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Water-soluble hydroxyalkylated phosphines: examples of their differing behaviour toward ruthenium and rhodium

Lee J. Higham,*[a] Michael K. Whittlesey[b] and Paul T. Wood[c]

[a] *Chemistry Department, The Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Sciences, University College Dublin, Belfield, Dublin 4, Ireland*

[b] *Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY*

[c] *University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW*

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The reaction of $P(CH_2OH)_3$ (**I**) and $P(C_6H_5)(CH_2OH)_2$ (**II**) with $RuCl_3$ in methanol eliminates two equivalents of formaldehyde to yield the mixed tertiary and secondary phosphine complexes all-*trans*-$[RuCl_2(P(CH_2OH)_3)_2(P(CH_2OH)_2H)_2]$ (**1**) and $[RuCl_2(P(C_6H_5)(CH_2OH)_2)_2(P(C_6H_5)(CH_2OH)H)_2]$ (**2**), respectively. There is a high degree of hydrogen-bonding interactions between the hydroxymethyl groups in **1** and **2**, although the phenyl groups of the latter reduce the extent of the network compared to **1**. The generation of these mixed secondary and tertiary phosphine complexes is unprecedented. Under the same reaction conditions, the tris(hydroxypropyl)phosphine **III** formed no ruthenium complex. The reaction of $P(CH_2OH)_3$, $P(C_6H_5)(CH_2OH)_2$ and $P\{(CH_2)_3OH\}_3$ with $[RhCl(1,5\text{-cod})]_2$ in an aqueous/dichloromethane biphasic medium yielded $[RhH_2(P(CH_2OH)_3)_4]^+$ (**3**), $[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ (**4**) and $[Rh(P(C_6H_5)(CH_2OH)_2)_4]^+$ (**5**) and $[Rh(P\{(CH_2)_3OH\}_3)_4]^+$ (**6**), respectively. Treating **5** with dihydrogen rapidly gave **4**. The hydroxypropyl compound **6** formed the corresponding dihydride much more slowly in aqueous solution, although $[RhH_2(P\{(CH_2)_3OH\}_3)_4]^+$ (**7**) was readily formed by reaction with dihydrogen. Two separate reaction pathways are therefore involved; for $P(CH_2OH)_3$ and to a lesser extent $P(C_6H_5)(CH_2OH)_2$, the hydride source in the product is likely to be the aqueous solvent or the hydroxyl protons, whilst for $P\{(CH_2)_3OH\}_3$ an oxidative addition of H_2 is favoured. The protic nature of **3** and **4** was illustrated by the H–D exchange observed in d_2-water. Dihydrides **3** and **4** reacted with carbon monoxide to yield the dicarbonyl cations $[Rh(CO)_2(P(CH_2OH)_3)_3]^+$ (**8**) and $[Rh(CO)_2(P(C_6H_5)(CH_2OH)_2)_3]^+$ (**9**). The analogous experiment with $[RhH_2(P\{(CH_2)_3OH\}_3)_4]^+$ resulted in phosphine exchange, although our experimental evidence points to the possibility of more than one fluxional process in solution.

Introduction

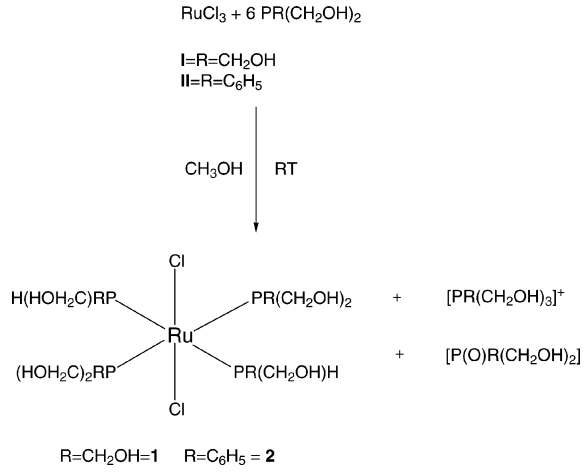
Despite continued interest in the development of water-soluble phosphines for use in biphasic catalysis and medicinal chemistry,[1] there is still much to be done on studying the fundamental reactivity of the hydroxyalkyl derivatives. Rhenium and technetium complexes of this ligand family have been shown to possess desirable attributes for use in radiopharmaceuticals.[2] Rh^{III},[3] Pd^{II}, Pt^{II} and Re^{V} complexes [1c] have been shown to be kinetically stabilised by such groups, and both rhodium[4] and ruthenium[5] compounds are active hydroformylation and hydrogenation catalysts, respectively. We have previously communicated[6] that the reaction of tris(hydroxymethyl)phosphine and ruthenium trichloride forms the all-*trans* complex $[RuCl_2(P(CH_2OH)_3)_2(P(CH_2OH)_2H)_2]$ **1** with the highly unusual generation of two secondary phosphine groups on the metal. Ikariya *et al.* have since shown this compound to be a superior catalyst than $P(CH_3)_3$ or water-soluble aryl phosphine complexes for the hydrogenation of supercritical carbon dioxide.[7] In light of the growing number of applications of these ligands, this novel reactivity prompted us to extend our study of water-soluble monodentate phosphines to both ruthenium and rhodium precursors. We report here our findings that the behaviour of these ligands differs widely between the two metals.

Results and discussion

Ruthenium reactions

The striking formation of all-*trans*-$[RuCl_2(P(CH_2OH)_3)_2(P(CH_2OH)_2H)_2]$ (**1**) prompted us to prepare the ligand $P(C_6H_5)(CH_2OH)_2$ **II** for its simple synthesis,[8] the presence of two α-carbons bearing hydroxyl groups (to confer water solubility) and the fact that the hydrophobic phenyl moiety would be expected to alter the solubility/hydrogen bonding properties of any complex. The compound $[Mo(CO)_5(P(C_6H_5)(CH_2OH)_2)]$ is a rare report of its coordination chemistry.[9] We also included the commercially available phosphine $P\{(CH_2)_3OH\}_3$ **III** in our study, to determine the effects of extending the number of CH_2 spacer groups between the alcohol and the phosphorus. In addition, aside from the use of this ligand in metallodendrimers,[10] telomerisations[11] and some hydrogenation reactions[5,7,12] its coordination chemistry is seldom encountered in the literature.

The $P(C_6H_5)(CH_2OH)_2$ reaction was carried out in an analogous fashion to that of **I** (Scheme 1), with the solution changing from dark red to a green colour and the subsequent precipitation



Scheme 1 Formation of the all-*trans*-complexes **1** and **2**.

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of small yellow crystals of **2** over 24 h. These were suitable for an X-ray crystallographic study (Fig. 1).

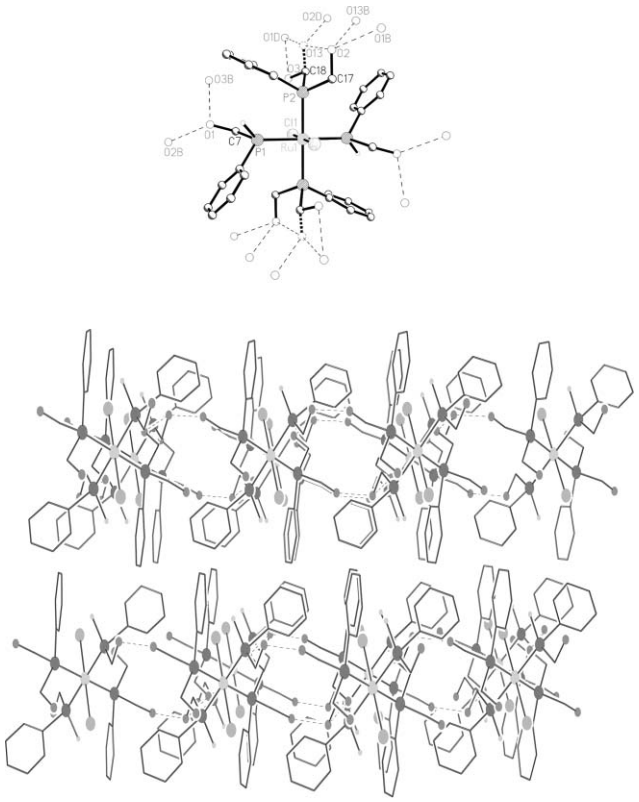


Fig. 1 View of **2** showing the atom numbering scheme and the possible hydrogen-bonding (dashed lines). The bold dashed lines indicate disorder in one of the hydroxymethyl groups (see text). The inset displays the [110] direction showing the hydrogen bonding (dashed line).

The compound crystallises in a centrosymmetric space group with the metal on an inversion centre which imposes an all-*trans* geometry and also dictates that both isomers of the chiral secondary phosphine ligand are present in each molecule. The position of one of the oxygen atoms of the tertiary phosphine is disordered over two sites. The site with one-third occupancy (O(13)) is eclipsed with respect to the other alcohol function on that ligand whilst that with two-thirds occupancy (O(3)) points away. In common with the other oxygen atoms in the molecule both of these positions have a number of intermolecular hydrogen bonds shorter than 2.8 Å. These give rise to sheets that lie in the *ab* plane but the presence of the hydrophobic phenyl ring interactions between these sheets prevents the formation of a three-dimensional hydrogen-bonded network, and helps to explain the apparent insolubility of **2**. There are similarities with the $P(CH_2OH)_3$ complex **1**; both the tertiary and secondary phosphines are involved in intermolecular hydrogen bonding, but with the P–H group playing no part in this.

Important bond lengths and angles for **2** are summarised in Table 1. In the case of **2** the metal to phosphine bond lengths are similar in both the tertiary and secondary cases, unlike **1** where there is a difference of about 0.1 Å (for **1**: ^{sec}P–Ru 2.414(2) *cf.* ^{ter}P 2.318(2) Å). The increased steric bulk of the ligand and lowered basicity of **II** may be expected to increase the Ru–P bond length with respect to **1**, and this is observed when the tertiary phosphine bond lengths are compared (for **2**: ^{ter}P–Ru 2.383(2) Å). However the reverse trend is found when comparing the respective secondary phosphines (for **1**: ^{sec}P–Ru 2.414(2) *cf.* ^{sec}P 2.352(2) Å for **2**). These differences may be attributable to the extensive hydrogen bonding. The $P(C_6H_5)(CH_2OH)H$ bond length in **2** is in close agreement with that found in the analogous organo-soluble complexes *trans*-$[RuCl_2(P(CH_3)_2H)_4]$ (2.323 and 2.331 Å)[13] and *trans*-$[RuCl_2(P(C_6H_5)_2H)_4]$ (2.3665(8) and 2.3505(8) Å).[14]

Table 1 A comparison of relevant bond lengths and angles for **2**

Ru–P(1)	2.352(2)	P(1)–Ru–P(1A)	180
Ru–P(2)	2.383(2)	P(2)–Ru–P(2A)	180
Ru–Cl(1)	2.443(2)	Cl(1)–Ru–Cl(1A)	180
P(1)–H(1)	1.55(8)	P(1)–Ru–P(2A)	91.45(7)
P(1)–C(1)	1.853(8)	P(1)–Ru–P(2)	88.55(7)
P(1)–C(7)	1.871(9)	P(1)–Ru–Cl(1A)	87.09(7)
C(7)–O(1)	1.390(11)	P(1)–Ru–Cl(1)	92.91(7)
P(2)–C(11)	1.834(8)	P(2)–Ru–Cl(1)	94.26(7)
P(2)–C(18)	1.849(8)	P(2)–Ru–Cl(1A)	85.74(7)
P(2)–C(17)	1.863(9)	C(1)–P(1)–C(7)	104.3(4)
C(17)–O(2)	1.426(11)	C(1)–P(1)–Ru	124.1(2)
C(18)–O(3)	1.395(12)	C(7)–P(1)–Ru	114.1(3)
C(18)–O(13)	1.34(2)	C(11)–P(2)–C(18)	102.5(4)
		C(11)–P(2)–C(17)	98.9(4)
O···O distances (Å)[a]		C(18)–P(2)–C(17)	100.3(4)
O(1)···O(2B)	2.698(13)	C(11)–P(2)–Ru	118.8(3)
O(1)···O(3B)	2.775(14)	C(18)–P(2)–Ru	118.8(3)
O(2)···O(1B)	2.698(13)	C(17)–P(2)–Ru	114.2(3)
O(2)···O(13B)	2.67(2)		
O(3)···O(1D)	2.775(14)		
O(13)···O(2D)	2.67(2)		

[a] Selected possible H-bonds based on O···O distances (the concerned OH hydrogen atoms could not be localised).

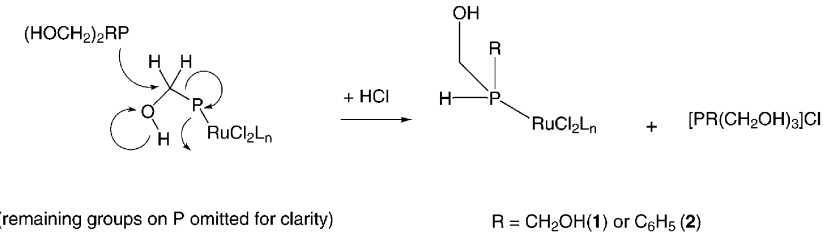
The ^{31}P NMR spectra of the reaction mixtures of both **1** and **2** share common features; the formation of $O{=}PR(CH_2OH)_2$ and $[PR(CH_2OH)_3]^+$ is observed in both cases (see later). For **1** the resonances are observed as an A_2B_2 pattern at δ 9.7 ppm (t, $^2J_{PP}$ = 37.5 Hz) and δ 13.5 ppm (t, $^2J_{PP}$ = 37.5 Hz), with the higher field triplet assigned to the secondary phosphine on account of the large P–H coupling ($^1J_{PH}$ = 253.0 Hz) in the ^{31}P–^{1}H coupled spectrum. The IR spectrum (KBr) shows a band at 2374 cm^{-1} assigned to ν(P–H).

The formation of **1** and **2** is not instantaneous but occurs slowly over time out of a complicated spectral region (reaction time <1 h) which precluded identification of the initial ruthenium phosphine species present. There is no NMR evidence for uncoordinated $P(CH_2OH)_2H$ or $P(C_6H_5)(CH_2OH)H$, and for **1** we see no scrambling of the phosphine ligands when the solutions are kept in the dark at 0 °C (light appears to promote isomerisation/scrambling). Only dimethyl sulfoxide and dimethylformamide dissolved **2**. Upon dissolution of **2** in d_6-dimethyl sulfoxide, the ^{31}P NMR spectrum was recorded immediately and showed signals similar to **1**; the $^2J_{P-P}$ coupling is comparable (35.0 Hz compared to 37.5 Hz for **1**) and the presence of the secondary phosphine was confirmed by the $^1J_{P-H}$ coupling on the upfield resonance (263.9 Hz compared to 253.0 Hz for **1**). Other complicated areas of the NMR spectrum are probably attributable to the 'non-innocent' behaviour of the solvent. The solvent reactivity may also explain why neither **1** nor **2** can be synthesised from the commonly used precursor $[RuCl_2(DMSO)_4]$, which in both cases yield a complex mixture of products. Solutions of **2** in deuterated dimethylformamide showed essentially the same behaviour.

Grosselin *et al.*[15] noted a number of pertinent points in their reactions of ruthenium chloride with TPPTS (TPPTS = tris(*m*-sulfophenyl)phosphine trisodium salt) when conducted in a polar solvent (in this case water). They postulate that the reduction of Ru^{III} to Ru^{II} and phosphine oxidation occurs prior to coordination (Scheme 2) and invoke a similar mechanism to

$$Ru^{III}Cl_3 + (n + {}^1/_2)TPPTS + {}^1/_2H_2O \rightarrow Ru^{II}Cl_2(TPPTS)_m + {}^1/_2OTPPTS + (n\text{-}m)TPPTS + HCl$$

Scheme 2 Grosselin's proposed reduction of Ru^{III} and concomitant phosphine oxidation.



Scheme 3 Proposed formation for the secondary phosphine groups in **1** and **2**.

that which accounts for the aqueous oxidation of TPPTS by rhodium chloride.[16]

A similar mechanism would explain many of the observations made during the formation of **1** and **2**, including the presence of $O{=}PR(CH_2OH)_2$ and the generation of HCl – necessary for the formation of the observed $[PR(CH_2OH)_3]^+$ (together with a mole of eliminated formaldehyde from the secondary phosphine forming step).

The synthesis of a bidentate phosphine–phosphinite complex $[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ prepared by Pringle *et al.* [17] requires the elimination of two units of formaldehyde, and was accompanied by the formation of $[P(CH_2OH)_4]Cl$. The elimination proceeds *via* nucleophilic attack by uncoordinated $P(CH_2OH)_3$ on the α-carbon of a cyclic adduct intermediate, which then eliminates as $[P(CH_2OH)_4]^+$. Upon ring closure the formation of the bidentate ligand is complete. We propose that the formation of the secondary phosphine in **1** and **2** occurs by attack of free $PR(CH_2OH)_2$ on the α-carbon of a coordinated $PR(CH_2OH)_2$ ligand. The formation of $[PR(CH_2OH)_3]^+$ can then be accounted for by elimination of formaldehyde and the presence of HCl, generated as a by-product of the metal reduction by phosphine (Scheme 3). This supports our findings that a ratio of 6 : 1 phosphine : ruthenium is required, and that additional phosphine (up to 10 equivalents) has no effect on the yield.

These results clearly demonstrate that the hydroxymethyl group is significantly activated by coordination to the ruthenium centre even when only two such groups are present on the ligand. It is unclear at present why an all-*trans* arrangement prevails for **1** and **2** and we found no evidence of further formaldehyde elimination when sodium hydrogen sulfite [18] or sodium metabisulfite [19] were added to solutions of **1**; instead they only promoted phosphine oxidation. The addition of formaldehyde solution to **1** and **2** did not lead to any detectable insertion into the P–H bonds, whilst ligand solutions give hemiacetal mixtures with the same reagent *i.e.*, a reaction which is in effect the reversal of the purification step of $P(CH_2OH)_3$.

It is plausible that the formation of **1** and **2** occurs by a secondary process of ligand rearrangement after formaldehyde elimination, driven perhaps by favourable hydrogen bonding. This is supported by the stability of **1** to ligand dissociation/exchange. The reactions were repeated using aqueous methanol (75 : 25 and 50 : 50 methanol : water) and we found increased amounts of phosphonium salt and oxide with increased water content. When water was employed as sole solvent these were the only products observed in the ^{31}P NMR spectrum, together with colloidal ruthenium. The proportion of phosphine oxide present is also substantially increased if the methanolic reaction is carried out under reflux.

The common factor to both phosphines is the hydroxymethyl groups and thus we carried out the analogous reaction with $P\{(CH_2)_3OH\}_3$ **III** to see if the functionality at the end of the propyl chain affects the reaction in any way. Surprisingly there was no complex formation (given that **III** has been used as a ligand for ruthenium based catalysis – see earlier); only a precipitate of what appeared to be ruthenium metal and a green solution containing phosphine oxide was observed. This contrasts to **1** and **2**, where the immediate presence of substantial amounts of $[PR(CH_2OH)_3]^+$ was observed.

An alternate precursor was employed, and in a biphasic reaction of $P(CH_2OH)_3$ and $[RuCl_2(P(C_6H_5)_3)_3]$ (water/dichloromethane) ligand exchange took place to yield **1**, with less phosphine oxide and phosphonium salt present, but other ruthenium–phosphine species evident by ^{31}P NMR. However, when $P\{(CH_2)_3OH\}_3$ was used in this manner no reaction took place (^{31}P NMR showed only uncoordinated $P\{(CH_2)_3OH\}_3$). The synthesis of $[Ru_4H_4(CO)_8(P(CH_2OH)_3)_4]$ [20] and the preparation[5] of the catalytic precursors $[(\eta^5\text{-}C_5H_5)RuCl(CO)L]$ where L is **I** or **III** are evidence that both ligands can coordinate to ruthenium in a 'regular' way depending on the other ligands present. As a comparison, we reacted 2 equivalents of $P(CH_2OH)_3$ and $[(\eta^5\text{-}C_5H_5)RuCl(P(C_6H_5)_3)_2]$ in a biphasic reaction but found no exchange took place. In an attempt to generate ruthenium hydride complexes, biphasic ligand exchange reactions were attempted using $P(CH_2OH)_3$ and $RuH_2(PPh_3)_4$ [21] and $RuH(CH_3CO_2)(PPh_3)_3$, [22] but no compounds could be isolated. No hydride was generated either by reaction of **1** with sodium borohydride.

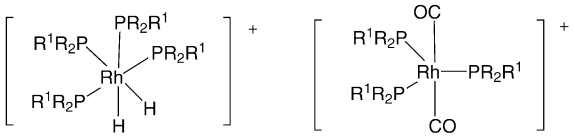
Rhodium reactions

Chatt *et al.*[23] reported the synthesis of *mer*-$[RhCl_3(P(CH_2OH)_3)_3]$, by reaction of $P(CH_2OH)_3$ and $RhCl_3$ in refluxing alcohol, and *trans*-$[RhCl(CO)(P(CH_2OH)_3)_2]$ was prepared by a ligand exchange reaction with $[RhCl(CO)_2]_2$ in methanol. Of significance is the more recent report describing the formation of *fac*-$[RhCl_3(P(CH_2OH)_3)_3]$ from the reaction of $RhCl_3$ and **I** in aqueous solution.[3] To the best of our knowledge, no rhodium complexes of $P(C_6H_5)(CH_2OH)_2$ and only one of $P\{(CH_2)_3OH\}_3$ have been reported.[10] We have found that reactions of **I** with $[RhCl(1,5\text{-cod})]_2$ in a biphasic reaction (water/dichloromethane) led to the instantaneous formation of the dihydride *cis*-$[RhH_2(P(CH_2OH)_3)_4]^+$ **3**; water-soluble phosphine hydrides are uncommon in the literature but they are increasingly attracting attention.[24–26]

The reaction is easily monitored by the transfer of coloration from the dichloromethane layer to the aqueous phase (the ^{31}P NMR spectrum of **3**: δ 33.7 ppm, dt, $^1J_{Rh-P} = 86.3$ Hz, δ 21.0 ppm, dt, $^1J_{Rh-P} = 98.8$ Hz, $^2J_{P-P} = 22.0$ Hz). A $^2J_{P-H}$ coupling constant of 120.3 Hz is observed for the phosphorus signal at δ 21.0 ppm, indicating these phosphines are *trans* to the hydride ligands which appear at δ −11.10 ppm in the ^1H NMR spectrum. Broadband ^{31}P decoupling of the spectrum shows a doublet splitting of $^1J_{H-Rh} = 12.1$ Hz. Selective decoupling of the phosphines *trans* to the hydrides produced a broadened pseudo-quartet, and signifies that the magnitude of $^2J_{P_{axial}-H}$ must be similar in magnitude to $^1J_{Rh-H}$ – approximately 12 Hz. Selective decoupling of the axial phosphines produces a second-order spectrum. There are strong similarities with *cis*-$[RhH_2(P(CH_3)_3)_4]^+$,[27] where the authors calculated a best-fit spectrum and established that the hydride multiplet consisted of a seven-spin $AA'MXX'Y_2$ system, rather than the more simple $A_2X_2MY_2$ with the equatorial *cis*-hydrides and equatorial phosphines assigned as AA′ and XX′, respectively. This is because of the chemical equivalence but magnetic non-equivalence of these groups in the equatorial plane, where both the larger *trans*- and smaller *cis*-$^2J_{P-H}$ coupling must be considered. The axial

phosphines, *i.e.* the phosphines *trans* to one another are denoted as Y_2. Accordingly a AA′MXX′Y_2 system is also assigned for **3**.

During this time Komiya *et al.* noted the unexpected formation of the same compound in tetrahydrofuran (along with other uncharacterised species) and speculated that traces of adventitious water may be the source of the hydride.[4] We find that the reaction of $[RhI(1,5\text{-cod})]_2$, $[RhCl(1,5\text{-cod})(P(C_6H_5)_3)]$, and $[Rh(1,5\text{-cod})(P(C_6H_5)_3)_2]B(C_6H_5)_4$ with excess $P(CH_2OH)_3$ (ratio = 1 Rh : 4.5 P) in dichloromethane/water all gave **3** (Fig. 2) as the main Rh containing product. The complexes $[RhI(1,5\text{-cod})]_2$ and $[RhCl(1,5\text{-cod})(P(C_6H_5)_3)]$ gave the cleanest routes with **3** as the only Rh complex. In our hands the reaction of $RhCl_3$ with $P(CH_2OH)_3$ in aqueous solution led to the formation of $O{=}P(CH_2OH)_3$, $[P(CH_2OH)_4]^+$ (as seen for **1** and **2**) and two independent doublets (δ 37.2 and 15.2 ppm) as part of a mixture of rhodium-phosphine species (one of which may be the *fac*-$[RhCl_3(P(CH_2OH)_3)_3]$ compound communicated by Katti[3]). Complex **3** was not formed under these conditions, but when $RhCl_3$, tetrakis(hydroxymethyl)phosphonium chloride and triethylamine were combined in aqueous solution it *was* synthesised relatively cleanly (by ^{31}P NMR spectroscopy).



R=R¹=CH_2OH = **3**
R=CH_2OH, R¹=C_6H_5 = **4**
R=R¹=$(CH_2)_3OH$ = **7**

R=R¹=CH_2OH = **8**
R=CH_2OH, R¹=C_6H_5 = **9**

Fig. 2 The rhodium dihydride and dicarbonyl compounds.

The reaction of $[RhCl(1,5\text{-cod})]_2$ with $P(CH_2OH)_3$ in *d*-chloroform/d_2-water gave a yellow aqueous layer after 30 min. A $^{31}P\{^1H\}$ NMR spectrum of the d_2-water layer was recorded and showed that the upfield resonance observed for **3** *i.e.* that of the phosphorus *trans* to the hydride ligands had changed to a broad signal, resulting from *trans* $J_{P\text{-}D}$ coupling. No hydride signal was seen in the proton spectrum. Unfortunately no M–D band was identified in the IR spectrum as the region (~1410 cm^{-1}) was obscured, although the M–H band at ν = 1966 cm^{-1} was no longer evident. Addition of water to these solutions sees the reappearance of the dihydride **3**. We carried out some selective decoupling experiments on **3** and found that when the water resonance was irradiated and a $^{31}P\text{–}^1H$ coupled spectrum recorded, $^2J_{P\text{-}H}$ coupling was observed, which indicates that exchange must be slow on the NMR timescale.

The reaction with $[RhCl(1,5\text{-cod})]_2$ was repeated with $P(C_6H_5)(CH_2OH)_2$ and the ^{31}P NMR spectrum after 10 min showed two doublets of triplets (δ 28.5 ppm, $^1J_{Rh\text{-}P}$ = 99.0 Hz, $^2J_{P\text{-}P}$ = 21.1 Hz; 15.8 ppm, $^1J_{Rh\text{-}P}$ = 87.0 Hz, $^2J_{P\text{-}P}$ = 21.1 Hz), consistent with the formation of the analogous complex *cis*-$[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ **4**. A measure of the splitting on the upfield resonance gives an approximate value of ~113 Hz, indicative of *trans* $^2J_{P\text{-}H}$ coupling for **4** (compared to 120.7 Hz for **3**). It was not possible to record a more accurate value owing to the broad nature of the signal. The hydride chemical shift (δ −11.20 ppm) of the multiplet is similar to that observed for the $P(CH_2OH)_3$ analogue **3**, and also to that reported for the closely related $[RhH_2(P(C_6H_5)(CH_3)_2)_4]^+$.[27]

Also evident in the ^{31}P NMR spectrum after 10 min reaction time was a large doublet resonance at δ −17.5 ppm ($^1J_{Rh\text{-}P}$ = 134.7 Hz), which we attribute to the four-coordinate rhodium(I) complex $[Rh(P(C_6H_5)(CH_2OH)_2)_4]^+$ **5** on account of the magnitude of $^1J_{Rh\text{-}P}$ and the absence of significant P–H coupling. Furthermore **4** is formed gradually over 60 min with a concomitant decrease in the signal for **5**. Treating **5** with dihydrogen resulted in the immediate conversion to the dihydride **4**. This correlates with the report by Osborn *et al.* who synthesised $[Rh(P(C_6H_5)(CH_3)_2)_4]^+$ ($^1J_{Rh\text{-}P}$ = 132 Hz) and converted it into the dihydride, an organo-soluble analogue of **4**, in a similar fashion.[27]

Further experiments showed **4** can also be formed in the *absence* of water, using alcoholic solvents, excess ligand and dihydrogen, although the stability of both **5** and **4** in such solvents appeared to be greatly reduced to that found in aqueous solution.

Analogous to the reaction with $P(CH_2OH)_3$, the dideuteride $[RhD_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ was prepared and the spectra showed essentially the same features; notably $^2J_{P\text{-}D}$ coupling which again broadened the upfield equatorial phosphine signal in the ^{31}P NMR spectrum, and no hydride signal in the proton spectrum. Addition of water regenerates the dihydride **4**, as discussed for **3**. The doublet species $[Rh(P(C_6H_5)(CH_2OH)_2)_4]^+$ (**5**) was present throughout these experiments, indicating the conversion of **5** to $[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ was slower than the D–H exchange process and serves to demonstrate the protic character of **4**.

Next we reacted $P\{(CH_2)_3OH\}_3$ with $[RhCl(1,5\text{-cod})]_2$ and found that after 5 min stirring, complete colour transfer to the aqueous layer had taken place.

There was however, no evidence of two doublets of triplets even after a 24 h period, only a doublet species **6** which showed no $J_{P\text{-}H}$ coupling at δ 4.4 ppm (136.3 Hz). This echoes the formation of **5**, and the highly hydrophilic compound is likely to be the analogous Rh^I cation $[Rh(P\{(CH_2)_3OH\}_3)_4]^+$. The notable difference between **5** and **6** however, is the time required for the latter to show even partial conversion to the dihydride (several months *cf.* 60 min). Further support for this assignment came from treating solutions of **6** with dihydrogen; a colour change was observed from orange to light yellow over a 15 min period and the familiar AA'MXX'Y_2 spin system became evident as **6** was quantitatively converted to the dihydride $[RhH_2(P\{(CH_2)_3OH\}_3)_4]^+$ **7** (δ_P 13.7 ppm, $^1J_{Rh\text{-}P}$ = 99.6 Hz, $^2J_{P\text{-}P}$ = 22.3 Hz; −0.4 ppm, $^1J_{Rh\text{-}P}$ = 87.4 Hz, $^2J_{P\text{-}P}$ = 22.3 Hz). The upfield resonance broadens in the $^{31}P\text{–}^1H$ coupled NMR, but the signal for the hydrides is very similar to that of **3** and **4** and appears at δ −11.85 ppm in the proton spectrum.

Solutions of **7** are stable in d_6-dimethyl sulfoxide and d_2-water, and show no sign of H–D exchange. The former behaviour mirrors that of **4**, but contrasts with that observed with the $P(CH_2OH)_3$ complex **3**, where dimethyl sulfoxide promotes decomposition *via* phosphine dissociation. The absence of exchange suggests the protic nature of **7** is considerably less than either $[RhH_2(P(CH_2OH)_3)_4]^+$ or $[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$, an unsurprising observation given the lack of reactivity of $[Rh(P\{(CH_2)_3OH\}_3)_4]^+$ in aqueous solution.

Of the three dihydride complexes, the phenyl derivative **4** is the least soluble on account of the lower number of hydroxyl groups present. Solutions of **3**, **4** and **7** show similar stability at room temperature, of up to two weeks, when stored under an inert atmosphere, and none of the complexes demonstrated reversible or irreversible loss of H_2 under reduced pressure. Exposure to oxygen and/or light promoted decomposition, whilst the alcoholic solutions show a marked decrease in stability, leading to decomposition to the corresponding oxides.

The addition of excess phosphine to aqueous solutions of the dihydrides showed no effect on the $^{31}P\{^1H\}$ NMR spectrum for **3**, suggesting there is no $P(CH_2OH)_3$ exchange. With $P(C_6H_5)(CH_2OH)_2$ however, there was a broadening of the resonances of **4** and uncoordinated phosphine, although the $^1J_{Rh\text{-}P}$ and $^2J_{P\text{-}P}$ couplings were retained. In the case of $P\{(CH_2)_3OH\}_3$, the addition of excess phosphine to aqueous solutions of **7** resulted in a broad phosphine signal and the re-emergence of the doublet resonance assigned to **6** *i.e.* $[Rh(P\{(CH_2)_3OH\}_3)_4]^+$. This appears to suggest that the phosphine promotes a reductive elimination reaction not observed with $P(CH_2OH)_3$ and $P(C_6H_5)(CH_2OH)_2$.

The formation of **3** proceeds without any evidence for the tetrakisphosphine complex $[Rh(P(CH_2OH)_3)_4]^+$. NMR analysis of the reaction analysed immediately showed only signals for **3**, phosphine oxide and a large signal for $P(CH_2OH)_3$. Even with low phosphine ratios of 1 : 1 $[RhCl(1,5\text{-cod})]_2$: $P(CH_2OH)_3$, the only metal complex observed in the ^{31}P NMR spectrum of the aqueous layer was **3**.

Conversely, interconversion of **5** into the dihydride **4** can be monitored over time, and unlike the reaction with $P(CH_2OH)_3$, reactant ratios of P : Rh lower than 4 : 1 for $P(C_6H_5)(CH_2OH)_2$ often show only phosphine oxide in the aqueous layer. This slower rate of formation may be due to the electron-withdrawing properties of the phenyl substituent. The rate is dramatically increased however upon the addition of H_2 to the aqueous solution of **5**, in an oxidative addition to a d^8 square-planar complex. Such reactions are common, but there are notable exceptions; for instance $[Rh(P(C_6H_5)_2CH_3)_4]^+$ does not react with H_2,[27] and $[Rh(P(CH_3)_3)_4]^+$ is more reactive but tends to dissociate $P(CH_3)_3$ in the absence of excess phosphine.[23]

The tetrakis-cation $[Rh(P\{(CH_2)_3OH\}_3)_4]^+$ **6** reacted very slowly toward water to give **7** after several months. Hence the formation of the dihydrides $[RhH_2(P(CH_2OH)_3)_4]^+$ and $[RhH_2(P\{(CH_2)_3OH\}_3)_4]^+$ proceed primarily *via* two independent pathways, whilst for the phenyl derivative $[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ both protonation and oxidative addition of H_2 appear accessible. These observations are supported by the H–D exchange reactions discussed earlier. The non-conversion of **6** to **7** in aqueous solution (in the absence of hydrogen) is surprising if water is the protonating agent during the formation of **3** and **4**, in that one may expect the most basic phosphine to promote protonation. One possible explanation of this trend is that the source of the hydride is not water but the hydroxyl protons of the ligands, a hypothesis which also supports the reported synthesis of **3** under anhydrous conditions (but which is currently attributed to trace amounts of water [4]). This may also account for the slow formation of **7** from **6** in aqueous solution, where the hydroxyl groups could be repelled from the metal centre by the longer, hydrophobic propyl chains. The synthesis of the dideuteride analogues of **3** and **4** could then be explained by the hydroxyl ligand protons undergoing prior exchange in the deuterated solvent, followed by reaction at the rhodium centre.

Reactivity of 3, 4 and 7 towards carbon monoxide

Bubbling aqueous or methanolic solutions of **3** with carbon monoxide for 15 min gave the phosphine oxide and a new species **8**, which appeared as a doublet at δ 24.4 ($^1J_{Rh-P} = 107.2$ Hz in d_4-methanol) in the ^{31}P NMR spectrum (there was no evidence for any hydride ligands). The analogous spectrum of ^{13}CO labelled **8**, showed coupling between the $P(CH_2OH)_3$ ligands and ^{13}CO, and the original doublet appeared as a doublet of triplets. The $^1J_{Rh-P}$ coupling remained at 107.2 Hz, with the $^2J_{PC}$ triplet splitting equal to 13.4 Hz. The ^{13}C NMR spectrum showed the methylene resonances at δ 58.2 ppm, and a clear, well-defined doublet of quartets at δ 197.1 ppm, with a $^1J_{Rh-C}$ coupling constant of 48.8 Hz and $^2J_{P-C}$ of 13.4 Hz. The IR spectrum of ^{12}CO labelled **8** showed a strong, single band at 2020 cm^{-1} (1958 cm^{-1} for ^{13}CO labelled **8**) indicative of a *trans*-disposition of the carbonyl ligands. The data is consistent with a trigonal bipyramidal structure for *trans*-$[Rh(CO)_2(P(CH_2OH)_3)_3]^+$.

For $[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ (**4**), stirred under a ^{12}CO atmosphere over 17 h, a broad doublet species **9** was observed at 19.0 ppm ($^1J_{Rh-P} \sim 107.8$ Hz). As in the corresponding $P(CH_2OH)_3$ reaction, no other rhodium–phosphine species were observed. When ^{13}CO was used, the signal resolves at 0 °C into a doublet of triplets, with $^1J_{Rh-P} = 106.6$ Hz and $^2J_{PC} = 11.3$ Hz. The ^{13}C NMR spectrum shows a corresponding doublet of quartets at the same temperature, with $^1J_{Rh-C} = 53.2$ Hz. An IR spectrum of ^{12}CO labelled **9** gave a single strong band at ν(CO) = 2018 cm^{-1}, with the ^{13}CO analogue showing the expected isotopic shift (1976 cm^{-1}). On this basis **9** is assigned as *trans*-$[Rh(^{13}CO)_2(P(C_6H_5)(CH_2OH)_2)_3]^+$. No evidence for phosphine dissociation was observed by ^{31}P NMR, suggesting the fluxionality of **9** is not due to phosphine ligand exchange.

The solution behaviour of **9** resembles is some ways that of $[Rh(CO)_2(P(C_6H_5)_3)_3]^+$, which exhibits significant dynamic behaviour in solution; only on cooling solutions to ≤ -60 °C does the broad singlet observed for the carbonyl ligands become a well defined doublet of quartets (δ 198.6 ppm, $^1J_{C-Rh} = 50$ Hz, $^2J_{C-P} = 14$ Hz).[28] However, in contrast to **8** and **9**, there is considerable phosphine dissociation at room temperature, with $^1J_{Rh-P}$ coupling only resolved below −40 °C (113.0 Hz), and two CO bands in the room-temperature solution IR spectrum, suggestive of a *cis* arrangement of these ligands. These results demonstrate that the $P(CH_2OH)_3$ and $P(C_6H_5)(CH_2OH)_2$ complexes **8** and **9** differ from many $[Rh(CO)_2(PR_3)_3]^+$ complexes reported in the literature which are commonly unstable and readily dissociate PR_3 and/or CO.

The reaction with $[RhH_2(P\{(CH_2)_3OH\}_3)_4]^+$ **7** and ^{13}CO saw the emergence of a doublet species (**10**) at δ 11.0 ppm ($^1J_{Rh-P} = 95.5$ Hz), accompanied by a broad resonance for uncoordinated $P\{(CH_2)_3OH\}_3$. On warming d_4-methanolic solutions of **10** to + 55 °C, loss of $^1J_{Rh-P}$ coupling was observed as both resonances broadened; the chemical shift for the uncoordinated phosphine flattened over an area of ~15 ppm, consistent with a phosphine exchange process. On lowering the temperature the doublet resolved again until at −60 °C the signal broadened and the coupling was lost. The ^{13}C NMR spectra showed a broadened doublet resonance at 198.5 ppm ($^1J_{Rh-C} = 53.7$ Hz) at room temperature, which lost the $^1J_{Rh-C}$ coupling at +50 °C. At −60 °C the resonance was also significantly broadened. ^{13}CO labelled **10** kept under a ^{12}CO atmosphere fully incorporated that isotope, indicating facile CO exchange. In contrast to **8** and **9** neither the ^{13}C nor the ^{31}P variable-temperature NMR spectra showed J_{PC} coupling. The IR spectrum of ^{12}CO labelled **10** gave a strong intensity band at ν(CO) = 1966 cm^{-1} (another medium band at 1989 cm^{-1} was also present), with a corresponding value of 1916 cm^{-1} for the ^{13}CO analogue. The spectroscopic evidence of rapid dissociation and exchange precludes definitive assignment of **10** other than as a $[Rh(CO)_n(P\{(CH_2)_3OH\}_3)_m]^+$ type species and serves to illustrate further the difference in reactivity of $P\{(CH_2)_3OH\}_3$ to the hydroxymethyl phosphines.

Aqueous and methanolic solutions of all the dicarbonyl cationic complexes are prone to oxidation on standing, and prolonged exposure to a reduced pressure also leads to decomposition. Repeated attempts at recrystallising the chloride salts of **8** and **9** from aqueous solution, methanol, and methanol–diethyl ether solvent systems were unsuccessful.

Attempts were also made to insert carbon dioxide into the Rh–H bond/s of the dihydrides, but when aqueous solutions of **3**, **4** and **7** were stirred under an atmosphere of the gas for 24 h, no reactivity was observed.

Experimental

General methods

All manipulations of oxygen sensitive compounds were carried out using vacuum-line techniques. All organic solvents were distilled and stored under nitrogen; from sodium (hexane and toluene), sodium/potassium (diethyl ether), sodium and benzophenone (tetrahydrofuran), phosphorus pentoxide (dichloromethane) and magnesium/iodine (methanol and ethanol). The solvent d_4-methanol (Cambridge Isotope Laboratories) was dried over 4 Å molecular sieves, and degassed with argon, as was the d_6-dimethyl sulfoxide and d-chloroform. The d_2-water was purchased from Apollo Scientific Ltd and was also purged with argon. Triethylamine (Aldrich) was dried and distilled from phosphorus pentoxide and stored under argon. The gases carbon monoxide (both isotopes), carbon dioxide

and dihydrogen were used as supplied (Aldrich). Lancaster Synthesis Ltd supplied $NaB(C_6H_5)_4$, $NaPF_6$, $NaBF_4$, $AgBF_4$ and 1,5-cyclooctadiene, which was used without further purification. The phosphines $P(C_6H_5)H_2$ and $P\{(CH_2)_3OH\}_3$ were purchased from Strem Chemicals Inc. The phosphonium salt $[P(CH_2OH)_4]Cl$ was donated as an 80% w/w aqueous solution by Rhodia.

The metal salts $RuCl_3{\cdot}H_2O$ and $RhCl_3$ were loaned by Johnson Matthey plc. The ruthenium compound $[RuCl_2(P(C_6H_5)_3)_3]$ was prepared by following the literature method.[29] The rhodium starting materials $[RhCl(1,5\text{-cod})]_2$, $[RhI(1,5\text{-cod})]_2$ and $[RhCl(1,5\text{-cod})P(C_6H_5)_3]$ [30] and $[Rh(1,5\text{-cod})(P(C_6H_5)_3)_2][B(C_6H_5)_4]$ [27] were all prepared according to the literature methods.

Physical and analytical measurements

NMR spectra were recorded on Jeol JNM-Ex 270 MHz FT-NMR and Varian Mercury 400 MHz NMR spectrometers (δ relative to tetramethylsilane for ^1H and ^{13}C spectra and 85% phosphoric acid for ^{31}P spectra). IR spectra were recorded on a Nicolet Impact 410 FT-IR System spectrometer in aqueous solutions between calcium fluoride plates or as Nujol mulls/potassium bromide disks. Elemental analyses were carried out at the University of East Anglia (UEA). Electrospray mass spectra were recorded on a Fison VG Autospec mass spectrometer in 1 : 1 water–methanol with 1% acetic acid.

Syntheses

$P(CH_2OH)_3$ (I). This was based on the literature procedure.[31]

An 80% w/w solution of $[P(CH_2OH)_4]Cl$ was evaporated to dryness on a rotary evaporator. The crystalline product (24 g, 0.19 mol) was further dried by azeotropic toluene distillation (110 °C, 1 atm). The anhydrous salt was then transferred to a 250 cm^3 round-bottomed flask, to which was added 150 cm^3 of dry triethylamine. This was stirred on an oil-bath at 60 °C for 1 h. After cooling, the resultant amine salt was removed by filtration. The excess triethylamine and formaldehyde by-product were then removed by distillation (88 °C, 1 atm), the formaldehyde subliming out into the condenser. The remaining product fraction consisted of $P(CH_2OH)_3$ and a quantity of hemiacetal impurities. The product was purified by vacuum distillation (90 °C, 0.1 mmHg) using a nitrogen-bleed inlet to prevent decomposition of $P(CH_2OH)_3$ to PH_3. The yield is quantitative (Found: C, 29.23; H, 7.12. Calc. for $C_3H_9O_3P$: C, 29.04; H, 7.31%). NMR (d_2-water, ppm): δ_H 4.15 (6 H, d, $^2J_{P\text{-}H} = 5.5$ Hz, CH_2); δ_P −23.7 (s). m/z 124 (M^+). Other physical properties of $P(CH_2OH)_3$ can be found in the literature.[32]

$P(C_6H_5)(CH_2OH)_2$ (II). Based on a private communication by Prof. Katti.[8]

Ethanol (15 cm^3) was added to an aqueous solution of formaldehyde (40% w/v, 2.2 g, 29.5 mmol) and degassed with argon. $P(C_6H_5)H_2$ (1.6 g, 14.5 mmol) was added dropwise to the solution and stirred for 5 h. The solvent was removed *in vacuo* to yield $P(C_6H_5)(CH_2OH)_2$ as a viscous, colourless oil in near quantitative yield (2.37 g, 96%). NMR (d_2-water, ppm): δ_H 7.34 (5 H, m, Ar*H*), 4.11 (4 H, d, $^2J_{P\text{-}H} = 5.9$ Hz, CH_2); δ_P −20.4 (s).

***trans*-[$RuCl_2(P(CH_2OH)_3)_2(P(CH_2OH)_2H)_2$] (1).** $RuCl_3{\cdot}xH_2O$ (50 mg, 0.24 mmol) was dissolved in dry methanol (5 cm^3), and to this 6 equivalents of $P(CH_2OH)_3$ (178 mg, 1.44 mmol) as a methanol solution (8 cm^3) was added. After 10 min a green colour resulted, and a precipitate appeared to form, which quickly redissolved. After 1 h the solvent was removed under vacuum, and the resultant oil solidified. This was dissolved in the minimum amount of methanol and hexane was added (20 cm^3). The hexane layer became opaque as impurities precipitated out. This layer was filtered off and the process repeated until a yellow solid started to precipitate. This was filtered off, dissolved in the minimum amount of warm methanol, layered with hexane and left for 2 weeks at 0 °C. Small yellow crystals were deposited and examined by X-ray crystallography which gave the structure as all-*trans*-$[RuCl_2(P(CH_2OH)_3)_2(P(CH_2OH)_2H)_2]$ (**1**). Yield = 35 mg, 24.2% (Found: C, 20.64; H, 5.38. $C_{10}H_{32}O_{10}P_4RuCl_2$ requires C, 19.75; H, 5.30%). IR (KBr, cm^{-1}) 2374 m, ν(P–H). NMR (d_4-methanol, ppm): δ_H 4.48 (8 H, br s, CH_2), 4.53 (12 H, br s, CH_2); δ_C 57.4 (vt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ 27.2 Hz), 57.9 (vt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ 26.8 Hz); δ_P 13.5 (t, $^2J_{P\text{-}P} = 37.5$ Hz), 9.7 (t, $^2J_{P\text{-}P} = 37.5$ Hz). Crystallographic data for **1** have been reported previously (CCDC 182/861).

***trans*-[$RuCl_2(P(C_6H_5)(CH_2OH)_2)_2(P(C_6H_5)(CH_2OH)H)_2$] (2).** $P(C_6H_5)(CH_2OH)_2$ (281 mg, 1.7 mmol) was dissolved in methanol (10 cm^3) and added to a solution (20 cm^3) of $RuCl_3$ in the same solvent (76 mg, 0.4 mmol). The red solution became green in colour on stirring overnight, after which time the product precipitated as small yellow crystals. The crystals were filtered off, washed with methanol and dried *in vacuo*. The structure by X-ray crystallography was found to be *trans*-$[RuCl_2(P(C_6H_5)(CH_2OH)_2)_2(P(C_6H_5)(CH_2OH)H)_2]$ (**2**). Yield = 30 mg, 10.5% (Found: C, 45.71; H, 5.04; Cl, 8.88. $C_{30}H_{40}O_6P_4RuCl_2$ requires C, 45.47; H, 5.09; Cl, 8.95%).

***cis*-[$RhH_2(P(CH_2OH)_3)_4]^+$ (3) and *cis*-[$RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$ (4).** The relevant phosphine (9.0 mmol) was dissolved in a degassed aqueous solution (20 cm^3) and slowly added to $[RhCl(1,5\text{-cod})]_2$ (0.51 g, 1.0 mmol) in dichloromethane (10 cm^3). Over a 10 min period complete colour transfer took place; the organic layer became colourless and the aqueous layer turned yellow. For $P(CH_2OH)_3$ (**I**), the ^{31}P NMR spectrum indicated that dihydride **3** was the only rhodium phosphine species in solution, but for $P(C_6H_5)(CH_2OH)_2$ (**II**) longer reaction times are required (typically 1 h) for complete conversion of **5** to **4**. The organic layer was then discarded and the aqueous phase washed with dichloromethane (20 cm^3). The water was removed under vacuum (at 40 °C) and the orange oil dissolved in methanol (5 cm^3). This was then washed repeatedly with diethyl ether to remove phosphine oxide that precipitated from the solution. The resultant oil was redissolved in methanol and the process repeated three times to give **3** as a fine yellow powder and **4** as a sticky solid. Attempts to characterise **4** by elemental analysis were thwarted by the presence of small quantities of remaining oxide. Separating the aqueous layer after 5 min reaction time and slowly bubbling dihydrogen through the solution for 10 min can also be used to prepare **4**.

3: (Found: C, 23.14; H, 5.25. $C_{12}H_{38}O_{12}P_4RhCl$ requires C, 22.60; H, 6.02%). NMR (d_4-methanol, ppm}: δ_H 3.48 (12 H, s, CH_2), 3.39 (12 H, s, CH_2), −11.10 (2 H, m, Rh*H*); δ_C 61.0 (vt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$17.7 Hz), 59.9 (vt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ 35.4 Hz); δ_P 33.7 (dt, $^1J_{Rh\text{-}P} = 86.3$ Hz, $^2J_{P\text{-}P} = 22.0$ Hz), 21.0 (dt, $^1J_{Rh\text{-}P} = 98.8$ Hz, $^2J_{P\text{-}P} = 22.0$ Hz); IR (KBr, cm^{-1}) 1966 w, ν(Rh–H). When biphasic reaction conditions were again employed and the Rh : P ratio was 1 : 4.5 then **3** was similarly prepared from $[RhCl(1,5\text{-cod})P(C_6H_5)_3]$, $[RhI(1,5\text{-cod})]_2$, and $[Rh(1,5\text{-cod})(P(C_6H_5)_3)_2][B(C_6H_5)_4]$, with $[Cl]^-$, $[I]^-$, and $[B(C_6H_5)_4]^-$ acting as the respective counter-ions.

4: IR (KBr, cm^{-1}) 1974 w, ν(Rh–H). NMR (d_4-methanol, ppm): δ_H 7.35 (20 H, m, Ar*H*), 4.07 (16 H, m, CH_2), −11.20 (2 H, m, Rh*H*); δ_C 62.6 (vt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ 13.4, 19.5, 18.3 Hz), 61.0 (vt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ 13.4, 17.0 Hz); δ_P 28.5 (dt, $^1J_{Rh\text{-}P} = 99.0$ Hz, $^2J_{P\text{-}P} = 21.1$ Hz), 15.8 (dt, $^1J_{Rh\text{-}P} = 87.0$ Hz, $^2J_{P\text{-}P} = 21.1$ Hz); ESMS m/z 785 $[RhH_2(P(C_6H_5)(CH_2OH)_2)_4]^+$.

***cis*-[$RhH_2(P\{(CH_2)_3OH_3\}_4]^+$ (7).** $P\{(CH_2)_3OH\}_3$ (110 mg, 0.53 mmol) was dissolved in deoxygenated water (10 cm^3) and added by cannula transfer to a stirred dichloromethane solution (10 cm^3) of $[RhCl(1,5\text{-cod})]_2$ (29 mg, 0.06 mmol). After stirring for 5 min the aqueous layer became orange in colour, and the colourless dichloromethane layer was discarded. The solution

at this stage contained $[Rh(P\{(CH_2)_3OH\}_3)_4]^+$ (**6**) as the major product. Dihydrogen was bubbled through the stirred solution for 5 min, the resultant light yellow solution indicative of the full conversion of **6** to **7**. As with **4**, removal of the solvent yielded **7** as a yellow oil with a small amount of phosphine oxide present as an impurity. Most of the oxide can be removed by diethyl ether extraction of methanolic solutions, but our attempts to remove all oxide impurity for elemental analysis purposes were unsuccessful.

IR (KBr, cm^{-1}) 2012 w, ν(Rh–H). NMR (d_6-dimethyl sulfoxide, ppm): δ_H 3.63 (24 H, m, CH_2), 1.90 (48 H, m, CH_2), −11.85 (2 H, m, RhH); δ_P 13.7 (dt, $^1J_{Rh-P} = 99.6$ Hz, $^2J_{P-P} = 22.3$ Hz), −0.4 (dt, $^1J_{Rh-P} = 87.4$ Hz, $^2J_{P-P} = 22.3$ Hz).

Synthesis of the rhodium dicarbonyl cations (8) and (9) and data for species $Rh(^{13}CO)_n(P\{(CH_2)_3OH\}_3)_m]^+$ 10. These compounds were all prepared by stirring the aqueous or methanolic solutions of the corresponding dihydride under an atmosphere of CO for 48 h. The ^{13}CO derivatives were prepared in an entirely analogous fashion.

Spectroscopic data for $[Rh(^{13}CO)_2(P(CH_2OH)_3)_3]^+$ (**8**): NMR (d_4-methanol, 298 K, ppm): δ_C 197.1 (dq, $^1J_{Rh-C} = 48.8$ Hz, $^2J_{P-C} = 13.4$ Hz, RhC); δ_P 24.4 (dt, $^1J_{Rh-P} = 107.2$ Hz, $^2J_{P-C} = 13.4$ Hz). For $[Rh(^{12}CO)_2(P(CH_2OH)_3)_3]^+$ IR: (water, cm^{-1}) 2020 s, ν(CO) (1958 for ^{13}CO **8**).

Spectroscopic data for $[Rh(^{13}CO)_2(P(C_6H_5)(CH_2OH)_2)_3]^+$ **9**: NMR (d_4-methanol, 273 K, ppm): δ_C 197.6 (dq, $^1J_{Rh-C} = 53.2$ Hz, $^2J_{P-C} = 11.3$ Hz, RhC): δ_P 19.0 (dt, $^1J_{Rh-P} = 106.6$ Hz, $^2J_{P-C} = 11.3$ Hz). For $[Rh(^{12}CO)_2(P(C_6H_5)(CH_2OH)_2)_3]^+$ IR: (water, cm^{-1}) 2018 s, ν(CO) (1976 for ^{13}CO **9**).

Spectroscopic data for (**10**): NMR (d_4-methanol, 273 K, ppm): δ_C 198.5 (d, $^1J_{Rh-C} = 53.7$ Hz, RhC); δ_P 11. 0 (d, $^1J_{Rh-P} = 95.5$ Hz). For $[Rh(^{12}CO)_2(P\{(CH_2)_3OH\}_3)_3]^+$ IR: (water, cm^{-1}) 1966 s, ν(CO) (1916 for ^{13}CO **10**).

Attempts to isolate pure samples of the dicarbonyl products were hindered due to contamination by small quantities of the phosphine oxides.

Crystal structure determination for complex 2

$C_{30}H_{40}Cl_2O_6P_4Ru$, $M = 792.48$, triclinic, space group $P\bar{1}$, $a = 9.283(2)$, $b = 10.008(6)$, $c = 10.568(1)$ Å, $\alpha = 99.87(2)$, $\beta = 105.12(1)$, $\gamma = 109.15(1)°$, $U = 859.1(6)$ Å^3, $T = 293$ K, $Z = 1$, μ(Mo-Kα) = 0.838 mm^{-1}, D_c= 1.516 Mg m^{-3}, $\lambda = 0.71073$ Å. 5570 data were collected on a Rigaku RAXIS IIc image plate of which 2962 were unique ($R_{int} = 0.0825$), 2003 had $F_o > 4\sigma(F_o)$, $4.94 < 2\theta < 51.18°$, no absorption correction was applied. Structure solved by direct methods using SHELXS and all non-hydrogen atoms refined anisotropically using full-matrix least squares on F^2 (SHELXL-93).[33] $R1 = 0.0641$ (for 4σ data), $wR2 = 0.2084$, $S = 1.010$ (for all data).

CCDC reference number 228753.

See http://www.rsc.org/suppdata/dt/b4/b411701h/ for crystallographic data in CIF or other electronic format.

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