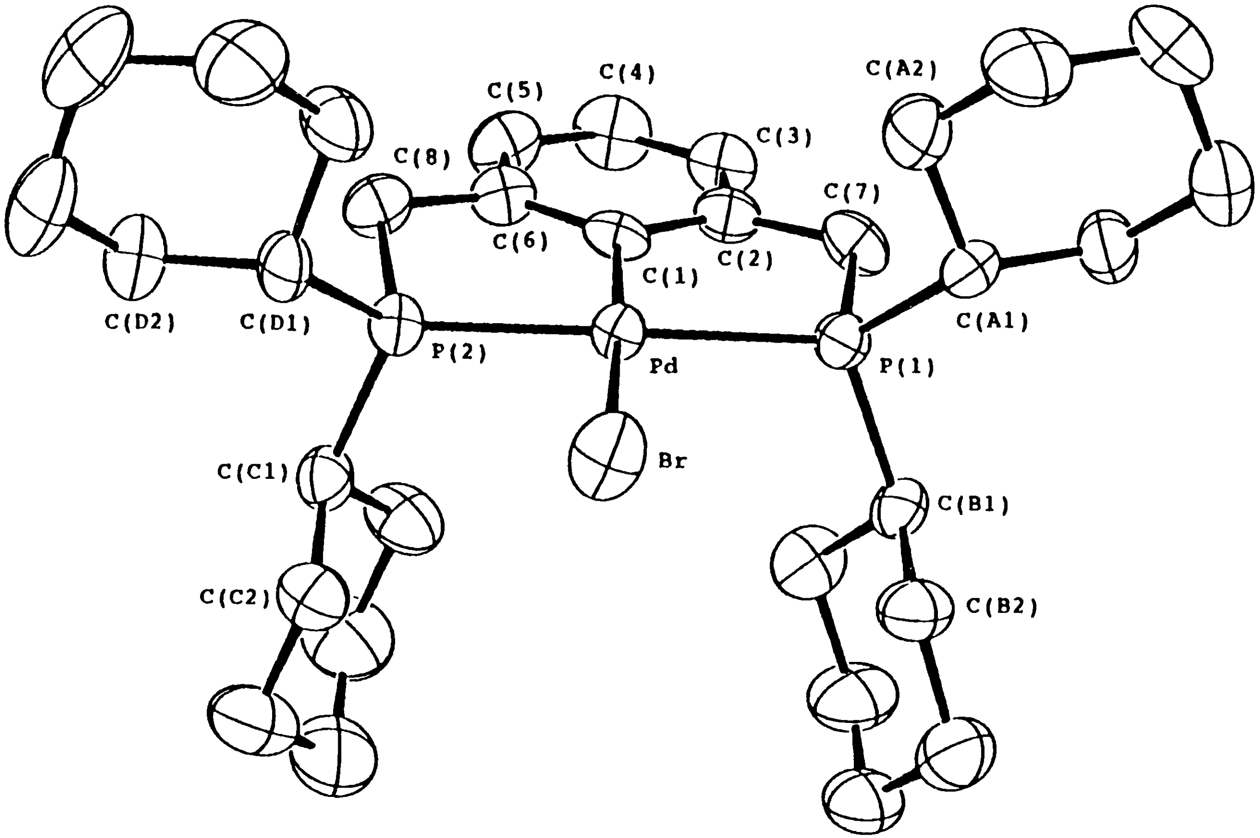

Fig.3,4iii Structure of [PdBr(PCP)].

Table 3,4iv Bond lengths (Å) for [PdBr(PCP)].

Pd - Br	2.514(2)	Pd - P(1)	2.296(2)
Pd - P(2)	2.268(2)	Pd - C(1)	2.009(8)
P(1) - C(7)	1.840(8)	P(1) - C(A1)	1.847(7)
P(1) - C(B1)	1.838(8)	P(2) - C(8)	1.814(8)
P(2) - C(C1)	1.837(8)	P(2) - C(D1)	1.834(7)
C(1) - C(2)	1.403(11)	C(1) - C(6)	1.412(11)
C(2) - C(3)	1.392(11)	C(2) - C(7)	1.499(11)
C(3) - C(4)	1.372(12)	C(4) - C(5)	1.370(13)
C(5) - C(6)	1.387(11)	C(6) - C(8)	1.513(11)
C(A1) - C(A2)	1.512(11)	C(A1) - C(A6)	1.518(11)
C(A2) - C(A3)	1.539(12)	C(A3) - C(A4)	1.533(13)
C(A4) - C(A5)	1.507(13)	C(A5) - C(A6)	1.527(12)
C(B1) - C(B2)	1.529(11)	C(B1) - C(B6)	1.527(11)
C(B2) - C(B3)	1.522(12)	C(B3) - C(B4)	1.518(13)
C(B4) - C(B5)	1.491(14)	C(B5) - C(B6)	1.525(13)
C(C1) - C(C2)	1.525(11)	C(C1) - C(C6)	1.532(11)
C(C2) - C(C3)	1.529(13)	C(C3) - C(C4)	1.511(14)
C(C4) - C(C5)	1.502(16)	C(C5) - C(C6)	1.536(13)
C(D1) - C(D2)	1.530(10)	C(D1) - C(D6)	1.529(11)
C(D2) - C(D3)	1.522(12)	C(D3) - C(D4)	1.504(14)
C(D4) - C(D5)	1.516(14)	C(D5) - C(D6)	1.515(12)

Table 3,4v Bond angles (°) for [PdBr(PCP)].

Br-Pd-P(1)	98.3(1)	Br-Pd-P(2)	94.3(1)
Br-Pd-C(1)	177.1(3)	P(1)-Pd-P(2)	165.6(1)
P(1)-Pd-C(1)	84.4(3)	P(2)-Pd-C(1)	83.1(3)
Pd-P(1)-C(7)	102.4(3)	Pd-P(1)-C(A1)	122.2(3)
Pd-P(1)-C(B1)	113.2(3)	C(7)-P(1)-C(A1)	106.1(4)
C(7)-P(1)-C(B1)	105.0(4)	C(A1)-P(1)-C(B1)	106.3(4)
Pd-P(2)-C(8)	104.2(3)	Pd-P(2)-C(C1)	114.7(3)
Pd-P(2)-C(D1)	118.4(3)	C(8)-P(2)-C(C1)	103.7(4)
C(8)-P(2)-C(D1)	107.0(4)	C(C1)-P(2)-C(D1)	107.5(4)
Pd-C(1)-C(2)	121.8(6)	Pd-C(1)-C(6)	121.7(6)
C(2)-C(1)-C(6)	116.4(7)	C(1)-C(2)-C(3)	121.8(7)
C(1)-C(2)-C(7)	119.6(7)	C(3)-C(2)-C(7)	118.6(7)
C(2)-C(3)-C(4)	119.8(8)	C(3)-C(4)-C(5)	120.4(8)
C(4)-C(5)-C(6)	120.3(8)	C(1)-C(6)-C(5)	121.3(8)
C(1)-C(6)-C(8)	119.1(7)	C(5)-C(6)-C(8)	119.6(7)
P(1)-C(7)-C(2)	110.6(5)	P(2)-C(8)-C(6)	107.9(5)
P(1)-C(A1)-C(A2)	110.3(5)	P(1)-C(A1)-C(A6)	113.9(5)
C(A2)-C(A1)-C(A6)	111.4(6)	C(A1)-C(A2)-C(A3)	110.6(7)
C(A2)-C(A3)-C(A4)	111.0(7)	C(A3)-C(A4)-C(A5)	112.0(8)
C(A4)-C(A5)-C(A6)	111.4(7)	C(A1)-C(A6)-C(A5)	112.7(7)
P(1)-C(B1)-C(B2)	113.5(6)	P(1)-C(B1)-C(B6)	109.4(5)
C(B2)-C(B1)-C(B6)	110.5(6)	C(B1)-C(B2)-C(B3)	111.7(7)
C(B2)-C(B3)-C(B4)	112.2(7)	C(B3)-C(B4)-C(B5)	111.6(8)
C(B4)-C(B5)-C(B6)	111.2(8)	C(B1)-C(B6)-C(B5)	111.3(7)
P(2)-C(C1)-C(C2)	113.5(6)	P(2)-C(C1)-C(C6)	110.2(6)
C(C2)-C(C1)-C(C6)	110.3(7)	C(C1)-C(C2)-C(C3)	110.1(7)
C(C2)-C(C3)-C(C4)	112.1(8)	C(C3)-C(C4)-C(C5)	111.1(9)
C(C4)-C(C5)-C(C6)	111.3(8)	C(C1)-C(C6)-C(C5)	111.5(7)
P(2)-C(D1)-C(D2)	114.3(5)	P(2)-C(D1)-C(D6)	109.9(5)
C(D2)-C(D1)-C(D6)	111.3(6)	C(D1)-C(D2)-C(D3)	110.9(7)
C(D2)-C(D3)-C(D4)	111.3(8)	C(D3)-C(D4)-C(D5)	111.0(8)
C(D4)-C(D5)-C(D6)	112.7(8)	C(D1)-C(D6)-C(D5)	111.8(7)

3, 4c STRUCTURE OF $[NiBr\{PCy_2CH_2)_2(C_6H_3)\}]$.

This structure (Fig. 3, 4iv) is similar to those of [PdCl(PCP)] and [PdBr(PCP)]. The square-planar geometry around the nickel atom is subject to a slightly greater distortion towards tetrahedral geometry than in the palladium complexes, as is shown by the displacement of the P(1), P(2), Br and C(1) atoms by 0.108(1), 0.112(1), -0.068(1) and -0.105(4) Å, respectively, from the metal coordination plane. However this distortion is still small. Despite being smaller than a palladium atom the nickel atom does not relieve the ring strain in the chelate ligand very greatly. The P(1)-M-P(2) angle is 167.6(1)°, as compared to 165.6(1)° in [PdBr(PCP)], and the angles M-P(1)-C(7) and M-P(2)-C(8) are 103.6(2) and 105.0(2)° for [NiBr(PCP)] and 102.4(3) and 104.2(3) for its Pd analogue. This indicates that metal size does not strongly influence the conformation of the PCP ligand. Complete lists of bond lengths and angles are given in Tables 3, 4vi and 3, 4vii.

The Ni-Br distance of 2.360(1) Å compares well with similar distances of 2.374(1) and 2.350(1) Å given for the complexes *trans*-$[NiBr(PEt_3)_2\{2,6\text{-}(PhMeNCH_2)_2(C_6H_3)\}]$[67] and *trans*-$[NiBr(PPh_3)_2(MeOCOCHCH(C_6H_3Cl_2)COOMe)]$[68] which both contain two phosphine ligands and Br *trans* to σ-bonded carbon. The Ni-C distance of 1.909(5) Å is identical to the analagous distance of 1.908(6) Å in the non-chelated complex mentioned above (see ref. 67). The Ni-P(1) and Ni-P(2)

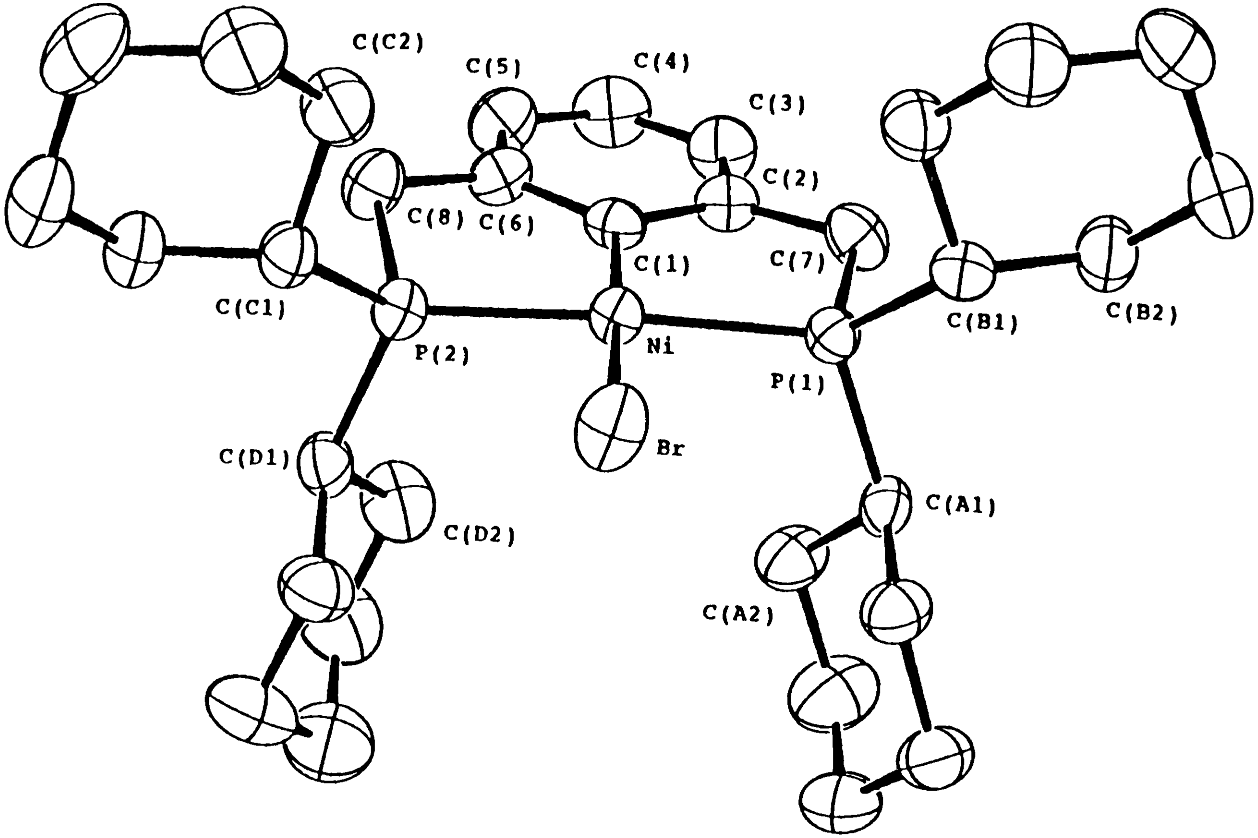

Fig.3,4iv Structure of [NiBr(PCP)].

Table 3,4vi Bond lengths (Å) for [NiBr(PCP)].

Ni - Br	2.360(1)	Ni - P(1)	2.185(2)
Ni - P(2)	2.168(2)	Ni - C(1)	1.909(5)
P(1) - C(7)	1.824(5)	P(1) - C(A1)	1.836(5)
P(1) - C(B1)	1.833(5)	P(2) - C(8)	1.817(5)
P(2) - C(C1)	1.830(5)	P(2) - C(D1)	1.844(5)
C(1) - C(2)	1.406(7)	C(1) - C(6)	1.420(7)
C(2) - C(3)	1.387(7)	C(2) - C(7)	1.506(7)
C(3) - C(4)	1.383(8)	C(4) - C(5)	1.370(9)
C(5) - C(6)	1.389(7)	C(6) - C(8)	1.505(7)
C(A1) - C(A2)	1.528(7)	C(A1) - C(A6)	1.521(7)
C(A2) - C(A3)	1.523(8)	C(A3) - C(A4)	1.509(9)
C(A4) - C(A5)	1.516(8)	C(A5) - C(A6)	1.531(7)
C(B1) - C(B2)	1.537(7)	C(B1) - C(B6)	1.534(7)
C(B2) - C(B3)	1.522(8)	C(B3) - C(B4)	1.523(8)
C(B4) - C(B5)	1.522(9)	C(B5) - C(B6)	1.526(8)
C(C1) - C(C2)	1.526(7)	C(C1) - C(C6)	1.530(7)
C(C2) - C(C3)	1.530(8)	C(C3) - C(C4)	1.518(9)
C(C4) - C(C5)	1.503(8)	C(C5) - C(C6)	1.520(8)
C(D1) - C(D2)	1.519(7)	C(D1) - C(D6)	1.525(7)
C(D2) - C(D3)	1.526(8)	C(D3) - C(D4)	1.497(10)
C(D4) - C(D5)	1.524(9)	C(D5) - C(D6)	1.514(8)

Table 3,4vii Bond angles (°) for [NiBr(PCP)].

Br-Ni-P(1)	95.4(1)	Br-Ni-P(2)	94.0(1)
Br-Ni-C(1)	177.3(2)	P(1)-Ni-P(2)	167.6(1)
P(1)-Ni-C(1)	86.3(2)	P(2)-Ni-C(1)	84.7(2)
Ni-P(1)-C(7)	103.6(2)	Ni-P(1)-C(A1)	114.2(2)
Ni-P(1)-C(B1)	122.0(2)	C(7)-P(1)-C(A1)	103.9(3)
C(7)-P(1)-C(B1)	106.0(3)	C(A1)-P(1)-C(B1)	105.4(2)
Ni-P(2)-C(8)	105.0(2)	Ni-P(2)-C(C1)	119.2(2)
Ni-P(2)-C(D1)	114.8(2)	C(8)-P(2)-C(C1)	106.5(3)
C(8)-P(2)-C(D1)	103.0(3)	C(C1)-P(2)-C(D1)	106.9(3)
Ni-C(1)-C(2)	122.2(4)	Ni-C(1)-C(6)	122.2(4)
C(2)-C(1)-C(6)	115.6(5)	C(1)-C(2)-C(3)	122.3(5)
C(1)-C(2)-C(7)	118.4(4)	C(3)-C(2)-C(7)	119.2(5)
C(2)-C(3)-C(4)	120.0(5)	C(3)-C(4)-C(5)	119.9(5)
C(4)-C(5)-C(6)	120.4(5)	C(1)-C(6)-C(5)	121.7(5)
C(1)-C(6)-C(8)	118.4(4)	C(5)-C(6)-C(8)	119.9(5)
P(1)-C(7)-C(2)	108.3(4)	P(2)-C(8)-C(6)	105.6(4)
P(1)-C(A1)-C(A2)	109.3(3)	P(1)-C(A1)-C(A6)	113.8(4)
C(A2)-C(A1)-C(A6)	109.9(4)	C(A1)-C(A2)-C(A3)	111.5(5)
C(A2)-C(A3)-C(A4)	111.2(5)	C(A3)-C(A4)-C(A5)	110.5(5)
C(A4)-C(A5)-C(A6)	112.4(5)	C(A1)-C(A6)-C(A5)	111.5(4)
P(1)-C(B1)-C(B2)	114.1(4)	P(1)-C(B1)-C(B6)	110.4(4)
C(B2)-C(B1)-C(B6)	110.4(4)	C(B1)-C(B2)-C(B3)	112.2(5)
C(B2)-C(B3)-C(B4)	111.9(5)	C(B3)-C(B4)-C(B5)	111.1(5)
C(B4)-C(B5)-C(B6)	112.1(5)	C(B1)-C(B6)-C(B5)	111.1(4)
P(2)-C(C1)-C(C2)	110.0(4)	P(2)-C(C1)-C(C6)	114.3(4)
C(C2)-C(C1)-C(C6)	111.1(4)	C(C1)-C(C2)-C(C3)	111.9(5)
C(C2)-C(C3)-C(C4)	110.9(5)	C(C3)-C(C4)-C(C5)	111.3(5)
C(C4)-C(C5)-C(C6)	111.2(5)	C(C1)-C(C6)-C(C5)	110.5(4)
P(2)-C(D1)-C(D2)	111.2(4)	P(2)-C(D1)-C(D6)	114.3(4)
C(D2)-C(D1)-C(D6)	110.5(4)	C(D1)-C(D2)-C(D3)	112.2(5)
C(D2)-C(D3)-C(D4)	111.6(5)	C(D3)-C(D4)-C(D5)	110.7(6)
C(D4)-C(D5)-C(D6)	111.4(6)	C(D1)-C(D6)-C(D5)	110.5(5)

distances of 2.185(2) and 2.168(2) Å are in good agreement with average values of 2.187 Å for 15 Ni-PPh_3 bonds and 2.200 Å for 20 Ni-PMe_3 distances.[64]

The difference between the two Ni-P distances indicates that the two five-membered rings are not equivalent and this is highlighted by the torsion angles given in Table 3, 4iii. The angle between the plane of the aromatic ring and the coordination plane of the nickel is 4.1°. The PCP ligand exists in a similar conformation to that found for [PdBr(PCP)] and [PdCl(PCP)] with the P-C bonds nearly eclipsed when viewed along the P-Ni-P axis.

3, 4d STRUCTURE OF *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$].

As described in Section 2, 7k the solution of this structure was not trivial and it must be remembered that the geometrical parameters described below may in fact be averages from three closely similar conformations. This disorder may be evinced by the high thermal displacement parameters of some of the atoms (Tables 2, 7xxiv and xxv); however, the bond lengths and angles presented in Tables 3, 4viii and 3, 4ix and described in detail below all appear normal as do the thermal ellipsoids in Fig. 3, 4v.

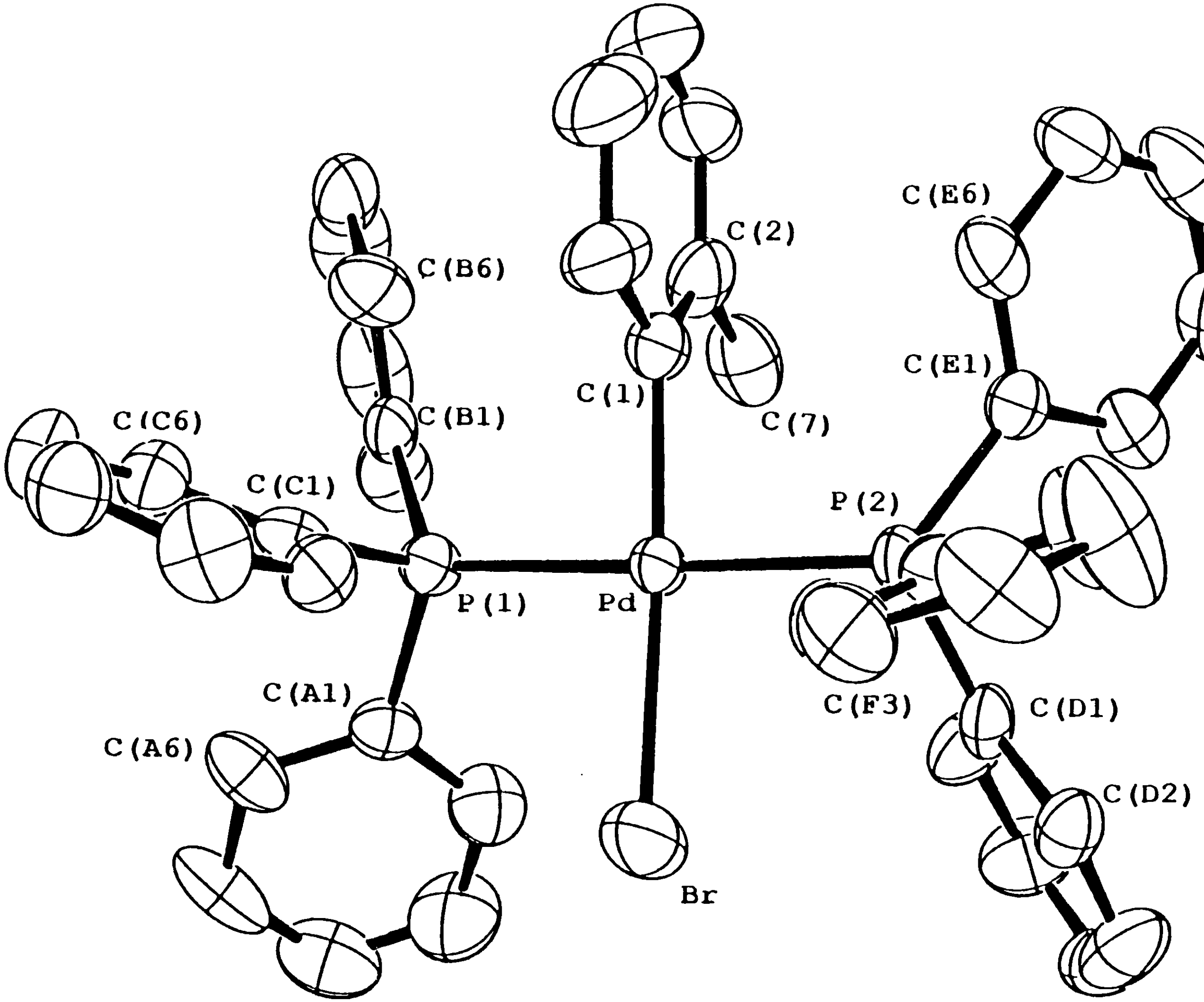

Fig.3,4v Structure of *trans*-[PdBr(*o*-tolyl)$(PPh_3)_2$].

The coordination geometry about the palladium atom is essentially square-planar with a small tetrahedral distortion, indicated by the bond angles subtending Pd (Table 3, 4ix) and by the deviations from the coordination plane of Br, C(1), P(1) and P(2) by -0.114(2), -0.150(11), 0.112(3) and 0.111(3) Å, respectively.

The Pd-P(1) and Pd-P(2) distances of 2.319(4) and 2.327(4) Å are effectively identical and are only marginally larger than the average Pd-P distance found for 51 Pd-PPh_3 interactions (2.308 Å).[64] The Pd-Br bond length of 2.523(3) Å is, as demonstrated in Section 3, 4b, very long but is in good agreement with other Pd-Br distances *trans* to σ bonded carbon, such as that of 2.514(2) Å in [PdBr(PCP)]. The Pd-C bond length of 1.999(13) Å is identical, within experimental error, to the value for [PdBr(PCP)] (2.009(8) Å). This is discussed further in Section 3, 4k.

The plane of the tolyl ring is at an angle of 92.5° to the coordination plane of palladium. The difference between the angles Pd-C(1)-C(2) (125.4(10)°) and Pd-C(1)-C(6) (115.8(10)°) shows that additionally the tolyl ring is skewed to one side to hold the methyl group clear of the palladium atom (Pd...C(7) = 3.29(2) Å). The closest approach of a hydrogen atom to the palladium atom is 2.93 Å for H(7C). It is therefore concluded that there are no significant Pd...methyl interactions.

The triphenylphosphine ligands are mutually eclipsed when viewed

Table 3,4viii Bond lengths (Å) for $[PdBr(o\text{-}tolyl)(PPh_3)_2]$.

Pd - Br	2.523(3)	Pd - P(1)	2.319(4)
Pd - P(2)	2.327(4)	Pd - C(1)	1.999(13)
P(1) - C(A1)	1.834(17)	P(1) - C(B1)	1.832(11)
P(1) - C(C1)	1.807(10)	P(2) - C(D1)	1.812(12)
P(2) - C(E1)	1.840(17)	P(2) - C(F1)	1.803(8)
C(1) - C(2)	1.398(18)	C(1) - C(6)	1.430(21)
C(2) - C(3)	1.412(23)	C(2) - C(7)	1.425(21)
C(3) - C(4)	1.35(4)	C(4) - C(5)	1.36(4)
C(5) - C(6)	1.38(4)	C(A1) - C(A2)	1.370(26)
C(A1) - C(A6)	1.397(19)	C(A2) - C(A3)	1.373(17)
C(A3) - C(A4)	1.313(16)	C(A4) - C(A5)	1.386(22)
C(A5) - C(A6)	1.401(16)	C(B1) - C(B2)	1.418(16)
C(B1) - C(B6)	1.360(17)	C(B2) - C(B3)	1.408(15)
C(B3) - C(B4)	1.373(16)	C(B4) - C(B5)	1.340(15)
C(B5) - C(B6)	1.417(14)	C(C1) - C(C2)	1.394(10)
C(C1) - C(C6)	1.416(17)	C(C2) - C(C3)	1.387(12)
C(C3) - C(C4)	1.337(16)	C(C4) - C(C5)	1.401(10)
C(C5) - C(C6)	1.363(12)	C(D1) - C(D2)	1.382(15)
C(D1) - C(D6)	1.361(12)	C(D2) - C(D3)	1.352(15)
C(D3) - C(D4)	1.393(10)	C(D4) - C(D5)	1.355(14)
C(D5) - C(D6)	1.365(14)	C(E1) - C(E2)	1.415(26)
C(E1) - C(E6)	1.380(22)	C(E2) - C(E3)	1.354(16)
C(E3) - C(E4)	1.351(17)	C(E4) - C(E5)	1.351(21)
C(E5) - C(E6)	1.352(15)	C(F1) - C(F2)	1.381(20)
C(F1) - C(F6)	1.371(20)	C(F2) - C(F3)	1.401(14)
C(F3) - C(F4)	1.371(18)	C(F4) - C(F5)	1.370(18)
C(F5) - C(F6)	1.391(14)		

Table 3,4ix Bond angles (°) for [PdBr(o-tolyl)(PPh$_3$)$_2$].

Br-Pd-P(1)	92.8(1)	Br-Pd-P(2)	89.9(1)
Br-Pd-C(1)	171.0(4)	P(1)-Pd-P(2)	175.8(2)
P(1)-Pd-C(1)	87.3(4)	P(2)-Pd-C(1)	90.5(4)
Pd-P(1)-C(A1)	113.9(6)	Pd-P(1)-C(B1)	118.5(6)
Pd-P(1)-C(C1)	110.3(4)	C(A1)-P(1)-C(B1)	102.0(7)
C(A1)-P(1)-C(C1)	107.1(6)	C(B1)-P(1)-C(C1)	103.8(6)
Pd-P(2)-C(D1)	108.6(4)	Pd-P(2)-C(E1)	120.8(6)
Pd-P(2)-C(F1)	114.8(5)	C(D1)-P(2)-C(E1)	103.5(7)
C(D1)-P(2)-C(F1)	104.8(6)	C(E1)-P(2)-C(F1)	102.8(7)
Pd-C(1)-C(2)	125.4(10)	Pd-C(1)-C(6)	115.8(10)
C(2)-C(1)-C(6)	118.8(13)	C(1)-C(2)-C(3)	119.2(13)
C(1)-C(2)-C(7)	119.9(13)	C(3)-C(2)-C(7)	120.9(13)
C(2)-C(3)-C(4)	119.3(17)	C(3)-C(4)-C(5)	123.4(24)
C(4)-C(5)-C(6)	119.2(21)	C(1)-C(6)-C(5)	120.0(15)
P(1)-C(A1)-C(A2)	120.0(12)	P(1)-C(A1)-C(A6)	120.7(11)
C(A2)-C(A1)-C(A6)	119.3(14)	C(A1)-C(A2)-C(A3)	120.9(14)
C(A2)-C(A3)-C(A4)	120.9(10)	C(A3)-C(A4)-C(A5)	120.9(12)
C(A4)-C(A5)-C(A6)	119.8(12)	C(A1)-C(A6)-C(A5)	118.2(10)
P(1)-C(B1)-C(B2)	118.5(10)	P(1)-C(B1)-C(B6)	121.9(9)
C(B2)-C(B1)-C(B6)	119.4(11)	C(B1)-C(B2)-C(B3)	117.8(12)
C(B2)-C(B3)-C(B4)	121.4(10)	C(B3)-C(B4)-C(B5)	120.4(10)
C(B4)-C(B5)-C(B6)	120.0(11)	C(B1)-C(B6)-C(B5)	120.8(10)
P(1)-C(C1)-C(C2)	119.9(8)	P(1)-C(C1)-C(C6)	123.0(6)
C(C2)-C(C1)-C(C6)	117.0(8)	C(C1)-C(C2)-C(C3)	120.3(10)
C(C2)-C(C3)-C(C4)	121.7(8)	C(C3)-C(C4)-C(C5)	119.9(7)
C(C4)-C(C5)-C(C6)	119.4(10)	C(C1)-C(C6)-C(C5)	121.6(8)
P(2)-C(D1)-C(D2)	124.3(8)	P(2)-C(D1)-C(D6)	119.0(9)
C(D2)-C(D1)-C(D6)	116.6(10)	C(D1)-C(D2)-C(D3)	121.3(9)
C(D2)-C(D3)-C(D4)	120.8(10)	C(D3)-C(D4)-C(D5)	118.2(9)
C(D4)-C(D5)-C(D6)	119.9(8)	C(D1)-C(D6)-C(D5)	123.0(11)
P(2)-C(E1)-C(E2)	122.5(12)	P(2)-C(E1)-C(E6)	120.9(12)
C(E2)-C(E1)-C(E6)	116.6(14)	C(E1)-C(E2)-C(E3)	120.2(13)
C(E2)-C(E3)-C(E4)	120.6(10)	C(E3)-C(E4)-C(E5)	120.7(12)
C(E4)-C(E5)-C(E6)	119.9(11)	C(E1)-C(E6)-C(E5)	121.9(12)
P(2)-C(F1)-C(F2)	120.2(11)	P(2)-C(F1)-C(F6)	122.4(9)
C(F2)-C(F1)-C(F6)	117.4(9)	C(F1)-C(F2)-C(F3)	122.4(12)
C(F2)-C(F3)-C(F4)	118.8(11)	C(F3)-C(F4)-C(F5)	119.5(9)
C(F4)-C(F5)-C(F6)	121.1(12)	C(F1)-C(F6)-C(F5)	120.9(11)

along the P-Pd-P axis. The torsion angles C(1)-Pd-P(1)-C(B1) and C(1)-Pd-P(2)-C(E1) of 32.3(7) and -24.4(8)° show that the *o*-tolyl ring positions lies towards the B and E phenyl rings.

3, 4e STRUCTURE OF $[RhCl_2\{(PCy_2CH_2)_2(C_6H_3)\}(OH_2)].CH_3COHCH_3$.

ORTEP drawings showing the atom numbering system are given in Figs. 3, 4vi and vii. Tables 3, 4x and 3, 4xi give details of bond lengths and angles.

The coordination geometry about the rhodium atom in the complex $[RhCl_2(PCP)(OH_2)]$.propan-2-ol is octahedral, with mutually *trans* chlorine atoms positioned *cis* to the chelate ligand and with the water molecule placed *trans* to the σ-bonded carbon atom. The only significant deviation from octahedral geometry is the closure of the P(1)-Rh-P(2) angle to 165.8(1)° due to the steric demands of the PCP ligand.

The increased spatial demands of the non-chelate ligands, as compared to the square-planar [MX(PCP)] structures (Section 3, 4a - c), leads to changes in the geometry of the chelate PCP ligand. In order to accommodate six ligands around the metal the two PCy_2R units, which in the square-planar structures were held in a mutually eclipsed

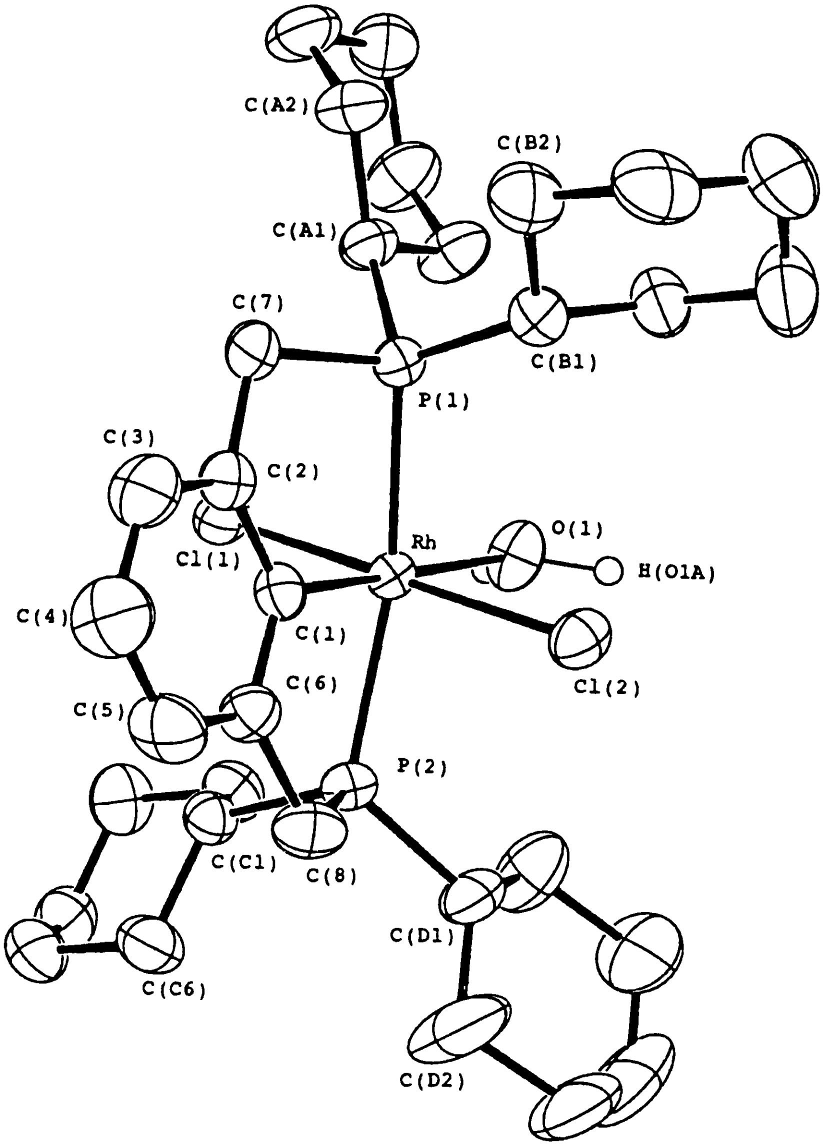

Fig.3,4vi Structure of [$RhCl_2(PCP)(OH_2)$].popan-2-ol.

conformation, have rotated in opposite directions about the P-Rh-P axis to give a staggered conformation. This has resulted in the two five-membered chelate rings becoming even less planar, as is shown by the torsion angles given in Table 3, 4iii. The twist also results in the large angle of 14.6° between the plane of the aromatic ring and the coordination plane Rh P(1) P(2) O(1) C(1). This distortion is also illustrated by the torsion angles P(1)-Rh-C(1)-C(2) and P(2)-Rh-C(1)-C(6) given in Table 3, 4iii. Further changes in the chelate ligand geometry, indicative of increasing ring strain in the complex, are the closing of the chelate-ring Rh-P(1)-C(7) and Rh-P(2)-C(8) angles to 99.3(2) and 98.6(2)° respectively. These angles are smaller than the corresponding values for the square-planar complexes [MX(PCP)] (range 102.4(3) to 105.0(2)°) which in turn are themselves smaller than the values for the five-membered ring in *cis*-[$PdCl_2$(dppe)] (108.5(2) and 107.9(2)°).[69] For comparison, the Rh-P-C angles in *trans*-[Rh(OH_2)(CO)(PPh_3)$_2$][ClO_4].CH_2Cl_2 (Section 3, 4m) range from 112.8(2) to 117.9(2)°.

The Rh-P(1) and Rh-P(2) bond lengths of 2.351(1) and 2.354(2) Å are essentially identical and are in good agreement with those found in [$RhCl_2$(PCP)(HOMe)].0.41CH_2Cl_2 and [$RhCl_2$(PCP)(HOEt)].H_2O. The Rh-Cl bond lengths of 2.345(2) and 2.371(2) Å are not equivalent. The greater length of Rh-Cl(2) is probably a consequence of hydrogen bonding between Cl(2) and the hydroxyl group of the propan-2-ol solvent. Details of this and other hydrogen bonds are given in Table 3, 4xii. The Rh-C distance

Table 3,4x Bond lengths (Å) for [RhCl$_2$(PCP)(OH$_2$)].propan-2-ol.

Rh - Cl(1)	2.345(2)	Rh - Cl(2)	2.371(2)
Rh - P(1)	2.351(1)	Rh - P(2)	2.354(2)
Rh - O(1)	2.274(3)	Rh - C(1)	2.004(4)
P(1) - C(7)	1.823(5)	P(1) - C(A1)	1.856(4)
P(1) - C(B1)	1.836(4)	P(2) - C(8)	1.835(5)
P(2) - C(C1)	1.842(4)	P(2) - C(D1)	1.843(5)
O(S) - C(S1)	1.423(7)	C(1) - C(2)	1.405(6)
C(1) - C(6)	1.404(6)	C(2) - C(3)	1.387(6)
C(2) - C(7)	1.502(6)	C(3) - C(4)	1.381(7)
C(4) - C(5)	1.384(7)	C(5) - C(6)	1.375(7)
C(6) - C(8)	1.509(6)	C(A1) - C(A2)	1.528(6)
C(A1) - C(A6)	1.527(6)	C(A2) - C(A3)	1.522(7)
C(A3) - C(A4)	1.508(7)	C(A4) - C(A5)	1.518(7)
C(A5) - C(A6)	1.536(7)	C(B1) - C(B2)	1.526(6)
C(B1) - C(B6)	1.516(6)	C(B2) - C(B3)	1.540(7)
C(B3) - C(B4)	1.506(8)	C(B4) - C(B5)	1.506(8)
C(B5) - C(B6)	1.521(7)	C(C1) - C(C2)	1.536(6)
C(C1) - C(C6)	1.536(6)	C(C2) - C(C3)	1.517(7)
C(C3) - C(C4)	1.518(7)	C(C4) - C(C5)	1.510(7)
C(C5) - C(C6)	1.520(7)	C(D1) - C(D2)	1.462(8)
C(D1) - C(D6)	1.499(7)	C(D2) - C(D3)	1.508(9)
C(D3) - C(D4)	1.465(9)	C(D4) - C(D5)	1.454(10)
C(D5) - C(D6)	1.524(8)	C(S1) - C(S2)	1.465(8)
C(S1) - C(S3)	1.489(9)		

Table 3,4xi Bond angles (°) for [$RhCl_2$(PCP)(OH_2)].propan -2-ol.

Cl(1)-Rh-Cl(2)	177.2(1)	Cl(1)-Rh-P(1)	84.9(1)
Cl(1)-Rh-P(2)	93.6(1)	Cl(1)-Rh-O(1)	91.5(1)
Cl(1)-Rh-C(1)	90.9(2)	Cl(2)-Rh-P(1)	96.3(1)
Cl(2)-Rh-P(2)	85.9(1)	Cl(2)-Rh-O(1)	85.8(1)
Cl(2)-Rh-C(1)	91.8(2)	P(1)-Rh-P(2)	165.8(1)
P(1)-Rh-O(1)	95.8(1)	P(1)-Rh-C(1)	82.9(2)
P(2)-Rh-O(1)	98.4(1)	P(2)-Rh-C(1)	83.0(2)
O(1)-Rh-C(1)	177.1(2)	Rh-P(1)-C(7)	99.3(2)
Rh-P(1)-C(A1)	120.0(2)	Rh-P(1)-C(B1)	113.6(2)
C(7)-P(1)-C(A1)	102.3(2)	C(7)-P(1)-C(B1)	106.9(2)
C(A1)-P(1)-C(B1)	112.2(2)	Rh-P(2)-C(8)	98.6(2)
Rh-P(2)-C(C1)	114.9(2)	Rh-P(2)-C(D1)	121.5(2)
C(8)-P(2)-C(C1)	106.1(2)	C(8)-P(2)-C(D1)	102.9(3)
C(C1)-P(2)-C(D1)	110.2(2)	H(O1A)-O(1)-H(O1B)	115.3(3)
Rh-C(1)-C(2)	120.9(3)	Rh-C(1)-C(6)	120.9(3)
C(2)-C(1)-C(6)	118.1(4)	C(1)-C(2)-C(3)	120.1(4)
C(1)-C(2)-C(7)	119.4(4)	C(3)-C(2)-C(7)	120.5(4)
C(2)-C(3)-C(4)	120.8(5)	C(3)-C(4)-C(5)	119.5(5)
C(4)-C(5)-C(6)	120.6(5)	C(1)-C(6)-C(5)	120.9(4)
C(1)-C(6)-C(8)	119.1(4)	C(5)-C(6)-C(8)	119.9(4)
P(1)-C(7)-C(2)	109.0(3)	P(2)-C(8)-C(6)	109.0(3)
P(1)-C(A1)-C(A2)	115.6(3)	P(1)-C(A1)-C(A6)	115.5(3)
C(A2)-C(A1)-C(A6)	110.8(4)	C(A1)-C(A2)-C(A3)	110.0(4)
C(A2)-C(A3)-C(A4)	112.2(4)	C(A3)-C(A4)-C(A5)	111.2(4)
C(A4)-C(A5)-C(A6)	111.6(5)	C(A1)-C(A6)-C(A5)	109.4(4)
P(1)-C(B1)-C(B2)	118.9(3)	P(1)-C(B1)-C(B6)	111.8(3)
C(B2)-C(B1)-C(B6)	111.0(4)	C(B1)-C(B2)-C(B3)	109.9(4)
C(B2)-C(B3)-C(B4)	110.7(4)	C(B3)-C(B4)-C(B5)	112.1(5)
C(B4)-C(B5)-C(B6)	112.1(5)	C(B1)-C(B6)-C(B5)	111.1(4)
P(2)-C(C1)-C(C2)	111.9(3)	P(2)-C(C1)-C(C6)	117.2(3)
C(C2)-C(C1)-C(C6)	110.0(4)	C(C1)-C(C2)-C(C3)	110.9(4)
C(C2)-C(C3)-C(C4)	110.3(4)	C(C3)-C(C4)-C(C5)	111.2(4)
C(C4)-C(C5)-C(C6)	111.1(4)	C(C1)-C(C6)-C(C5)	111.1(4)
P(2)-C(D1)-C(D2)	118.8(4)	P(2)-C(D1)-C(D6)	115.7(4)
C(D2)-C(D1)-C(D6)	115.8(5)	C(D1)-C(D2)-C(D3)	114.4(5)
C(D2)-C(D3)-C(D4)	114.3(6)	C(D3)-C(D4)-C(D5)	115.1(6)
C(D4)-C(D5)-C(D6)	116.2(5)	C(D1)-C(D6)-C(D5)	112.8(5)
O(S)-C(S1)-C(S2)	108.5(5)	O(S)-C(S1)-C(S3)	111.9(5)
C(S2)-C(S1)-C(S3)	114.2(5)		

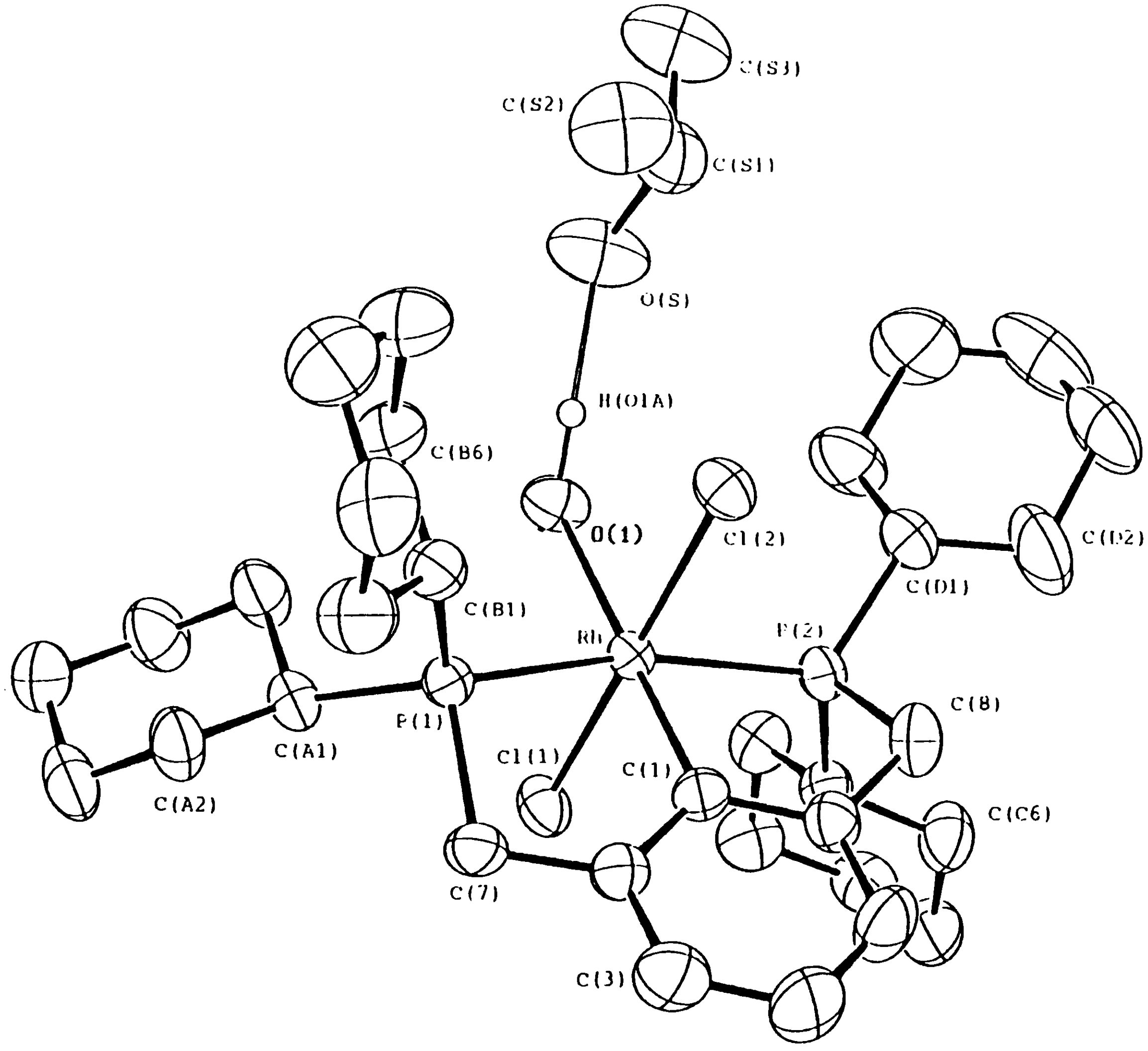

Fig.3,4vii View of $[RhCl_2(PCP)(OH_2)]$.propan-2-ol showing the solvent molecule.

TABLE 3, 4xii

HYDROGEN-BONDING DISTANCES, (Å), AND ANGLES, (°)

O-H..X	O-H	H..X	O...X	O-H..X
$[RhCl_2(PCP)(OH_2)]$.propan-2-ol				
O(1)-H(O1A)...O(S)	1.03	1.813	2.759(4)	152
$O(S)^*$-$H(OS)^*$...Cl(2)	1.10	2.116	3.133(3)	152
$[RhCl_2(PCP)(HOMe)]0.41CH_2Cl_2$				
O(1)-H(O1)...Cl(3)	1.04	1.63	2.64	164
O(1)-H(O1)...Cl(6)	1.04	1.66	2.58	145
$[RhCl_2(PCP)(HOEt)].OH_2$				
O(1)-H(O1)...O(2)	1.15	1.60	2.736(9)	172
$O(2)^*$-H^*...Cl(2)	-	-	3.214(7)	-
$[Rh(CO)(OH_2)(PPh_3)_2][ClO_4].CH_2Cl_2$				
O(1)-H(O1A)...$O(4)^i$	1.03	1.79	2.781(7)	161
O(1)-H(O1B)...O(3)	0.84	1.94	2.735(8)	158

SYMMETRY CODES:-
i = -x, -y, -z.
* = -½+x, ½-y, z.

TABLE 3, 4xiii

Rh-O BOND LENGTHS FOUND IN ALL KNOWN CRYSTAL STRUCTURES OF Rh(I) AND Rh(III) AQUA COMPLEXES

COMPLEX	OX. NO., COORD.NO	TRANS ATOM	Rh-O (Å)	Ref.
[Rh(CO)(OH$_2$)(PPh$_3$)$_2$][ClO$_4$] .CH$_2$Cl$_2$	I,4	C	2.127(4)	This work
[Rh(CO)(OH$_2$)(PPh$_3$)$_2$][BF$_4$] .¼C$_6$H$_{12}$.½H$_2$O	I,4	C	2.130(6)	6
"	I,4	C	2.115(5)	"
[Rh(CO){Ph$_2$P(C$_2$H$_4$O)$_3$C$_2$H$_4$PPh$_2$} (OH$_2$)][PF$_6$]	I,4	C	2.107(6)	80
[Rh{CH$_3$C(CH$_2$PPh$_2$)$_3$}(C$_2$H$_4$) (OH$_2$)][BF$_4$]	I,5	P	2.215(5)	81
[Rh(acac)(BTFBD)(OH$_2$)] .½H$_2$O	III,6	C	2.32(1)	82
[Rh(PMe$_2$Ph)$_2$(OCCH$_2$ClCH$_2$ClCO)Cl(O H2)]	III,6	C	2.28(06)	83
[RhCl$_2$(PCP)(OH$_2$)] .propan-2-ol	III,6	C	2.274(3)	This work
[RhCl$_2$(NCN)(OH$_2$)]	III,6	C	2.269(2)	77
[Rh(P(C$_6$H$_4$F)$_3$)(O$_2$CF$_3$)(QCOX)Ph(OH$_2$)]	III,6	C	2.243(6)	84
[Rh(AsMe$_3$)$_2$(TTFB)Cl(OH$_2$)]	III,6	C	2.241(12)	85
[RhCl$_2$(PPh$_3$)(NTHA)(OH$_2$)]	III,6	P	2.202(3)	86
[Rh(NN)(MOXB)(PMePh$_2$)(OH$_2$)] [ClO$_4$]	III,6	C	2.194(4)	87
[Rh(OQ)(η^2-Ph$_2$P (C$_6$F$_4$))Br(OH$_2$)]	III,6	P	2.175(6)	88
"	III,6	P	2.167(5)	"
[Rh(Cp*)(O$_2$CPh)$_2$(OH$_2$)]	III,6	πC	2.12(1)	89
[Rh(μ-OH) (TACN)(OH$_2$)]$_2$[ClO$_4$]$_4$	III,6	N	2.107(8)	90
[Rh(HEDTA)(H$_2$O)]	III,6	N	2.096(2)	91
[RhCl$_2$(SNS)(OH$_2$)][PF$_6$]	III,6	N	2.070(4)	92

of 2.004(4) Å is identical, to within experimental error, to that in the [RhCl$_2$(PCP)(HOEt)].H$_2$O complex and is similar to that in the coordinated methanol analogue (1.984(8) Å). It is also equivalent to the Rh-C distances in the square-pyramidal complexes [RhHCl{(PBu$^t_2$CH$_2$)$_2$(C$_6$H$_3$)}][45] and [RhPhCl$_2$(PPh$_3$)$_2$][61] of 1.999(7) and 2.016(3) Å respectively. The Rh-O distance of 2.274(3) Å is long for a Rh(III)-OH$_2$ complex but does agree well with other Rh-O distances in complexes in which the water ligand is *trans* to a σ-bonded carbon (Table 3, 4xiii). The water molecule is hydrogen-bonded to the oxygen atom of the propan-2-ol solvent molecule (see Table 3, 4xii).

3, 4f STRUCTURE OF [RhCl$_2${(PCy$_2$CH$_2$)$_2$(C$_6$H$_3$)}(HOMe)]0.41CH$_2$Cl$_2$.

The coordination geometry about the rhodium atom is similar to that found in the complex [RhCl$_2$(PCP)(OH$_2$)].propan-2-ol discussed in Section 3, 4e; coordinated methanol replaces the water ligand and closure of the P(1)-Rh-P(2) angle to 166.1(1)° is again the only significant deviation from octahedral coordination. Fig. 3, 4viii is an ORTEP drawing of the complex and Tables 3, 4xiv and xv contain bond lengths and bond angles.

Again, as in the aqua complex, the geometry of the chelate ligand is distorted away from the symmetrical conformation seen in the square-

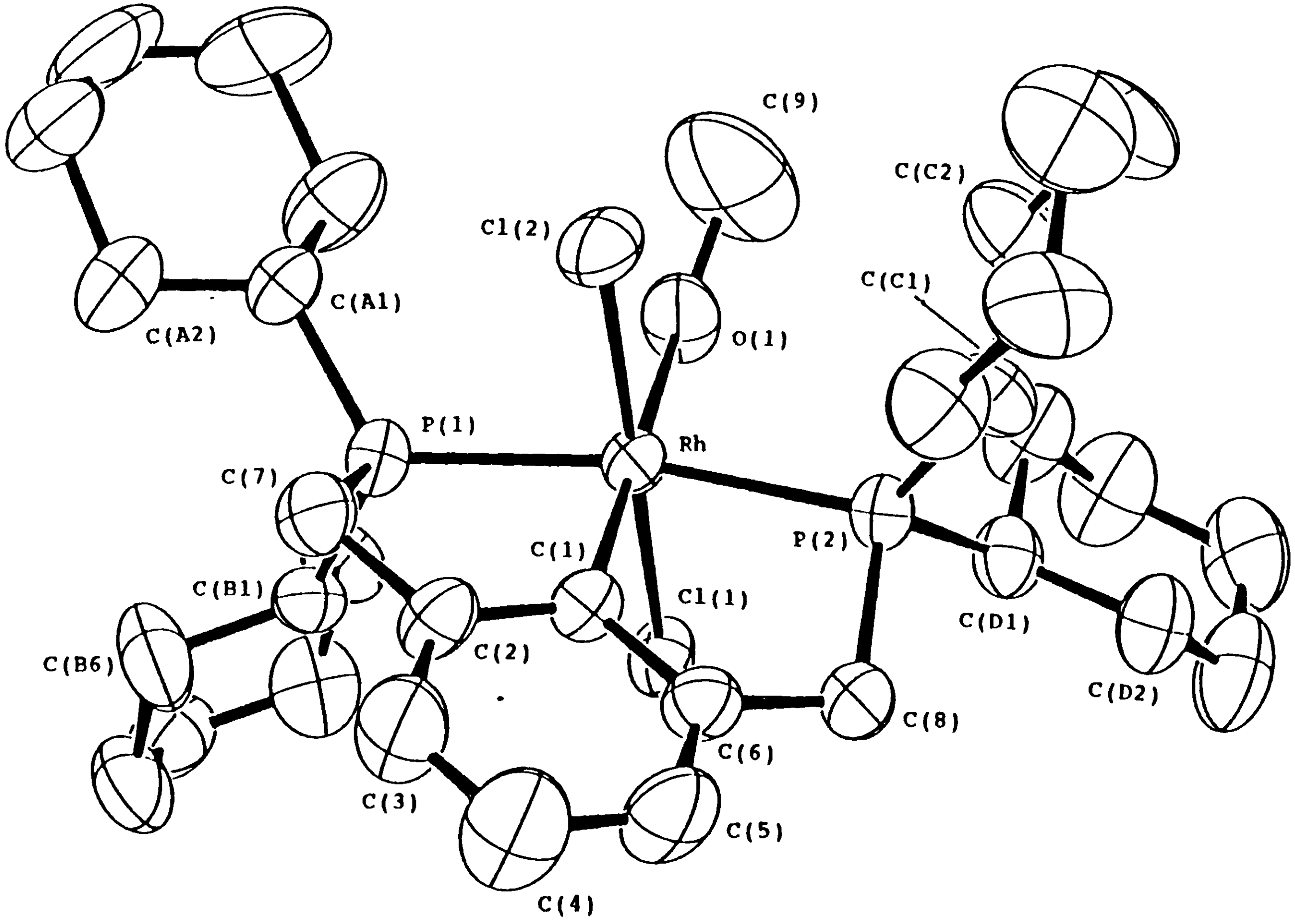

Fig.3,4viii Structure of $[RhCl_2(PCP)(MeOH)].0.41CH_2Cl_2$.

planar [MX(PCP)] species. Thus, the PCy_2R fragments are twisted into a staggered conformation which results in an angle of 14.8° between the aromatic ring plane and the coordination plane Rh P(1) P(2) O(1) C(1). The torsion angles given in Table 3, 4iii also show this and the greater puckering of the five-membered chelate rings compared with those in the [MX(PCP)] compounds. Further indication that the chelate system is strained comes from the closing of the Rh-P(1)-C(7) and Rh-P(2)-C(8) angles to 98.7(3) and 98.5(3)° respectively (Table 3, 4xxi).

In the absence of hydrogen bonding to the chlorine ligands, as seen in the aqua and ethanol analogues, the Rh-Cl distances of 2.342(3) and 2.347(3) Å are essentially identical and are consistent with the non-hydrogen-bonded Rh-Cl distances in these analogues. The Rh-P(1) and Rh-P(2) bond lengths of 2.346(3) and 2.361(3) Å differ by only 0.016(4) Å. The Rh-C distance of 1.984(8) Å is in good agreement with the Rh-C distances in the aqua and ethanol analogues (Sections 3, 4e and 3, 4k). The Rh-O distance of 2.239(7) Å is shorter than in the above analogues but only by *ca.* 0.03 Å. The possible significance of this is discussed in Section 3, 4l. The torsion angles P(1)-Rh-O(1)-C(9) and P(2)-Rh-O(1)-C(9) are 109.8(10) and -71.8(10)° respectively. A search of the Cambridge Structural Database found no previous structures of Rh^{III} compounds with methanol ligands* and only one square-planar Rh^{I} structure (Table 3, 4xvi), that of $[RhCl(CO)(\mu\text{-}Ph_2P(C_5NH_3)PPh_2)(CO)(HOMe)Rh][PF_6]$[70] in which the Rh-O bond length, *trans* to a carbonyl ligand, is 2.144(6) Å,

Table 3,4xiv Bond lengths (Å) for $[RhCl_2(PCP)(MeOH)].0.\ 41CH_2Cl_2$.

Rh - Cl(1)	2.342(3)	Rh - Cl(2)	2.347(3)
Rh - P(1)	2.346(3)	Rh - P(2)	2.361(3)
Rh - O(1)	2.239(7)	Rh - C(1)	1.984(8)
P(1) - C(7)	1.827(9)	P(1) - C(A1)	1.818(10)
P(1) - C(B1)	1.839(9)	P(2) - C(8)	1.842(9)
P(2) - C(C1)	1.846(9)	P(2) - C(D1)	1.845(9)
O(1) - C(9)	1.407(17)	C(1) - C(2)	1.390(12)
C(1) - C(6)	1.413(12)	C(2) - C(3)	1.368(14)
C(2) - C(7)	1.519(13)	C(3) - C(4)	1.340(17)
C(4) - C(5)	1.381(16)	C(5) - C(6)	1.365(13)
C(6) - C(8)	1.515(12)	C(A1) - C(A2)	1.501(15)
C(A1) - C(A6)	1.546(15)	C(A2) - C(A3)	1.525(19)
C(A3) - C(A4)	1.444(21)	C(A4) - C(A5)	1.494(24)
C(A5) - C(A6)	1.544(17)	C(B1) - C(B2)	1.523(13)
C(B1) - C(B6)	1.522(13)	C(B2) - C(B3)	1.527(15)
C(B3) - C(B4)	1.485(16)	C(B4) - C(B5)	1.528(17)
C(B5) - C(B6)	1.519(16)	C(C1) - C(C2)	1.523(15)
C(C1) - C(C6)	1.476(14)	C(C2) - C(C3)	1.561(16)
C(C3) - C(C4)	1.429(18)	C(C4) - C(C5)	1.501(21)
C(C5) - C(C6)	1.507(16)	C(D1) - C(D2)	1.500(13)
C(D1) - C(D6)	1.518(14)	C(D2) - C(D3)	1.521(15)
C(D3) - C(D4)	1.496(18)	C(D4) - C(D5)	1.475(18)
C(D5) - C(D6)	1.524(14)	Cl(3) - C(S)	1.859
Cl(4) - C(S)	1.781	Cl(5) - C(S)	1.862
Cl(6) - C(S)	1.886		

Table 3,4xv Bond angles (°) for $[RhCl_2(PCP)(MeOH)].0.\ 41CH_2Cl_2$.

Cl(1)-Rh-Cl(2)	178.0(1)	Cl(1)-Rh-P(1)	93.9(1)
Cl(1)-Rh-P(2)	84.9(1)	Cl(1)-Rh-O(1)	88.1(2)
Cl(1)-Rh-C(1)	90.4(3)	Cl(2)-Rh-P(1)	85.2(1)
Cl(2)-Rh-P(2)	96.4(1)	Cl(2)-Rh-O(1)	90.2(2)
Cl(2)-Rh-C(1)	91.2(3)	P(1)-Rh-P(2)	166.1(1)
P(1)-Rh-O(1)	96.8(2)	P(1)-Rh-C(1)	82.6(3)
P(2)-Rh-O(1)	97.0(2)	P(2)-Rh-C(1)	83.5(3)
O(1)-Rh-C(1)	178.4(3)	Rh-P(1)-C(7)	98.7(3)
Rh-P(1)-C(A1)	120.7(4)	Rh-P(1)-C(B1)	115.1(3)
C(7)-P(1)-C(A1)	103.2(5)	C(7)-P(1)-C(B1)	105.3(4)
C(A1)-P(1)-C(B1)	110.8(5)	Rh-P(2)-C(8)	98.5(3)
Rh-P(2)-C(C1)	121.9(3)	Rh-P(2)-C(D1)	119.7(3)
C(8)-P(2)-C(C1)	103.9(5)	C(8)-P(2)-C(D1)	102.4(5)
C(C1)-P(2)-C(D1)	106.7(4)	Rh-O(1)-C(9)	128.4(9)
Rh-C(1)-C(2)	122.2(7)	Rh-C(1)-C(6)	121.0(6)
C(2)-C(1)-C(6)	116.7(8)	C(1)-C(2)-C(3)	121.1(9)
C(1)-C(2)-C(7)	118.2(8)	C(3)-C(2)-C(7)	120.6(9)
C(2)-C(3)-C(4)	121.3(10)	C(3)-C(4)-C(5)	119.9(11)
C(4)-C(5)-C(6)	120.1(10)	C(1)-C(6)-C(5)	120.8(9)
C(1)-C(6)-C(8)	119.3(8)	C(5)-C(6)-C(8)	119.7(8)
P(1)-C(7)-C(2)	108.7(6)	P(2)-C(8)-C(6)	108.0(6)
P(1)-C(A1)-C(A2)	117.7(8)	P(1)-C(A1)-C(A6)	115.9(7)
C(A2)-C(A1)-C(A6)	111.6(9)	C(A1)-C(A2)-C(A3)	112.4(10)
C(A2)-C(A3)-C(A4)	113.7(12)	C(A3)-C(A4)-C(A5)	113.2(13)
C(A4)-C(A5)-C(A6)	114.3(11)	C(A1)-C(A6)-C(A5)	111.8(10)
P(1)-C(B1)-C(B2)	111.1(6)	P(1)-C(B1)-C(B6)	118.9(7)
C(B2)-C(B1)-C(B6)	112.6(8)	C(B1)-C(B2)-C(B3)	109.9(9)
C(B2)-C(B3)-C(B4)	110.4(9)	C(B3)-C(B4)-C(B5)	112.0(9)
C(B4)-C(B5)-C(B6)	110.0(10)	C(B1)-C(B6)-C(B5)	109.8(8)
P(2)-C(C1)-C(C2)	112.3(7)	P(2)-C(C1)-C(C6)	114.5(7)
C(C2)-C(C1)-C(C6)	112.7(8)	C(C1)-C(C2)-C(C3)	110.4(9)
C(C2)-C(C3)-C(C4)	114.2(11)	C(C3)-C(C4)-C(C5)	113.2(12)
C(C4)-C(C5)-C(C6)	112.7(10)	C(C1)-C(C6)-C(C5)	112.0(9)
P(2)-C(D1)-C(D2)	115.2(6)	P(2)-C(D1)-C(D6)	114.0(7)
C(D2)-C(D1)-C(D6)	110.7(8)	C(D1)-C(D2)-C(D3)	111.0(8)
C(D2)-C(D3)-C(D4)	113.4(11)	C(D3)-C(D4)-C(D5)	111.2(10)
C(D4)-C(D5)-C(D6)	114.1(9)	C(D1)-C(D6)-C(D5)	109.4(9)
Cl(3)-C(S)-Cl(4)	113.8	Cl(5)-C(S)-Cl(6)	112.7

TABLE 3, 4xvi

Rh-O BOND DISTANCES IN KNOWN STRUCTURES OF Rh-ALCOHOL COMPLEXES.

COMPLEX	OX. NO., COORD. NO.	TRANS ATOM	Rh-O (Å)	Ref.
$[Rh(CO)(Ph_2P(C_2H_40)_2C_2H_4PPh_2)(HOEt)]$ $[PF_6]$	I , 4	C	2.180(1)	73
$[RhCl(CO)(Ph_2P(C_6NH_3)PPh_2)_2(CO)(HOMe)Rh]$ $[PF_6]$	I , 4	C	2.144(6)	70
$[RhCl_2(PCP)(HOEt)].OH_2$	III, 6	C	2.264(6)	This work
$[RhCl_2(PCP)(HOMe)].xCH_2Cl_2$	III, 6	C	2.239(7)	This work
$[Br_4Rh(CO)(HOEt)][PPh_3Bu^n]$	III, 6	C	2.118(4)	72
"	III, 6	C	2.087(2)	72

considerably less than the corresponding value for $[RhCl_2(PCP)(HOMe)].0.41CH_2Cl_2$.

The CH_2Cl_2 solvent molecule is only partially present: its occupancy refined to 0.414(6), and it is disordered over two sites by rotation about an axis passing through the carbon atom. One chlorine from each of the two solvent conformations is hydrogen-bonded to the methanol ligand via the hydroxyl hydrogen atom. Hydrogen-bonding distances and angles are given in Table 3, 4xii.

* N.B. The structure of the Rh^{III} anion $[I_2Cl(CO)Rh(\mu\text{-}I)_2RhI_2(CO)(HOMe)]^-$ has been reported from a small crystal using synchrotron radiation[71] but the Rh-O distance is not reported and the methanol position is noted to be unreliable.

3, 4g STRUCTURE OF $[RhCl_2\{(PCy_2CH_2)_2(C_6H_3)\}(HOEt)].H_2O$.

As in the aqua and methanol analogues the coordination geometry about rhodium is essentially octahedral with mutually *trans* chlorine ligands lying *cis* to the chelate ligand. The ethanol molecule fills the sixth coordination site *trans* to the σ-bonding carbon atom. The principle deviation from octahedral geometry is the closure of the P(1)-Rh-P(2) angle

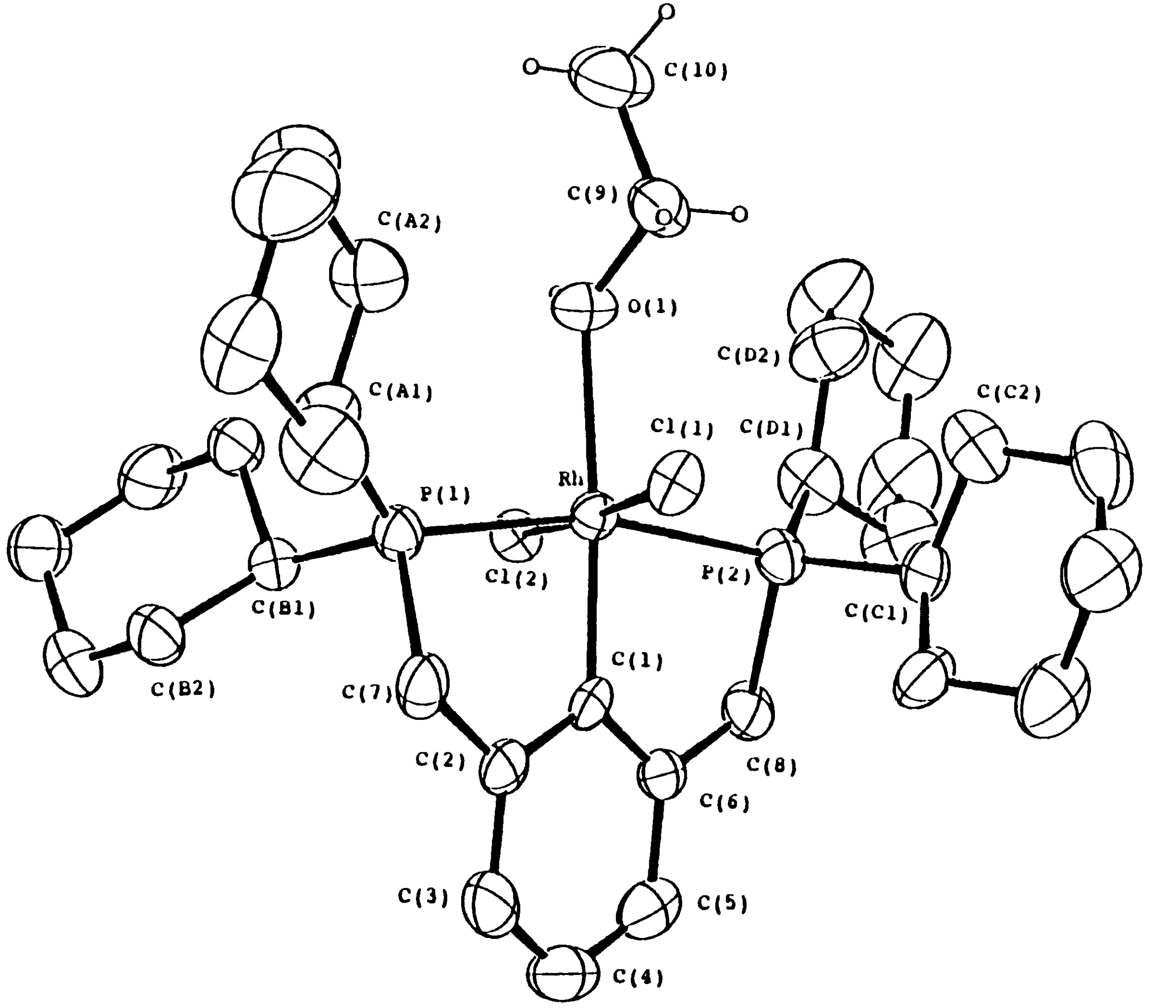

Fig.3,4ix Structure of [$RhCl_2$(PCP)(EtOH)].H_2O.

to 164.5(1)°, due to the intrinsically small bite angle of the PCP ligand. An ORTEP drawing of the complex is shown in Fig. 3, 4ix and bond lengths and angles are given in Tables 3, 4xvii and xviii. The ethanol ligand is bulkier than both methanol and water and it may be this that leads to larger distortions in the chelate ligand conformation away from the symmetrical, eclipsed geometry seen in the square-planar [MX(PCP)] complexes. Fig. 3, 4x illustrates this, with the atoms drawn as spheres of arbitrary size for clarity. The angle between the coordination plane Rh P(1) P(2) O(1) C(1) and the plane of the aromatic ring is thereby opened to 19.5° with corresponding puckering of the two five-membered chelate rings, as is evident from study of the torsion angles given in Table 3, 4iii.

The Rh-P distances of 2.363(3) and 2.357(3) Å are essentially identical but the Rh-Cl distances of 2.354(3) and 2.375(3) Å are not, probably because of the hydrogen-bonding interaction between Cl(2) and a solvent water molecule (see Table 3, 4xii). Both the Rh-P distances and the Rh-Cl distances are in good agreement with those found in the aqua and methanol analogues. The Rh-C(1) distance of 2.008(8) Å is identical, to within experimental error, to that of the aqua species and also to those in the square-pyramidal species $[RhPhCl_2(PPh_3)_2]$[61] and $[RhHCl\{(PBu^t_2CH_2)_2(C_6H_3)\}]$.[45] The Rh-O(1) distance is 2.264(6) Å and this is only 0.010(7) Å shorter than the Rh-O bond length in the aqua complex $[RhCl_2(PCP)(OH_2)]$.propan-2-ol. This indicates that there is very little difference between the two bond types. The Rh-O bond in the

Table 3,4xvii Bond lengths (Å) for [RhCl$_2$(PCP)(EtOH)].H$_2$O.

Rh - Cl(1)	2.354(3)	Rh - Cl(2)	2.375(3)
Rh - P(1)	2.363(3)	Rh - P(2)	2.357(3)
Rh - O(1)	2.264(6)	Rh - C(1)	2.008(8)
P(1) - C(7)	1.818(10)	P(1) - C(A1)	1.843(11)
P(1) - C(B1)	1.827(10)	P(2) - C(8)	1.832(10)
P(2) - C(C1)	1.824(10)	P(2) - C(D1)	1.870(11)
O(1) - C(9)	1.434(11)	O(1) - H(O1)	1.146(7)
C(1) - C(2)	1.429(13)	C(1) - C(6)	1.363(13)
C(2) - C(3)	1.393(13)	C(2) - C(7)	1.511(14)
C(3) - C(4)	1.359(17)	C(4) - C(5)	1.377(16)
C(5) - C(6)	1.411(13)	C(6) - C(8)	1.521(14)
C(9) - C(10)	1.489(15)	C(A1) - C(A2)	1.502(14)
C(A1) - C(A6)	1.477(16)	C(A2) - C(A3)	1.515(17)
C(A3) - C(A4)	1.504(19)	C(A4) - C(A5)	1.504(19)
C(A5) - C(A6)	1.541(17)	C(B1) - C(B2)	1.542(14)
C(B1) - C(B6)	1.535(13)	C(B2) - C(B3)	1.527(16)
C(B3) - C(B4)	1.505(15)	C(B4) - C(B5)	1.530(16)
C(B5) - C(B6)	1.523(14)	C(C1) - C(C2)	1.553(14)
C(C1) - C(C6)	1.535(14)	C(C2) - C(C3)	1.505(15)
C(C3) - C(C4)	1.536(17)	C(C4) - C(C5)	1.502(16)
C(C5) - C(C6)	1.523(14)	C(D1) - C(D2)	1.497(15)
C(D1) - C(D6)	1.508(17)	C(D2) - C(D3)	1.533(18)
C(D3) - C(D4)	1.472(20)	C(D4) - C(D5)	1.506(21)
C(D5) - C(D6)	1.522(19)		

Table 3,4xviii Bond angles (°) for $[RhCl_2(PCP)(EtOH)].H_2O$

Cl(1)-Rh-Cl(2)	177.1(1)	Cl(1)-Rh-P(1)	85.0(1)
Cl(1)-Rh-P(2)	95.8(1)	Cl(1)-Rh-O(1)	90.7(2)
Cl(1)-Rh-C(1)	94.1(3)	Cl(2)-Rh-P(1)	94.0(1)
Cl(2)-Rh-P(2)	85.9(1)	Cl(2)-Rh-O(1)	86.7(2)
Cl(2)-Rh-C(1)	88.4(3)	P(1)-Rh-P(2)	164.5(1)
P(1)-Rh-O(1)	95.6(2)	P(1)-Rh-C(1)	82.5(3)
P(2)-Rh-O(1)	99.8(2)	P(2)-Rh-C(1)	82.1(3)
O(1)-Rh-C(1)	174.7(3)	Rh-P(1)-C(7)	98.2(4)
Rh-P(1)-C(A1)	125.4(4)	Rh-P(1)-C(B1)	114.7(4)
C(7)-P(1)-C(A1)	107.0(5)	C(7)-P(1)-C(B1)	105.7(5)
C(A1)-P(1)-C(B1)	104.0(5)	Rh-P(2)-C(8)	98.3(4)
Rh-P(2)-C(C1)	122.6(4)	Rh-P(2)-C(D1)	118.7(4)
C(8)-P(2)-C(C1)	104.3(5)	C(8)-P(2)-C(D1)	101.0(5)
C(C1)-P(2)-C(D1)	107.6(5)	Rh-O(1)-C(9)	126.6(6)
Rh-O(1)-H(O1)	109.1(4)	C(9)-O(1)-H(O1)	116.7(6)
Rh-C(1)-C(2)	119.4(7)	Rh-C(1)-C(6)	121.5(7)
C(2)-C(1)-C(6)	119.0(8)	C(1)-C(2)-C(3)	118.3(9)
C(1)-C(2)-C(7)	119.0(8)	C(3)-C(2)-C(7)	122.6(9)
C(2)-C(3)-C(4)	122.1(10)	C(3)-C(4)-C(5)	119.7(9)
C(4)-C(5)-C(6)	119.8(10)	C(1)-C(6)-C(5)	120.9(9)
C(1)-C(6)-C(8)	119.5(8)	C(5)-C(6)-C(8)	119.5(9)
P(1)-C(7)-C(2)	107.0(7)	P(2)-C(8)-C(6)	108.5(7)
O(1)-C(9)-C(10)	111.9(8)	P(1)-C(A1)-C(A2)	113.4(8)
P(1)-C(A1)-C(A6)	117.0(8)	C(A2)-C(A1)-C(A6)	112.5(9)
C(A1)-C(A2)-C(A3)	113.9(10)	C(A2)-C(A3)-C(A4)	112.1(10)
C(A3)-C(A4)-C(A5)	114.7(11)	C(A4)-C(A5)-C(A6)	111.5(10)
C(A1)-C(A6)-C(A5)	112.9(10)	P(1)-C(B1)-C(B2)	116.1(7)
P(1)-C(B1)-C(B6)	111.8(7)	C(B2)-C(B1)-C(B6)	109.6(8)
C(B1)-C(B2)-C(B3)	109.7(9)	C(B2)-C(B3)-C(B4)	111.8(9)
C(B3)-C(B4)-C(B5)	111.7(10)	C(B4)-C(B5)-C(B6)	110.6(9)
C(B1)-C(B6)-C(B5)	111.7(8)	P(2)-C(C1)-C(C2)	114.4(7)
P(2)-C(C1)-C(C6)	111.9(7)	C(C2)-C(C1)-C(C6)	110.0(8)
C(C1)-C(C2)-C(C3)	111.8(9)	C(C2)-C(C3)-C(C4)	112.4(10)
C(C3)-C(C4)-C(C5)	109.9(9)	C(C4)-C(C5)-C(C6)	112.0(10)
C(C1)-C(C6)-C(C5)	112.6(9)	P(2)-C(D1)-C(D2)	116.3(8)
P(2)-C(D1)-C(D6)	115.6(8)	C(D2)-C(D1)-C(D6)	109.5(10)
C(D1)-C(D2)-C(D3)	112.7(10)	C(D2)-C(D3)-C(D4)	111.9(11)
C(D3)-C(D4)-C(D5)	111.5(12)	C(D4)-C(D5)-C(D6)	113.7(11)
C(D1)-C(D6)-C(D5)	110.6(10)		

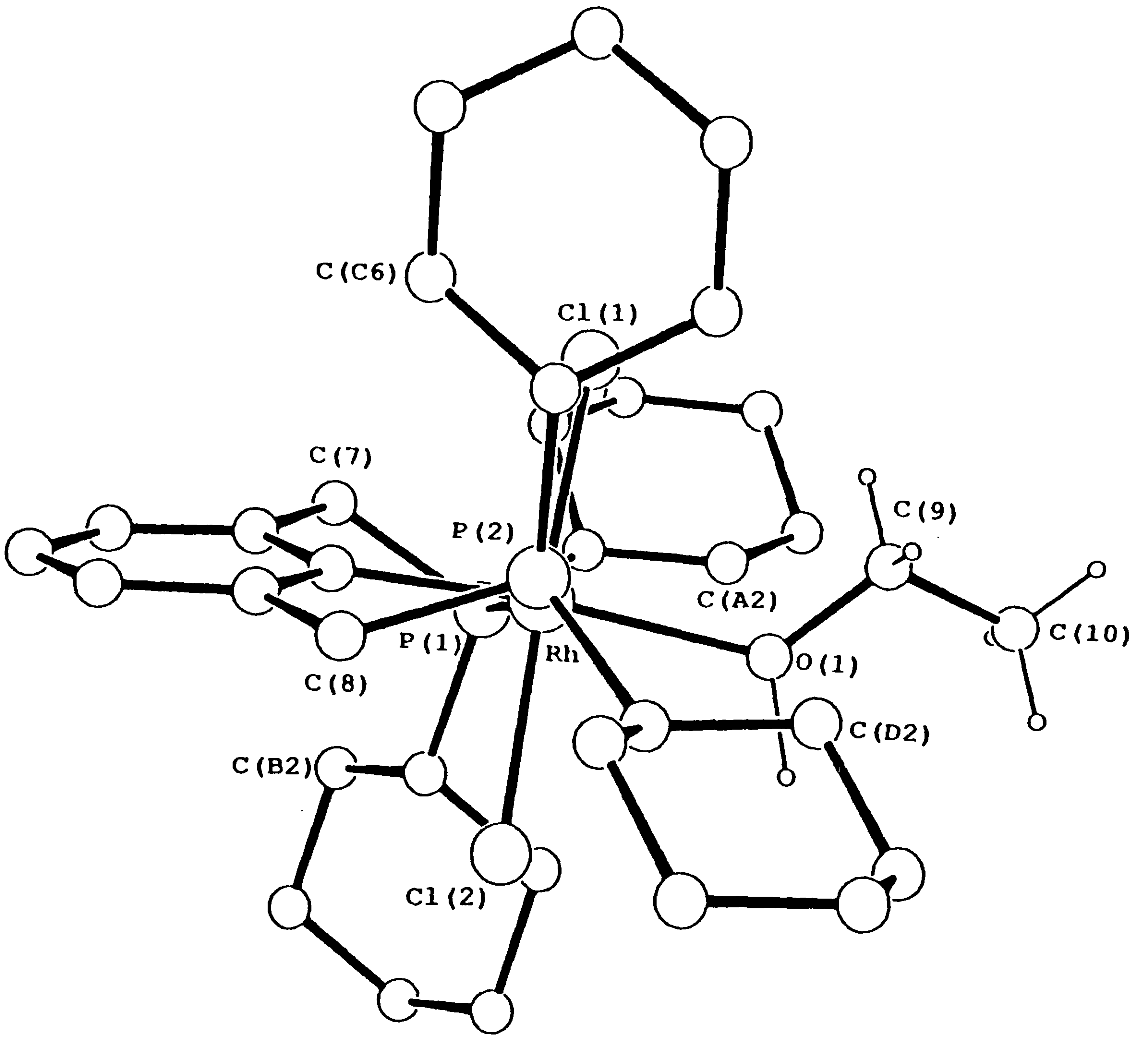

Fig.3,4x [$RhCl_2$(PCP)(EtOH)].H_2O viewed along the P(1)-Rh-P(2) axis.

corresponding methanol complex is 2.239(7) Å or 0.025(9) Å shorter. Again there is little evidence of a significant difference. The literature gives only one other example of a crystal structure involving a Rh^{III} complex with coordinated ethanol, the ionic species $[Rh(CO)(HOEt)Br_4][PPh_3Bu^n]$.[72] This compound has two separate anion geometries giving Rh-O bond lengths of 2.118(4) and 2.087(2) Å (Table 3, 4xvi). The table also shows that one Rh^I ethanol complex has had its crystal structure determined.[73] The Rh-O distance is again much shorter than in $[RhCl_2(PCP)(HOEt)].H_2O$. None of the complexes listed in Table 3, 4xvi, however, are comparable to the PCP complex. This is discussed further in Section 3, 4j. The ethanol ligand is hydrogen-bonded to the solvent water molecule via the hydrogen of the hydroxyl group as detailed in Table 3, 4xii.

The ethanol ligand is not quite perpendicular to the coordination plane Rh P(1) P(2) O(1) C(1) as is shown by the torsion angles P(1)-Rh-O(1)-C(9) and P(2)-Rh-O(1)-C(9) of 118.8(7) and -69.3(7)°, respectively. The internal geometric parameters of the ethanol ligand appear unexceptional with the O(1)-C(9) distance of 1.434(15) Å being equal to the average C-O distance of 1.436 Å found for 196 examples of coordinated ethanols.[64]

3, 4h STRUCTURE OF $[RhCl_2\{PCy_2CH_2)_2(C_6H_3)\}(HOEt)]$.

As can be seen from Fig. 3, 4xi and Tables 3, 4xix and 3, 4xx the geometry of this complex is similar to that of $[RhCl_2(PCP)(HOEt)].H_2O$. The crystals however are not isomorphous, indicating that the water molecules do not merely fill vacancies in the anhydrous crystals structure but do, presumably through hydrogen-bonding (see Section 3, 4g), influence the crystal packing.

As the structure analysis of the hydrated crystal is more accurate than that of the anhydrous complex and as the structures of the two rhodium complexes are generally similar, further discussion of the geometry of $[RhCl_2(PCP)(HOEt)]$ is confined to that found in the hydrate. One difference between the two structures is, however, worth noting. In the anhydrous structure the Rh-O bond length is 2.337(17) Å. This is longer than any other Rh-O bond length given in Tables 3, 4xvi and 3, 4xiii for Rh-alcohol or $Rh-OH_2$ complexes. It is felt however that the limitations of the analysis make any conclusions from this bond length unreliable.

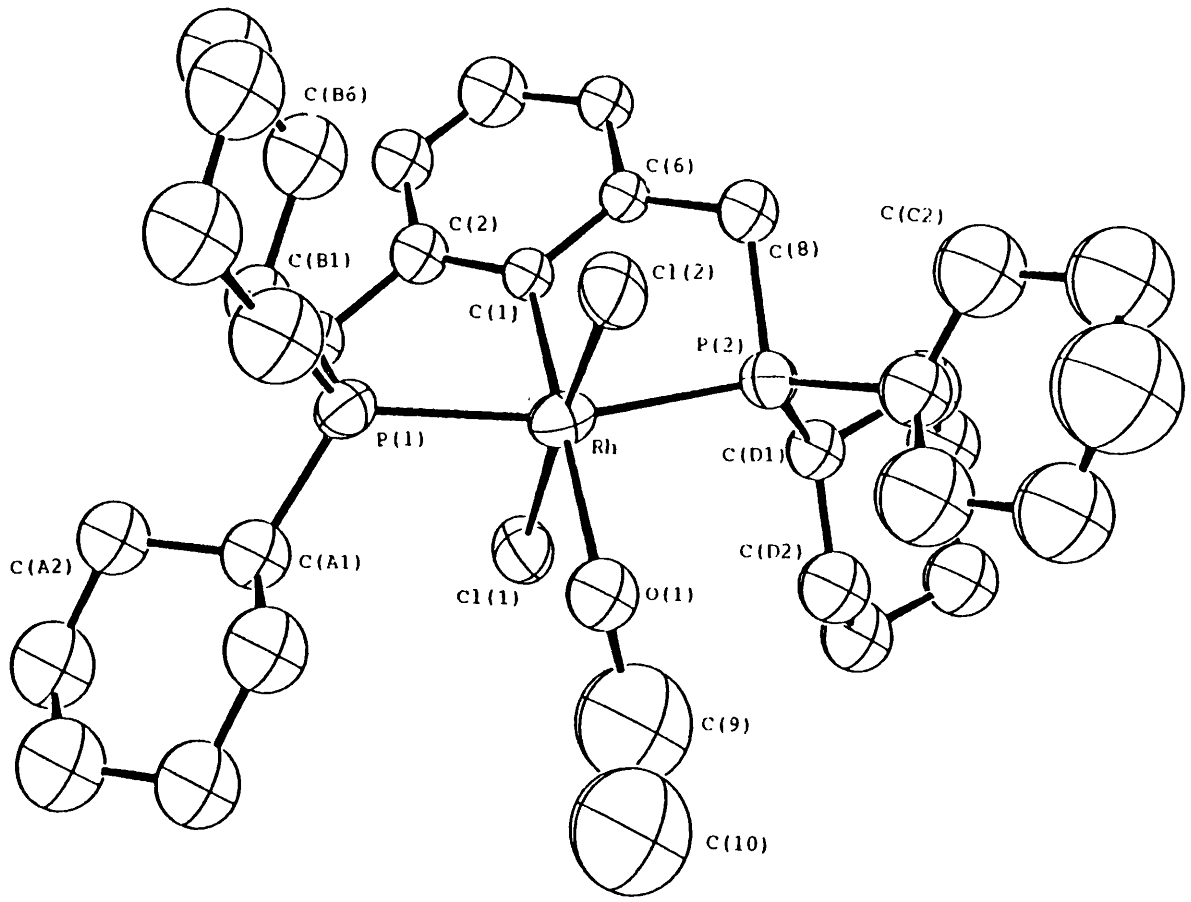

Fig.3,4xi Structure of $[RhCl_2(PCP)(EtOH)]$.

Table 3,4xix Bond lengths (Å) for [RhCl$_2$(PCP)(EtOH)].

Rh - Cl(1)	2.347(8)	Rh - Cl(2)	2.370(8)
Rh - P(1)	2.335(8)	Rh - P(2)	2.365(8)
Rh - O(1)	2.337(17)	Rh - C(1)	1.985(25)
P(1) - C(7)	1.823(25)	P(1) - C(A1)	1.80(3)
P(1) - C(B1)	1.865(25)	P(2) - C(8)	1.835(28)
P(2) - C(C1)	1.853(28)	P(2) - C(D1)	1.855(25)
O(1) - C(9)	1.45(5)	C(1) - C(2)	1.38(4)
C(1) - C(6)	1.43(4)	C(2) - C(3)	1.36(4)
C(2) - C(7)	1.54(4)	C(3) - C(4)	1.36(5)
C(4) - C(5)	1.38(4)	C(5) - C(6)	1.41(4)
C(6) - C(8)	1.50(4)	C(9) - C(10)	1.40(6)
C(A1) - C(A2)	1.57(4)	C(A1) - C(A6)	1.49(5)
C(A2) - C(A3)	1.52(5)	C(A3) - C(A4)	1.49(5)
C(A4) - C(A5)	1.51(5)	C(A5) - C(A6)	1.54(5)
C(B1) - C(B2)	1.57(5)	C(B1) - C(B6)	1.54(5)
C(B2) - C(B3)	1.58(5)	C(B3) - C(B4)	1.47(6)
C(B4) - C(B5)	1.48(5)	C(B5) - C(B6)	1.56(5)
C(C1) - C(C2)	1.43(5)	C(C1) - C(C6)	1.51(5)
C(C2) - C(C3)	1.55(5)	C(C3) - C(C4)	1.52(6)
C(C4) - C(C5)	1.39(6)	C(C5) - C(C6)	1.50(5)
C(D1) - C(D2)	1.50(4)	C(D1) - C(D6)	1.51(4)
C(D2) - C(D3)	1.54(4)	C(D3) - C(D4)	1.48(5)
C(D4) - C(D5)	1.55(5)	C(D5) - C(D6)	1.55(4)

Table 3,4xx Bond angles (°) for [$\mathrm{RhCl_2}$(PCP)(EtOH)].

Cl(1)-Rh-Cl(2)	175.1(3)	Cl(1)-Rh-P(1)	85.0(3)
Cl(1)-Rh-P(2)	94.8(3)	Cl(1)-Rh-O(1)	93.7(5)
Cl(1)-Rh-C(1)	88.8(8)	Cl(2)-Rh-P(1)	97.0(3)
Cl(2)-Rh-P(2)	84.6(3)	Cl(2)-Rh-O(1)	81.6(5)
Cl(2)-Rh-C(1)	95.9(8)	P(1)-Rh-P(2)	163.8(3)
P(1)-Rh-O(1)	98.3(5)	P(1)-Rh-C(1)	80.8(8)
P(2)-Rh-O(1)	97.8(5)	P(2)-Rh-C(1)	83.0(8)
O(1)-Rh-C(1)	177.3(8)	Rh-P(1)-C(7)	99.7(8)
Rh-P(1)-C(A1)	119.6(9)	Rh-P(1)-C(B1)	122.6(9)
C(7)-P(1)-C(A1)	101.7(13)	C(7)-P(1)-C(B1)	103.0(12)
C(A1)-P(1)-C(B1)	106.2(12)	Rh-P(2)-C(8)	97.2(8)
Rh-P(2)-C(C1)	125.5(10)	Rh-P(2)-C(D1)	117.2(9)
C(8)-P(2)-C(C1)	105.3(13)	C(8)-P(2)-C(D1)	104.8(12)
C(C1)-P(2)-C(D1)	104.0(12)	Rh-O(1)-C(9)	120.0(19)
Rh-C(1)-C(2)	123.1(20)	Rh-C(1)-C(6)	120.4(17)
C(2)-C(1)-C(6)	116.2(23)	C(1)-C(2)-C(3)	121.4(26)
C(1)-C(2)-C(7)	118.0(24)	C(3)-C(2)-C(7)	120.5(23)
C(2)-C(3)-C(4)	121.1(25)	C(3)-C(4)-C(5)	122.8(26)
C(4)-C(5)-C(6)	115.4(23)	C(1)-C(6)-C(5)	122.8(21)
C(1)-C(6)-C(8)	117.7(22)	C(5)-C(6)-C(8)	119.2(22)
P(1)-C(7)-C(2)	106.3(17)	P(2)-C(8)-C(6)	107.6(19)
O(1)-C(9)-C(10)	111.3(31)	P(1)-C(A1)-C(A2)	116.1(19)
P(1)-C(A1)-C(A6)	116.0(21)	C(A2)-C(A1)-C(A6)	106.5(22)
C(A1)-C(A2)-C(A3)	111.2(22)	C(A2)-C(A3)-C(A4)	113.3(26)
C(A3)-C(A4)-C(A5)	111.7(26)	C(A4)-C(A5)-C(A6)	111.6(25)
C(A1)-C(A6)-C(A5)	116.0(25)	P(1)-C(B1)-C(B2)	112.3(18)
P(1)-C(B1)-C(B6)	111.3(18)	C(B2)-C(B1)-C(B6)	105.9(22)
C(B1)-C(B2)-C(B3)	110.2(23)	C(B2)-C(B3)-C(B4)	109.6(26)
C(B3)-C(B4)-C(B5)	114.1(29)	C(B4)-C(B5)-C(B6)	109.2(26)
C(B1)-C(B6)-C(B5)	111.0(24)	P(2)-C(C1)-C(C2)	118.2(22)
P(2)-C(C1)-C(C6)	118.0(22)	C(C2)-C(C1)-C(C6)	113.4(26)
C(C1)-C(C2)-C(C3)	117.6(27)	C(C2)-C(C3)-C(C4)	109.2(30)
C(C3)-C(C4)-C(C5)	114.5(35)	C(C4)-C(C5)-C(C6)	113.1(31)
C(C1)-C(C6)-C(C5)	114.3(27)	P(2)-C(D1)-C(D2)	113.0(18)
P(2)-C(D1)-C(D6)	113.3(19)	C(D2)-C(D1)-C(D6)	111.1(21)
C(D1)-C(D2)-C(D3)	111.0(22)	C(D2)-C(D3)-C(D4)	111.4(24)
C(D3)-C(D4)-C(D5)	109.9(23)	C(D4)-C(D5)-C(D6)	111.3(23)
C(D1)-C(D6)-C(D5)	109.9(23)		

3, 4i CONFORMATIONS OF THE PCP LIGAND.

The six structures containing the PCP ligand clearly show a variety of conformations of the chelate ligand. Thus, in [NiBr(PCP)] the aromatic ring coincides with the coordination plane of the metal and the cyclohexyl rings adopt a mutually eclipsed arrangement, while in the [$RhCl_2$(PCP)(HOEt)].H_2O complex the aromatic ring has twisted away by 19.5° from coplanarity with the metal coordination plane and the staggered cyclohexyl rings are pulled out and back from the site of the ligand *trans* to the σ-bonded carbon. This change in conformation is illustrated by Figs. 3, 4ii and 3, 4x.

These changes in geometry are best quantified by the torsion angles around the chelate rings which are listed in Table 3, 4iii and by the bond angles given in Table 3, 4xxi.

Table 3, 4xxi. Selected Angles (°) of PCP Containing Complexes.

COMPLEX	x*	P-M-P	M-P(1)-C(7)	M-P(2)-C(8)
"IDEAL"	0	180	≈115	≈115
[NiBr(PCP)]	4.1	167.6(1)	103.6(2)	105.0(2)
[PdBr(PCP)]	5.0	165.6(1)	102.4(3)	104.2(3)
[PdCl(PCP)]	5.0	165.5(1)	102.6(2)	104.1(3)
[$RhCl_2(PCP)(OH_2)$] .propan-2-ol	14.6	165.8(1)	99.3(2)	98.6(2)
[$RhCl_2$(PCP)(HOMe)] .xCH_2Cl_2	14.8	166.1(1)	98.7(3)	98.5(3)
[$RhCl_2$(PCP)(HOEt)] .OH_2	19.5	164.5(1)	98.2(4)	98.3(4)

* The dihedral angle between the σ-bonded aryl ring and the MP_2CL coordination plane is denoted by x.

All other bond lengths and angles of the chelate system appear normal and do not vary greatly over the six complexes. Table 3, 4xxi also contains angles for a hypothetical idealised square-planar complex, where the aromatic ring is exactly coplanar with the coordination plane of the metal and where the M-P-C angles are those typical of tertiary phosphine complexes.

It is clear from the study of Tables 3, 4iii and xxi that [NiBr(PCP)], [PdBr(PCP)] and [PdCl(PCP)] all have nearly the same PCP conformation. The two palladium species are isostructural and so changing Br for Cl appears not to affect the PCP geometry. Neither does the geometry appear to be greatly affected by changing from Pd to the smaller Ni. Thus within these limits, metal size does not appear to be important to the conformation of PCP.

A major conformational change of the ligand does however occur on moving to the octahedral Rh^{III} species. The conformations of PCP in the aqua and methanol species are, by examination of Tables 3, 4iii and xxi, very similar. The differences between this conformation and that found for the square-planar conformation are shown by (i) the increased angle between the plane of the aromatic ring and the coordination plane M P(1) P(2) C(1) L, (ii) the generally increased magnitudes of the torsion angles within the five-membered chelate rings (Table 3, 4iii) and (iii) the changes in sign of these torsion angles. Additionally the closure (by ≈ 5°) of the M-P-C angles (tables 3, 4xxi) indicates that this new conformation of the PCP ligand introduces more ring strain into the chelate system. The conformation of PCP in the ethanol-Rh complex is similar to that in the aqua and methanol analogues but the twist in the ligand is greater, giving more extreme values for both bond angles and torsion angles.

It seems unlikely that the change in conformation of the ligand is due to changing from Pd(II) and Ni(II) to Rh(III), as it was shown above that changing from Pd(II) to Ni(II) made little difference. The change in conformation must thus come about from the greater spatial demands of the other ligands in the octahedral as compared to the square-planar complexes. It is impossible to say whether the two chlorine ligands *cis* to the chelate or the large, polyatomic ligands *trans* to the aromatic ring have the greater effect on PCP geometry. It is evident, however, from Fig. 3, 4i that the four bulky cyclohexyl rings appear to project away from the axial positions that the chlorine ligands would occupy and that they cluster around the site of the ligand *trans* to the aromatic ring. Also, it seems likely that the increased bulk of the EtOH ligand, compared to water or methanol, causes the extra distortions seen in $[RhCl_2(PCP)(HOEt)].H_2O$.

That the large distortions in PCP geometry caused by the ethanol ligand are indicative of stress in the complex is further illustrated by the experimental failure to synthesise $[RhCl_2(PCP)S]$ (S = acetone, propan-2-ol). In compounds where steric restraints are absent the ligation strength of these two ligands is comparable to that of ethanol[74] but with the PCP-containing substrate they appear to be too large to coordinate.

Two previous crystal structures of complexes containing PCP-type ligands have been reported. Data in refs. 44 and 45 have been used to calculate the dihedral angles, x, between the phenyl and MP_2CL coordination planes; the values are 11.4° for $[Pt(COOH)\{(Ph_2PCH_2)_2(C_6H_3)\}]$ and 6.9° for square-pyramidal $[RhHCl\{(Bu^t{}_2PCH_2)_2(C_6H_3)\}]$. As can be seen from Table 3, 4xxi the large angle of 11.4° found in the first of these complexes is closer to the values found for the octahedral $[RhCl_2(PCP)S]$

complexes than to the values found for the square-planar [MX(PCP)] complexes. This may reflect the steric bulk of the COOH ligand *trans* to the σ-bonded aryl ring. [RhHCl{$(PBu^t_2CH_2)_2(C_6H_3)$}], on the other hand, has very bulky tertiary butyl substituents and the metal atom has a coordination number of five, the angle of 6.9° between the plane of the aromatic ring and the coordination plane Rh Cl P(1) P(2) C(1) is, however, only slightly larger than those found for square-planar [MX(PCP)].

3, 4j TRENDS IN THE LENGTH OF THE Rh-O BOND.

The Rh-O bond lengths in the three complexes [$RhCl_2$(PCP)S] (S = OH_2, HOEt and HOMe) are 2.274(3), 2.264(6) and 2.239(7) Å, respectively. These values are quite similar and the experimental errors make it difficult to assess any systematic trend in them although the difference of 0.035(8) Å between the Rh-O distances in the aqua and methanol complexes is, at least formally, highly significant.

Work by Crabtree and coworkers gave a ligand strength series for solvents in complexes of the type [$IrH_2S_2L_2$] where S = solvent and L = phosphine.[74] This series, proposed from competition reactions, showed ligand strength increasing in the order $H_2O \approx$ T.H.F. < t-BuOH < i-PrOH <Me_2CO < EtOH < MeOH < MeCN. Other studies on Rh^I complexes confirm the relative weakness of the aqua ligand.[6] In [$RhCl_2(PCP)(OH_2)$].propan-2-ol, however, water is preferentially bound over propan-2-ol, apparently reversing the order given above. Also the Rh-O bond length in the aqua complex differs little from that in the ethanol complex. From ref. 74 it might be expected that ethanol, being a stronger ligand than OH_2, should exhibit a shorter Rh-O bond length. The results obtained here indicate that such shortening, if it occurs, is of the same order as the experimental uncertainty in the Rh-O bond lengths. In Section 3, 3d it was noted that recrystallisation of the aqua complex from acetone did not give [$RhCl_2(PCP)(OCMe_2)$]. Thus, in contrast to the ligand series above, the ligand strength series for [$RhCl_2(PCP)S$] is i-PrOH $\approx$ $OCMe_2 << OH_2 \leq$ EtOH < MeOH. This difference may be explained by the disfavouring of the larger solvents by the steric crowding around the solvent ligand site caused by the four cyclohexyl groups.

Comparison of the Rh-O distance in the aqua complex with those in other aqua-Rh complexes (Table 3, 4xiii) does not suggest that steric crowding causes lengthening of the bond in [$RhCl_2(PCP)(OH_2)$]. The dominant factor appears to be *trans*-influence. The Rh(III)-O bond length shows a very large range from 2.32(1) to 2.070(4) Å. This corresponds to a change of more than 10% in the bond length, indicating that the Rh-O bond is very sensitive to *trans*-influence. (By contrast a study of *trans*-influence on Pt-Cl bond lengths gave a range of about 0.07 Å or 3% of the bond length).[75] Taube[76] pointed out that organometallic complexes of hard ligands such as water are rare but that the positive charge in cationic complexes may be a stabilising factor as it could be delocalised over the hydrogen atoms of an aqua ligand. The data in Table 3, 4xiii lend some support to this view. The only Rh-OH$_2$ (*trans* to σ-C) bond length in Table 3, 4xiii which is comparable with the Rh-OH$_2$ (*trans* to PR$_3$) distances occurs in a cationic complex. There is no evidence that steric crowding lengthens the Rh-O bond length in [RhCl$_2$(PCP)(OH$_2$)].propan-2-ol but most of the complexes listed in Table 3, 4xiii are themselves fairly crowded species. The Rh-O distances in the square-planar aqua complexes are shorter than in the octahedral complexes. This is expected on steric and orbital hybridisational grounds and is a fairly general feature.[64]

Table 3, 4xvi shows that Rh-O distances in the species [RhCl$_2$(PCP)S] (S = MeOH or EtOH) are much larger than values found in other known Rh(I) or Rh(III) alcohol-complexes. The poverty of data available for comparison, however, does not allow any conclusions to be drawn from this. The two PCP alcohol complexes are the first organometallic Rh(III) alcohol complexes to be reported and are the first neutral rhodium alcohol complexes to be reported for either Rh(I) or Rh(III).

3, 4k TRENDS IN THE METAL TO CARBON BOND LENGTH.

The M-C bond lengths in the complexes [PdCl(PCP)], [PdBr(PCP)], [$RhCl_2(PCP)(OH_2)$].propan-2-ol and [$RhCl_2$(PCP)(HOEt)].H_2O are essentially the same (range 2.004(4) to 2.012(6) Å) and that in [$RhCl_2$(PCP)(HOMe)].xCH_2Cl_2 is similar (1.984(8) Å). Thus, within the range represented by these complexes, the M-C distance is insensitive to oxidation number, metal type, coordination geometry and the nature of the *trans* ligand. It is predictable that *trans*-influence is not a determining factor in the M-C distances found in these complexes since the ligands *trans* to carbon (halide or oxygen donors) all have weak *trans*-influences. It would also appear from the Rh-C bond length of 1.999(7) Å in [$RhHCl\{(PBu^t_2CH_2)_2(C_6H_3)\}$][45] that it is unaffected by changing the substituents on the phosphine ligands from $Cy_2(CH_2)$ to $Bu^t_2(CH_2)$.

Trans-[PdBr(*o*-tolyl)$(PPh_3)_2$] (Section 3, 4d) has a Pd-C bond length of 1.999(13) Å and the Rh-C distance in [$RhPhCl_2(PPh_3)_2$][61] is 2.016(3) Å. These figures indicate that the chelate nature of the PCP ligand does not greatly affect the M-C bond length.

3, 41 COMPARISONS WITH NCN COMPLEXES.

Van Koten and his coworkers have thoroughly investigated platinum group complexes with a series of terdentate ligands $[(R_2NCH_2)_2(C_6H_3)]^-$ (hereafter NCN); R is usually methyl or other alkyl or aryl groups. These NCN ligands bond to metal centres in a fashion similar to PCP, and crystal structure analyses of several analogues to the structures presented here have been published.[67, 77]

Table 3, 4xxii compares the coordination geometry of (1) [NiBr(PCP)], (2) $[NiBr\{(MePr^iNCH_2)_2(C_6H_3)\}]$, the more sterically hindered (3) $[NiBr\{(MeBu^tNCH_2)_2(C_6H_3)\}]$ and the non-chelated (4) *trans*-$[NiBr(PEt_3)_2\{(MePhNCH_2)_2(C_6H_3)\}]$ where the amine arms do not bond to the nickel atom.

Table 3, 4xxii. Selected Bond Lengths (Å) and Angles (°) for related Ni(II) Complexes.

	1	2	3	4
Ni-Br	2.360(1)	2.437(2)	2.4459(30)	2.3738(12)
Ni-C	1.909(5)	1.83(1)	1.825(17)	1.908(6)
Ni-P/N	2.185(2)	1.99(1)	2.060(12)	2.234(2)
Ni-P/N	2.168(2)	2.01(1)	2.105(13)	2.226(2)
P/N-Ni-P/N	167.6(1)	165.8(5)	165.3(6)	171.26(9)
Br-Ni-C	177.3(2)	176.6(4)	162.2(6)	171.04(19)

It is interesting that (1) and (4), the phosphorus-containing complexes, have similar Ni-Br distances and identical Ni-C distances. The Ni-C distances in (1) and (4) also compare well with the average value of 1.917 Å found for 18 similar bonds.[64]

In complexes (2) and (3) the Ni-C distances of 1.83(1) and 1.825(17) Å are significantly shorter than in (1) or (4). This must be a result of ring strain in the NCN complexes, the shortness of the Ni-N and N-CH_2 ring bonds requiring a shorter Ni-C bond than in free systems. [It was noted in section 3, 4k that PCP is large enough to allow the carbon atom to take up a normal position.] The relatively short Ni-C distances in (2) and (3) result in very long Ni-Br bonds, presumably indicating enhanced *trans*-influence.

Table 3, 4xxiii compares the coordination geometry of $[RhCl_2(PCP)(OH_2)]$.propan-2-ol (5) and $[RhCl_2\{(Me_2NCH_2)_2(C_6H_3)\}(OH_2)]$ (6).

Table 3, 4xxiii. **Comparison of Selected Bond Lengths (Å) and Angles (°) of Complexes 5 and 6.**

	5 $[RhCl_2(PCP)(OH_2)].S$	6 $[RhCl_2(NCN)(OH_2)]$
Rh-Cl	2.345(2)	2.3532(9)
Rh-Cl	2.371(2)	2.3528(9)
Rh-C	2.004(4)	1.913(3)
Rh-O	2.274(3)	2.269(2)
Rh-P/N	2.351(1)	2.160(3)
Rh-P/N	2.354(2)	2.152(3)
P/N-Rh-P/N	165.8(1)	163.1(1)
Cl-M-Cl	177.2(1)	177.68(3)

NCN = $(Me_2NCH_2)_2C_6H_3$

Here again it is seen that the smaller NCN chelate results in a smaller Rh-C distance (2.004(4) Å in (5) and 1.913(3) Å in (6)). There is no indication of a lengthening of the Rh-O bond in (6) compared with (5), so that the shorter Rh-C bond is not accompanied by the enhanced σ-C *trans*-influence found in the nickel(II) complexes.

3, 4m STRUCTURE OF *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$.

The coordination geometry about the rhodium atom is square-planar but is subject to a small tetrahedral distortion as is evident from the bond

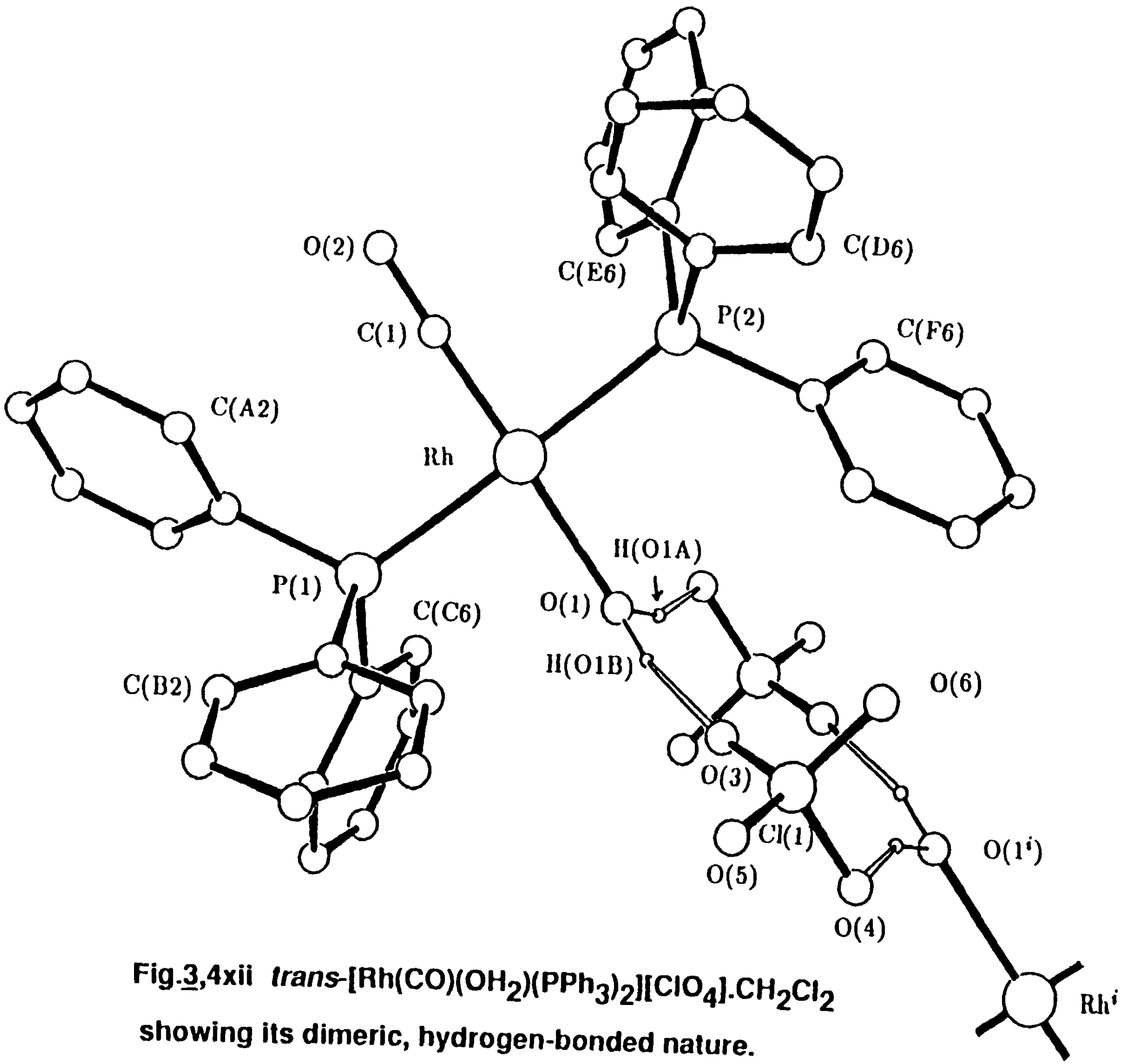

Fig.3,4xii *trans*-[Rh(CO)(OH$_2$)(PPh$_3$)$_2$][ClO$_4$].CH$_2$Cl$_2$ showing its dimeric, hydrogen-bonded nature.

angles subtended at the Rh centre (see Tables 3, 4xxiv and xxv) and from the displacements of the P(1), P(2), O(1) and C(1) atoms by 0.070(1), 0.068(1), -0.070(4) and -0.087(5) Å, respectively, from the coordination plane of the metal. Fig. 3, 4xii is an ORTEP drawing of the complex with atoms shown as arbitrary spheres for clarity.

The Rh-O distance of 2.127(4) Å is in good agreement with those given for the other two known Rh(I) square-planar aqua complexes (Table 3, 4xiii) and the Rh-P and Rh-C distances are also in good agreement with those of the related complexes *trans*-$[Rh(CO)Cl(PPh_3)_2]$[4, 78] and *trans*-$[Rh(CO)Cl(PMePh_2)_2]$.[79] The two PPh_3 fragments adopt a mutually staggered conformation with respect to the P-Rh-P axis and the geometrical parameters of the phenyl rings, the ClO_4^- anion and of the CH_2Cl_2 solvent molecule are as expected.

In the crystal structure the CH_2Cl_2 molecules are separated by van der Waals distances from the dimeric $[Rh(OH_2)(CO)(PPh_3)_2]_2[ClO_4]_2$ units, in which the cations and anions are held together by hydrogen-bonding involving H atoms of the coordinated water molecules (Tables 3, 4xii). The dimeric units are characterised by crystallographically imposed C_i symmetry, the centre of symmetry coinciding with the centre of the twelve-membered $Cl_2O_6H_4$ ring. While this work was being carried out, crystal structures were published of *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][BF_4].\frac{1}{2}H_2O.\frac{1}{4}C_6H_{12}$[6] and of *trans*-

Table 3,4xxiv Bond lengths (Å) for $[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$.

Rh - P(1)	2.352(2)	Rh - P(2)	2.351(2)
Rh - O(1)	2.127(4)	Rh - C(1)	1.785(6)
P(1) - C(A1)	1.828(6)	P(1) - C(B1)	1.821(5)
P(1) - C(C1)	1.813(5)	P(2) - C(D1)	1.821(5)
P(2) - C(E1)	1.821(5)	P(2) - C(F1)	1.822(5)
O(2) - C(1)	1.153(7)	C(A1) - C(A2)	1.390(8)
C(A1) - C(A6)	1.398(8)	C(A2) - C(A3)	1.389(9)
C(A3) - C(A4)	1.376(11)	C(A4) - C(A5)	1.365(10)
C(A5) - C(A6)	1.379(9)	C(B1) - C(B2)	1.388(9)
C(B1) - C(B6)	1.370(9)	C(B2) - C(B3)	1.353(10)
C(B3) - C(B4)	1.374(12)	C(B4) - C(B5)	1.374(12)
C(B5) - C(B6)	1.386(10)	C(C1) - C(C2)	1.372(7)
C(C1) - C(C6)	1.381(7)	C(C2) - C(C3)	1.383(8)
C(C3) - C(C4)	1.336(9)	C(C4) - C(C5)	1.366(10)
C(C5) - C(C6)	1.397(9)	C(D1) - C(D2)	1.398(8)
C(D1) - C(D6)	1.368(8)	C(D2) - C(D3)	1.381(9)
C(D3) - C(D4)	1.353(10)	C(D4) - C(D5)	1.356(11)
C(D5) - C(D6)	1.380(10)	C(E1) - C(E2)	1.381(7)
C(E1) - C(E6)	1.389(8)	C(E2) - C(E3)	1.379(7)
C(E3) - C(E4)	1.385(9)	C(E4) - C(E5)	1.353(9)
C(E5) - C(E6)	1.376(8)	C(F1) - C(F2)	1.396(7)
C(F1) - C(F6)	1.385(7)	C(F2) - C(F3)	1.392(9)
C(F3) - C(F4)	1.348(8)	C(F4) - C(F5)	1.376(10)
C(F5) - C(F6)	1.385(9)	Cl(1) - O(3)	1.368(8)
Cl(1) - O(4)	1.405(7)	Cl(1) - O(5)	1.359(6)
Cl(1) - O(6)	1.353(8)	Cl(2) - C(2)	1.714(11)
Cl(3) - C(2)	1.682(12)		

Table 3,4xxv Bond angles (°) for $[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$.

P(1)-Rh-P(2)	176.7(1)	P(1)-Rh-O(1)	88.3(1)
P(1)-Rh-C(1)	89.9(2)	P(2)-Rh-O(1)	94.1(1)
P(2)-Rh-C(1)	88.0(2)	O(1)-Rh-C(1)	173.8(2)
Rh-P(1)-C(A1)	117.9(2)	Rh-P(1)-C(B1)	113.0(2)
Rh-P(1)-C(C1)	113.1(2)	C(A1)-P(1)-C(B1)	103.5(3)
C(A1)-P(1)-C(C1)	102.5(3)	C(B1)-P(1)-C(C1)	105.3(3)
Rh-P(2)-C(D1)	113.4(2)	Rh-P(2)-C(E1)	112.8(2)
Rh-P(2)-C(F1)	117.7(2)	C(D1)-P(2)-C(E1)	103.1(3)
C(D1)-P(2)-C(F1)	104.2(3)	C(E1)-P(2)-C(F1)	104.2(3)
Rh-C(1)-O(2)	177.1(5)	P(1)-C(A1)-C(A2)	119.6(5)
P(1)-C(A1)-C(A6)	121.9(4)	C(A2)-C(A1)-C(A6)	118.5(5)
C(A1)-C(A2)-C(A3)	120.1(6)	C(A2)-C(A3)-C(A4)	120.2(6)
C(A3)-C(A4)-C(A5)	120.3(6)	C(A4)-C(A5)-C(A6)	120.3(7)
C(A1)-C(A6)-C(A5)	120.6(6)	P(1)-C(B1)-C(B2)	123.5(5)
P(1)-C(B1)-C(B6)	118.6(5)	C(B2)-C(B1)-C(B6)	117.8(6)
C(B1)-C(B2)-C(B3)	121.3(7)	C(B2)-C(B3)-C(B4)	120.9(7)
C(B3)-C(B4)-C(B5)	118.9(8)	C(B4)-C(B5)-C(B6)	120.0(8)
C(B1)-C(B6)-C(B5)	121.0(7)	P(1)-C(C1)-C(C2)	122.8(4)
P(1)-C(C1)-C(C6)	118.6(4)	C(C2)-C(C1)-C(C6)	118.4(5)
C(C1)-C(C2)-C(C3)	120.7(5)	C(C2)-C(C3)-C(C4)	121.0(6)
C(C3)-C(C4)-C(C5)	119.9(6)	C(C4)-C(C5)-C(C6)	120.1(6)
C(C1)-C(C6)-C(C5)	119.9(6)	P(2)-C(D1)-C(D2)	118.4(4)
P(2)-C(D1)-C(D6)	124.1(4)	C(D2)-C(D1)-C(D6)	117.5(5)
C(D1)-C(D2)-C(D3)	119.8(6)	C(D2)-C(D3)-C(D4)	121.7(6)
C(D3)-C(D4)-C(D5)	118.8(6)	C(D4)-C(D5)-C(D6)	120.9(7)
C(D1)-C(D6)-C(D5)	121.4(6)	P(2)-C(E1)-C(E2)	123.1(4)
P(2)-C(E1)-C(E6)	118.3(4)	C(E2)-C(E1)-C(E6)	118.6(5)
C(E1)-C(E2)-C(E3)	120.8(5)	C(E2)-C(E3)-C(E4)	119.8(6)
C(E3)-C(E4)-C(E5)	119.4(6)	C(E4)-C(E5)-C(E6)	121.4(6)
C(E1)-C(E6)-C(E5)	119.9(5)	P(2)-C(F1)-C(F2)	119.1(4)
P(2)-C(F1)-C(F6)	121.4(4)	C(F2)-C(F1)-C(F6)	119.5(5)
C(F1)-C(F2)-C(F3)	119.2(5)	C(F2)-C(F3)-C(F4)	121.4(6)
C(F3)-C(F4)-C(F5)	119.2(6)	C(F4)-C(F5)-C(F6)	121.5(6)
C(F1)-C(F6)-C(F5)	119.1(6)	O(3)-Cl(1)-O(4)	107.7(5)
O(3)-Cl(1)-O(5)	115.6(6)	O(3)-Cl(1)-O(6)	109.7(5)
O(4)-Cl(1)-O(5)	106.0(4)	O(4)-Cl(1)-O(6)	103.4(6)
O(5)-Cl(1)-O(6)	113.5(6)	Cl(2)-C(2)-Cl(3)	115.9(6)

$[Rh(OH_2)(CO)(PPh_3)_2][CF_3SO_3]$.[17] The molecular geometry of the BF_4^- salt closely resembles that of the ClO_4^- salt, but the crystal structures are not isomorphous, whilst that of the $CF_3SO_3^-$ salt was not sufficiently reliable for comparison. It has been suggested that hydrogen bonding may be present in the crystal structure of the BF_4^- salt (as it is in the ClO_4^- salt) but the hydrogen atoms were not located. That the Rh-O bond distance in the ClO_4^- salt falls between two independent values found in the BF_4^- salt suggests that this is indeed the case (Table 3, 4xiii).

3, 4n STRUCTURE OF *trans*-$[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].OCMe_2$.

As detailed in Section 2, 7j this structure has not been satisfactorily refined. No rhodium complex of a simple ketone has previously been structurally characterised and it is therefore felt that a brief report of the structural results is worthwhile.

The cations exist as discrete monomeric entities and the coordination geometry is square-planar about the rhodium atom with no significant out-of-plane deviations. Bond lengths and angles are given in Tables 3, 4xxvi and xxvii respectively. Fig. 3, 4xiii shows an ORTEP drawing of the cation with the atoms represented as arbitrary spheres. The geometric parameters of the metal coordination sphere, of the

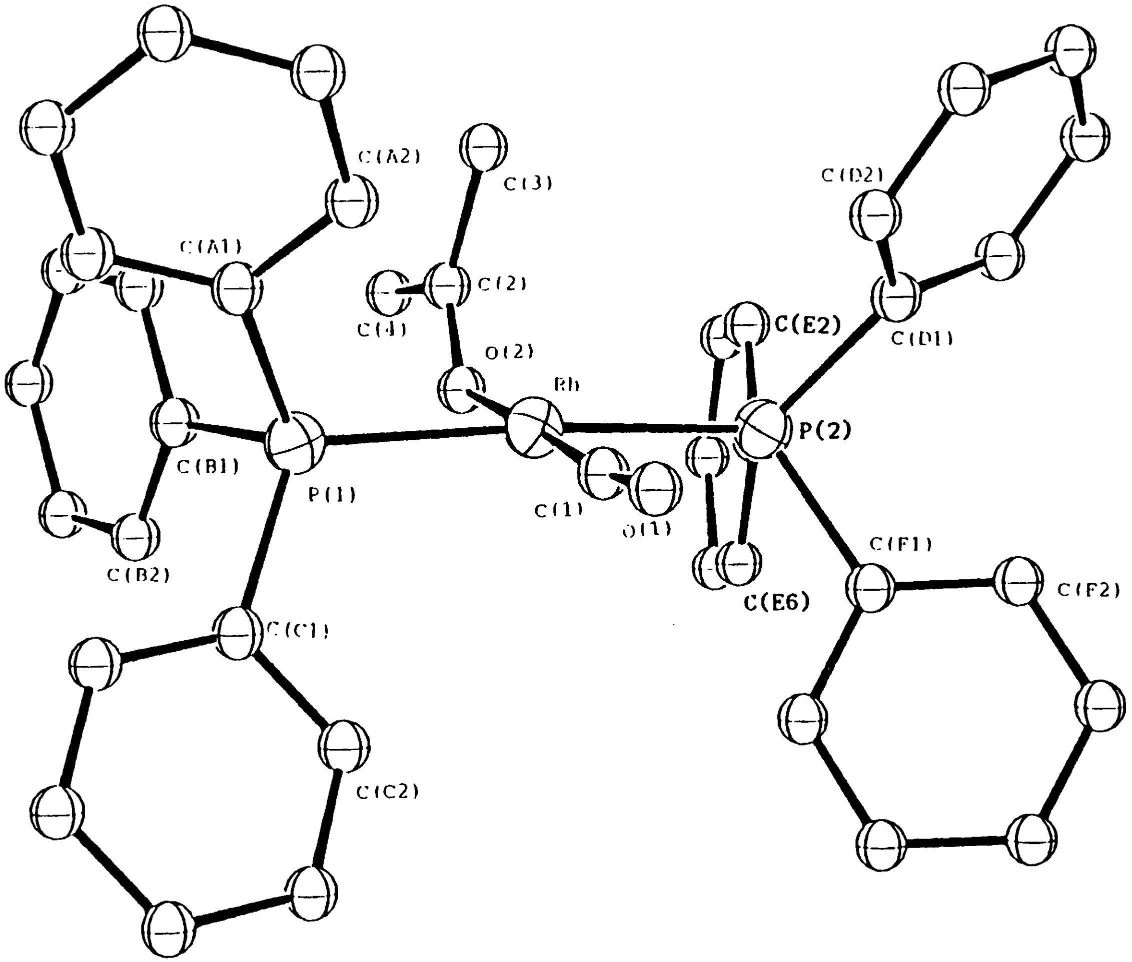

Fig.3,4xiii *trans*-$[Rh(CO)(OCMe_2)(PPh_3)_2][ClO_4].OCMe_2$.

carbonyl and acetone ligands and of the two triphenylphosphine groups, which adopt a mutually eclipsed conformation, are all within normal limits and compare well with those in *trans*-$[Rh(OH_2)(CO)(PPh_3)_2][ClO_4].CH_2Cl_2$. The Rh-O bond is shorter in the acetone complex than in the aqua complex. The plane of the acetone ligand makes an angle of 95° with the plane of the metal coordination sphere. The acetone ligand is bonded via the oxygen atom not through the C=O bond (Rh-C(2) = 3.03(7) Å).

The ClO_4^- anion and the $OCMe_2$ solvent molecule are separated by van der Waals distances from each other and from the cation. There is evidence of unresolved disorder in both units.

Table 3,4xxvi Selected bond lengths (Å) for $[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].OCMe_2$.

Rh - P(1)	2.341(15)	Rh - P(2)	2.352(15)
Rh - O(2)	2.02(4)	Rh - C(1)	1.70(5)
P(1) - C(A1)	1.87(6)	P(1) - C(B1)	1.80(4)
P(1) - C(C1)	1.88(6)	P(2) - C(D1)	1.86(8)
P(2) - C(E1)	1.76(6)	P(2) - C(F1)	1.86(7)
O(1) - C(1)	1.25(7)	O(2) - C(2)	1.24(8)
C(2) - C(3)	1.57(11)	C(2) - C(4)	1.44(14)

Table 3,4xxvii Selected bond angles (°) for $[Rh(OCMe_2)(CO)(PPh_3)_2][ClO_4].OCMe_2$.

P(1)-Rh-P(2)	176.3(7)	P(1)-Rh-O(2)	89.2(11)
P(1)-Rh-C(1)	92.1(16)	P(2)-Rh-O(2)	91.2(11)
P(2)-Rh-C(1)	87.3(16)	O(2)-Rh-C(1)	176.6(18)
Rh-P(1)-C(A1)	114.0(21)	Rh-P(1)-C(B1)	113.5(18)
Rh-P(1)-C(C1)	114.1(20)	C(A1)-P(1)-C(B1)	102.9(28)
C(A1)-P(1)-C(C1)	110.6(25)	C(B1)-P(1)-C(C1)	100.4(25)
Rh-P(2)-C(D1)	118.8(30)	Rh-P(2)-C(E1)	110.8(20)
Rh-P(2)-C(F1)	114.7(15)	C(D1)-P(2)-C(E1)	113.5(34)
C(D1)-P(2)-C(F1)	93.9(32)	C(E1)-P(2)-C(F1)	103.0(23)
Rh-O(2)-C(2)	134.7(39)	Rh-C(1)-O(1)	171.7(38)
O(2)-C(2)-C(3)	111.6(57)	O(2)-C(2)-C(4)	122.6(66)
C(3)-C(2)-C(4)	125.3(67)		

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