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Crystal structures of the solvates *trans*-$[RhCl_2(MeOH)\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$. $0.41CH_2Cl_2$ and *trans*-$[RhCl_2(EtOH)\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$. H_2O. Factors influencing the reactions of $C_6H_4\text{-}1,3\text{-}(CH_2PR_2)_2$ with $RhCl_3$

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Abstract

The terdentate ligands $C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2$ (PCP: Cy = cyclohexyl) in the octahedral solvento complexes *trans*-$[RhCl_2(MeOH)(PCP)]$ and *trans*-$[RhCl_2(EtOH)(PCP)]$ adopt conformations which minimise the interactions between the sterically demanding Cy groups and the *trans* chlorides. Comparison of these structures with those of related molecules, including square-pyramidal and square-planar species, suggests an explanation for the different structural types obtained as products from reactions of $RhCl_3.3H_2O$ and various ligands $C_6H_4\text{-}1,3\text{-}(CH_2ER_2)_2$ with E = N or P.

Keywords: Rhodium; Terdentate ligands; Crystal structure; Orthometallation

1. Introduction

As part of their studies on the interaction of bulky ligands with transition metal ions, Shaw and his coworkers showed that $RhCl_3.3H_2O$ or $IrCl_3.xH_2O$ reacted with $C_6H_4\text{-}1,3\text{-}(CH_2PR_2)_2$ ($R = {}^tBu$) to produce the chlorohydrido complexes **1** [1]. Compounds of similar composition, **2**, were formed from the reactions with the α,ω-diphosphines ${}^tBu_2P(CH_2)_5P^tBu_2$ [2,3], ${}^tBu_2P(CH_2)_2CHMe(CH_2)_2P^tBu_2$ [3], and ${}^tBu_2PCH_2CHMe(CH_2)_3P^tBu_2$ [4].

The formation of these latter complexes was always accompanied by $[MHCl_2\{{}^tBu_2PCH_2CHR^1CHR^2(CH_2)_2P^tBu_2\}]_2$, and there was evidence that these dimeric species might be intermediates en route to **2**. The reaction of $RhCl_3.3H_2O$ with the nitrogen donor ligand $C_6H_4\text{-}1,3\text{-}(CH_2NMe_2)_2$, however, has been shown to yield octahedrally coordinated *trans*-$[RhCl_2(OH_2)\{C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2\}]$ [5], and no hydrides were detected.

Recently we reported that the diphosphine $C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2$ reacted with $RhCl_3.3H_2O$ to produce octahedral *trans*-$[RhCl_2(OH_2)(PCP)]$ ($PCP = C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2$), characterised by a single-crystal X-ray structure determination [6]. We report here the formation and structure analyses of the solvates *trans*-$[RhCl_2(MeOH)\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}].0.41CH_2Cl_2$ and *trans*-$[RhCl_2(EtOH)\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}].H_2O$, which allow a rationalisation to be made of the products of the reactions of $RhCl_3.3H_2O$ with $C_6H_4\text{-}1,3\text{-}(CH_2PR_2)_2$ or $C_6H_4\text{-}1,3\text{-}(CH_2NR_2)_2$.

2. Results and discussion

Recrystallisation of *trans*-$[RhCl_2(OH_2)(PCP)]$ from methanol or ethanol, respectively, produced the new solvates *trans*-$[RhCl_2(MeOH)(PCP)]$ and *trans*-$[RhCl_2(EtOH)(PCP)]$, but attempts to prepare 2-propanol or acetone solvates failed, probably for steric reasons (vide infra). Since the MeOH and EtOH adducts were stable in moist air it appears that the ligand strength series for these weakly bonded groups at this rhodium(III) centre is ${}^iPrOH$, $Me_2CO < H_2O < EtOH$,

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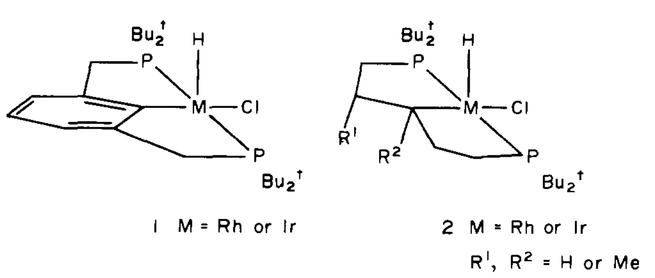

Form 1.

MeOH. This differs from the series $H_2O < {}^iPrOH <$ EtOH < MeOH established from ligand competition reactions at Ir(III) [7], and the most likely explanation is that steric crowding by our PCP ligand hinders the coordination of the more bulky solvents.

Heating either of the orange-coloured alcohol complexes under vacuum gave pink, unsolvated [$RhCl_2$(PCP)], as did recrystallisation of [$RhCl_2$(MeOH)(PCP] from warm $CHCl_3$. The unsolvated [$RhCl_2$(PCP)] has a single absorption at 330 cm^{-1} in its IR spectrum, which we assign to ν(Rh–Cl) of mutually *trans* chlorides. This indicates a square-pyramidal structure with Rh–C in the apical position, similar to the known [$RhCl_2Ph(PPh_3)_2$] [8]. Exposure of the pink [$RhCl_2$(PCP)] to moist air allows its immediate conversion into orange [$RhCl_2(OH_2)$(PCP)], a process that can be reversed by flushing with dry N_2. Solutions of [$RhCl_2$(PCP)] in $CDCl_3$ are orange in colour, indicating the presence of an octahedral species. The ^{31}P NMR spectra of all the PCP complexes in $CDCl_3$ are practically identical, as are the ^1H resonances assignable to the [$RhCl_2$(PCP)] fragments (see Experimental details). We take this as an indication that the weak oxygen donors have been replaced by the halogenated solvent (there are precedents for such coordination of chlorocarbons) [9].

We describe here the crystal structures of *trans*-[$RhCl_2$(MeOH)(PCP)].0.41CH_2Cl_2 and *trans*-[$RhCl_2$(EtOH)(PCP)].H_2O (see Figs. 1 and 2, Table 1). We have also determined the structure of anhydrous *trans*-[$RhCl_2$(EtOH)(PCP)]. The crystals are monoclinic, space group $P2_1/a$, with $a = 14.485(4)$ Å, $b = 10.792(3)$ Å, $c = 22.962(12)$ Å, $\beta = 103.18(3)°$, $V = 3495$ Å^3, $Z = 4$. $R = 0.070$ for 1186 unique reflections with $I > 3\sigma(I)$ and 186 refined parameters. The results establish that the anhydrous and hydrated forms of *trans*-[$RhCl_2$(EtOH)(PCP)] are not isomorphous, but that they contain *trans*-[$RhCl_2$(EtOH)(PCP)] molecules with very similar geometries. Because the accuracy of the analysis of the anhydrous complex is compromised by the low data/parameter ratio we have confined our discussion to the hydrate complex, for which more satisfactory data are available.

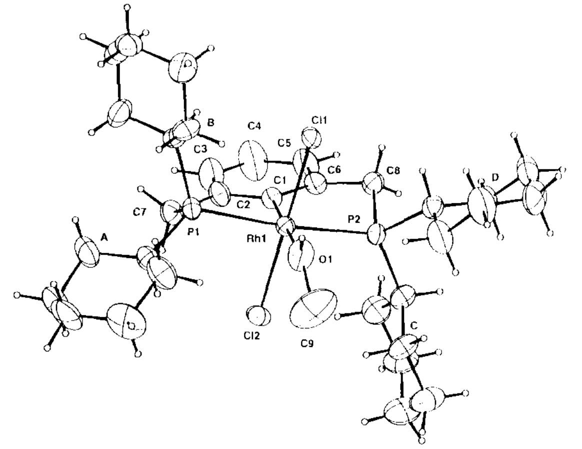

Fig. 1. A view of the molecule *trans*-[$RhCl_2$(MeOH){C_6H_3-2,6-($CH_2PCy_2)_2$}]. Here and in Fig. 2 50% probability ellipsoids are displayed except for hydrogen atoms which are represented by spheres of arbitrary size. Cyclohexyl C atoms are numbered cyclically C(*n*1)–C(*n*6) for rings *n* = A, B, C and D, starting with the *ipso* carbon atom. The label for each ring is placed beside C(*n*2).

There are no previous structural reports of methanol bonded to Rh(III) (the structure of the anion [$Rh_2(\mu$-$I)_2I_4Cl(CO)_2(MeOH)]^-$, determined by use of synchrotron radiation on an exceptionally small crystal, did not satisfactorily locate the methanol) [10] and only one (the anion [$RhBr_4$(CO)(EtOH)]$^-$[11]) of an ethanol complex. Both the methanol and ethanol solvate complexes are broadly similar in their geometry to *trans*-[$RhCl_2(H_2O)$(PCP)]. ^{i}PrOH [6], with the most significant deviation from octahedral coordination being that involving the P(1)–Rh–(2) angles, which are constrained to 166 · 1(1)° and 164 · 5(1)° in the MeOH and EtOH complexes, respectively.

The Rh–C, Rh–P and Rh–Cl distances in the MeOH and EtOH complexes are unexceptional (see Ref. [6]). The crystal of the methanol complex contains 0.41(1) of a poorly defined CH_2Cl_2 solvent molecule per rhodium. The partially present CH_2Cl_2 is disordered over two sites by rotation about an axis passing through its

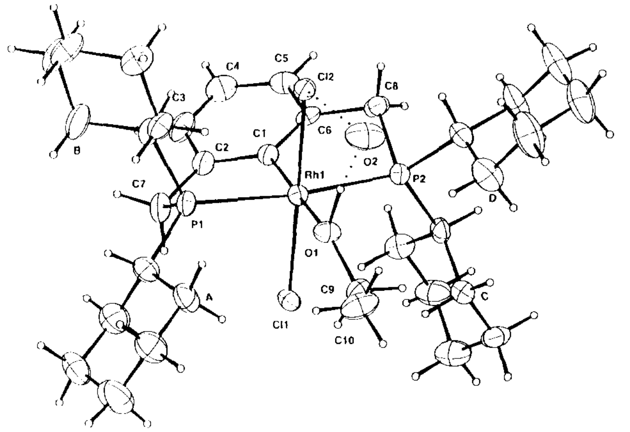

Fig. 2. A view of the molecule *trans*-[$RhCl_2$(EtOH){C_6H_3-2,6-($CH_2PCy_2)_2$}] and of its associated water molecule. Broken lines indicate hydrogen bonds. Ring labels are indicated in the same way as in Fig. 1.

carbon atom; each orientation appears to permit one chlorine to hydrogen bond to the methanol hydroxy group (the O…Cl contacts of ca. 2.6 Å are short and suggest systematic error in the CH_2Cl_2 chlorine atom positions). In the EtOH complex a water molecule is weakly hydrogen bonded to the coordinated ethanol

Table 1
Selected distances (Å) and angles (°) in *trans*-$[RhCl_2(EtOH)\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}].H_2O$ (**A**) and *trans*-$[RhCl_2(MeOH)\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}].0.41CH_2Cl_2$ (**B**)

Bond lengths	(**A**)	(**B**)		(**A**)	(**B**)
Rh–Cl(1)	2.354(3)	2.342(3)	Rh–Cl(2)	2.376(3)	2.347(3)
Rh–P(1)	2.363(3)	2.346(3)	Rh–P(2)	2.357(3)	2.361(3)
Rh–O(1)	2.264(6)	2.239(6)	Rh–C(1)	2.008(8)	1.984(8)
P(1)–C(7)	1.818(9)	1.827(9)	P(1)–C(A1)	1.843(11)	1.819(9)
P(1)–C(B1)	1.827(10)	1.839(9)	P(2)–C(8)	1.831(9)	1.842(9)
P(2)–C(C1)	1.823(10)	1.847(9)	P(2)–C(D1)	1.870(11)	1.845(9)
O(1)–C(9)	1.434(10)	1.407(15)	C(1)–C(2)	1.429(12)	1.390(11)
C(1)–C(6)	1.363(12)	1.413(11)	C(2)–C(3)	1.393(12)	1.369(12)
C(2)–C(7)	1.511(13)	1.519(12)	C(3)–C(4)	1.359(14)	1.340(14)
C(4)–C(5)	1.377(14)	1.381(13)	C(5)–C(6)	1.411(12)	1.365(12)
C(6)–C(8)	1.521(13)	1.515(11)	C(9)–C(10)	1.489(13)	
Bond angles					
Cl(1)–Rh–Cl(2)	177.1(1)	178.0(1)	Cl(1)–Rh–P(1)	85.0(1)	93.9(1)
Cl(1)–Rh–P(2)	95.8(1)	84.9(1)	Cl(1)–Rh–O(1)	90.7(2)	88.1(2)
Cl(1)–Rh–C(1)	94.1(3)	90.4(3)	Cl(2)–Rh–P(1)	94.0(1)	85.2(1)
Cl(2)–Rh–P(2)	85.9(1)	96.4(1)	Cl(2)–Rh–O(1)	86.7(2)	90.2(3)
Cl(2)–Rh–C(1)	88.4(3)	91.3(3)	P(1)–Rh–P(2)	164.6(1)	166.1(1)
P(1)–Rh–O(1)	95.6(2)	96.8(2)	P(1)–Rh–C(1)	82.5(3)	82.6(3)
P(2)–Rh–O(1)	99.8(2)	97.0(2)	P(2)–Rh–C(1)	82.1(3)	83.5(3)
O(1)–Rh–C(1)	174.7(3)	178.4(3)	Rh–P(1)–C(7)	98.2(4)	98.7(3)
Rh–P(1)–C(A1)	125.4(4)	120.7(4)	Rh–P(1)–C(B1)	114.7(4)	115.1(3)
C(7)–P(1)–C(A1)	107.0(5)	103.2(5)	C(7)–P(1)–C(B1)	105.8(5)	105.3(4)
C(A1)–P(1)–C(B1)	104.0(5)	110.8(5)	Rh–P(2)–C(8)	98.3(4)	98.5(3)
Rh–P(2)–C(C1)	122.6(4)	121.9(4)	Rh–P(2)–C(D1)	118.7(4)	119.7(3)
C(8)–P(2)–C(C1)	104.3(5)	103.9(5)	C(8)–P(2)–C(D1)	101.0(5)	102.4(5)
C(C1)–P(2)–C(D1)	107.6(5)	106.7(4)	Rh–O(1)–C(9)	126.6(6)	128.4(8)
Rh–C(1)–C(2)	119.4(7)	122.2(6)	Rh–C(1)–C(6)	121.5(7)	121.0(6)
C(2)–C(1)–C(6)	119.0(8)	116.7(8)	C(1)–C(2)–C(3)	118.3(9)	121.1(9)
C(1)–C(2)–C(7)	119.0(8)	118.2(8)	C(3)–C(2)–C(7)	122.6(9)	120.6(9)
C(2)–C(3)–C(4)	122.1(10)	121.3(10)	C(3)–C(4)–C(5)	119.7(9)	119.9(10)
C(4)–C(5)–C(6)	119.8(10)	120.1(9)	C(1)–C(6)–C(5)	120.9(10)	120.8(9)
C(1)–C(6)–C(8)	119.5(8)	119.3(7)	C(5)–C(6)–C(8)	119.5(9)	119.7(8)
P(1)–C(7)–C(2)	107.0(7)	108.7(6)	P(2)–C(8)–C(6)	108.5(7)	108.0(6)
O(1)–C(9)–C(10)	111.9(8)				
Torsion angles	(**A**)	(**B**)			
Cl(1)–Rh–P(1)–C(B1)	−178.9(4)	2.1(4)			
Cl(1)–Rh–P(2)–C(C1)	5.6(4)	179.6(4)			
Cl(2)–Rh–P(1)–C(B1)	3.8(4)	−179.7(4)			
Cl(2)–Rh–P(2)–C(C1)	−176.7(4)	1.1(4)			
P(1)–Rh–C(1)–C(2)	−15.9(7)	−16.5(7)			
C(1)–Rh–P(1)–C(7)	27.5(4)	23.7(4)			
C(1)–Rh–P(1)–C(A1)	145.1(5)	134.8(5)			
C(1)–Rh–P(1)–C(B1)	−84.1(5)	−87.8(4)			
P(2)–Rh–C(1)–C(6)	−20.0(7)	−13.4(7)			
C(1)–Rh–P(2)–C(8)	25.2(4)	22.9(4)			
C(1)–Rh–P(2)–C(C1)	−87.7(5)	−89.4(5)			
C(1)–Rh–P(2)–C(D1)	132.7(5)	132.4(4)			
Rh–P(1)–C(7)–C(2)	−36.8(6)	−30.2(6)			
Rh–P(2)–C(8)–C(6)	−30.2(6)	−30.8(6)			
Rh–C(1)–C(2)–C(3)	171.5(12)	−179.6(12)			
Rh–C(1)–C(2)–C(7)	−6.3(7)	−0.9(6)			
Rh–C(1)–C(6)–C(5)	−173.3(13)	179.2(12)			
Rh–C(1)–C(6)–C(8)	3.6(7)	−5.5(6)			
C(1)–C(2)–C(7)–P(1)	32.0(7)	23.8(7)			
C(1)–C(6)–C(3)–P(2)	21.4(7)	27.0(7)			

[O(2)...O(1) 2.74(1) Å] and to one of the *cis* chlorides [O(2)...Cl(2) 3.22(1) Å]; it also participates in a contact of 3.24(1) Å with Cl(2) of a neighbouring complex molecule. Otherwise there are no intermolecular contacts significantly shorter than the sum of the appropriate van der Waals radii.

We have previously noted the sensitivity of $Rh-OH_2$ bond lengths to the nature of the *trans* ligands [6]. The Rh–O bonds in our PCP complexes are long, but are typical of such bonds *trans* to σ-bonded carbon: $Rh-OH_2$ is 2 · 274(3) Å, Rh–OHMe is 2 · 239(7) Å, and Rh–OHEt is 2 · 264(6) Å. The small variations in the lengths of these Rh–O bonds are unsurprising in view of the differences both in the substituents on oxygen and in the crystallographic environments: each O-donor ligand also participates in intermolecular hydrogen bonding. Much shorter Rh–O bonds of 2.087(2) Å and 2.118(4) Å are found in the anion $[RhBr_4(CO)(EtOH)]^-$ *trans* to carbonyl, a π-acidic ligand of low *trans* influence [11].

A feature of interest in complexes of terdentate ligands of the PCP type is the conformation adopted by the substituents on phosphorus. We have observed that in square-planar compounds [MX(PCP)] (M = Ni, Pd or Pt) and related derivatives, bulky ligand substituents Cy or ^tBu adopt an eclipsed conformation (when viewed along the P...P axis of the PCP ligand) so that the local symmetry at the metal approximates to C_s, but less bulky substituents prefer staggered conformations and an overall C_2 symmetry, leading to increased twisting of the chelate rings out of the coordination plane and corresponding reductions in the observed M–P–C(chelate) angles [12,13]. Table 2 compares the salient structural features of our Rh(III) solvates with those of other five- and six-coordinate complexes containing ligands similar to either PCP or its NCN analogue. In each of the octahedral complexes the substituents of the P or N donor atoms are found to be staggered relative to the P...P or N...N axis, irrespective of whether they are sterically demanding Cy or smaller Me groups. This marked difference from the structures of square-planar complexes is most likely caused by the interactions of the ligand substituents with the groups coordinated *cis* to the terdentate PCP or NCN. This argument is consistent with trends in torsion and bond angles apparent in Table 1: each Cl ligand participates in one eclipsed and one staggered Cl–Rh–P–C(Cy) conformation (torsion angles respectively ca. 0° and 180°); the Cl–Rh–P angles associated with the eclipsed conformations are 94–96° compared with 85–86° for the staggered arrangements. Overall C_s symmetry would require one Cl ligand to participate in two, rather than one, eclipsed Cl–Rh–P–C(Cy) conformations. A further consequence of the adoption of the C_2 (staggered) conformation in the octahedral complexes is a constriction of about 4° in the Rh–P–C(chelate ring) angles (see Table 2).

Square-pyramidal hydrido complexes of types **1** or **2**, in which the H atoms are in apical position, have structures resembling those of square-planar analogues, with bulky ligand substituents lying eclipsed. Presumably the hydride *cis* to the terdentate ligands is not large enough to interfere with this conformation. We note, however, that five-coordinate complexes which have larger (*cis*) apical atoms, $[NiI_2(NCN)]$ and $[PtI(I_2)(NCN)]$, adopt an intermediate geometry tending towards eclipsed.

The steric interactions indicated by the adopted conformations offer a clue to rationalising the different product types of the reactions between $RhCl_3.3H_2O$ and C_6H_4-1,3-$(CH_2PR_2)_2$ or C_6H_4-1,3-$(CH_2NR_2)_2$. In the first place, it seems clear that the steric demand of the terdentate ligands produced by the metallation reactions imposes constraints on the nature of the final products. We have previously shown that in square-planar compounds of type[MX(PCP)] and [MX(NCN)] the terdentate ligand is flexible enough to allow a molecular geometry approximating to either C_s, in which the terminal R groups are eclipsed along the P...P or

Table 2
Selected distances (Å) and angles (°) in octahedral and square pyramidal complexes with terdentate PCP or NCN ligands

Compound	Geometry (ref.)	M–C	M–P(1) M–P(2) or M–N(1) M–N(2)	PMP or NMN	M–P–C(ring) or M–N–C(ring)	Aromatic [a] tilt.	Substituent Conformation
$[RhCl_2(OH_2)\{(Cy_2PCH_2)_2C_6H_3\}]$	Oct. [6]	2.004(4)	2.351(1) 2.354(2)	165.8(1)	99.3(2) 98.6(2)	14.6	staggered
$[RhCl_2(MeOH)\{(Cy_2PCH_2)_2C_6H_3\}]$	Oct.	1.984(8)	2.346(3) 2.361(3)	166.1(1)	98.7(3) 98.5(3)	14.8	staggered
$[RhCl_2(EtOH)\{(Cy_2PCH_2)_2C_6H_3\}]$	Oct.	2.008(8)	2.363(3) 2.357(3)	164.6(1)	98.2(4) 98.3(4)	19.5	staggered
$[RhHCl\{(Bu_2{}^tPCH_2)_2C_6H_3\}]$	Sq. pyr. [14]	1.999(7)	2.306(2) 2.302(2)	168.82(8)	102.3(4) 102.5(3)	6.9	eclipsed
$[RhHCl(Bu_2{}^tP(CH_2)_5PBu_2{}^t)]$	Sq. pyr. [2]	2.082(2)	2.310(1) 2.318(1)	167.8	102.9 102.3	–	eclipsed
$[IrHCl(Bu_2{}^tP(CH_2)_5PBu_2{}^t)]$	Sq. pyr. [3]	2.106(7)	2.308(2) 2.311(2)	167.5(1)	103.5(2) 103.1(3)	–	eclipsed
$[IrHCl(Bu_2{}^tPCH_2CHMe(CH_2)_3PBu_2{}^t)]$	Sq. pyr. [4]	2.073(14)	2.299(3) 2.315(3)	167.4(1)	103.7(4) 103.7(4)	–	eclipsed
$[RhCl_2(OH_2)\{(Me_2NCH_2)_2C_6H_3\}]$	Oct. [5]	1.913(3)	2.160(3) 2.152(3)	163.1(1)	104.5(2) 104.7(2)	14.6	staggered
$[NiI_2\{(Me_2NCH_2)_2C_6H_3\}]$	Sq. pyr. [15]	1.898(5)	2.050(4) 2.038(4)	152.0(2)	108.4 109.5	11.5	eclipsed
$[PtI(I_2)\{(Me_2NCH_2)_2C_6H_3\}]$	Sq. pyr. [16]	1.937(9)	2.116(7) 2.106(8)	160.7(3)	108.0 108.9	9.26	eclipsed
$[PtCl_3\{(Me_2NCH_2)_2C_6H_3\}]$	Oct. [17,18]	1.948(12)	2.152(12) 2.143(9)	160.3(6)	106.1(7) 106.9(7)	16.3	staggered
$\{PtI_2(p\text{-}tol)\{(Me_2NCH_2)_2C_6H_3\}]$	Oct. [18]	1.99(2)	2.15(2) 2.21(2)	162.5(8)	106.1 106.9	12.9	staggered

[a] The angle at which the aromatic ring tilts (about C(1)–C(4)) relative to the mean coordination plane.

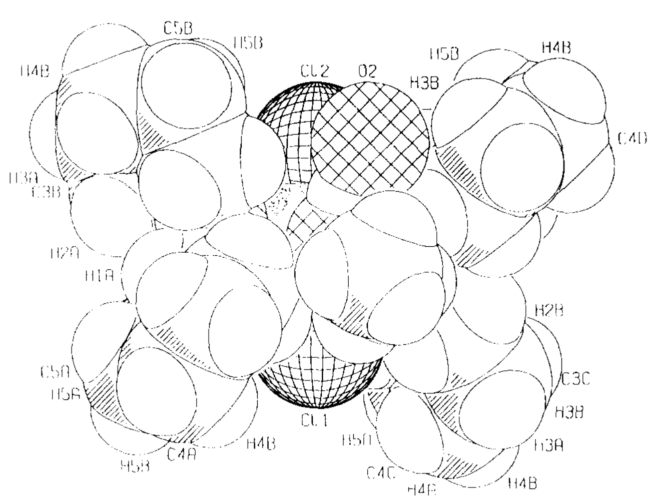

Fig. 3. A view of a space-filling model of the molecule *trans*-[$RhCl_2(EtOH)$-{C_6H_3-2,6-$(CH_2PCy_2)_2$}] and of its associated water molecule. The view direction is approximately the same as that of Fig. 2.

N...N axis, or C_2, with staggered R groups, and that bulky Cy or ^tBu substituents favour C_i to minimise R · · · X interactions [13]. In the octahedral molecules of the present study, the adoption of an approximate C_2 symmetry is necessary to avoid conflict between the terminal R groups and the "axial" chloride ligands. This necessarily leads to an increased interaction between R and the solvento ligands *trans* to σ-C, but with the smaller solvent molecules involved it is clear that even with R = Cy this can be achieved (though the space-filling diagram of *trans*-[$RhCl_2$(EtOH)(PCP)] (Fig. 3) reveals how crowded this arrangement is). It appears that with the even more sterically demanding ^tBu substituents [20] neither configuration can be achieved, although a single axial H atom can be accommodated. The fact that [Rh(CO){C_6H_3-2,6-$(CH_2P^tBu_2)_2$}] fails to undergo oxidative addition with Cl_2 [1], an unusual behaviour for a square-planar Rh(I) species, is compatible with this rationalisation.

With the formation of complexes [$RhCl_2$(L){C_6H_3-2,6-$(CH_2P^tBu_2)_2$}], or even [$RhCl_2${C_6H_3-2,6-$(CH_2P^tBu_2)_2$}], precluded on steric grounds, another reaction path must operate. There is evidence that the formation of five-coordinate complexes of types **1** and **2** is preceded by binuclear [$Rh_2H_2Cl_4(PCHP)_2$] [2] and [$RhCl_2(OH_2)$(NCN)] by [$RhCl_3$(NCHN)] [5]. The metallation step is thus probably the slowest, after both coordination of the P or N donor atoms and, when appropriate, the reduction of a Rh–Cl to Rh–H. Also, the metallation step might require preformation of *trans*-spanning P–P or N–N chelates [13,21]. We suggest, therefore, that the presence of the highly sterically demanding *tert*-butyl groups prevents the formation of the key structures en route to metallated complexes until one Cl ligand has been replaced by H.

3. Experimental details

NMR spectra were recorded on Bruker AM200 or SW200 instruments operating in the Fourier transform mode. IR spectra were recorded for KBr discs on a Phillips FTIR spectrophotometer. Microanalyses were performed at Glasgow University Chemistry Department microanalytical laboratory. Reactions were carried out under dry, oxygen-free nitrogen. All solvents were degassed.

3.1. [$RhCl_2$(MeOH)(PCP)]

A mixture of [$RhCl_2(OH_2)$(PCP)]. ^iPrOH [6] (0.22 g, 0.29 mmol) and methanol (30 ml) was refluxed for 24 h. After evaporation of the solvent in a nitrogen stream, the residual pale-brown powder was recrystallised from a mixture of methanol (20 ml) and CH_2Cl_2 (4 ml) at −5°C to yield orange needles of [$RhCl_2$(MeOH)-(PCP)].CH_2Cl_2 (0.51 g, 51%), M.Pt. 268–271°C (dec). The dichloromethane molecule was rapidly lost on standing (20 min) to leave an orange powder of [$RhCl_2$(MeOH)(PCP)]. ^{31}P NMR spectrum in $CHCl_3$, δ 39.5, *J*(Rh–P), 95.1 Hz; ^1H NMR spectrum, δ(CH_2 chelate ring) 3.31(t, $|^2J_{(P-H)} + ^4J_{(P-H)}| = 8.32$ Hz).

3.2. [$RhCl_2$(EtOH)(PCP)]

A similar recrystallisation of [$RhCl_2(OH_2)$-(PCP)].^iPrOH from hot ethanol produced [$RhCl_2$ (EtOH)(PCP)] as orange needles, M.Pt. 254–256°C (dec). Anal. Found: C, 56.6; H, 7.75; Cl, 10.2. $C_{34}H_{57}Cl_2OP_2Rh$ calc.: C, 56.9; H, 8.0; Cl, 9.9%. ^{31}P NMR spectrum in $CHCl_3$, δ 39.9, *J*(Rh–P) = 95.3 Hz; ^1H NMR spectrum, δ(CH_2 chelate ring) 3.31(t, $|^2J_{(P-H)} + ^4J_{(P-H)}| = 8.32$ Hz)

3.3. X-ray analysis of *trans*-[$RhCl_2$(MeOH)-(PCP)].0.41CH_2Cl_2

Measurements were made at 26°C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo-*K*α radiation, $\lambda = 0.71073$ Å, using a fragment 0.40 × 0.35 × 0.33 mm cut from a larger crystal and mounted in a capillary.

3.3.1. Crystal data

$C_{33}H_{55}Cl_2OP_2Rh.0.41CH_2Cl_2$, $M = 738.45$, monoclinic, space group $P2_1/a$, $a = 11.003(1)$ Å, $b = 27.322(1)$ Å, $c = 13.391(2)$ Å, $\beta = 113.55(1)°$, $V = 3690(2)$ Å^3, $Z = 4$, $D_c = 1.329$ g cm^{-3}, μ(Mo-*K*α) = 7.1 cm^{-1}.

3.3.2. Measurements

Cell dimensions are based on the setting angles of 22 reflections with $11.7 < \theta(\text{Mo-}K\alpha) < 22.8°$. The intensities of 11,720 reflections with $2.6 < \theta(\text{Mo-}K\alpha) < 30.0°$, $h\,\overline{15}$–15, k0–39, l 0–19, were estimated from

Table 3
Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for *trans*-[RhCl$_2$(MeOH)(PCP)].0.41CH$_2$Cl$_2$.

Atom	*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′(5)	−0.24393	0.13333	0.07899	0.086

$\omega/2\theta$ scans and corrected for Lp and absorption effects (empirical correction factors on F 0.83–1.05) [22]. On averaging 425 duplicate measurements ($R_{\text{int}} = 0 \cdot 042$) intensities for 11,295 unique reflections were obtained. Further calculations used only the 3971 unique reflections with $I > 3\sigma(I)$.

3.3.3. Structure analysis

The structure was solved by Patterson and Fourier methods. Refinement on F with $w = 1/\sigma^2(F)$ of 354 parameters (Table 3) converged ($\Delta/\sigma < 0.003$) at $R = 0.062$, $R = 0.066$, $S = 2.2$. Anisotropic U_{ij} were used for all non-H atoms of the Rh complex. The H atom of the MeOH hydroxyl group was positioned from a difference synthesis and its U_{iso} was refined. MeOH methyl H atoms were not included in the calculations. The structure contains 0.414(6) of a CH$_2$Cl$_2$ molecule disordered so that there are four Cl sites. Many unsuccessful attempts were made to model this disorder. Finally the positional and U_{iso} parameters of the CH$_2$Cl$_2$ C and Cl atoms were estimated from a difference synthesis and only the occupancy parameter of the solvent molecule was refined. The H atoms of this molecule were not included in the calculations. Other H atom positions were calculated using stereochemical criteria with C–H = 0.96 Å and $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Final $\Delta\rho$ values were −0.73 to +0.88 e Å^{-3}. Tables of hydrogen atom coordinates and anisotropic displacement parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Table 4
Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for *trans*-[RhCl$_2$(EtOH)(PCP)].H$_2$O.

Atom	*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

3.4. X-ray analysis of trans-$[RhCl_2(EtOH)(PCP)].H_2O$.

Unless stated otherwise the experimental and computational methods employed were similar to those used in the previous analysis. The crystal was a yellow plate of dimensions 0.45 × 0.30 × 0.05 mm obtained from EtOH/hexane solution.

3.4.1. Crystal data

$C_{34}H_{59}Cl_2O_2P_2Rh$, $M = 735.68$, monoclinic, space group $P2_1/a$, $a = 12.389(1)$ Å, $b = 22.575(2)$ Å, $c = 12.937(2)$ Å, $\beta = 93.27(1)°$, $V = 3612.3(7)$ Å^3, $Z = 4$, $D_c = 1.353$g cm^{-3}, μ(Mo–$K\alpha$) = 7.3 cm^{-1}.

3.4.2. Measurements

Cell dimensions are based on the setting angles of 25 reflections with $15.4 < \theta(\text{Mo–}K\alpha) < 22.0°$. The intensities of 8,859 reflections with $2.2 < \theta(\text{Mo–}K\alpha) < 27.8°$, h $\overline{16}$–16, k 0–29, l $\overline{16}$–0, were estimated from $\omega/2\theta$ scans and corrected for Lp and absorption effects (empirical correction factors on F 0.82–1.10) [22]. On averaging 361 duplicate measurements ($R_{\text{int}} = 0.059$) intensities for 8,498 unique reflections were obtained. Further calculations used only the 3089 unique reflections with $I > 3\sigma(I)$.

3.4.3. Structure analysis

Refinement on F with $w = 1/\sigma^2(F)$ of 371 parameters (Table 4) converged ($\Delta/\sigma < 0.002$) at $R = 0.055$, $R_w = 0.054$, $S = 1.7$. Final $\Delta\rho$ values were -0.77 to $+0.98$ e Å^{-3}. Water H atoms were not located; the position of the H atom of the ethanol hydroxy group was obtained from a difference synthesis. The GX package was used for all calculations [23]. Scattering factors and anomalous dispersion corrections were taken from Ref. [24]. Tables of hydrogen atom coordinates and of anisotropic displacement parameters;and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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