The Reactions of Chlorohydrido- and Dichloro-tris(triphenylphosphine)-ruthenium(II) with Alkali Hydroxides and Alkoxides. Hydridohydroxobis-(triphenylphosphine)ruthenium(II) Monosolvates, their Reactions and Related Compounds †

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The interaction of chlorohydridotris(triphenylphosphine)ruthenium(II) with NaOH or KOH in tetrahydrofuran, acetone, or t-butyl alcohol leads, depending on conditions, first to red, five-co-ordinate complexes $RuH(OH)(PPh_3)_2(sol)$ (sol = thf or H_2O) secondly to hydroxo-bridged dimers, $(PPh_3)_2H(sol)Ru(\mu\text{-}OH)_2Ru(sol)H(PPh_3)_2$ (sol = Me_2CO, H_2O, or Bu^tOH) and thirdly to a tetranuclear complex of stoicheiometry $Ru_4H_4(OH)_2(PPh_2)_2(CO)_2(PPh_3)_6(Me_2CO)_2$.

Interaction of dichlorotris(triphenylphosphine)ruthenium(II) with KOH gives similar compounds, $RuCl(OH)(PPh_3)_2(sol)_2$ and $\{RuCl(OH)(PPh_3)_2(sol)\}_2$ (sol = H_2O or thf) as well as $\{RuH(OH)(PPh_3)_2(thf)\}_2$.

The interaction of $RuHCl(PPh_3)_3$ with sodium methoxide gives rise to two compounds that are formulated, respectively as having Ru–CHO and $Ru\text{–}OCH_2$ groups. The mechanism of decarbonylation of alcohols is discussed and the compounds $RuH_2(CO)(PPh_3)_2\cdot ROH$ (R = Me or Et) are synthesised.

I.r. and ^1H and ^{31}P n.m.r. spectra of the various complexes are given and structures for the compounds proposed on this basis.

ALTHOUGH some hydroxo-complexes of ruthenium have been known for nearly 90 years,[1-10] no systematic attempts to prepare them have been reported, perhaps on account of the supposed lack of affinity between the hard OH^- ligand and the presumed soft class B metal centre. With the class A metals, cobalt and nickel, on the other hand, many such reactions have been attempted and proved successful.[11]

Following the observation that *ortho*-metallated tri-

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† No reprints available.

[1] A. Joly, *Compt. rend.*, 1889, **108**, 854.

[2] M. Mukaida, M. Kusakari, T. Togani, T. Isomae, T. Nomura, and T. Ishinori, *Bull. Chem. Soc. Japan*, 1975, **48**, 1095.

[3] D. Scargill, *J. Chem. Soc.*, 1961, 4444.

[4] R. B. King and P. N. Kapoor, *Inorg. Chem.*, 1972, **11**, 336.

[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2285.

[6] T. Ishiyama, *Bull. Chem. Soc. Japan*, 1975, **48**, 443.

[7] F. P. Dwyer, M. A. Goodwin, and E. L. Gyarfas, *Austral. J. Chem.*, 1963, 544.

[8] K. R. Grundy, K. R. Laing, and W. R. Roper, *Chem. Comm.*, 1970, 1500.

[9] K. R. Laing and W. R. Roper, *J. Chem. Soc. (A)*, 1970, 2149.

[10] B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *J.C.S. Dalton*, 1972, 1239.

[11] A. Orlandini and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 78, and references therein.

phenylphosphine complexes of ruthenium, *e.g.*, $RuH(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$ will react with water:[12]

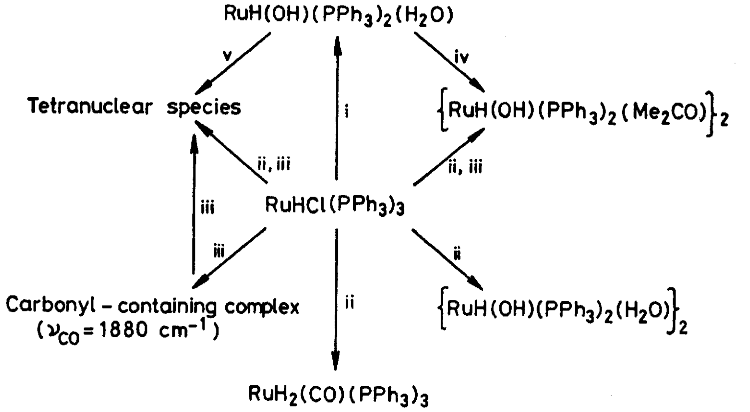
$$RuH(C_6H_4PPh_2)(PPh_3)_2(Et_2O) + 2H_2O \longrightarrow RuH(OH)(PPh_3)_2(H_2O) + PPh_3 + Et_2O$$

we attempted to prepare hydridohydroxo-complexes of this kind by more direct methods.

Since alkoxo-complexes of a similar nature have been proposed[13,14] as intermediates in the decarbonylation of alcohols by low-valent ruthenium phosphine complexes, on the basis of i.r. evidence alone, we have also attempted to isolate such complexes both by direct and indirect methods. A few examples of alkoxo-complexes are known for other group 8B metals.[15-18]

RESULTS AND DISCUSSION

Reactions of $RuHCl(PPh_3)_3$ *with Hydroxide Ion.*—The reactions of $RuHCl(PPh_3)_3$ with an excess of aqueous carbonate-free NaOH or KOH in tetrahydrofuran (thf) yield red solutions from which a red crystalline compound of stoicheiometry $RuH(OH)(PPh_3)_2(thf)$ may be isolated. If, however, the reaction is carried out in acetone, the nature of the products is critically dependent upon the reaction conditions. Thus, if the reaction of $RuHCl(PPh_3)_3$ with NaOH or KOH in acetone at room temperature is carried out in the presence of >10% by volume of water, a red solid, the analysis for which is consistent with the formulation $RuH(OH)(PPh_3)_2(H_2O)$, is precipitated. The yellow filtrate contains only triphenylphosphine and NaCl or KCl. The complex $RuH(OH)(PPh_3)_2(H_2O)$ is also formed from $RuHCl(PPh_3)_3$ and KOH in toluene–water mixtures.



i, NaOH, 10% H_2O, 25 °C; ii, KOH, <1% H_2O, 25 °C; iii, KOH, <1% H_2O, reflux; iv, reflux dry acetone; v, KOH, dry acetone, 25 °C

SCHEME 1 Reactions of $RuHCl(PPh_3)_3$ with KOH or NaOH in acetone

On reducing the percentage of water in the acetone, the yield of $RuH(OH)(PPh_3)_2(H_2O)$ decreases and more ruthenium now remains in solution. If only one drop (*ca.* 0.1 cm^3) of water is added to 50 cm^3 of acetone, an orange-red solution is formed. From this solution, red and yellow crystalline complexes may be isolated, together with small amounts of $RuH_2(CO)(PPh_3)_3$.[19] The red complex is considered on the basis of i.r., ^1H n.m.r., and ^{31}P data, as well as its crystallographic molecular weight (*ca.* 2 500), to be a polynuclear * species probably of stoicheiometry $Ru_4H_4(OH)_2(PPh_2)_2(CO)_2(PPh_3)_6(Me_2CO)_2$ and is discussed in detail later.

The two yellow complexes which are obtained have analyses consistent with their formulation as $\{RuH(OH)(PPh_3)_2(sol)\}_2$ (sol = H_2O or Me_2CO), the complex with co-ordinated water being less soluble and obtained in higher yield after longer reaction times.

In the absence of added water, $RuHCl(PPh_3)_3$ will not react with KOH pellets in acetone, presumably on account of the insolubility of KOH.

From the prolonged reaction of $RuHCl(PPh_3)_3$ with KOH in refluxing acetone in the presence of traces (<1%) of water, the tetranuclear species and $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ are the only products, but if the reaction is stopped after a short time (*ca.* 1 h), spectroscopic evidence indicates the presence of $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ and a small amount of another CO-containing compound ($\nu_{C=O}$ = 1 880 cm^{-1}).

The tetranuclear species may also be prepared by reaction of $RuH(OH)(PPh_3)_2(H_2O)$ with KOH in acetone in the presence of less than 1% water, whilst $RuH(OH)(PPh_3)_2(H_2O)$ when refluxed in dry acetone for several days produces $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$, indicating that $RuH(OH)(PPh_3)_2(H_2O)$ is intermediate in the formation of both $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ and the tetranuclear species. These reactions are outlined in

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* Hereinafter referred to as 'the tetranuclear species.'

[12] D. J. Cole-Hamilton and G. Wilkinson, *Nouveau Journal de Chimie*, 1977, **1**, 141.

[13] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

[14] E. Benedetti, G. Bracci, G. Shrana, F. Salvetti, and B. Grassi, *J. Organometallic Chem.*, 1972, **37**, 361.

[15] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1014 and 1370.

[16] M. A. Bennett, G. R. Robertson, P. A. Whimp, and T. Yoshida, *J. Amer. Chem. Soc.*, 1973, **95**, 3028.

[17] R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1965, 5422.

[18] T. Yoshida, T. Okano, and S. Otsuka, *J.C.S. Dalton*, 1976, 993, and references therein.

[19] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3143.

Scheme 1 and the mechanism of formation of the tetranuclear species is discussed later.

The reaction of $RuHCl(PPh_3)_3$ with KOH pellets in t-butyl alcohol yields $RuH_2(PPh_3)_4$ together with yellow crystals of $\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$. The latter complex is also formed on reacting $RuHCl(PPh_3)_3$ with potassium t-butoxide in t-butyl alcohol (see later).

All these hydridohydroxo-complexes have been fully characterised by elemental analysis, as well as by i.r., ^1H, and ^{31}P n.m.r. spectroscopy. Chemical evidence for the presence of hydroxide ion in $RuH(OH)(PPh_3)_2(H_2O)$ is also afforded by its reaction with aqueous fluoroboric acid in methanol to yield the known[20] complex ion, $[RuH(PPh_3)_2(H_2O)(MeOH)_2]^+$, presumably by protonation of the co-ordinated hydroxo-group:

$$RuH(OH)(PPh_3)_2(H_2O) + H^+ + BF_4^- \xrightarrow{MeOH} [RuH(PPh_3)_2(H_2O)(MeOH)_2][BF_4]$$

Evidence that $RuH(OH)(PPh_3)_2(sol)$ (sol = H_2O or thf) contain only one co-ordinated solvent molecule per ruthenium atom comes from analytical data and from integration of solvent resonances in the ^1H n.m.r. spectrum against those of the phenyl groups of PPh_3.

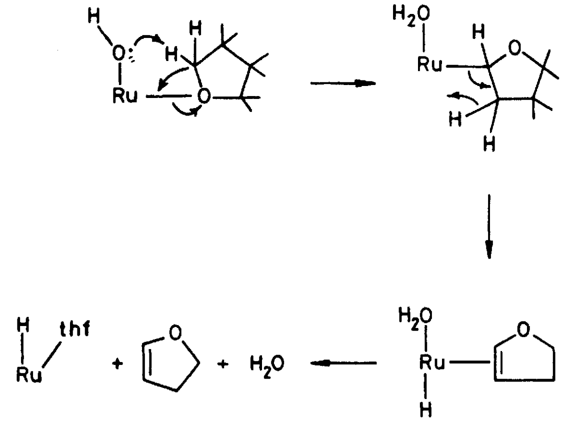
It has not proved possible to measure molecular weights of these complexes on account of their insolubility (dimeric species) and air sensitivity (monomers), but $RuH(OH)(PPh_3)_2(sol)$ (sol = H_2O or thf) are considered to be monomeric on the basis of their solubility and scarlet colour which appears to be characteristic of five-co-ordinate, sixteen-electron complexes of ruthenium(II).[21,22,*] The yellow colour and relative insolubility, together with i.r. evidence (two ν_{OH}), on the other hand, suggest dimeric formulations for $\{RuH(OH)(PPh_3)_2L\}_2$ [L = H_2O, Me_2CO, Bu^tOH, or thf (see below)].

Finally $RuH(OH)(PPh_3)_2(sol)$ (sol = thf or H_2O) react with CO to give $Ru(CO)_3(PPh_3)_2$. We have followed the reaction of $RuH(OH)(PPh_3)_2(thf)$ with CO by i.r. spectroscopy, and although the reaction is complex with several transient species being formed, it is clear that *water* (broad peaks near 3 300 and 1 600 cm^{-1}) not formic acid is formed, presumably by reductive elimination.

Reactions of $RuCl_2(PPh_3)_3$ *with Hydroxide Ion.*—$RuCl_2(PPh_3)_3$ does not react with KOH or NaOH in dry tetrahydrofuran at room temperature but if 10% by volume of water is added, a reaction does occur despite there being no apparent change in the orange-brown colour of the solution.

The first complex that may be isolated from the tetrahydrofuran solution is $RuCl(OH)(PPh_3)_2(H_2O)_2$ which may be recrystallised unchanged from toluene but which is converted into $RuCl(OH)(PPh_3)_2(thf)_2$ on recrystallisation from tetrahydrofuran–light petroleum. Longer reaction times lead to the isolation of yellow-brown microcrystals of stoicheiometry $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$ which may also be obtained by recrystallisation of $RuCl(OH)(PPh_3)_2(H_2O)_2$ from warm toluene–light petroleum mixtures.

In refluxing tetrahydrofuran containing 10% water, $RuCl_2(PPh_3)_3$ and NaOH give a mixture of $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$ and, more surprisingly, $\{RuH(OH)(PPh_3)_2(thf)\}_2$, which is the sole product if refluxing is prolonged for several hours. The origin of the hydride in this complex is not clear but it is possible that it occurs by preliminary formation of a dihydroxo-species followed by elimination of water from the hydroxide and an α-hydrogen atom of a *cis*-co-ordinated tetrahydrofuran moiety then β-elimination of dihydrofuran from the alkyl, as in Scheme 2. A similar mechanism is thought to account for the reaction of $RuMe(C_6H_4PPh_2)(PPh_3)_nL_{3-n}$ (n = 2, L = Et_2O; n = 1, L = $MeLi{\cdot}Et_2O$) with tetrahydrofuran to give $RuH(C_6H_4PPh_2)(PPh_3)_n(thf)_{3-n}$ and methane.[23,†] If this mechanism does account for the formation of $\{RuH(OH)(PPh_3)_2(thf)\}_2$, it is probable that it occurs in a dimeric species $\{Ru(OH)_2(PPh_3)_2(thf)\}_2$ since there is no evidence for formation of the dimeric hydridohydroxo-compound from $RuH(OH)(PPh_3)_2(thf)$ even on prolonged reflux in tetrahydrofuran, the monomer being recovered unchanged.



SCHEME 2 Formation of hydride from co-ordinated hydroxide ion and tetrahydrofuran

Although $RuCl(OH)(PPh_3)_2(H_2O)_2$ does not react with sodium borohydride in tetrahydrofuran, in toluene–water mixtures both $RuHCl(PPh_3)_3$ and $RuH_2(PPh_3)_4$ are formed in the presence of an excess of triphenylphosphine, suggesting that, although both the OH and Cl groups are reducible, the OH group is reduced preferentially. This may reflect the higher six-co-ordinate *trans*-effect of the Cl^- group, or may simply be due to the greater intrinsic strength of the Ru–Cl bond over the Ru–OH bond, or to the different lattice energies of NaCl and NaOH.

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[*] But see below for $RuH_2(CO)(PPh_3)_2(ROH)$.

[†] A similar mechanism may also operate in transfer hydrogenation reactions catalysed by low-valent ruthenium compounds.[24]

[20] R. J. Young and G. Wilkinson, *J.C.S. Dalton*, 1976, 719.

[21] J. R. Sanders, *J.C.S. Dalton*, 1973, 743.

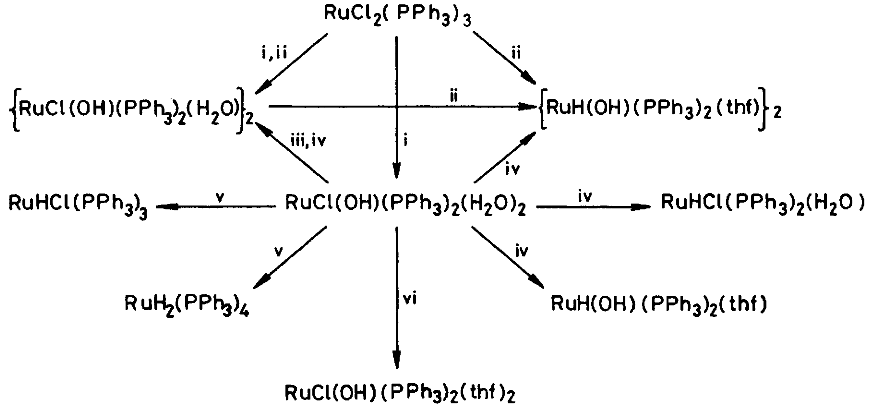
[22] P. R. Hoffmann and R. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221.

[23] D. J. Cole-Hamilton and G. Wilkinson, *J.C.S. Dalton*, 1977, 797.

[24] Y. Yasson, P. Albin, and J. Blum, *Tetrahedron Letters*, 1974, 83; H. Imai, T. Nishiguchi, and K. Fukuzumi, *Chem. Letters*, 1975, 807.

Using the milder reducing agent, hydrogen in the presence of base (KOH) in tetrahydrofuran, a mixture of $\{RuH(OH)(PPh_3)_2(thf)\}_n$ ($n = 1$ or 2) is formed. Although this appears to indicate that the chloride group is preferentially reduced under these conditions, this is in fact not the case, since, if less KOH is employed in the reaction, the main product is the red-purple complex $RuHCl(PPh_3)_2(H_2O)$, which is presumably analogous to the previously reported,[25] though not isolated, '$RuHCl(PPh_3)_2$.' The hydridohydroxo-complexes are then presumably formed by attack of OH^- on this complex.

As in previous studies,[26] a qualitative order of the *trans*-effects of the anionic ligands ($H^- > Cl^- > OH^-$) in five- and six-co-ordinate complexes of ruthenium(II) is indicated by the much slower reaction of $RuCl_2(PPh_3)_3$ with OH^- than of $RuHCl(PPh_3)_3$, and the observation that only one chloride ion of $RuCl_2(PPh_3)_3$ is replaced by hydroxide ion under mild conditions.



i, NaOH, 10% H_2O, thf, 25 °C; ii, NaOH, 10% H_2O, thf, under reflux; iii, recrystallised from toluene–light petroleum, 60 °C; iv, H_2, excess of KOH, thf, under reflux; v, $NaBH_4$, PPh_3, toluene, water, 25 °C; vi, recrystallised from thf–light petroleum

SCHEME 3 Preparation and reactions of $RuCl(OH)(PPh_3)_2(H_2O)_2$

Reactions of $RuHCl(PPh_3)_3$ *with Alkoxide Ions.*—The reaction of $RuCl_2(PPh_3)_3$ with NaOR (R = Et or Pr^i) has previously been studied[27] under various conditions and dihydridoruthenium complexes, $RuH_2(PPh_3)_3X$ (X = N_2, H_2, CO, or PPh_3) invariably result.

The prolonged reaction of $RuHCl(PPh_3)_3$ with NaOMe in diethyl ether or tetrahydrofuran in the presence of *ca.* 2% methanol also leads to the formation of $RuH_2(CO)(PPh_3)_3$. However, the reaction in tetrahydrofuran in addition gives a yellow crystalline complex, $RuH_2(PPh_3)_3(thf)$ * in *ca.* 20% yield. If this reaction in tetrahydrofuran is stopped as soon as the purple colour of $RuHCl(PPh_3)_3$ has disappeared, $RuH_2(PPh_3)_3(thf)$ is obtained in higher yield (*ca.* 50%), indicating that $RuH_2(PPh_3)_3(thf)$ is probably an intermediate in the formation of $RuH_2(CO)(PPh_3)_3$ but that not all of it is carbonylated in the long term.

Since the isolation of other intermediates from this reaction should shed some light on the mechanism of decarbonylation of alcohols in basic media by low-valent ruthenium phosphine complexes (which has been postulated[13,14] from i.r. evidence but never proved), we have investigated the reactions of $RuHCl(PPh_3)_3$ with NaOMe in the presence of methanol under different conditions.

Thus, if the reaction of $RuHCl(PPh_3)_3$ with solid NaOMe is carried out in ether in the presence of *ca.* 1% methanol at low temperature (0 °C) a yellow micro-crystalline solid is deposited after several hours.

This solid (A) has absorptions in its i.r. spectrum arising from $RuH_2(CO)(PPh_3)_3$,[19] as well as extra peaks at 2 010w, 1 632vs,br, and 825m cm^{-1}.† On some occasions another yellow compound (B), with extra peaks in its i.r. spectrum at 2 720w, 2 030w, 1 600vs, 875m, and 780s is isolated under ostensibly the same reaction conditions. The strong peaks near 1 600 cm^{-1} for both complexes are presumably indicative of aldehydic C=O linkages. Complex (B) which has an extra weak peak at 2 720 cm^{-1} (ν_{C-H}) probably contains a co-ordinated formyl group since $\nu_{C=O}$ of the only other known formyl complex[29]‡ $[Fe(CO)_4(CHO)]^-$ is in the range 1 590—1 610 cm^{-1}, the value depending upon the nature of the cation, and since this compound, as well as other aliphatic aldehydes, although not formaldehyde have ν_{C-H} of the aldehydic moiety near 2 700 cm^{-1}.[30]

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* This compound is also the sole product from the reaction in tetrahydrofuran of $RuHCl(PPh_3)_3$ with Me_3SiCH_2Li which has been set aside in air for several days and hence formed Me_3SiCH_2OLi.[28]

† It is unlikely that all the absorptions (see Experimental section) arise from one compound since the relative intensities of the peaks at 1 940 and 1 632 cm^{-1} are variable.

‡ *Note added in proof*: Recently, other metal formyl complexes have been synthesised. Once again $\nu_{C=O}$ is near 1 600 cm^{-1}. C. P. Casey and S. M. Neumann, *J. Amer. Chem. Soc.*, 1976, **98**, 5395.

[25] B. R. James, L. D. Markham, and D. K. W. Wang, *J.C.S. Chem. Comm.*, 1974, 439.

[26] See, T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335, and references therein.

[27] S. Cenini, A. Mantovani, A. Fusi, and M. Keubler, *Gazzetta*, 1975, **105**, 255.

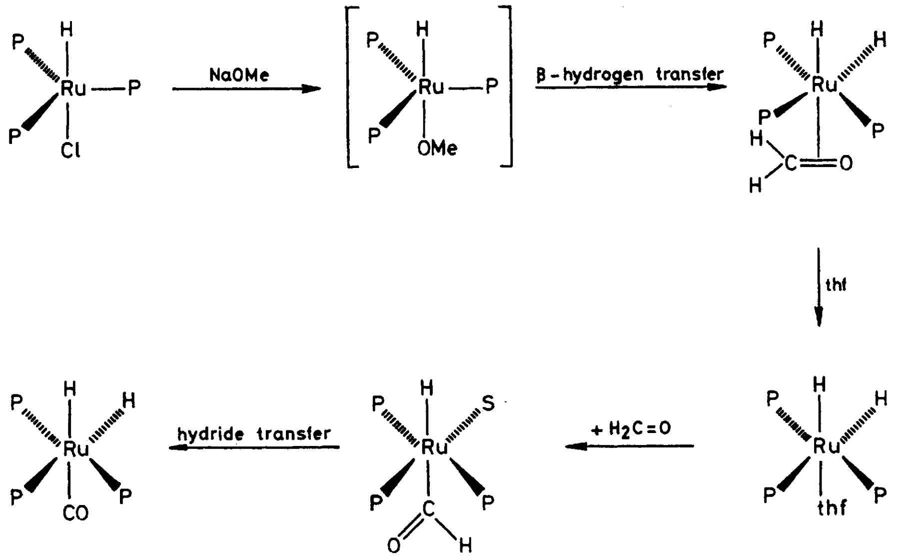
[28] See, ' Organometallic Compounds,' G. E. Coates and K. Wade, Methuen, 1967, vol. 1, p. 10.

[29] J. P. Collman and S. R. Winter, *J. Amer. Chem. Soc.*, 1973, **95**, 4089.

[30] 'Aldrich Library of Infrared Spectra,' C. J. Pouncher, Aldrich Chemical Co. Inc., 1970.

Further, alkyl aldehydes, *e.g.* acetaldehyde, have C–H deformations at 875 and 780 cm^{-1},[30] exactly the positions of the other two extra peaks in the i.r. spectrum of (B). We, *therefore*, suggest that this compound is $RuH(CHO)(PPh_3)_3(sol)$ with the acyl group bound through the carbon atom rather than through the C=O bond as is found for the related $RuCl\{C(O)R\}(CO)(PPh_3)_2$,[31] since in these complexes $\nu_{C=O}$ is at much lower frequency (1 505—1 510 cm^{-1}).

Compound (A), on the other hand, like formaldehyde itself,[30] does not have ν_{C-H} below 2 800 cm^{-1} and we formulate the compound as $RuH_2(OCH_2)(PPh_3)_3$. Since $\nu_{C=O}$ in this complex is 113 cm^{-1} below that of the free ligand (1 745 cm^{-1}) it is probable that the formaldehyde group is bound to the metal *via* the C=O double-bond, rather than through a lone pair on oxygen.



SCHEME 4 Mechanism of formation of $RuH_2(CO)(PPh_3)_3$ from $RuHCl(PPh_3)_3$ and NaOMe [compound in brackets not isolated]

Unfortunately, it has not proved possible to purify these compounds since recrystallisation leads only to $RuH_2(CO)(PPh_3)_3$, which is also obtained from the filtered reaction solutions.

It is not clear what the difference is between the preparations of complexes (A) and (B) but it may be that small changes in the percentage of methanol in the system tip the balance one way or the other, since $RuHCl(PPh_3)_3$ will not react with NaOMe in diethyl ether in the absence of methanol, whilst if 5% methanol is employed, spectroscopic evidence indicates that a mixture of $RuH_2(CO)(PPh_3)_3$, $RuH_2(PPh_3)_4$, and $RuH_4(PPh_3)_3$ [32] is formed.

Finally, the reaction of $RuH_2(PPh_3)_4$ with gaseous formaldehyde gives $RuH_2(CO)(PPh_3)_3$ in high yield.

These reactions are summarised in Scheme 4 and suggest a similar mechanism for alcohol decarbonylation to those which have previously been postulated;[13,14] the only difference being that formaldehyde, having left the co-ordination sphere of the ruthenium atom oxidatively adds a C–H bond to form a hydridoformyl derivative which, on hydride transfer, leads directly to a C-bound CO group and precludes the necessity of postulating an O-bound CO group.[13]

Since it appears that the β-hydrogen transfer reaction is important in the decarbonylation of alkoxo-complexes of ruthenium, those which do not contain β-hydrogen atoms on the alkoxide moiety (OPh, OBu^t) should be elimination-stabilised and should be isolable.

We have described[33] the reaction of $RuHCl(PPh_3)_3$ with sodium phenoxide, which leads to $RuH(OPh)(PPh_3)_2$, in which the phenoxo-group is co-ordinated to the ruthenium atom *via* its ring system rather than the oxygen atom. However, all attempts to prepare a t-butoxo-complex have been fruitless, giving only $\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$ and small amounts of $RuH_2(PPh_3)_4$, despite numerous attempts to remove any water from t-butyl alcohol, by drying over sieves, distillation from magnesium or both. Using sublimed $KOBu^t$ in thf the reaction is not clean and a mixture of a hydroxo-compound and $RuH_2(PPh_3)_4$ is formed.

The isolation of hydroxo-complexes from these reactions with Bu^tO^- suggests that water may be present and KOH formed *in situ*. However, this does not appear to be the case, since reaction of $RuHCl(PPh_3)_3$ with KOH in Bu^tOH under similar conditions is much slower (3 days as against 3 h) and produces higher yields of $RuH_2(PPh_3)_4$. It may be that the t-butoxide forms but decomposes as shown in Scheme 5 to give a co-ordinated hydroxo-group and isobutylene. When heated to 500 °C t-butyl alcohol undergoes dehydration *via* a similar four-centred transition state to give isobutylene.[34]

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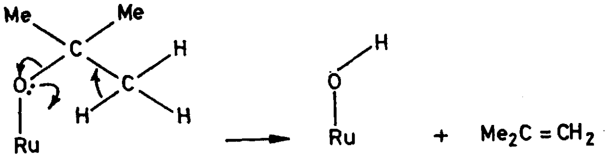
[31] R. R. Hitch, S. K. Gondal, and C. T. Sears, *Chem. Comm.*, 1971, 777.

[32] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3011; R. O. Harris, N. K. Hota, L. Sadavay, and J. M. C. Yuen, *J. Organometallic Chem.*, 1973, **54**, 259.

[33] D. J. Cole-Hamilton, R. J. Young, and G. Wilkinson, *J.C.S. Dalton*, 1976, 1995.

[34] See H. Knözinger in 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience Publishers, 1971, ch. 12, p. 662, and references therein.

Further Attempts to Isolate Alkoxo-complexes.—In a further attempt to prepare alkoxo-complexes, the reactions of $RuH(OH)(PPh_3)_2(H_2O)$ with alcohols, ROH (R = Me, Et, or Bu^t) were attempted. Although no reaction was observed with t-butyl alcohol, methanol, and ethanol gave red solids, $RuH_2(CO)(PPh_3)_2{\cdot}ROH$, together with small amounts of $RuH_2(CO)_2(PPh_3)_2$[35] and $Ru(CO)_3(PPh_3)_2$[36] (i.r. evidence) on prolonged reflux.



SCHEME 5 Mechanism of decomposition of co-ordinated t-butoxide ligand

The bright red colours of these complexes suggest five-co-ordinate formulations[21,22] with one molecule of alcohol of crystallisation. The ${}^1H$ n.m.r. spectrum of the methanol complex, however, indicates a non-fluxional *cis*-dihydride with one of the phosphines *trans* to a hydride, so it seems likely that the complex is six-co-ordinate with structure (I) (Figure 1). We cannot, however, rule out the possibility that the complex has structure (II) and is rearranging slowly at room temperature. The observations that the methanol is retained on recrystallisation of $RuH_2(CO)(PPh_3)_2{\cdot}MeOH$ from benzene–light petroleum mixtures and that ν_{C-O} of the alcohol is at 1 050 cm^{-1} (*cf.* 1 030 cm^{-1} for free methanol[37]) strongly support the contention that methanol is co-ordinated.

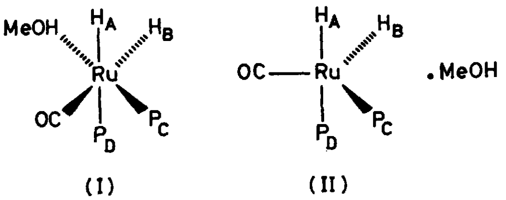


FIGURE 1 Possible structures of $RuH_2(CO)(PPh_3)_2(MeOH)$

These complexes are presumably formed by trans-esterification of the co-ordinated hydroxo-group with alkoxide followed by decarbonylation *via* a pathway similar to that shown in Scheme 4.

The failure to prepare alkoxides of low-valent ruthenium-phosphine complexes is perhaps not surprising since to our knowledge the only phosphine-containing alkoxo-complex of a metal in the iron triad is *fac*-$Os(OEt)(S_2CNMe_2)(PMe_2Ph)_3$.[38]

Spectroscopic Properties.—*Infrared spectra* (*Table* 1). All the complexes show absorptions in their i.r. spectra characteristic of co-ordinated triphenylphosphine groups, together with other peaks which give some structural information.

TABLE 1

Infrared spectra of ruthenium complexes[a]

Compound	ν_{Ru-H}/cm^{-1}	ν_{O-H}/cm^{-1}	Other bands
$RuH(OH)(PPh_3)_2(H_2O)$	2 100w	3 600m	
$RuH(OH)(PPh_3)_2(thf)$	2 080w	3 590m	
$\{RuH(OH)(PPh_3)_2(H_2O)\}_2$	1 980w	3 570m, 3 590m	
$\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$	1 980w	3 580m, 3 600m	1 715m[b]
$\{RuH(OH)(PPh_3)_2(thf)\}_2$	2 110m	3 570mbr	
$\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$	1 890m	3 590m, 3 610m	
$RuCl(OH)(PPh_3)_2(H_2O)_2$		3 600m	300w[c]
$RuCl(OH)(PPh_3)_2(thf)_2$		3 580m	300w[c]
$\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$		3 580m, 3 605m	280w[c]
$RuHCl(PPh_3)_2(H_2O)$	2 020m		265w[c]
$RuH_2(CO)(PPh_3)_2(MeOH)$			1 935s,[d] 1 050m, br[e]
$RuH_2(CO)(PPh_3)_2(EtOH)$			1 940s,[d] 1 050m, br[e]
$RuH_2(PPh_3)_3(thf)$	1 985w, 2 045w		
Tetranuclear species	2 005w	3 585m	1 910s,[d] 1 715m[b]

[a] In Nujol mulls. [b] $\nu_{C=O}$ of co-ordinated acetone. [c] ν_{Ru-Cl}. [d] $\nu_{C\equiv O}$. [e] ν_{C-O} of co-ordinated alcohol.

For $RuH(OH)(PPh_3)_2(sol)$ and $RuCl(OH)(PPh_3)_2(sol)_2$ (sol = H_2O or thf) a single peak near 3 600 cm^{-1} is indicative of co-ordinated hydroxide ion,[3,15-17,39,40] whilst two peaks in this region for $\{RuH(OH)(PPh_3)_2L\}_2$ (L = H_2O, Me_2CO, or Bu^tOH) and $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$ indicate either terminal hydroxo-groups which are mutually *cis* or, more likely, bridging hydroxo-groups. For $\{RuH(OH)(PPh_3)_2(thf)\}_2$ only one ν_{O-H} is seen but since this is significantly broader than the single ν_{O-H} of $RuH(OH)(PPh_3)_2(thf)$, it is probable that two absorptions of very similar energies are in fact present.

A single absorption near 2 000 cm^{-1} for $RuH(OH)(PPh_3)_2(sol)$ (sol = H_2O or thf), $\{RuH(OH)(PPh_3)_2L\}_2$ (L = H_2O, Me_2CO, thf, or Bu^tOH) and $RuHCl(PPh_3)_2(H_2O)$ indicates the presence of an Ru–H bond. For $RuH_2(PPh_3)_3(thf)$, the presence of two ν_{Ru-H} at 1 985 and 2 045 cm^{-1} confirms it as a *cis*-dihydride and, although ν_{Ru-H} in the other dihydrido-complexes, $RuH_2(CO)(PPh_3)_2{\cdot}ROH$ (R = Me or Et), are not immediately apparent, slight asymmetry of $\nu_{C=O}$ indicates that they are probably near 1 950 cm^{-1}.

The metal–chlorine stretches of $RuCl(OH)(PPh_3)_2(sol)_2$ (sol = H_2O or thf) and $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$ being near 300 cm^{-1} are indicative of terminal chlorine atoms[41] and ν_{Ru-Cl} at 265 cm^{-1} for $RuHCl(PPh_3)_2(H_2O)$ is close to the value found[19] in the monomeric $RuHCl(PPh_3)_3$ in which the chloride is *trans* to the hydride[42] and since

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[35] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

[36] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 3504.

[37] 'Uvasols Solvents for Spectroscopy,' E. Merck, Darmstadt, W. Germany.

[38] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1976, 2396.

[39] P. M. Treichel, W. K. Dean, and J. C. Calabrese, *Inorg. Chem.*, 1973, **12**, 2908.

[40] G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Canad. J. Chem*,. 1972, **50**, 3694.

[41] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 1749.

[42] A. C. Skapski and P. G. H. Troughton, *Chem. Comm.*, 1968, 1230.

$RuHCl(PPh_3)_2(H_2O)$ is deeply coloured, it seems likely that it is a five-co-ordinate monomer with the chloride *trans* to hydride.

$RuH_2(CO)(PPh_3)_2\cdot ROH$ (R = Me or Et) show absorptions near 1 950 cm^{-1} indicative of terminal CO groups *trans* to hydride (*cf.* 1 940 cm^{-1} for ν_{CO} of $RuH_2(CO)(PPh_3)_3$[19]). Absorptions near 1 050 cm^{-1} are in the region accepted for co-ordinated alcohol moieties.[43]

Finally, although absorptions arising from co-ordinated solvent molecules (sol = thf, H_2O, or Bu^tOH) do not appear to be present (they may be weak and hidden under phosphine absorptions) a peak near 1 715 cm^{-1} in the i.r. spectrum of $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ is assigned to $\nu_{C=O}$ of co-ordinated acetone.

^1H *and* ^{31}P *n.m.r. spectra* (*Table* 2). Peaks between τ 2.4 and 3.5 for all the complexes herein reported indicate the presence of co-ordinated triphenylphosphine groups, although little stereochemical information is available from the broad resonances.

TABLE 2

^1H N.m.r. spectra of ruthenium complexes [a]

Compound	Hydride τ(J_{PH})	Hydroxide τ	Co-ordinated solvent τ(J_{HH})
$RuH(OH)(PPh_3)_2(H_2O)$	34.1 (39)t	9.95s	8.5s
$RuH(OH)(PPh_3)_2(thf)$	34.0 (39)t	10.0s	6.30s [b] 8.45 [b]
$\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$	27.7 (29)t	11.30s	8.3s
$\{RuH(OH)(PPh_3)_2(thf)\}_2$	27.9 (32)t	11.65s	6.33 [b] 8.48 [b]
$\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$	27.95 (29)t	11.75s	7.9s 8.9s
$RuCl(OH)(PPh_3)_2(H_2O)_2$		10.0s	9.4s
$RuCl(OH)(PPh_3)_2(thf)_2$		10.0s	6.05 [b] 8.25 [b]
$\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$		14.85	9.6s
$RuHCl(PPh_3)_2(H_2O)$	30.10 (34)t		9.0s
$RuH_2(PPh_3)_3(thf)$	20.3 (36)q		6.54 [b] 8.68 [b]
$RuH_2(CO)(PPh_3)_2(EtOH)$			6.2(7)q [c] 8.7(7)t [c]
$RuH_2(CO)(PPh_3)_2(MeOH)$	H_A 21.1 [e] (6, H_AH_B) [d] H_B 30.0 (16, H_AP_C) (76, H_AP_D) (33, H_BP_C) (42, H_BP_D)		6.7s [c]

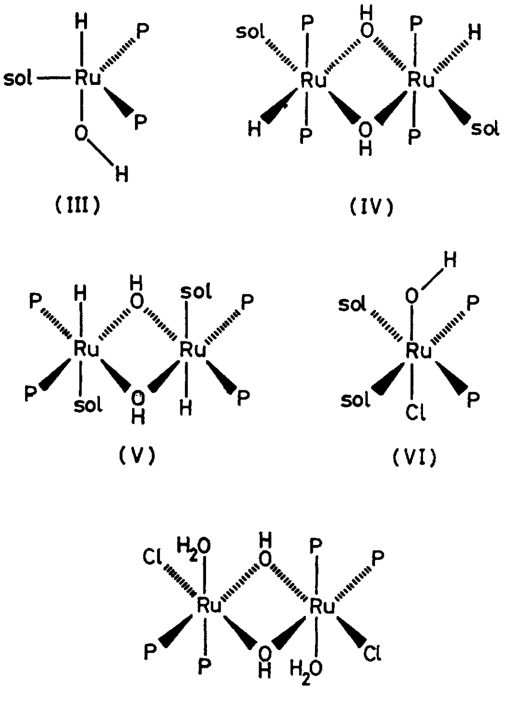
s = Singlet; d = doublet; t = triplet; q = quartet.

[a] In C_6D_6 at 36 °C at 60 MHz, J in Hz. [b] Second-order pattern for co-ordinated thf. [c] Co-ordinated alcohol. [d] For assignments see Figure 1. [e] Broad.

The presence of co-ordinated water in $\{RuH(OH)(PPh_3)_2(H_2O)\}_n$ (n = 1 or 2), $RuCl(OH)(PPh_3)_2(H_2O)_2$, $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$, and $RuHCl(PPh_3)_2(H_2O)$ is confirmed by peaks near τ 9, whilst the characteristic second-order resonances for co-ordinated tetrahydrofuran are observed near τ 6.2 and 8.5 for $\{RuH(OH)(PPh_3)_2(thf)\}_n$ (n = 1 or 2), $RuCl(OH)(PPh_3)_2(thf)_2$, and $RuH_2(PPh_3)_3(thf)$. In $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ co-ordinated acetone resonates near τ 8.3 whilst the tertiary butanol moieties in $\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$ resonate at τ 7.9 (OH) and 8.9 (Bu^t).

More structural information is available from analysis of the high-field region of the ^1H n.m.r. spectrum since many of the complexes show well resolved hydride resonances.

For $RuH(OH)(PPh_3)_2(sol)$ (sol = thf or H_2O), as well as for $RuHCl(PPh_3)_2(H_2O)$, a triplet near τ 30 indicates coupling of the hydride to two equivalent phosphorus atoms as would be expected for the presumably fluxional five-co-ordinate species. The proton noise decoupled ^{31}P n.m.r. spectrum of $RuH(OH)(PPh_3)_2(thf)$ in benzene, which shows a single line, split into a doublet (J_{PH} = 39 Hz) when only the phenyl region of the proton spectrum is decoupled, is in total agreement with this structure; whilst its chemical shift (76.2 p.p.m.) * is close to that found for the unique phosphorus atom of $RuH(OAc)(PPh_3)_3$ and of $RuCl_2(PPh_3)_3$ at low temperatures,[22] indicating that the phosphines are probably *trans* to ligands of low *trans*-influence [structure (III), Figure 2], since for P *trans* to P typical chemical shifts are closer to 40 p.p.m.[22] and for P *trans* to H negative chemical shifts are often observed.[12,23]



(III) (IV)

(V) (VI)

(VII)

FIGURE 2 Structures of some hydroxoruthenium complexes (P = PPh_3 and sol = solvent)

Once isolated, the dimeric species, $\{RuH(OH)(PPh_3)_2(sol)\}_2$ (sol = H_2O, Me_2CO, thf), as well as $RuH_2(CO)(PPh_3)_2\cdot EtOH$, are all too insoluble for observation of their hydride resonances in the proton n.m.r. spectra, but the presence of a resonance (τ 4.8) corresponding to $CHDCl_2$ when they are dissolved in $CDCl_3$ strongly indicates that the hydride is indeed present. For $\{RuH(OH)(PPh_3)_2(sol)\}_2$ (sol = Me_2CO or

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* Chemical shifts are to high frequency of external 85% H_3PO_4.

[43] L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1770.

thf) it has also proved possible to observe the hydride resonances in supersaturated reaction solutions prior to isolation of the complexes. Thus, both these complexes, as well as the more soluble $\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$ show triplet resonances near τ 28 (J_{PH} *ca.* 30 Hz). This suggests that the hydride is *cis* to the two phosphines and that the phosphines are equivalent, as in (IV) or (V) (Figure 2), although it is possible that the phosphines are non-equivalent but are fortuitously equally coupled to the hydride, as in $RuH(OAc)(PPh_3)_3$.[22] For $\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$, the observation of a singlet in the proton-noise-decoupled ^{31}P n.m.r. spectrum at 75.5 p.p.m. which splits into a doublet ($J_{PH} = 36$ Hz) when only the phenyl region is decoupled confirms that the phosphorus atoms are equivalent and are in the thermodynamically more favourable[44,45] *cis* configuration, as in structure (V).

The observation of a quartet at τ 20.3 ($J_{PH} = 36$ Hz) for $RuH_2(PPh_3)_3(thf)$ indicates that like $RuH_2(PPh_3)_3(C_5H_{10})$[46,*] but unlike $RuH_2(PPh_3)_3L$ (L = CO,[19] MeCN,[12] or dimethylformamide[47]), this is a fluxional dihydrido-complex. Eight-line resonances for each of the hydrides of $RuH_2(CO)(PPh_3)_2(MeOH)$, on the other hand indicate a non-fluxional *cis*-dihydrido-stereochemistry.

Finally, the resonances of the protons of the co-ordinated hydroxo-moieties are of interest since they provide unequivocal correlations of chemical shift with mode of co-ordination. Thus, in $RuH(OH)(PPh_3)_2(sol)$ and $RuCl(OH)(PPh_3)_2(sol)_2$ (sol = H_2O or thf), where terminal hydroxo-groups are indicated by their colours, i.r. spectra, and stoicheiometries, the resonance is near τ 10 whilst for the bridging hydroxides of $\{RuH(OH)(PPh_3)_2(sol)\}_2$ (sol = H_2O, Me_2CO, thf, or Bu^tOH) and $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$, the resonances are to higher field (τ 12—15).

At first sight these resonances appear to be to somewhat higher field than is usual for transition-metal hydroxo-compounds (τ 6—8),[15,40,48] however, for the bridging hydroxo-groups in $Fe_2(CO)_6(OH)\{P(p\text{-}C_6H_4Me)_2\}$,[39] and $\{Ni(CCl{=}CCl_2)(OH)(PPh_3)\}_2$[18] the chemical shifts are τ 12.86 and 13.62 respectively whilst for *trans*-$PtR(OH)(PPh_3)_2$,[18] the terminal OH proton resonates between τ 9 and 12.5.

The fact that the bridging O–H protons in all the dimeric hydridohydroxo-complexes appear as a single line suggests that the two O–H groups are equivalent, as in structure (V) (Figure 2). We do not observe coupling of the O–H protons to the phosphorus atoms in these complexes, as is sometimes reported,[18] for any of the complexes apart from the tetranuclear species (see below) but since the resonances are slightly broad, it is possible that this broadening is produced by small P–H couplings.

The solvent groups in $RuH_2(CO)(PPh_3)_2{\cdot}ROH$ resonate at τ 6.7 (OMe) and τ 6.2 and 8.7 (OEt) which are typical chemical shifts for co-ordinated alcohol moieties.

It is not possible to ascertain unequivocally the structures of the chlorohydroxo-complexes but, on the basis of their preparations [from *trans*-$RuCl_2(PPh_3)_3$ under mild conditions] and the non-lability of the second chloride ligand we propose that the hydroxide moiety is *trans* to chloride and that the phosphines are mutually *cis*, as in (VI) and (VII) (Figure 2). This structure (VII) for the dimeric species is in part supported by the very different chemical shift of the bridging O–H protons, compared with those in $\{RuH(OH)(PPh_3)_2(sol)\}_2$ (sol = H_2O, thf, Me_2CO, or Bu^tOH) and the observation of only one O–H resonance, indicating that the O–H groups are chemically equivalent but that the structure is different from those of the hydridohydroxo-dimers.

Nature and Mechanism of Formation of the Tetranuclear Complex.—As noted above, the prolonged reaction between $RuHCl(PPh_3)_3$ and NaOH in acetone in the presence of $<1\%$ water gives a red crystalline complex which, on the basis of its crystallographic molecular weight (*ca.* 2 500) and complex spectra is evidently a polynuclear, probably tetranuclear species.

The i.r. spectrum of this complex shows absorptions attributable to co-ordinated triphenylphosphine and acetone (1 715 cm^{-1}), as well as peaks at 3 585, 2 005, and 1 910 cm^{-1} indicating the presence of co-ordinated OH^-, H^-, and CO respectively. The presence of only one ν_{CO} indicates that no more than two CO groups are present in the molecule.

The ^1H and ^{31}P n.m.r. spectra are collected in Table 3. Integration of the resonances arising from the OH, H^1, and H^2 protons indicates that there is an equal number of each of these three different types of hydrogen atom. Further, since the region for bridging hydroxo-groups contains two resonances of equal intensity, one a doublet ($J_{P^3H^3} = 3$ Hz) (OH^3) and the other a singlet (OH^4),† it seems probable that there are two of each kind of hydride atom, H^1 and H^2, and two non-equivalent hydroxo-moieties.

The proton noise decoupled ^{31}P n.m.r. spectrum shows that there are four different types of phosphorus atom in the intensity ratio 1 : 1 : 1 : 1, numbered in order of decreasing chemical shift. Of these, P^2 is coupled to all the other phosphorus atoms whilst P^1 is only coupled to P^2. P^3 and P^4 couple to one another as well as to P^2.

The only possible explanation of these coupling phenomena which does not invoke zero coupling between phosphorus atoms on the same ruthenium atom is that

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* *Note added in proof*: We have since shown[12] this compound to have been erroneously formulated.

† This singlet resonance moves to higher field (τ 12.4) on addition of water to the n.m.r. tube and we suggest that this is probably due to the replacement of co-ordinated acetone by co-ordinated water. Support from this contention comes from the observation that recrystallisation of the tetranuclear complex from wet benzene gives a less-soluble red solid which has an identical n.m.r. spectrum to that of the starting compound except that there is no resonance at τ 8.3, indicating loss of co-ordinated acetone.

[44] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[45] B. E. Prater, *J. Organometallic Chem.*, 1972, **34**, 379.

[46] F. Penella, *Coord. Chem. Rev.*, 1975, **16**, 51.

[47] S. Komiya, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1975, **48**, 101.

[48] M. Herberhold and G. Suss, *Angew. Chem. Internat. Edn.*, 1975, **14**, 700.

TABLE 3

^1H and ^{31}P n.m.r. data for tetranuclear species [a]

Chemical shifts				Coupling constants/Hz [d]							
τ [b]		δ [c]									
Me_2CO	8.3	P^1	75.3	H^1P^1	8.0	H^2P^1	26.4	P^1P^2	35.0	P^2P^4	44.8
OH^3	12.08	P^2	71.5	H^1P^2	22.3	H^2P^2	36.0	P^1P^3	0	P^3P^4	13.6
OH^4	12.25	P^3	55.4	H^1P^3	16.5	H^2P^3	0	P^1P^4	0	H^1H^2	0
H^1	19.4	P^4	26.6	H^1P^4	88.0	H^2P^4	0	P^2P^3	3.6	H^3P^3	3.0
H^2	27.8										

[a] In C_6D_6 at 36 °C, for assignments see text. [b] Me_4Si at τ 10. [c] In p.p.m. to high frequency of external 85% H_3PO_4. [d] Assignments based on heteronuclear double resonance and partial decoupling studies.

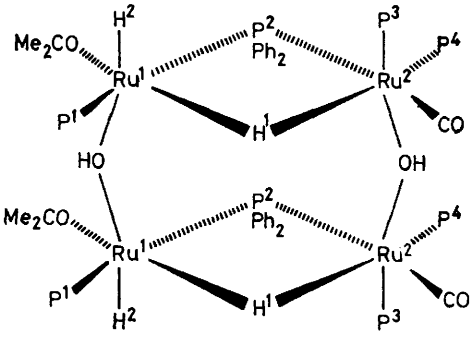
P^2 bridges two ruthenium atoms one of which (Ru^1) has P^1 bonded to it and the other (Ru^2) accommodates P^3 and P^4. Since bridging triphenylphosphine groups are unknown and unlikely, it is probable that P^2 is the phosphorus atom of a bridging diphenylphosphido-group.

Since H^2 is coupled only to P^1 and P^2 it seems probable that it is a terminal hydride on Ru^1. H^1, on the other hand, being coupled to all four phosphorus atoms probably bridges the two ruthenium atoms. The chemical shifts of the two hydrides are somewhat unusual since, in general, bridging hydrides resonate at higher fields than do terminal ones.[49,50] However, in the recently isolated [51] $[Ir_2H_5(PPh_3)_4][PF_6]$ the bridging hydrides resonate at lower fields (τ 16.9, 18.4) than do the terminal ones (τ 33.9); also, with different *trans*-ligands and different chemical environments, shielding effects of the phenyl rings may be sufficiently different to render assignments based on chemical-shift data alone relatively meaningless.

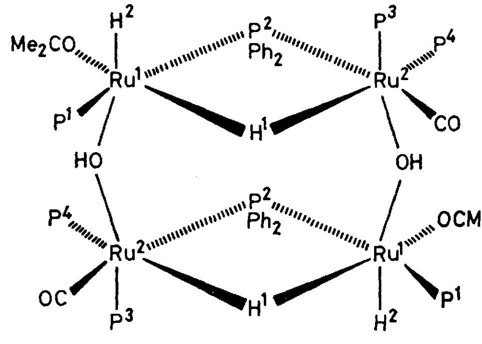
Since $J_{P^4H^1}$ is so large (80 Hz), P^4 and H^1 are likely to be mutually *trans*. The chemical shift of P^4 (26.6 p.p.m.) being of much lower frequency than those of the other phosphorus atoms is also consistent with its being *trans* to a hydride, although since the resonance is not to such low field as is sometimes observed [12,24] for phosphorus *trans* to hydride, it suggests that the bridging hydride does not have such a marked effect on the chemical shift of the phosphorus atom *trans* to it as do terminal hydride ligands.

Unfortunately, little information is available on the chemical shifts and coupling constants of bridging phosphido-groups so it is not possible to deduce structural information from the coupling constants of P^2 to the other magnetic nuclei but the values of $J_{P^1H^1}$, $J_{P^1H^2}$, $J_{P^2H^1}$, and $J_{P^2H^2}$ strongly suggest that both H^1 and H^2 are *cis* to both P^1 and P^2, as well as to one another, which is only possible if P^1 and P^2 are mutually *trans*. The very low value of $J_{P^2H^3}$ suggests that these two phosphorus atoms are not mutually *trans*.

We are not able, on the basis of spectroscopic studies alone, unequivocally to assign a structure to this complex but we suggest that it is similar to one of those shown in Figure 3. Both of these structures fit *ca.* 90% of the data but in (VIII), although the OH protons are non-equivalent, as required, it is expected that if the OH proton on Ru^2 couples to one P^3 it should also be coupled to the other one and a triplet rather than a doublet should be observed. In (IX), on the other hand, the two O–H protons are equivalent, and coupling to P^3 should give a single doublet. A similar type of skeleton containing single and double bridges has recently been reported [52] for $Na_4[Mo_4O_4(OH)_2(edta)_2]\cdot 12H_2O$.



(VIII)



(IX)

FIGURE 3 Two possible structures of the tetranuclear species (P = PPh_3); CO and acetone may be interchanged in a dimeric unit

If the structure is similar to one of those illustrated in Figure 3, it is clear that the dinuclear species which constitutes half of the molecule could be formed from reaction of $RuH(OH)(PPh_3)_2(Me_2CO)$ and $RuH_2(CO)(PPh_3)_3$, with loss of benzene and a triphenylphosphine group. Indeed, the reaction between these two complexes in acetone under reflux or at room temperature

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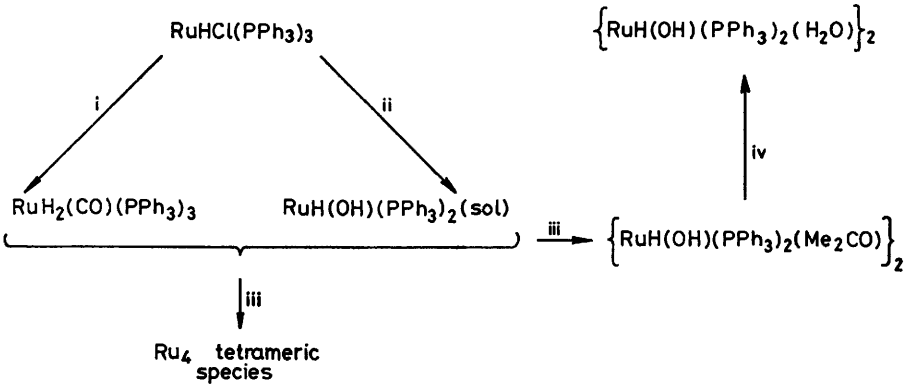
[49] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231, and references therein.

[50] D. C. Harris and H. B. Gray, *Inorg. Chem.*, 1975, **14**, 1215, and references therein.

[51] R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Organometallic Chem.*, 1976, **113**, C7.

[52] T. Shibahara, B. Sheldrick, and A. G. Sykes, *J.C.S. Chem. Comm.*, 1976, 523.

does give the tetranuclear species and benzene is detected in the reaction solution by g.l.c. Benzene is also present in the reaction mixture when the tetranuclear species is prepared from $RuHCl(PPh_3)_3$ and KOH.



i, Base-catalysed decarbonylation of acetone; ii, KOH; iii, dimerisation; iv, solvent exchange.

SCHEME 6 Mechanism of reaction of $RuHCl(PPh_3)_3$ with KOH in acetone containing <1% water

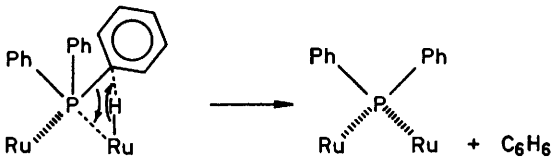
TABLE 4

Analytical data for new ruthenium complexes

Compound	Colour	Found				Required			
		C	H	P	Other	C	H	P	Other
$RuH(OH)(PPh_3)_2(H_2O)$	Scarlet	64.7	5.1	8.8		65.4	5.1	9.4	
$RuH(OH)(PPh_3)_2(thf)$	Scarlet	65.9	5.3	8.7		67.1	5.6	8.7	
$\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$	Yellow	66.6	4.9	8.7		66.8	5.4	8.8	
$\{RuH(OH)(PPh_3)_2(thf)\}_2$	Yellow	67.3	5.2	8.6		67.1	5.6	8.7	
$\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$	Yellow	65.9	5.0	8.8		66.9	5.9	8.7	
$RuCl(OH)(PPh_3)_2(H_2O)_2$	Yellow-brown	61.5	4.4	8.4	Cl, 5.0	60.5	4.9	8.7	Cl, 7.1
$RuCl(OH)(PPh_3)_2(thf)_2$	Yellow-brown	65.6	5.5	6.9	Cl, 6.2	64.3	5.7	7.6	Cl, 4.3
$\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$ [a]	Yellow-brown	61.3	5.1	8.5	Cl, 5.4	62.1	4.7	8.9	Cl, 5.1
$RuHCl(PPh_3)_2(H_2O)$ [b]	Red-purple	63.6	4.8	9.8		63.6	4.9	9.1	
$RuH_2(CO)(PPh_3)_2(MeOH)$	Crimson	64.4	5.0	9.0		63.8	4.8	8.7	
$RuH_2(CO)(PPh_3)_2(EtOH)$ [c]	Crimson	65.0	5.3	8.6		64.2	4.9	8.5	
$RuH_2(PPh_3)_3(thf)$	Yellow	72.9	5.6	10.0		72.4	5.7	9.7	
Tetranuclear species [d]	Red-orange	65.5	6.2	8.2	O, 5.2	65.7	5.0	9.7	O, 3.8

[a] *M* 750 (713.5) cryoscopically in benzene. [b] Chlorine analysis for this complex is consistently low (*ca.* 1%). [c] *M* 672 (701) osmometrically in benzene. [d] *M* 2 500 (2 556) crystallographically.

Cleavage of a P–C bond of a triphenylphosphine group is not unusual and a similar reaction[53] to the one postulated here is the thermolysis of $RuH(NO)(PPh)_3$ in decalin which leads to $\mu\mu'$-$(PPh_2)_2{\cdot}Ru_2(NO)_2(PPh_3)_2$. These reactions presumably occur *via* a transition state such as that shown in Scheme 7.



SCHEME 7 Formation of a bridging phosphido-group from co-ordinated PPh_3 and hydride

The mechanism of the reaction of $RuHCl(PPh_3)_3$ with NaOH in acetone is outlined in Scheme 6.

EXPERIMENTAL

Microanalyses are by Butterworth Microanalytical Consultancy Limited. I.r. spectra were obtained using a Perkin-Elmer PE457 grating diffractometer, n.m.r. spectra using Perkin-Elmer R12 (60 MHz) and Varian Associates XL-100-12 spectrometers (^{31}P), the latter in the Fourier-transform mode with proton-noise decoupling. Melting points were determined in closed capillaries under argon on an Electrothermal melting-point apparatus and are uncorrected.

All solvents were thoroughly degassed before use and all operations were carried out in an argon atmosphere, using standard suba-seal and catheter tubing techniques. The light petroleum used had boiling range 40—60 °C.

NaOMe and $KOBu^t$ were made from the alcohol (purified by distillation from magnesium) and the metal followed by evaporation to dryness and sublimation ($KOBu^t$).

$RuHCl(PPh_3)_3$,[54] $RuCl_2(PPh_3)_3$,[55] and $RuH_2(CO)(PPh_3)_3$ [19] were prepared by published procedures.

Microanalytical data for the new complexes are given in Table 4.

(1) *Hydridohydroxo(tetrahydrofuran)bis(triphenylphosphine)ruthenium*(II).—(*a*) $RuHCl(PPh_3)_3$ (1 g, 1.08 mmol) was stirred in tetrahydrofuran (100 cm^3) containing carbonate-free NaOH (10 cm^3, 0.5M in water, 5 mmol) for

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[53] J. Reed, A. J. Schultz, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 2949.

[54] R. A. Schunn and E. R. Wonchoba, *Inorg. Synth.*, 1972, *XIII*, 131.

[55] P. S. Hallman, T. A. Stephenson, and G. Wilkinson, *Inorg. Synth.*, 1970, *XII*, 237.

16 h. On evaporation to small volume and addition of an excess of water the very air-sensitive scarlet *complex* was precipitated. This was collected and recrystallised from tetrahydrofuran–light petroleum; yield *ca.* 90%.

(*b*) This reaction was carried out as described in (*a*) but using KOH pellets and 10 cm^3 water.

(2) *Aquahydridohydroxobis(triphenylphosphine)ruthenium*(II).—(*a*) The experiment was as described in 1(*a*) or (*b*) but using acetone (100 cm^3) as solvent. After either 3 h of stirring or 0.5 h of refluxing the *complex* precipitated from the solution as very air-sensitive scarlet *microcrystals*. It was washed several times with water; yield *ca.* 100%. Evaporation of the residual pale yellow solution left only a white solid identified as triphenylphosphine from its i.r. spectrum.

(*b*) $RuHCl(PPh_3)_3$ (0.5 g, 0.54 mmol) and KOH (0.2 g, 3.6 mmol) were stirred overnight in a 1 : 1 mixture of toluene and water (50 cm^3). The scarlet *solid* that collected at the interface was filtered off, washed several times with water, and dried *in vacuo*; yield *ca.* 80%, m.p. 172 °C (decomp.).

(3) *Reaction of* $RuHCl(PPh_3)_3$ *with* KOH *in Acetone containing* <1% *Water.*—(*a*) $RuHCl(PPh_3)_3$ (1 g, 1.08 mmol) and KOH (0.57 g, 10 mmol) were stirred in acetone (100 cm^3) containing 2 drops (*ca.* 0.1 cm^3) of water for 2 days. The yellow solid that precipitated (*ca.* 20%) was filtered off and, after being washed with water, was dried *in vacuo*. It was identified as *di-μ-hydroxo-bis[aquahydridobis(triphenylphosphine)ruthenium*(II)]. On evaporation to 20 cm^3 and addition of light petroleum to the orange filtered solution, orange crystals of the tetranuclear species (40%) were isolated. These were sometimes contaminated with a yellow powder, $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ (*ca.* 20%), but these two compounds were separated by extraction of the orange crystals with acetone followed by addition of light petroleum. After crystallisation of the orange and yellow solids the filtrate was further reduced in volume (to *ca.* 2 cm^3) and addition of light petroleum caused precipitation of a white solid identified as $RuH_2(CO)(PPh_3)_3$ (i.r. evidence) (*ca.* 10%). The yield of $\{RuH(OH)(PPh_3)_2(H_2O)\}_2$ from this reaction was increased after longer reaction times (7 days) and it was also prepared by washing $\{RuH(OH)(PPh_3)_2(Bu^tOH)\}_2$ with water.

(4) *The Tetranuclear Complex.*—(*a*) $RuHCl(PPh_3)_3$ (1 g, 1.08 mmol) and KOH (0.57 g, 10 mmol) were refluxed in acetone (100 cm^3) containing *ca.* 0.1 cm^3 of water for 3 h. A small amount of the red complex $RuH(OH)(PPh_3)_2(H_2O)$ precipitated and was filtered off. The red solution which was shown to contain benzene (g.l.c. evidence) was evaporated to 20 cm^3 and light petroleum was added until the solution just became turbid. The yellow solid that formed (*ca.* 10%) was identified as $\{RuH(OH)(PPh_3)_2(Me_2CO)\}_2$ and after filtration, addition of more light petroleum, and cooling the orange *crystals* of the complex were collected, washed with light petroleum, and dried *in vacuo*; yield *ca.* 50%, m.p. 118 °C. When shorter reaction times (*ca.* 0.5 h) were employed and the solution was evaporated to dryness, there was i.r. evidence of another CO-containing compound (ν_{CO} 1 880 cm^{-1}).

(*b*) $RuH(OH)(PPh_3)_2(H_2O)$ (0.5 g, 0.76 mmol) and KOH (0.28 g, 5 mmol) were stirred in acetone (100 cm^3) containing *ca.* 0.1 cm^3 of water for 16 h. Filtration of the solution followed by evaporation to 20 cm^3 and addition of light petroleum (100 cm^3) caused red *needles* of the complex to be precipitated; yield *ca.* 50%.

(*c*) $RuH(OH)(PPh_3)_2(H_2O)$ (0.17 g, 0.26 mmol) and $RuH_2(CO)(PPh_3)_3$ (0.24 g, 0.26 mmol) were refluxed in acetone (10 cm^3) for 3 h. The orange solution, which was shown to contain benzene (g.l.c. evidence), was filtered to remove an excess of $RuH_2(CO)(PPh_3)_3$ and $RuH(OH)(PPh_3)_2(H_2O)$ and evaporated to dryness. I.r. and ^1H n.m.r. evidence confirmed the presence of the *complex* as the only acetone-soluble product; yield *ca.* 50%.

(5) *Di-μ-hydroxo-bis[acetonehydridobis(triphenylphosphine)ruthenium*(II)].—$RuH(OH)(PPh_3)_2(H_2O)$ (0.5 g, 0.76 mmol) was stirred in dry acetone for several days, after which the yellow *complex* which had precipitated was collected, washed with acetone, and dried *in vacuo*; yield *ca.* 50%.

(6) *Di-μ-hydroxo-bis[hydrido(t-butyl alcohol)bis(triphenylphosphine)ruthenium*(II)].—(*a*) Potassium (0.5 g, 25 mg-atom) was dissolved in dry t-butyl alcohol 40 cm^3) and the resulting solution filtered onto $RuHCl(PPh_3)_3$ (0.5 g, 0.54 mmol). After the mixture had been stirred for several hours the yellow precipitate was collected. It was recrystallised from toluene–light petroleum as yellow-orange *crystals*; yield *ca.* 60%. Addition of light petroleum to the t-butyl alcohol filtrate produced $RuH_2(PPh_3)_4$ in low yield.

(*b*) $RuHCl(PPh_3)_3$ (0.5 g, 0.54 mmol) and KOH (0.57 g, 10 mmol) were stirred in t-butyl alcohol (50 cm^3) for several days. The yellow solid that precipitated was identified by i.r. spectroscopy as a mixture of $RuH_2(PPh_3)_4$ and the *complex*. Recrystallisation from toluene–light petroleum yielded $RuH_2(PPh_3)_4$ as yellow *crystals*.

(7) *Reaction of* $RuHCl(PPh_3)_3$ *with* $KOBu^t$ *in Tetrahydrofuran.*—$RuHCl(PPh_3)_3$ (0.6 g, 0.65 mmol) and $KOBu^t$ (0.15 g, 1.34 mmol) were stirred in tetrahydrofuran (50 cm^3) for 16 h. The resulting brown solution was evaporated to dryness and extracted with toluene (10 cm^3). After filtration and addition of light petroleum (20 cm^3) a small amount of a brown amorphous solid, which was not identified but contained co-ordinated-OH (n.m.r. evidence), separated. When set aside, the filtrate deposited yellow crystals identified as $RuH_2(PPh_3)_4$ from their i.r. spectrum.

(8) *Carbonyldihydridomethanolbis(triphenylphosphine)ruthenium*(II).—$RuH(OH)(PPh_3)_2(H_2O)$ (0.5 g, 0.76 mmol) was stirred under methanol (100 cm^3) for 16 h during which time the colour changed from scarlet to crimson. The *complex* was collected and dried *in vacuo*; yield *ca.* 80%. Evaporation of the yellow filtrate to dryness produced a small amount of yellow solid which contained $RuH_2(CO)_2(PPh_3)_3$ and $RuH_2(CO)(PPh_3)_3$ (i.r. evidence).

(9) *Carbonylethanoldihydridobis(triphenylphosphine)ruthenium*(II).—This reaction was carried out as in (8) by refluxing in ethanol for 4 days to give crimson *microcrystals*; yield *ca.* 80%, m.p. 160 °C (decomp.).

(10) *Bis(aqua)chlorohydroxobis(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (1 g, 1.04 mmol) and carbonate-free NaOH (5 cm^3, 0.5M aqueous, 2.5 mmol) were stirred in tetrahydrofuran for 16 h. On evaporation to 10 cm^3 and addition of water (50 cm^3), an orange tar was formed. Recrystallisation of this from toluene by concentrating a solution in a stream of argon at room temperature gave the complex as orange *microcrystals*; yield *ca.* 20%, m.p. 160 °C. Warming the solution during recrystallisation from toluene–light petroleum caused some dimerisation to $\{RuCl(OH)(PPh_3)_2(H_2O)\}_2$. Recrystallisation from tetrahydrofuran–light petroleum gave yellow–brown *needles* of *chlorohydroxobis(tetrahydrofuran)bis(triphenylphosphine)ruthenium*(II) in high yield.

(11) *Di-μ-hydroxo-bis[aquachlorobis(triphenylphosphine)-ruthenium*(II)].—The experiment was carried out as in (9) but with a reaction time of 5 days; yield *ca.* 60%, m.p. 144 °C.

(12) *Di-μ-hydroxo-bis[hydridohydroxo(tetrahydrofuran)bis-(triphenylphosphine)ruthenium*(II)].—$RuCl_2(PPh_3)_3$ (1 g, 1.04 mmol) and NaOH (6 cm^3, 0.5M aqueous; 3 mmol) were refluxed in tetrahydrofuran (50 cm^3) for 2 days. The yellow-brown solution was evaporated to 5 cm^3 and water (20 cm^3) added. The resulting oil was recrystallised from tetrahydrofuran–light petroleum as a yellow *microcrystalline* powder; yield *ca.* 30%. Using a reaction time of 16 h, and a similar work-up procedure, but recrystallisation from toluene–light petroleum, $\{RuCl(OH)(PPh_3)_2H_2O\}_2$ and the *complex* were obtained successively in approximately equal yield (*ca.* 20%).

(13) *Aquachlorohydridobis(triphenylphosphine)ruthenium*-(II).—$RuCl(OH)(PPh_3)_2(H_2O)_2$ (0.6 g, 0.85 mmol) and KOH (0.16 g, 2.85 mmol) were refluxed in tetrahydrofuran with passage of hydrogen for 6 h. On evaporation to 20 cm^3 and addition of water (50 cm^3) a dark oil separated. This was collected and recrystallised from toluene–light petroleum as red-purple *microcrystals*; yield *ca.* 70%.

An n.m.r. spectrum of the reaction solution obtained from the same reaction but with 0.2 g of $RuCl(OH)(PPh_3)_2(H_2O)_2$ showed only $\{RuH(OH)(PPh_3)_2(thf)\}_n$ (n = 1 or 2) to be present.

(14) *Reaction of* $RuCl(OH)(PPh_3)_2(H_2O)_2$ *with* $NaBH_4$ *in the Presence of an Excess of* PPh_3.—$RuCl(OH)(PPh_3)_2(H_2O)_2$ (0.5 g, 0.7 mmol), PPh_3 (0.3 g, 1.14 mmol), and $NaBH_4$ (0.1 g, 2.5 mmol) were stirred in toluene (60 cm^3) containing water (10 cm^3) for 16 h. Separation of the toluene followed by evaporation to 30 cm^3 and addition of light petroleum (50 cm^3) gave $RuH_2(PPh_3)_4$ (*ca.* 60%) and $RuHCl(PPh_3)_3$ (*ca.* 30%), identified by their i.r. spectra.

(15) *Dihydrido(tetrahydrofuran)tris(triphenylphosphine)-ruthenium*(II).—$RuHCl(PPh_3)_3$ (0.7 g, 0.75 mmol) and NaOMe (0.08 g, 1.5 mmol) were stirred in tetrahydrofuran (30 cm^3) containing methanol (1 cm^3) for 0.5 h. The orange solution was filtered and evaporated to half-volume. On addition of light petroleum (20 cm^3) and cooling, the *complex* separated as yellow *crystals* which were collected and dried *in vacuo*; yield *ca.* 50%, m.p. 170—200 °C (decomp.). When set aside the orange filtrate deposited white *needles* of $RuH_2(CO)(PPh_3)_3$ (i.r. evidence). Longer reaction times (16 h) led to reduced yields (*ca.* 20%) of the complex, and increased yields of $RuH_2(CO)(PPh_3)_3$.

(16) *Reaction of* $RuHCl(PPh_3)_3$ *with Sodium Methoxide in Diethyl Ether at Low Temperature*.—$RuHCl(PPh_3)_3$ (0.5 g, 0.54 mmol) and NaOMe (0.05 g, 0.9 mmol) were stirred in diethyl ether (20 cm^3) and methanol, which had not been pre-dried (0.25 cm^3), at 0 °C. After 3 h the yellow precipitate was collected and dried *in vacuo*. I.r.: 2 010w, 1 960w, 1 940vs, 1 632vs,br, and 825m. Recrystallisation from toluene–light petroleum afforded white crystals of $RuH_2(CO)(PPh_3)_3$ (i.r. comparison with an authentic sample). On some occasions a different yellow complex (i.r. 2 720w, 2 030w, 1 600vs, 875m, and 780s) was isolated from an ostensibly identical reaction.

(17) *Reaction of* $RuH_2(PPh_3)_4$ *with Formaldehyde*.—Formaldehyde, prepared by heating paraformaldehyde to 180 °C in a slow stream of argon, was passed through a solution of $RuH_2(PPh_3)_4$ (0.5 g, 0.43 mmol) in tetrahydrofuran (25 cm^3). After 5 min the white solid formed was collected and identified as paraformaldehyde. When set aside the pale filtrate deposited white *needles* of $RuH_2(CO)(PPh_3)_3$.

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