Carboxylato-triphenylphosphine Complexes of Ruthenium, Cationic Triphenylphosphine Complexes derived from them, and their Behaviour as Homogeneous Hydrogenation Catalysts for Alkenes †

By **Robert W. Mitchell, Alwyn Spencer,** and **Geoffrey Wilkinson,*** Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

The two-electron reduction of the oxo-centred triangular acetato-complex, $Ru_3O(CO_2Me)_6(PPh_3)_3$, in which the metal has mean oxidation state $2\frac{2}{3}$, gives a yellow ruthenium(II) species, probably $Ru(CO_2Me)_2PPh_3$. In methanol containing a non-complexing strong acid and additional triphenylphosphine to give a minimum PPh_3:Ru ratio of 2:1, the complex acts as a catalyst for the hydrogenation of alkenes. Similar catalyst solutions in methanol are obtained by the action of acids on the hydrido-acetate, $RuH(CO_2Me)(PPh_3)_3$, or the dihydride, $Ru(H)_2(PPh_3)_4$; aqueous fluoroboric acid, *p*-toluenesulphonic acid hydrate or trifluoromethylsulphonic acid have been used. The initial product is evidently the (solvated) cation $[Ru(PPh_3)_3]^{2+}$, but in presence of alkene a bis species, such as $[Ru(PPh_3)_2(alkene)]^{2+}$ is formed. On standing, or on treatment with H_2 or CO in absence of alkene, the orange-red tris species are converted to catalytically inactive yellow species, this reaction being faster in presence of water. From aged solutions the salt $[(Ph_3P)_2Ru(OH)_2Ru(PPh_3)_2](BF_4)_2$ has been isolated. The yellow solutions of $Ru(CO_2Me)_2PPh_3$ are oxidised by air to a new type of oxo-bridged ruthenium(III) complex, $Ru_2O(CO_2Me)_4(PPh_3)_2$, which is shown to be an intermediate in the preparation of $RuH(CO_2Me)(PPh_3)_3$ from commercial hydrated ruthenium chloride. The diacetate, $Ru(CO_2Me)_2(PPh_3)_2$ has also been prepared and the reduction of the tetra-μ-acetato-complex $[Ru_2(CO_2Me)_4]Cl$ investigated. Analogues of some of the compounds with other carboxylate groups are described.

We have previously shown[1] that the oxo-centred triangular ruthenium(III) carboxylates of the type $[Ru_3O(CO_2R)_6L_3]^+$, where L = water or pyridine undergo successive one- and two-electron reductions to form the species $Ru_3O(CO_2R)_6L_3$ and $Ru_3(CO_2R)_6L_3$, respectively, and that the first reduction is electrochemically reversible. The structure of the green intermediate complex $Ru_3O(CO_2Me)_6(PPh_3)_3$ has been determined by *X*-ray diffraction[2] and the oxo-centred formulation confirmed. This complex, in which the metal atoms are in the mean oxidation state $2\frac{2}{3}$ (or II, III, III), also undergoes a two-electron reduction. Unlike the similar yellow solutions obtained when water and pyridine are the ligands and which are trimeric species without the central oxygen atom,[1] the yellow phosphine solutions cannot be re-oxidised with molecular oxygen to the oxo-centred complex.

We now report details of the reduction of the phosphine carboxylates and use of the reduced species in acidified methanol solutions as hydrogenation catalysts for alkenes and the formation of similar species by action of acids on the complexes $RuH(CO_2Me)(PPh_3)_3$, $Ru(H)_2(PPh_3)_4$, and $Ru(CO_2Me)_2(PPh_3)_2$.

Reduction of Tris(triphenylphosphine)hexa-μ-acetato-μ$_3$-oxo-triruthenium(II, III, III).—The green complex, $Ru_3O(CO_2Me)_6(PPh_3)_3$, is not reduced in methanol by hydrogen at 2 atm pressure in the presence of a platinum oxide (Adams) catalyst at room temperature, but reduction occurs in *ca.* 3 h at 40° to give a yellow solution. In methanol, containing aqueous fluoroboric acid, reduction also occurs[3] in 6—8 h at 1 atm pressure and *ca.* 45°. The reduction may also be effected electrochemically (see below). The electronic absorption spectra of the solutions are given in Table 1.

The solutions are very air-sensitive, but unlike the pyridine aquo-complexes, the oxo-centred trimer is not regenerated, although the solutions initially turn green. The acidified solutions are similarly air-sensitive. On standing in air the solutions become black and finally after two days or so, deep purple. We have shown that the purple species is a new complex of stoicheiometry $Ru_2O(CO_2Me)_4(PPh_3)_2$ (see below).

The failure of the reduced solutions of $Ru_3O(CO_2Me)_6(PPh_3)_3$ to re-oxidise cleanly, suggests that break-up of the trinuclear structure has occurred to give species, doubtless solvated, of the type $Ru(CO_2Me)_2(PPh_3)$,*n*MeOH.

It may be noted that if triphenylphosphine is added to

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† No reprints available.

[1] A. Spencer and G. Wilkinson, *J.C.S. Dalton*, 1972, 1570.

[2] F. A. Cotton and J. G. Norman, jun., *Inorg. Chim. Acta*, 1972, 6, 411.

[3] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.

the reduced aquo-species, under rigorously air-free conditions and even under hydrogen, oxidation to form $Ru_3O(CO_3Me)_6(PPh_3)_3$ occurs quite rapidly. This provides additional confirmation of the preservation of the trinuclear structure in $Ru_3(CO_2Me)_6(H_2O)_3$. The reaction probably involves the reduction of one co-ordinated water molecule per complex, with the oxygen atom being inserted into the centre of the metal triangle:

TABLE 1

Electronic absorption spectra of ruthenium complexes

Complex	λ/nm (ε in parentheses)
$Ru_3O(CO_2Me)_6(PPh_3)_3$ [a]	974(6 280); *ca.* 790sh; *ca.* 410sh; 347(11 900)
$Ru_3O(CO_2Et)_6(PPh_3)_3$ [a]	974(6 630); *ca.* 790sh; *ca.* 410sh; 343(12 000)
$Ru_3O(CO_2Pr^n)_6(PPh_3)_3$ [a]	974(5 060); *ca.* 790sh; *ca.* 410sh; 338(12 200)
$Ru_2O(CO_2Me)_4(PPh_3)_2$ [a]	559(5 300); 372(4 300); 313(12 700)
$Ru_2O(CO_2Et)_4(PPh_3)_2$ [a]	555(5 780); 371(4 990); 310(16 100)
$Ru_2O(CO_2Pr^n)_4(PPh_3)_2$ [a]	557(5 840); 371(5 240); 312(15 900)
$Ru_2O(CO_2Ph)_4(PPh_3)_2$ [a]	563(5 590); *ca.* 384sh (*ca.* 5 900); 291(23 300)
$Ru_2O(CO_2Me)_4\{(p\text{-}FC_6H_4)_3P\}_2$ [a]	560(5 500); 369(4 920); 310(13 000)
Electrochemically reduced [b] solution from	
$Ru_3O(CO_2Me)_6(PPh_3)_3$	440(800); 353(3 200)
$Ru_2O(CO_2Me)_4(PPh_3)_2$	440(880); 353(3 800)
Acidified solutions of [c]	
$RuH(CO_2Me)(PPh_3)_3$ red	543(1 080); 460(1 500); 341(11 600)
aged yellow	560(340); *ca.* 460sh (*ca.* 1 000)
Acidified solutions of [c]	
$Ru(H)_2(PPh_3)_4$ red	530(800); 460(1 500)
aged yellow	558(320); *ca.* 450sh (*ca.* 1 300)

[a] In $CHCl_3$. [b] In methanol under H_2, Ru : PPh_3 = 1 : 3, $H^+ : CO_2Me^- = 4 : 1$. [c] In methanol under N_2 with CF_3SO_3H or HBF_4 (42% aqueous).

$$Ru_3(CO_2Me)_6(H_2O)_3 + 3PPh_3 \longrightarrow Ru_3O(CO_2Me)_6(PPh_3)_3 + 2H_2O + H_2$$

where an intermediate such as $Ru_3(CO_2Me)_6(H_2O)_2PPh_3$, must be presumed capable of reducing water.

The polarogram of $Ru_3O(CO_2Me)_6(PPh_3)_3$ in acetone with sodium perchlorate as supporting electrolyte shows a reduction wave at −1·05 V *vs.* the aqueous s.c.e., while macrocoulometry at controlled potential gave *n*-values of 2·01 and 1·88. For the corresponding n-butyrate a value of $n = 2{\cdot}10$ was obtained. The yellow solutions obtained by electrolytic reduction are similar to those formed by hydrogen reduction. Electronic spectra are given in Table 1.

The polarogram of $Ru_3O(CO_2Me)_6(PPh_3)_3$ in methanol containing fluoroboric acid shows only irregular reduction waves attributed to catalytic reduction of hydrogen ions. Although coulometric determination of the reduction was impossible, electrolysis of the acid solution at a potential of −0·6 V *vs.* silver wire again gave a greenish yellow solution. On addition to such solutions of triphenylphosphine to give a minimum ratio Ru : PPh_3 = 1 : 2, the resulting solution was catalytically active in the reduction of alkenes (see later). The extra PPh_3 was commonly added before electrolysis and good reproducibility was obtained when solutions of equal concentrations of $Ru_3O(CO_2Me)_6(PPh_3)_3$, PPh_3, and HBF_4 (42% aqueous) were electrolysed at 40° and −0·6 V *vs.* Ag, until the same quantity of electricity had passed. The current–time curves were reproducible to within a few per cent.

We have been unable to isolate a well defined solid complex from the reduced solutions but it would seem most likely that they contain the triphenylphosphine species $Ru(CO_2Me)_2PPh_3$, probably solvated. Since an extra mole of PPh_3 as well as acid is required to produce catalytically active solutions, these probably contain the bis(triphenylphosphine)ruthenium(II) cation, $[Ru(PPh_3)_2,n\text{MeOH}]^{2+}$, and substantiating evidence for this formulation is given later.

The reduced yellow species clearly are related to hydridoacetatotris(triphenylphosphine)ruthenium(II),[4] $RuH(CO_2Me)(PPh_3)_3$, whose crystal structure has been determined by *X*-ray diffraction.[5] Thus when a methanol solution of $Ru_3O(CO_2Me)_6(PPh_3)_3$ containing additional PPh_3 (one PPh_3 per Ru) and acid (one equivalent HBF_4 per two acetate groups) is reduced electrochemically and the yellow solution then treated with further triphenylphosphine (under hydrogen), the hydrido-complex is obtained essentially quantitatively:

$$Ru_3O(CO_2Me)_6(PPh_3)_3 \xrightarrow[3H^+,\ 2e]{3PPh_3} 3[Ru(CO_2Me)(PPh_3)_2]^+ \xrightarrow[H_2]{PPh_3} RuH(CO_2Me)(PPh_3)_3$$

If an excess of acid is used complete protonation occurs to give cations of the type $[Ru(PPh_3)_2]^{2+}$ and acetic acid. The cationic species should thus be obtainable by action of acid on the hydridoacetate.

The hydridoacetate is almost insoluble in cold methanol, but on addition of trifluoromethylsulphonic acid or *p*-toluenesulphonic acid monohydrate, red solutions are formed rapidly upon warming (40°), although using aqueous (42%) fluoroboric acid, it is necessary to heat the solution to 65°. The red solutions are air-sensitive. N.m.r. study shows that there is no Ru–H group present, and that acetic acid is formed. Attempts to obtain ^{31}P n.m.r. spectra (Fourier transform) failed due to the low concentration and conversion to a yellow species (see below). The isolation of crystalline salts from the solutions has proved difficult, but a fluoroborate and a trifluoromethylsulphonate appear to be salts of the ion $[Ru(PPh_3)_3]^{2+}$. Since this ion is co-ordinatively unsaturated it is likely that the anions occupy sites in the co-ordination sphere and indeed the conductivities are

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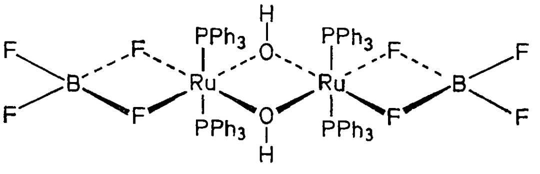
[4] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610.

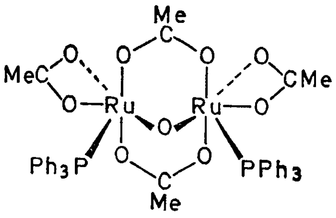
[5] A. C. Skapski and F. A. Stephens, *Chem. Comm.*, 1969, 1008.

lower than expected for a 1 : 2 electrolyte in nitromethane. The formulation as a tris(triphenylphos-*phine*)*ruthenium*(II) cation is supported by the reaction of the red species in methanol with chloride ion to give quantitatively $\mathrm{RuCl_2(PPh_3)_3}$ and with acetate ion under hydrogen to give $\mathrm{RuH(CO_2Me)(PPh_3)_3}$ (see later). The cation may also be obtained by the interaction of a stoicheiometric amount of silver tetrafluoroborate with $\mathrm{RuCl_2(PPh_3)_3}$. After removal of the precipitated AgCl, the solution is orange, and has identical properties to the cationic solutions above.

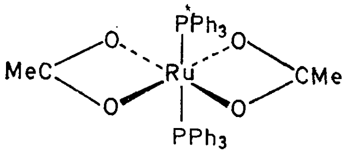
The life time of the red ion in methanol depends on the conditions. For the fluoroboric acid case, it is stable under nitrogen for *ca.* 1 h, whereupon the solution turns yellow. This change is much more rapid under hydrogen (15 min). On admission to the red solution under hydrogen of carbon monoxide or ethylene, the change is immediate. No carbonyl or ethylene complex can be isolated or even detected in solution, and g.l.c. study shows that traces of formaldehyde and ethane, respectively, are formed. From the yellow solutions, a well defined crystalline salt slowly separates. This has the stoicheiometry $\mathrm{Ru(OH)(PPh_3)_2BF_4}$ and its i.r. spectrum has bands at 845 and 540 $\mathrm{cm^{-1}}$ for the antisymmetric and symmetric RuORu vibrations, characteristic of bridging hydroxo-groups.[6] The low conductivity in nitromethane again suggests anion co-ordination or ion-pairing. One possible structure for the solid is (I).



(I)



(II)



(III)

When $\mathrm{CF_3SO_3H}$ or *p*-$\mathrm{MeC_6H_4SO_3H,H_2O}$ are used the red solutions only very slowly become yellow, even under hydrogen, but no crystalline solid can be isolated, presumably because of the absence or deficiency of water.

On addition of liquid alkenes to the red solutions or to methanol solutions of the isolated red salts, no colour change occurs under nitrogen, but under hydrogen, lightening of the colour is immediate, as is the rapid uptake of hydrogen (see later). None of the yellow solutions obtained by ageing under nitrogen or hydrogen or by treatment with carbon monoxide or ethylene will act as hydrogenation catalysts.

Similar red (and yellow) solutions can be obtained analogously from the dihydride, $\mathrm{Ru(H)_2(PPh_3)_4}$, by treatment with acid (see below).

μ-*Oxo-bis*[(*triphenylphosphine*)*diacetatoruthenium*(III)].—It was noted earlier than reduced solutions of $\mathrm{Ru_3O(CO_2Me)_6(PPh_3)_3}$ on long exposure to air turn purple. Similarly the red solutions described above, on addition of acetate ion followed by oxygenation, turn purple. Purple solutions are also rapidly formed (5 min) when '$\mathrm{RuCl_3,3H_2O}$' is refluxed in methanol containing triphenylphosphine and sodium acetate trihydrate. Prolonged heating of the latter solution yields the hydrido-acetate $\mathrm{RuH(CO_2Me)(PPh_3)_3}$, whose formation is enhanced by increasing the excess of triphenylphosphine (which is presumably acting as reducing agent). The pure purple complex in methanol containing $\mathrm{PPh_3}$ is slowly reduced to the hydride under nitrogen even at room temperature.

Purple needle crystals of the acetate and of similar carboxylates may be obtained on slow evaporation in air of the methanolic solutions. These analyse as $\mathrm{Ru_2O(CO_2R)_4(PPh_3)_2,MeOH}$. The methanol of solvation can be readily detected in the i.r. or n.m.r. spectra. The n-butyrate may be obtained solvent free on crystallisation from benzene. The trifluoroacetate was obtained only as a powder. The complexes are soluble in common organic solvents and, in methanol and benzene, the n-butyrate has a molecular weight corresponding to $\mathrm{Ru_2O(CO_2Pr^n)_4(PPh_3)_2}$. They are insoluble in alkanes and in water. The solutions are stable to oxygen; in aromatic solvents slow conversion to brown, as yet unidentified, species occur. The electronic spectra of several carboxylates are given in Table 1.

Confirmation of the oxidation state as $\mathrm{Ru^{III}}$ comes from polarographic reduction of the acetate in acetone using sodium perchlorate as supporting electrolyte. There is a well defined reduction wave at —0·99 V *vs.* s.c.e. and coulometric reduction at —1·3 V gave an *n* value of 1·99 per $\mathrm{Ru_2O}$ unit. The reduced solutions are yellow and are evidently identical with those formed by reduction of $\mathrm{Ru_3O(CO_2Me)_6(PPh_3)_3}$ (see Table 1). Hence we have

$$\mathrm{Ru_2O(CO_2Me)_4(PPh_3)_2} \underset{\mathrm{O_2}}{\overset{2e}{\rightleftharpoons}} \mathrm{2Ru(CO_2Me)_2PPh_3} \xleftarrow{2e} \mathrm{Ru_3O(CO_2Me)_6(PPh_3)_3}$$

Also, electrochemical reduction in methanol containing $\mathrm{HBF_4}$ and $\mathrm{PPh_3}$ gives yellow solutions whose electronic spectra, polarograms, and behaviour as hydrogenation catalysts are similar to those produced from $\mathrm{Ru_3O(CO_2Me)_6(PPh_3)_3}$.

The acetate is diamagnetic both as solid (Gouy method) and in solution (Evans method) and has no e.s.r. signal in the solid or solution states. There is no band in the i.r. spectrum of any of the purple complexes

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[6] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 472.

in the region 800—940 cm^{-1} which is considered to be characteristic for bands due to linear M–O–M systems. Ruthenium complexes (of Ru^{IV}, however) with a linear Ru–O–Ru group absorb at 860—870 cm^{-1}. We conclude that the Ru–O–Ru group is bent, despite the view that spin-pairing leading to diamagnetism is possible only in linear systems.[7] Since spin-pairing occurs in the oxo-centred systems with six electrons per ruthenium atom,[1,2] there seems no good reason why it should not occur in a bent $Ru^{III}–O^{2-}–Ru^{III}$ bridge where there are also six electrons per ruthenium. Whether the complexes also have bridging carboxylato-groups or whether both these are chelated is uncertain as neither i.r. nor n.m.r. spectra are definitive. However a structure such as (II) seems reasonable. Consistent with this, the n.m.r. spectrum shows two methyl resonances (ratio 1 : 1). The methanol of solvation could be hydrogen bonded to the bridge oxygen. The n.m.r. spectra of the propionato-, n-butyrato-, and the tris(*p*-fluorophenyl)phosphine acetato-complexes also show similar non-equivalence of the carboxylates; this is not due to ^{31}P coupling as shown by spectra at 60 and 100 MHz.

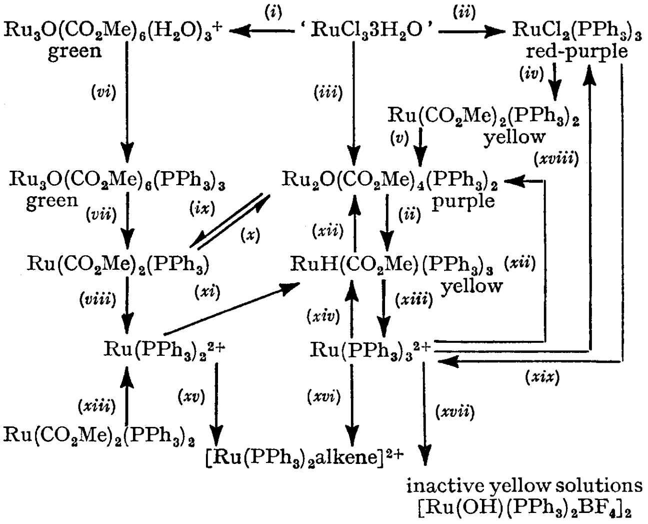
Diacetatobis(triphenylphosphine)ruthenium(II).— Since bistriphenylphosphine species appear to be involved in the above chemistry, we prepared the previously unknown orange-yellow diacetate, $Ru(CO_2Me)_2(PPh_3)_2$. This is obtained by interaction of $RuCl_2(PPh_3)_3$ with sodium acetate in refluxing t-butyl alcohol (to prevent hydride abstraction and formation of the hydridoacetate) under nitrogen. The molecular weight is normal, there is only a single methyl resonance in the n.m.r. and the structure is presumably as in (III), where the carboxylate groups are chelate as in $RuH(CO_2Me)(PPh_3)_3$.[5]

The complex is protonated by CF_3SO_3H and other acids in methanol to give catalytically active solutions: the acetate is lost and there is no high field line in the n.m.r. spectrum. The yellow acid solutions doubtless contain the solvated $Ru(PPh_3)_2^{2+}$ ion. The yellow methanol solutions of the complex are stable for weeks under nitrogen, but in air, oxidation to the purple μ-oxo-species occurs slowly.

The accompanying Scheme sets out the relationships of the various complexes discussed above.

Tetra-μ-acetato-bis(triphenylphosphine)diruthenium(II).—During the early studies[3] on the protonation of ruthenium carboxylates, it was believed that the phosphine adduct of the unknown tetra-μ-acetato-diruthenium(II) had been obtained, but this turned out to be $Ru_3O(CO_2Me)_6(PPh_3)_3$.[1]

On treatment of the paramagnetic complex $[Ru_2(CO_2Me)_4]Cl$, for which the proposed[8] tetra-μ-acetato-structure has been confirmed by *X*-ray diffraction,[9] with triphenylphosphine in methanol under nitrogen, a light brown precipitate is formed (24 h). This may be separated into buff and yellow components. The latter has the stoicheiometry $Ru(CO_2Me)_2PPh_3$, but the solubility is too low for molecular weight determination, as is also that of the corresponding n-butyrate. It seems reasonable to assume that these are the dimers with four bridging carboxylates and phosphine end groups.



SCHEME (*i*), $MeCO_2H$; (*ii*), PPh_3 + MeOH; (*iii*), $MeCO_2Na$ + PPh_3 + MeOH; (*iv*), $MeCO_2Na$ + Bu^tOH; (*v*), MeOH + O_2; (*vi*), MeOH + PPh_3 + e; (*vii*), H_2(Pt) + MeOH or 2e; (*viii*), H^+ + MeOH + PPh_3; (*ix*), +2e; (*x*), O_2 + PPh_3; (*xi*), $MeCO_2Na$ + PPh_3; (*xii*), O_2 + $MeCO_2Na$ + MeOH; (*xiii*), H^+; (*xiv*), $MeCO_2Na$; (*xv*), alkene; (*xvi*), alkene − PPh_3; (*xvii*) ageing, H_2, CO, *etc.*; (*xviii*), LiCl; (*xix*), Ag^+

The polarograms of the acetato-, propionato-, and n-butyrato-chlorides, in methanol containing sodium perchlorate as supporting electrolyte, all show oxidation and reduction waves of approximately equal height. For the n-butyrate, the reduction wave has $E_{\frac{1}{2}} = -0{\cdot}09$ V and the oxidation wave $E_{\frac{1}{2}} = +0{\cdot}12$ V *vs.* aqueous s.c.e. The reduction waves of the acetate and propionate are obscured by maxima of the first kind, which are not suppressed by addition of a surfactant (Triton X-100), but are roughly at the same potential as the n-butyrate. The oxidation waves are at +0·14 V (acetate) and +0·08 V (propionate). Coulometric reduction at the mercury pool at −0·5 V gave *n*-values of 0·99 (acetate), 1·03 (propionate), and 0·92 (n-butyrate). Attempts to obtain the yellow phosphine complex from the electrolytically reduced solutions were unsuccessful. The polarogram of the electrochemically reduced solution of $[Ru_2(CO_2Pr^n)_4]Cl$ shows an oxidation wave at the same half wave potential as the original reduction wave, indicating thermodynamic reversibility:

$$Ru_2(CO_2Pr)_4^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} Ru_2(CO_2Pr)_4$$

The occurrence of maxima with the other two complexes precludes a similar comparison of potentials in methanol.

The oxidation waves doubtless arise from oxidation to Ru^{III}, but the waves are irregular and more than simple electron transfer is probably involved. It may be

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[7] J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 1953, 2594.

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

[9] M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1.

noted in passing that the original synthesis of $Ru_2(CO_2R)_4Cl$ leads to appreciable amounts of green $Ru_3O(CO_2R)_6L_3^+$ species.[1] The addition of excess anhydrous lithium chloride to the reaction mixture suppresses the formation of oxo-species and results in the yield of the acetato-chloride being raised to *ca.* 80%. The yield is the same whether the reaction is carried out under nitrogen or under oxygen. A similar yield was obtained for the propionate (under oxygen) but for the n-butyrate nitrogen must be used and the best yield is still only *ca.* 40%.

Catalytic Hydrogenation of Alkenes.—The following general points can be made concerning the catalyst systems.

(*a*) Similar catalytically active solutions can be made by (i), reduction in acidified methanol of $Ru_3O(CO_2Me)_6(PPh_3)_3$ or $Ru_2O(CO_2Me)_4(PPh_3)_2$; (ii), action of non-complexing strong acids on $RuH(CO_2Me)(PPh_3)_3$, $Ru(CO_2Me)_2(PPh_3)_2$ or $Ru(H)_2(PPh_3)_4$, or (iii), by removal of chloride ion from $RuCl_2(PPh_3)_3$ with the stoicheiometric amount of silver perchlorate. Use of an excess of silver salt leads to green solutions of unknown composition.

(*b*) Where the PPh_3 : Ru ratio is less than 2 : 1, as in the reduction of $Ru_3O(CO_2Me)_6(PPh_3)_3$, the solutions are inactive and become active only on addition of triphenylphosphine sufficient to give a minimum ratio PPh_3 : Ru of 2 : 1. Addition of an excess of phosphine to the yellow solutions up to a PPh_3 : Ru ratio of 8—10 : 1 produces no appreciable change in the rate of hydrogenation.

(*c*) The active catalytic species appear to be a cationic ruthenium(II) species with two triphenylphosphine groups, the other co-ordination sites being occupied by either solvent (methanol) molecules or co-ordinated alkene molecules. Where the initial ruthenium species have a ratio PPh_3 : Ru greater than 2 : 1, dissociation, presumably induced by alkene and/or hydrogen is assumed to occur.

From $Ru_3O(CO_2Me)_6(PPh_3)_3$. The complex in methanol containing excess of PPh_3 and fluoroboric acid sufficient to give a ratio Ru : PPh_3 = 1 : 2, and H^+ : CO_2Me^- = 1 : 1 was reduced electrochemically. Further acid or triphenylphosphine as required was added after reduction. Table 2 gives data for the competitive reactions of hydrogenation and isomerisation of hex-1-ene; isomerisation is not induced by the acid in methanol alone. At high acid concentrations hydrogenation predominates, although the rate falls off, possibly due to attack by hydrogen ion on ruthenium hydrogen bonds of intermediate species.

From $Ru_2O(CO_2Me)_4(PPh_3)_2$. This complex on reduction behaves similarly to $Ru_3O(CO_2Me)_6(PPh_3)_3$. However, alone in acidified methanol at 60° under hydrogen it gives a blue solution after *ca.* 1 h; on addition of PPh_3 and HBF_4 to give ratios of Ru : PPh_3, 1 : 2 and H^+ : CO_2Me^-, 1 : 1, the solution becomes mauve and reduces hex-1-ene with essentially no accompanying isomerisation. However, the slow initial rate increases with time when the solution begins to turn yellow. Thus it appears that slow reduction by hydrogen gives the same species as electrochemical reduction. This is confirmed by the addition of a little zinc to a solution of the complex containing an excess of PPh_3 and acid; the solution rapidly turns yellow and the rates of hydrogenation are similar to those of solutions made in other ways (Table 3).

TABLE 2

Dependence of hydrogenation and isomerisation of hex-1-ene on acidity. Catalyst, 7.5×10^{-4} mol l^{-1} Ru from electrolytic reduction of $Ru_3O(CO_2Me)_6(PPh_3)_3$; Ru : PPh_3 = 1 : 2; hexene, 1 mol l^{-1}; 40 °C; H_2 pressure 40 cmHg; methanol plus 42% aqueous HBF_4

$MeCO_2^-$: H^+	Uptake of H_2 in ml min^{-1} at s.t.p.	Unchanged[a] hex-1-ene (%)	n-hexane[a] (%)	*trans*-hex-2-ene[a] (%)
1 : 1	8·6	43·0	55·0	2·0
2 : 1	17·0	31·0	68·0	<0·5
3 : 1	26·8	28·0	71·5	0·5
4 : 1	36·0	0·7	99·0	0·3
5 : 1	27·4	14·0	85·0	1·0
6 : 1	25·0			
8 : 1	22·1	23·0	75·0	2·0

[a] Compositions determined after 1 h at 40 cmHg pressure, the hydrogen pressure was adjusted to 40 cmHg throughout the catalytic run.

TABLE 3

Rates of hydrogenation of hex-1-ene using different sources of ruthenium. Ruthenium concentration 7.5×10^{-4} mol l^{-1}; hexene, 1 mol l^{-1}; rates measured at 40 cmHg hydrogen pressure; methanol at 40° using aqueous fluoroboric acid except where noted

Source	PPh_3 : Ru	H^+ : $MeCO_2^-$	Hydrogen uptake in ml min^{-1} at s.t.p.
$Ru_3O(CO_2Me)_6(PPh_3)_3$ [a]	2	4	36·0
	3	4	38·0
$Ru_2O(CO_2Me)_4(PPh_3)_2$ [a]	2	4	53·2
	3	4	50·1
$RuH(CO_2Me)(PPh_3)_3$	3	4	48·0
	3	8 [b]	56·8
	3	16 [c]	17·2
	4	4	56·8
	10	4	56·8
$Ru(CO_2Me)_2(PPh_3)_2$	2	8	36·1
	2	8 [b]	41·2
	3	8	31·0
$Ru(PPh_3)_3(CF_3SO_3)_2$	3	0	38·8 [e]

[a] Catalyst solution made by electrolytic reduction. [b] CF_3SO_3H used. [c] CF_3SO_3H in t-butanol as solvent. [d] Solid complex used. [e] The red chloride free solution of $RuCl_2(PPh_3)_3$ under these conditions gave a rate for hex-1-ene of 39·8 ml min^{-1}.

From $Ru(CO_2Me)_2(PPh_3)_2$. Addition of acid to this acetate in methanol gives yellow solutions which are catalytically active. It is necessary to have a slight excess of acid present otherwise there is some loss of activity, possibly due to partial re-association to give an acetato-species. There is no change in colour on addition of alkenes to the solution, under either nitrogen or hydrogen.

From $RuH(CO_2Me)(PPh_3)_3$. In benzene solution this complex is moderately active for the reduction of alk-1-enes[4] and the rate is enhanced by the addition of alcohols.

The orange-red solution, formed on treating the hydride suspended in methanol with acid, on addition of alkenes is catalytically active (Table 3). The aged yellow solutions are inactive but in presence of an excess of acid show very weak activity.

From $Ru(H)_2(PPh_3)_4$. Although this complex has been known for some time[10] its properties as a hydrogenation catalyst do not appear to have been noted, although it is possible that if alkenes other than alk-1-enes (for which it is very selective, *cf.* ref. 4) were used, this ability could have been overlooked.*

In methanol (Ru concentration $7{\cdot}5 \times 10^{-4}$M) containing hex-1-ene (1M) at 40°, the rate of hydrogen uptake was 45·4 ml min^{-1} at hydrogen pressure 40 cmHg which can be compared directly with the rates given in Tables 2 and 3.

Dissociation of the solid in methanol containing HBF_4, CF_3SO_3H, or p-$MeC_6H_4SO_3H$ gives an orange-red solution having electronic spectra (Table 1) and catalytic properties similar to those obtained from $RuH(CO_2Me)(PPh_3)_3$; these solutions also age to give an inactive yellow species. Since an extra phosphine is present in the solution a comparison of $Ru(H)_2(PPh_3)_4$ with $RuH(CO_2Me)(PPh_3)_3$ containing an extra mole PPh_3 and at the same acid concentration ($H^+ : Ru = 4 : 1$) is more valid. Under the standard conditions of Tables 2 and 3, the rates were 57·6 and 56·8 ml min^{-1} respectively, suggesting that the catalyst species are indeed the same.

DISCUSSION

The catalytically active system appears to involve bis(triphenylphosphine)ruthenium(II) cations; the properties appear to be closely similar regardless of the method of formation, the most straightforward way being interaction of acid with $Ru(CO_2Me)_2(PPh_3)_2$.

The action of acids on $RuH(CO_2Me)(PPh_3)_3$ or $Ru(H)_2(PPh_3)_4$ gives initially red solutions in methanol. Since in the former, the three phosphine groups are known to be approximately meridional we can assume that the red species is a cation with the same *mer*-configuration. The quantitative reversal of the reaction under hydrogen by addition of sodium acetate is good evidence for this and additional evidence that the red species is a trisphosphine is the quantitative reaction with lithium chloride to give $RuCl_2(PPh_3)_3$. Thus we have:

$$RuH(CO_2Me)(PPh_3)_3 + 2H^+ = Ru(PPh_3)_3{}^{2+} + H_2 + MeCOOH$$

It is reasonable to assume that in presence of alkene under hydrogen (hydrogen appears to be required since there is no colour change with alkene under nitrogen) promoted dissociation of one of the PPh_3 groups occurs to give the bisphosphine species similar to those obtained in other ways.

The catalytic cycle may then proceed by steps commonly accepted for other homogeneous systems, namely oxidative addition of molecular hydrogen to the cationic alkene complex, hydride transfer to give an alkyl followed by a second hydride transfer and alkane elimination. It is possible that more than one alkene is co-ordinated in view of the rapid hydrogenation of cyclo-octadiene (see below). The other vacant co-ordination sites are presumably occupied by methanol. Since the addition of an excess of phosphine has little effect on the rate, the alkene complexes must be fairly resistant to substitution, although it must be remembered that the alkene concentration is vastly greater than either the Ru or PPh_3 concentration. Attempts to isolate alkene cationic species have failed. However, such complexes are known for rhodium and iridium, *e.g.*, $[Ir(cod)(PPh_3)_2]^+$, (where cod = cyclo-octa-1,5-diene). These cations also activate molecular hydrogen and will hydrogenate alkenes and other substrates by a mechanism similar to that given above.[11]

$$\begin{tikzcd} {[Ru(PPh_3)_2]^{2+}} \arrow[r, shift left, "\text{alkene}"] & {[Ru(PPh_3)_2\ \text{alkene}]^{2+}} \arrow[l, shift left] \arrow[d, shift left, "H_2"] \\ & {[Ru(H)_2(PPh_3)_2\ \text{alkene}]^{2+}} \arrow[u, shift left] \arrow[ul, "-\text{alkane}"] \end{tikzcd}$$

In Table 4 are given rates for various alkenes. Although like $RuH(CO_2Me)(PPh_3)_3$ in benzene,[3] there is high selectivity for alk-1-enes over alk-2-enes, the cationic species will hydrogenate cyclo-octene and cyclo-octa-1,5-diene. For the latter only traces of the expected intermediate cyclo-octene could be detected by g.l.c. This suggests that reduction proceeds directly to cyclo-octane. Presumably both double bonds in the diene can be chelated to the metal and reduced successively, the second being still bound to the metal after the reduction of the first. The failure to reduce conjugated dienes may be due to the formation of stronger, possibly allylic complexes. It may be noted that although in absence of liquid alkenes, the red species are converted to the inactive yellow species, this conversion does not occur in their presence and there is no change in the rate of hydrogenation with time over a period of an hour or so.

All the solutions are partially inactivated by addition of excess acetate ion and can be reactivated by addition of acid. It is also quite possible that hydrogen transfer reactions involving the α-hydrogen atoms of the triphenylphosphine groups are occurring also, as is well known in other similar complexes;[12] this aspect has no been studied.

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* *Added in proof.* The hydrogenation of styrene and ethylene has now been noted (S. Komiya, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1972, **42**, C65).

[10] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3010; W. H. Knoth, *J. Amer. Chem. Soc.*, 1972, **94**, 104; T. I. Eliades, R. O. Harris, and M. C. Zia, *Chem. Comm.*, 1970, 1709. For a simpler synthesis see J. J. Levison and S. D. Robinson, *J. Chem. Soc. (A)*, 1970, 2947.

[11] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1969, **91**, 2816.

[12] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

Although the nature of the yellow crystalline product which separates from the aqueous fluoroboric acid–methanol solution seems reasonably certain, the nature of the inactive yellow species in solution, especially when little or no water is present are not. It is possible that isomerisation of the red cation occurs to give a *fac*-tristriphenylphosphine cation.

The latter would be less likely to dissociate a phosphine readily to provide the necessary co-ordinative unsaturation.

EXPERIMENTAL

Microanalyses by Bernhardt, Mülheim, Yarsley, Surrey, and Imperial College laboratories.

Molecular weights by Perkin-Elmer–Hitachi model 115 osmometer. Spectroscopic instruments: i.r., Perkin-Elmer models 257, 457, and 325; electronic Cary model 14; n.m.r., Perkin-Elmer R12A (60 MHz) and R14 (100 MHz). Polarography by Beckman Electroscan TM30. Controlled potential electrolysis by Chemical Electronics TR 70/2A potentiostat. G.l.c. analyses by Perkin-Elmer F11 with Kent Chromalog integrator. For alkenes and alkanes, a silver nitrate–diethyleneglycol column and flame ionisation detector were used; for ethane and formaldehyde a silica gel column and hot wire detector.

Ruthenium chloride, ' $RuCl_3,3H_2O$ ' was from Johnson Matthey Ltd. The hydrogenation procedure, purification of substrates, *etc.* have been described.[13]

All preparations and other operations were normally carried out under oxygen-free argon, nitrogen, or hydrogen. Transfers were made by conventional thin steel tubing, syringe, serum cap, *etc.* techniques.

Hydridoacetatotris(triphenylphosphine)ruthenium(II).—These preparations are a considerable improvement on the original preparation.

(a) *From* $RuCl_2(PPh_3)_3$. This complex[8] (1 g) and sodium acetate trihydrate (1·42 g) in ethanol (250 ml) or methanol were heated under reflux under nitrogen. After *ca.* ½ h the solution was allowed to cool to room temperature. The yellow complex was collected in air, washed with ethanol, water, and again with ethanol and dried *in vacuo* over silica gel. Yield 0·85 g (85%).

(b) *From* $RuCl_3,3H_2O$. The chloride (0·3 g), triphenylphosphine (1·8 g), and sodium acetate trihydrate, (1·56 g) in methanol (50 ml) were heated under reflux for 4 h. The hydride which separates from the purple solution was collected from the hot solution, washed with methanol and ether and dried as above. Yield 0·64 g (59%).

TABLE 4

Rates of hydrogenation of various alkenes

Alkene	Hydrogen uptake in ml min^{-1} at s.t.p. $RuH(CO_2Me)(PPh_3)_3$ MeOH + H$^+$	 $RuH(CO_2Me)(PPh_3)_3$ Benzene[c]	 $Ru_3O(CO_2Me)_6(PPh_3)_3$[b]
Hex-1-ene	48·0, 49·1[d]	15·1	36·0
Pent-1-ene	37·0, 38·8[d]		30·7
cis-Hex-2-ene	<0·1, <0·1[d]	<0·1	<0·1
cis-Pent-2-ene	<0·1, <0·1[d]	<0·1	<0·1
trans-Hex-2-ene	<0·1, <0·1[d]	<0·1	<0·1
Cyclo-octene	31·9, 30·6[d]	<0·1	28·0
Cyclo-octa-1,3-diene	<0·1	<0·1	<0·1
Cyclo-octa-1,5-diene	58·8	<0·1	51·5
Bicyclohepta-2,5-diene	1·0	<0·1	0·7

[a] Conditions as given in Table 3. Electrolytically reduced in methanol; $PPh_3 : Ru = 2 : 1$. [c] Data of ref. 4. p-MeC_6H_4-SO_3H,H_2O used.

TABLE 5

Analytical data for the ruthenium complexes

Complex	Found C	Found H	Found P	Required C	Required H	Required P
$Ru_2O(CO_2Me)_4(PPh_3)_2MeOH$[a]	53·2	4·6	6·6	53·4	4·6	6·1
$Ru_2O(CO_2Et)_4(PPh_3)_2MeOH$	55·0	5·0	5·8	55·1	5·1	5·8
$Ru_2O(CO_2Pr^n)_4(PPh_3)_2$	56·9	5·5	5·7	57·0	5·1	5·8
$Ru_2O(CO_2Ph)_4(PPh_3)_2MeOH$	61·9	4·3	5·3	62·0	4·3	4·9
$Ru_2O(CO_2Me)_4\{(p\text{-}FC_6H_4)_3P\}_2MeOH$	47·9	3·3	5·0	48·3	3·6	5·5
$Ru(CO_2Me)_2(PPh_3)_2$[c]	64·7	5·1	8·5	64·6	4·9	8·3
$Ru(PPh_3)_3(CF_3SO_3)_2$	56·0	3·5	7·7	56·7	3·8	7·8
$Ru_2(OH)_2(PPh_3)_4(BF_4)_2$[d]	59·0	4·7	9·1	59·3	4·1	8·6
$[Ru(CO_2Me)_2PPh_3]_n$[e]	54·6	4·4	6·4	54·8	4·4	6·4

[a] Oxygen analysis, found 14·6, required 15·0%. [b] *M* 990 in benzene, 1180 in methanol, required 1080. [c] *M* 740 in chloroform, required 743. [d] Fluorine analysis, found 10·4, required 10·4; boron analysis, found 1·6, required 1·5%. [e] Complex too insoluble for *M* to be determined.

(c) *From* $Ru_3O(CO_2Me)_6(PPh_3)_3$. A methanol (100 ml) solution of this complex (36·6 mg), triphenylphosphine (19·8 mg), and fluoroboric acid (20 ml of a solution of 0·42 g, 42% aqueous HBF_4 in 500 ml methanol) was reduced under nitrogen at −0·6 V *vs.* the silver wire electrode for *ca.* 2 h. The yellow air-sensitive solution was transferred under hydrogen to a solution of PPh_3 (*ca.* 1 g) in methanol (50 ml). After refluxing under hydrogen for *ca.* 12 h, the hydride was collected as above. Yield 80%.

Tetra-μ-acetato-diruthenium(II, III) *Chloride*.—The following is a much improved procedure for this complex.[8]

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[13] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

Ruthenium chloride hydrate (0·5 g) and anhydrous lithium chloride (0·5 g) were added to a mixture of glacial acetic acid (17·5 ml) and acetic anhydride (3·5 ml). The solution was refluxed for 4 h in a slow stream of oxygen. After cooling at 10° for 12 h the red brown salt was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·36 g, (80%).

μ-Oxo-bis[diacetatotriphenylphosphineruthenium(III)] *Methanolate*.—(a) *From* $RuCl_3,3H_2O$. The chloride (2 g), triphenylphosphine (4 g), and $NaCO_2Me,3H_2O$ (4·2 g) in methanol (200 ml) were heated under reflux in nitrogen for 15 min. The mixture was cooled to room temperature (under nitrogen) and then filtered (in air) into water (200 ml) which was stirred rapidly. The purple precipitate was centrifuged, washed (water), and re-centrifuged until the washings were colourless. The crude complex was dried *in vacuo*, dissolved in hot methanol (*ca*. 70 ml) and the solution filtered. The filtrate was cooled at −40° for 24 h and any precipitate removed by filtration. Slow evaporation of the methanol solution in a conical flask in air at room temperature gave, in 4—5 days, purple crystals of the *complex*. These were collected, washed with methanol (*ca*. 10 ml) and light petroleum and dried *in vacuo*. Yield 1·53 g (41%).

(b) *From* $Ru_2(CO_2Me)_4Cl$. A solution of this salt (0·2 g) and PPh_3 (0·22 g) in methanol (30 ml) was stirred in air for 24 h. The resulting purple solution was cooled to −40° (6 h) and filtered. Addition of water to the solution precipitated the complex, which was collected, washed with water and ether, and dried. Yield *ca*. 100%.

μ-Oxo-bis[dipropionatotriphenylphosphineruthenium(III)] *Methanolate*.—Sodium hydroxide (0·31 g) was dissolved in warm methanol (50 ml) and to the cold solution was added propionic acid (0·567 g), PPh_3 (1 g) and $RuCl_3,3H_2O$ (0·5 g). The mixture was refluxed under nitrogen for 15 min and worked up as the acetate. Yield 0·43 g (44%).

μ-Oxo-bis[di-n-butyratotriphenylphosphineruthenium(III)].—As for the propionate from NaOH (0·3 g), n-butyric acid (0·67 g), PPh_3 (1 g), and $RuCl_3,3H_2O$ (0·5 g). The crude product was dissolved in benzene (50 ml) and the filtered solution left to evaporate in a conical flask. The first dark precipitate was removed and further evaporation gave the *complex* which was collected, washed with methanol, and dried *in vacuo*. Yield 0·51 g (50%).

μ-Oxo-bis[dibenzoatotriphenylphosphineruthenium(III)] *Methanolate*.—As before but using sodium benzoate (1·1 g). Cooling of the filtered methanol solution at −40° for 12 h gave almost complete precipitation of a purple-black solid. This was collected, dissolved in hot methanol, and the solution filtered and left to evaporate. The *complex* as purple needles was collected after *ca*. 2 days. Yield 0·63 g (54%).

μ-Oxo-bis[diacetatotris(p*-fluorophenyl)phosphineruthenium*-(III)] *Methanolate*.—As for the acetato-triphenylphosphine complex but using $RuCl_3,3H_2O$ (0·5 g), $(p\text{-}FC_6H_4)_3P$ (1·21 g), and $NaCO_2Me,3H_2O$ (1·03 g) in methanol (50 ml). Yield 0·36 g (36%).

Diacetatobis(triphenylphosphine)ruthenium(II).— Finely ground $RuCl_2(PPh_3)_3$ (2 g) and $NaCO_2Me,3H_2O$ (2·84 g) in t-butanol (100 ml) were heated under reflux in nitrogen for 1 h then cooled to *ca*. 30°. The orange crystalline *complex* was collected by centrifugation then transferred to a sintered filter with ether, washed well with water, methanol and ether and dried *in vacuo*. Yield 1·1 g (71%).

Electrochemistry.—Polarography and controlled potential electrolysis were carried out in conventional H-cells. All solutions were deoxygenated by nitrogen purified by passage through a chromous solution then two bubblers of the organic solvent. A conventional d.m.e. was used for polarographic studies and all controlled potential electrolyses were performed at a mercury pool. The anode was of platinum foil in a 0·1M aqueous solution of the supporting electrolyte separated from the ruthenium solutions by a 3% agar bridge.

Acetone Solutions.—AnalaR $NaClO_4$ dried at 80° *in vacuo* was used as supporting electrolyte. An aqueous s.c.e. in contact with a 0·1M aqueous $NaClO_4$ solution separated from the acetone solution by an agar bridge was used as reference electrode. Concentrations were in the range 5×10^{-3}—10^{-4}M. The half-wave potentials for reduction of the oxo-species $Ru_3O(CO_2R)_6(PPh_3)_3$ have been listed.[1] The *n*-values were obtained on reduction at −1·3 V. The oxo-bridged complex $Ru_2O(CO_2Me)_4(PPh_3)_2$ showed a half-wave potential of −0·99 V for reduction to Ru^{II} with an *n* value of 1·99 at −1·3 V.

Catalytic Studies.—In Table 3 and 4, the rates of hydrogen uptake were determined at a standard pressure of 40 cm^{-1} from the plot of pressure *vs*. time. The rates quoted in the Tables are at s.t.p.

(a) *Electrolysis of* $Ru_3O(CO_2Me)_6(PPh_3)_3$. The complex (0·0366 g) and PPh_3 (0·0198 g) were dissolved in warm methanol (70 ml) and to the cooled solution was added fluoroboric acid [20 ml of a solution containing 0·825 g aqueous HBF_4 (42%) in 500 ml MeOH] and the volume made up to 100 ml with methanol. This gives a ratio $H^+ : CO_2Me^-$ of one. The solution was reduced at −0·6 V *vs*. internal silver wire electrode for 1 h at 40°. The green-yellow solution was transferred to a 100 ml burette on the hydrogenation apparatus under hydrogen. The solution (50 ml) was then run into the reaction flask which contained methanol (10 ml) plus any desired excess of PPh_3 or acid.

The silver wire reference was preferred as the s.c.e. gave poor reproducibility of the current–time curves. If the electrolysis was continued for *ca*. 2 h the yellow solution was catalytically inactive, presumably due to the same ageing process observed in the action of acids on, for example, $RuH(CO_2Me)(PPh_3)_3$.

(b) $Ru_2O(CO_2Me)_4(PPh_3)_2$. The complex (0·038 g) and PPh_3 (0·0198 g) in methanol (70 ml) plus methanolic fluoroboric acid (20 ml), made up to 100 ml was electrolysed above to give in *ca*. 1 h a yellow solution.

(c) *Action of acids on ruthenium complexes*. The complexes $Ru(CO_2Me)_2(PPh_3)_2$, $RuH(CO_2Me)(PPh_3)_3$, or $Ru(H)_2(PPh_3)_4$ were added from a polythene bucket suspended in the hydrogenation apparatus to the methanol solution containing HBF_4, $p\text{-}MeC_6H_4SO_3H,H_2O$, or CF_3SO_3H, previously degassed by evacuation and flushing with hydrogen.

Tris(triphenylphosphine)ruthenium(II) *Tetrafluoroborate and Trifluoromethylsulphonate*.—The complexes $RuH(CO_2Me)(PPh_3)_3$ or $Ru(H)_2(PPh_3)_4$ in degassed methanol (*ca*. 100 ml) containing an excess of the acid (for fluoroboric 1—2 ml of 42% aqueous acid) were warmed to 65° until the solution was deep red. After filteration under nitrogen, hot water was added to the hot filtrate and the pink solids which were immediately precipitated were collected, washed with water, and vacuum dried. Conductivity measurements on both compounds in nitromethane over a range 10^{-2}—10^{-4}M gave straight line plots of Λ_c against $\sqrt{c}$ which was extrapolated to give Λ_0; a second plot of $\Lambda_0 - \Lambda_c$ *vs*. $\sqrt{c}$ gave a straight line passing through the origin. Slopes of 159 and

181 for the fluoroborate and trifluoromethylsulphonate are somewhat greater than that expected for fully dissociated 1 : 1 electrolytes but are less than that for 1 : 2 electrolytes. This would suggest that some degree of association of the anions is occurring.[14]

Bis(μ-hydroxo-bistriphenylphosphineruthenium) Bistetrafluoroborate.—To degassed methanol (250 ml) containing fluoroboric acid (0·8 ml, 42% aqueous) was added $RuH(CO_2Me)(PPh_3)_3$ (0·25 g) under nitrogen and the mixture was warmed to 65°. The red solution turned pale yellow under nitrogen after *ca.* 1 h and was then reduced to *ca.* 10 ml. Addition of diethyl ether gave the yellow *complex* which was collected, washed with a little methanol and ether, and dried *in vacuo*. Yield 0·15 g, 57%.

Conductivity measurements as above gave a slope of $\Lambda_0 - \Lambda_c$ *vs.* $\sqrt{c}$ of 112·0.

Interaction of the ' Red Cationic Solution ' with LiCl *and* LiOAc.—To a methanolic solution containing the red cation (as obtained above using 42% aq. HBF_4) was added an excess of LiCl. The solution immediately turned deep purple, the electronic absorption and solution i.r. spectra of which were identical to that of a methanol solution of $RuCl_2(PPh_3)_3$.

Addition of an excess of solid lithium acetate to the red cationic solution immediately produced a yellow solution, which on continued heating at 65° precipitated the hydridoacetate $RuH(CO_2Me)(PPh_3)_3$ almost quantitatively.

Interaction of Dichlorotris(triphenylphosphine)ruthenium(II) with $AgBF_4$.—The dichloride $RuCl_2(PPh_3)_3$, (0·5 g) suspended in methanol (250 ml) was treated with a stoicheiometric amount of silver tetrafluoroborate (0·16 g) and the mixture was stirred under nitrogen for 15 min. The precipitated silver chloride was filtered off, and the red-orange solution had identical properties to that obtained by protonation of $RuH(CO_2Me)(PPh_3)_3$ above.

Tetra-μ-acetato-bistriphenylphosphinediruthenium(II).—The chloride, $[Ru_2(CO_2Me)_4]Cl$ (0·3 g) and triphenylphosphine (0·48 g), both finely ground, were stirred in methanol (40 ml) under nitrogen for 20 h. The resulting buff precipitate was washed well with nitromethane, and recrystallised under nitrogen from boiling methanol (250 ml). The complex separated as a yellow powder on storing the solution at −40° for several days. It was collected, washed with methanol and ether and dried *in vacuo* over silica gel. Yield 0·17 g (28%). The complex is almost completely insoluble in all common solvents.

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[14] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.