Cationic Hydrido- and Carboxylato-triphenylphosphine Complexes of Ruthenium †

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Previous work on the protonation of acetatohydridotristriphenylphosphineruthenium(II) by fluoroboric acid has been extended. The initial red species in methanol and acetone is shown to be $[RuH(PPh_3)_3L]^+$ where L = solvent. The methanol solution ages in the absence of an excess of triphenylphosphine to yellow $[RuH(PPh_3)_2(H_2O)_2(MeOH)]^+$ but in the presence of PPh_3 to the π-bonded $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2]^+$. In acetone the end product is $[Ru(CO_2Me)(PPh_3)_3(H_2O)]^+$.

The species are characterised by i.r., ^1H, and ^{31}P n.m.r. spectra and by conversion into other known or easily characterisable complexes by the action of carbon monoxide and acetonitrile.

New complexes described are fluoroborate salts of the ions $[RuH(PPh_3)_2(H_2O)_2(MeOH)]^+$, $[Ru(CO_2Me)(PPh_3)_3(H_2O)]^+$, $[Ru(CO_2Me)(PPh_3)_3CO]^+$, $[Ru(CO_2Me)(PPh_3)_3MeCN]^+$, $[Ru(H_2O)(PPh_3)_3(MeCN)_2]^{2+}$, $[RuH(PPh_3)_2(H_2O)(CO)_2]^+$, and $[RuH(PPh_3)_3(MeCN)_2]Cl$, and the neutral complex $RuH(CO_2C_{17}H_{35})(PPh_3)_3$.

THE action of fluoroboric or other non-complexing strong acids on several ruthenium phosphine complexes, notably $RuH_2(PPh_3)_4$, $RuH(CO_2Me)(PPh_3)_3$, and $Ru(CO_2Me)_2(PPh_3)_2$ in methanol solution gives labile red solutions that under hydrogen become yellow-orange and catalyse the homogeneous hydrogenation of alkenes.[1] The proper characterisation of these species proved difficult owing to their low solubility but it seemed that they were cationic. About the same time, it was shown [2] that interaction of trityl hexafluorophosphate with $RuH_2(PPh_3)_4$ gave a red salt, $[RuH(PPh_3)_4][PF_6]$, which when set aside in dichloromethane slowly gave a yellow salt $[RuH(PPh_3)_3]^+[PF_6]^-$. For the latter ion, Sanders proposed that one of the phenyl rings of triphenylphosphine was π-bonded to the metal. During additional work on the species produced in the protonation reactions now described in detail, this π-complex had been made by interaction of $RuH(CO_2Me)(PPh_3)_3$ with fluoroboric acid in methanol. The π-bonded structure was confirmed by ^{31}P n.m.r. and X-ray diffraction.[3] The π-complex, which is the final product of the interaction of fluoroboric or other non-complexing acids with $RuH(CO_2R)(PPh_3)_3$, $RuH_2(PPh_3)_4$, or $Ru(CO_2R)_2(PPh_3)_2$ in the presence of an excess of triphenylphosphine, and other related arene complexes such as $(\eta^6\text{-}C_6H_5O)RuH(PPh_3)_2$ and $[(\eta^6\text{-}C_6H_6)RuH(PPh_3)_2][BF_4]$ will be described separately.[4]

A further reason for these additional studies on the acid system was that during 1972, it was observed [5] that the addition to the yellow-orange acidic methanol solutions of $RuH(CO_2Me)(PPh_3)_3$ under hydrogen (but not nitrogen or argon) of saturated hydrocarbons caused a relatively fast (5—10 min) change in colour to purple. However, after a cleaning of the reactor vessel with chromic–nitric cleaning mixture, we were unable to reproduce the phenomenon, despite numerous attempts using different samples of the components of the system, addition of traces of other elements, free-radical initiations or inhibitions, action of light *etc.*

Protonation of Hydridoruthenium Complexes.—When $RuH(CO_2Me)(PPh_3)_3$, $RuH_2(PPh_3)_4$, or $RuH_4(PPh_3)_3$ in methanol or acetone under nitrogen are treated with aqueous 42% fluoroboric acid a deep red solution is formed. In the presence of an excess of triphenylphosphine the colour is more intense and persists longer. However, attempts to isolate the red species have not been successful. The solution ages, becoming yellow and from the aged solutions the π-complex $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$ can be recovered essentially quantitatively. The complex can be rapidly prepared by interaction of an excess of fluoroboric acid and $RuH(CO_2Me)(PPh_3)_3$ in hot methanol.

When $RuH(CO_2Me)(PPh_3)_3$ is protonated in methanol in the *absence* of an excess of PPh_3 the initial red colour quickly becomes yellow but instead of the π-bonded complex, a bright yellow crystalline complex can be isolated from the yellow solution. This complex was originally formulated [1] as bis(μ-hydroxo-bistriphenylphosphine)ruthenium tetrafluoroborate but more detailed study now shows that it must be $[RuH(PPh_3)_2(H_2O)_2(MeOH)][BF_4]$. This salt has i.r. bands at 3 640 and 3 560 cm^{-1}, assignable as OH stretches and weak bands at 2 060 and

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† No reprints available.

[1] R. W. Mitchell, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 846.

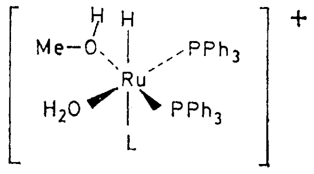
[2] J. R. Sanders, *J.C.S. Dalton*, 1973, 743.

[3] J. C. McConway, A. C. Skapski, L. Phillips, R. J. Young, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1974, 327.

[4] D. Cole-Hamilton, R. J. Young, and G. Wilkinson, to be published.

[5] R. W. Mitchell and A. Spencer, unpublished observations.

2 020 cm^{-1} assignable as Ru–H stretches, together with bands characteristic for PPh_3 and $[BF_4]^-$. The ^1H n.m.r. spectrum shows a broad pattern of aromatic protons due to PPh_3, weak lines due to water and methanol, and a high-field signal centred at τ 18.8 consisting of a doublet of doublets J_{P^1-H} 32 Hz, J_{P^2-H} 38 Hz. The proton noise decoupled ^{31}P spectrum of $[RuH(PPh_3)_2(H_2O)_2(MeOH)][BF_4]$ in $CDCl_3$ shows a typical AB pattern where $\Delta_{P^1P^2} \sim J_{P^1P^2}$ centred at $\delta + 55.77$ p.p.m. relative to free PPh_3 in $CDCl_3$. Selective decoupling of the phenyl protons produces only a splitting into an approximately symmetrical quintet with a mean P–H coupling for the central triplet of 35.3 Hz. The data suggest that the salt has structure (I) where the solvent L may be H_2O or MeOH. As isolated, the salt appears to be over 90% $[RuH(PPh_3)_2(H_2O)_2(MeOH)][BF_4]$ but clearly the water and methanol ratios can vary.



(I) L = H_2O or MeOH

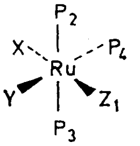
Study of the initial red species is difficult because of its transient nature and the impossibility of obtaining high concentrations in methanol. Three approaches were adopted: (*a*) the use of long chain carboxylates $RuH(CO_2R)(PPh_3)_3$ in order to increase the solubility of the starting material, (*b*) the use of $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$, (*c*) use of acetone instead of methanol as solvent.

The complexes $RuH(CO_2R)(PPh_3)_3$ [R = $C_{17}H_{35}$ and $-CH(Et)C_4H_9$] unlike the acetate were very soluble in methanol and acetone and the hydride resonances were easily observable as symmetrical quartets centred at *ca.* τ 28, with J_{PH} *ca.* 26 Hz. The spectra were similar to those of other carboxylates.[6] The selectively proton noise-decoupled ^{31}P n.m.r. spectrum of $RuH(CO_2Me)(PPh_3)_3$ in $CDCl_3$ (Table 1) shows that the hydridic proton to phosphorus coupling constants to the unique phosphorus nucleus ($J_{14} = 27.8$ Hz) and to the two equivalent phosphorus nuclei ($J_{12} = J_{13} = 25.3$ Hz) differ by 2.5 Hz. These data are in close agreement with recently published[7] ^{31}P n.m.r. spectra of $RuH(CO_2Me)(PPh_3)_3$ in CH_2Cl_2 and tetrahydrofuran. In the same paper a ^1H n.m.r. spectrum of $RuH(CO_2Me)(PPh_3)_3$ in CH_2Cl_2 measured at 220 MHz showed that the high field quartet was not of amplitude 1 : 3 : 3 : 1 and that the central peaks had shoulders identifying the pattern as a doublet of triplets. It is not surprising that in previous measurements at 60 and 100 MHz the expected fine structure was not observed. Indeed the ^{31}P n.m.r. spectrum of $[RuH(MeCN)_2(PPh_3)_3][BF_4]$ (Table 1) shows a difference in J_{PH} of 5.7 Hz for the different phosphorus environments, but the ^1H n.m.r. spectrum measured at 60 MHz is a broadened quartet with line width of *ca.* 5 Hz.

Addition of aqueous fluoroboric acid to the methanol or acetone solutions of $RuH(CO_2R)(PPh_3)_3$ containing an excess of triphenylphosphine produced an immediate intense red colour and the high-field signal disappeared. This might have suggested removal of the hydrogen bound to ruthenium in addition to removal of carboxylate, but there is good reason (see later) to believe that this is not so, and that the non-observance of the high-field line is due to non-rigidity and exchange processes.

TABLE 1

^{31}P n.m.r. spectra in $CDCl_3$. Shifts to high frequency from internal PPh_3 in $CDCl_3$; spectra proton noise decoupled from aromatic protons and selectively decoupled in region of Ru–H high-field proton resonance, measured at 25 °C



X,Y = CO_2Me, MeCN
Z = H, CO, H_2O

Compound	$\delta_2 = \delta_3$	δ_4	$J_{24} = J_{34}$	$J_{12} = J_{13}$	J_{14}
$RuH(CO_2Me)(PPh_3)_3$	+49.53	+85.74	27.4	25.3	27.8
$[Ru(CO)(CO_2Me)(PPh_3)_3][BF_4]$ [a]	+35.08	+45.75	20.5		
$[RuH(MeCN)_2(PPh_3)_3][BF_4]$	+52.58	+63.39	31.8	22.4	16.7
$[Ru(H_2O)(MeCN)_2(PPh_3)_3][BF_4]_2$	+27.32	+40.85	25.6		

[a] In CD_3OD referenced to internal PPh_3.

The red species produced on protonation in acetone is longer lived than in methanol but it too decays to give a yellow-orange solution. However, there are substantial differences in that (*a*) the acetone solutions under hydrogen do *not* act as hydrogenation catalysts for alkenes; (*b*) the π-bonded species $[RuH\{(\eta^6-C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$ is not formed either on ageing or in hot concentrated solutions; (*c*) the product isolated from the aged orange solution is an orange crystalline solid whose analysis is consistent with its formulation as $[Ru(CO_2Me)(H_2O)(PPh_3)_3][BF_4]$. I.r. and n.m.r. spectra indicate that the cation contains a bidentate acetate[6] ($\nu_{OO,asym}$, 1 500 cm^{-1}, $\nu_{OO,sym}$, 1 467 cm^{-1}; Δ_ν 33 cm^{-1}), does not have a Ru–H bond, and contains water (bands at 3 585,

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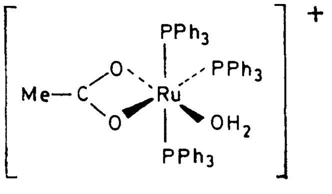
[6] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610; S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, **1973**, 1913.

[7] P. R. Hoffman and K. G. Caulton, *J. Amer. Chem. Soc.*, **1975**, **97**, 4221.

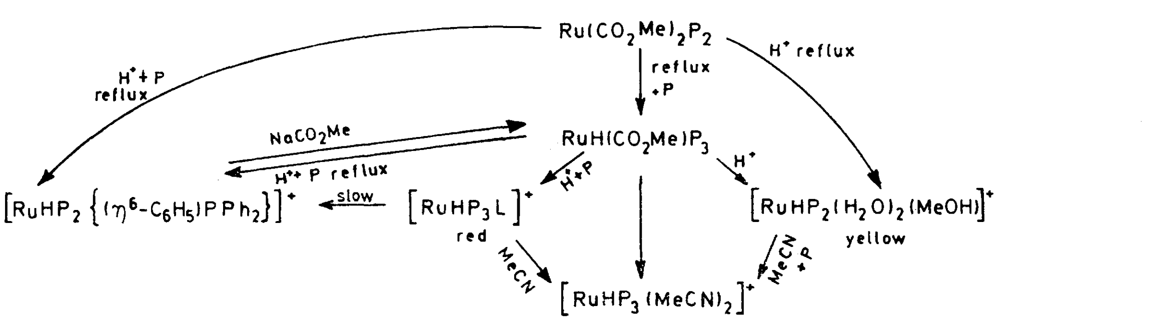
3 305, and 3 195 cm^{-1}) due to free OH and hydrogen bonded stretches. The difference between the methanol and acetone systems can be attributed to the fact that in the former the acetic acid liberated is rapidly converted by acid catalysis into methyl acetate (see Discussion).

The compound has conductivity in nitromethane corresponding to a 1 : 1 electrolyte. The ion thus appears to have structure (II) with meridional phosphines, as in $RuH(CO_2Me)(PPh_3)_3$ [8] from which it can be derived by

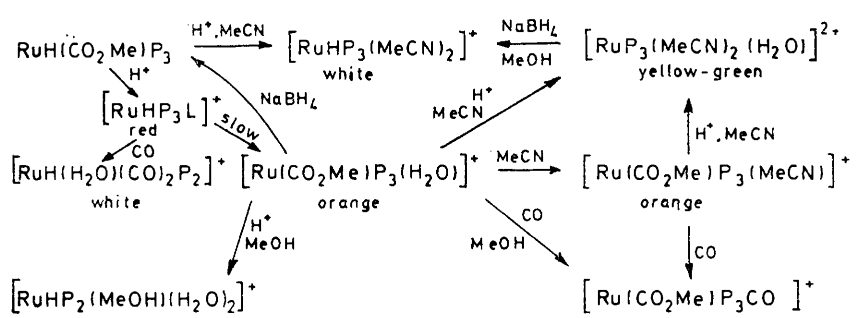


(II)

replacement of H^- by H_2O. The formulation (II) is supported by (*a*) the regeneration of $RuH(CO_2Me)(PPh_3)_3$ by the action of sodium borohydride on the salt in methanol or acetone, (*b*) the ready displacement of the water molecule by acetonitrile or carbon monoxide to give, respectively, the orange crystalline fluoroborates of the ions $[Ru(CO_2Me)(CO)(PPh_3)_3]^+$ and $[Ru(CO_2Me)(MeCN)(PPh_3)_3]^+$. The ^{31}P n.m.r. spectra of the various ions (Table 1) shows that in the octahedral tristriphenylphosphine species the PPh_3 are meridional. However, the ^{31}P n.m.r. spectrum of $[Ru(CO_2Me)(PPh_3)_3(H_2O)][BF_4]$ in $CDCl_3$ is a single sharp line, δ + 54.01 p.p.m. from PPh_3 in $CDCl_3$ suggesting that dissociation of water leads to a non-rigid 5-co-ordinate species in which the phosphorus nuclei are equivalent on the n.m.r. time scale.



SCHEME 1 Action of non-complexing acids on $RuH(CO_2Me)P_3$ in methanol. P = PPh_3, L = solvent. $RuH_4(PPh_3)_3$ and $RuH_2(PPh_3)_4$ behave similarly. Salts isolated as fluoroborates



SCHEME 2 Action of non-complexing acids on $RuH(CO_2Me)(PPh_3)_3$ in acetone. P = PPh_3, L = solvent. Salts isolated as fluoroborates

The action of aqueous HBF_4 on the orange acetonitrile solution of $[Ru(CO_2Me)(MeCN)(PPh_3)_3][BF_4]$ gives a yellow-green solution from which a pale yellow crystalline solid precipitates. This is a salt of the only dication confirmed in the system, namely $[Ru(H_2O)(MeCN)(PPh_3)_3]^{2+}$. The i.r. spectrum now has no acetate bands and the conductivity is in the range for a 2 : 1 electrolyte. Further, action of $NaBH_4$ on this salt in methanol yields the white microcrystalline salt $[RuH(PPh_3)_3(MeCN)_2][BF_4]$, previously obtained [2] by action of MeCN on $[RuH(PPh_3)_4][BF_4]$. The simplest synthesis of $[RuH(PPh_3)_3(MeCN)_2][BF_4]$ is merely to treat suspensions of $RuH(CO_2Me)(PPh_3)_3$ in methanol or acetone containing MeCN with aqueous fluoroboric acid, when the complex rapidly precipitates from the yellow solutions.

The ^1H n.m.r. spectrum of $[RuH(PPh_3)_3(MeCN)_2]^+$ is a symmetrical quartet suggesting meridional PPh_3 groups, and ^{31}P n.m.r. spectra (Table 1) indicate retention of the configuration in the sequence from $RuH(CO_2Me)(PPh_3)_3$[8] to $[RuH(MeCN)_2(PPh_3)_3]^+$.

Finally, action of aqueous fluoroboric acid on the orange methanol solution of $[Ru(CO_2Me)(H_2O)(PPh_3)_3][BF_4]$ under hydrogen gives immediately yellow crystals of $[RuH(MeOH)(H_2O)_2(PPh_3)_2][BF_4]$. The various reactions are summarized in Schemes 1 and 2 in methanol

[8] A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1974, 390.

and acetone respectively. The following additional reactions may be noted:

$$RuCl_2(PPh_3)_3 + 2AgBF_4 \xrightarrow[\text{reflux}]{\text{MeOH} + H_2O} [RuH(PPh_3)_2(H_2O)_2MeOH][BF_4] + 2AgCl$$

$$\begin{tikzcd}RuCl_2(PPh_3)_3 + NaCO_2Me \arrow[r, "\text{butan-2-ol}"] \arrow[dr, "\text{MeOH}"] & Ru(CO_2Me)_2(PPh_3)_2 \\ & RuH(CO_2Me)(PPh_3)_3\end{tikzcd}$$

The interaction of $RuCl_2(PPh_3)_3$ and hydrated sodium acetate in methanol gives $RuH(CO_2Me)(PPh_3)_3$ but in butan-2-ol $Ru(CO_2Me)_2(PPh_3)_2$ is obtained.[1] This ready abstraction of hydride ion from methanol is also shown by the quantitative conversion of $Ru(CO_2Me)_2(PPh_3)_2$ into $RuH(CO_2Me)(PPh_3)_3$ in refluxing methanol containing PPh_3. Alkoxide complexes are probably intermediates and for butan-2-ol an intermediate alkoxide complex could not yield hydride and aldehyde as can happen for an OCH_3 group by hydride transfer from carbon.

Reactions of Chlorohydridotris(triphenylphosphine)ruthenium.—The complexes discussed above can be related to the parent purple-red complex $RuHCl(PPh_3)_3$. On dissolving this compound in MeCN, a pale yellow-green solution is rapidly formed from which the white crystalline salt $[RuH(MeCN)_2(PPh_3)_3]Cl$ is readily isolated. The ^1H n.m.r. spectrum closely resembles that of the fluoroborate, but is solvent and temperature dependent. In methanol or MeCN, there is a high-field quartet, τ 23.6 ($J_{PH} = 22$ Hz). On addition of acetone a red colour appears together with an additional high-field multiplet, somewhat exchange-broadened, due to $RuHCl(PPh_3)_3$.

$$RuHCl(PPh_3)_3 \underset{\text{acetone}}{\overset{\text{MeCN}}{\rightleftharpoons}} [RuH(MeCN)_2(PPh_3)_3]^+ + Cl^-$$

Indeed if $[RuH(MeCN)_2(PPh_3)_3]Cl$ is heated under reflux in acetone $RuHCl(PPh_3)_3$ is formed quantitatively.

Similarly dichloromethane solutions of $[RuH(MeCN)_2(PPh_3)_3]Cl$ are red and have high-field signals in the regions τ 23—24 and 27—28, but on cooling to −10 °C the solution is yellow-green with the quartet at τ 23.5 only.

$$[RuH(MeCN)_2(PPh_3)_3]Cl \underset{-10\ {}^\circ C}{\overset{CH_2Cl_2}{\rightleftharpoons}} [RuHCl(PPh_3)_3] + 2MeCN$$

DISCUSSION

In the studies of homogeneous hydrogenation of alkenes,[1] the catalytically active species were assumed to be cationic but the nature of the red solutions was not properly established, although it was shown that similar catalytic solutions were obtained from $RuH(CO_2Me)(PPh_3)_3$, $RuH_2(PPh_3)_4$, $Ru(CO_2Me)_2(PPh_3)_2$, and in other ways. The present work shows that the presence of the $[RuH(PPh_3)_2]^+$ moiety is a common feature in all products isolated from the methanolic protonated solutions, and that the hydride ligand is retained throughout. The protonation of $RuH(CO_2Me)(PPh_3)_3$ proceeds differently in acetone and in methanol where the acetato-group is lost, evidently as acetic acid which is effectively removed as methyl acetate. G.l.c. study shows that methyl acetate is indeed produced essentially quantitatively:

$$RuH(CO_2Me)(PPh_3)_3 + H^+ \xrightarrow{\text{MeOH}} [RuH(PPh_3)_3L]^+ + MeCO_2H$$

$$MeCO_2H + MeOH \longrightarrow MeCO_2Me + H_2O$$

the result is the formation of the red trisphosphine species. The latter can dissociate so that in the absence of an excess of triphenylphosphine the yellow bisphosphine species is rapidly formed,

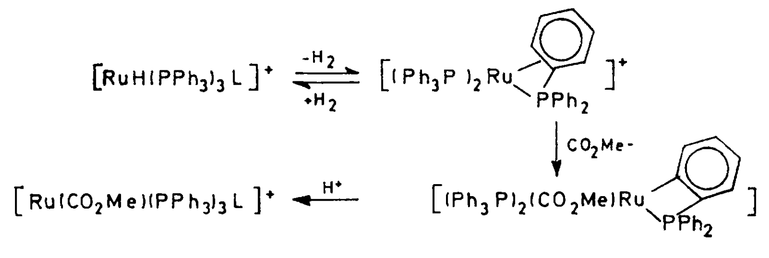
$$[RuH(PPh_3)_3L]^+ \overset{L}{\rightleftharpoons} [RuH(PPh_3)_2L_3]^+ + PPh_3$$

where L may be methanol or water as in the isolated yellow salt $[RuH(PPh_3)_2(H_2O)_2(MeOH)][BF_4]$. That the first stage of protonation yields a cationic trisphosphine species is confirmed by the protonation in methanol in the presence of acetonitrile or by addition of acetonitrile to the red solution produced on protonation of $RuH(CO_2Me)(PPh_3)_3$ in the presence of an excess of PPh_3, since in both cases the product is the tris-species $[RuH(MeCN)_2(PPh_3)_3][BF_4]$. By contrast with the methanol systems, in acetone acetic acid produced by protonation cannot be removed as methyl acetate. However, the initial red species formed in acetone must, as in methanol, be $[RuH(PPh_3)_3L]^+$ since (*a*) action of CO on the red solution gives a hydrido-species, namely $[RuH(CO)_2(PPh_3)_2(H_2O)][BF_4]$, which in turn is quantitatively converted by lithium chloride into the same isomer of $RuHCl(CO)_2(PPh_3)_2$ as that reported by James *et al.*;[9] (*b*) protonation of $RuH(CO_2Me)(PPh_3)_3$ in acetone in the presence of acetonitrile gives $[RuH(MeCN)_2(PPh_3)_3][BF_4]$.

However, the aged, orange-yellow solution in acetone does not contain a hydrido-species but gives only $[Ru(CO_2Me)(PPh_3)_3(H_2O)][BF_4]$. Hence it appears we have the slow overall reaction:

$$[RuH(PPh_3)_3(L)]^+ + MeCO_2H = [Ru(CO_2Me)(PPh_3)_3(L)]^+ + H_2$$

It seems likely that this reaction of the co-ordinatively unsaturated red species proceeds *via* the well known *ortho*-metallation reaction



The *ortho*-metallation reaction is known to occur in these types of ruthenium complexes[10,11] and when carried out under deuterium to lead to D substitution in the phenyl ring of PPh_3.

It may be noted further that when no acetate is present, as when $RuH_2(PPh_3)_4$ is protonated in acetone, the final product is the π-bonded species $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$.

Sanders[3] suggested that the red colour of some similar ruthenium(II) species is a characteristic of 16-electron systems. The tris-species $[RuH(PPh_3)_3(L)]^+$ is such a species. It would also, as a 5-co-ordinate species, be expected to be non-rigid and would be in dissociative equilibrium with the yellow 18-electron octahedral species $[RuH(H_2O)_2(MeOH)(PPh_3)_2]^+$ and $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2]^+$ as well as undergoing hydrogen exchange with the solvent and with *ortho*-hydrogens of the phenyl group. It is not surprising therefore that no high-field proton resonance could be detected for the red species, even in the presence of a large excess of PPh_3 which suppresses the dissociation, intensifying the red colour and prolonging the lifetime of the tris-species. The formation of the final hydrido π-arene complex clearly has to involve the dissociation steps discussed above. If an excess of another potential π-bonding arene ligand, *e.g.* benzene, is present, then the triphenylphosphine may be competitively displaced. Thus protonation of $RuH_2(PPh_3)_4$ in benzene or toluene results in an immediate red colour, which rapidly fades to give a pale yellow solution. The resulting arene complexes $[RuH(\eta^6\text{-arene})(PPh_3)_2][BF_4]$ will be described separately. The involvement of the *ortho*-hydrogen exchange in the system is shown by the preparation of $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$ in $[^2H_4]$methanol. The complex has several i.r. bands not present in the undeuteriated species. There are bands at 632, 782, 851, and 874 cm^{-1} all of which have been previously observed[11] in the products from deuterium gas-exchange studies[10,11] with $RuHCl(PPh_3)_3$, $RuH_2(PPh_3)_4$, $RuH_4(PPh_3)_3$, and $RhH(PPh_3)_4$ and ascribed to out-of-plane deformation vibrations of di- and/or tri-substituted benzene rings. A C–D stretch is also observed at 2 260 cm^{-1} [*cf.* Ru–D stretch in deuterium-substituted $RuHCl(PPh_3)_3$ ref. 10*a*], but the expected Ru–D stretch [at 1 467 cm^{-1} taking $\nu(RuD/\nu RuH) = 1.39$] is obscured by a strong band at 1 454 cm^{-1} which also appears in the spectra of deuteriated $RuH_2(PPh_3)_4$ and $RhH(PPh_3)_4$. It is most likely an aromatic C–C stretching frequency shifted by deuteriation at one carbon atom.

Finally, there is the matter of the nature of the catalytically active orange-yellow solution formed from $[RuH(PPh_3)_3L]^+$ in methanol containing an excess of PPh_3 under hydrogen. It seems most likely that we have:

$$[RuH(PPh_3)_3L] + H_2 \rightleftharpoons [RuH_3(PPh_3)_2L]^+ + PPh_3$$

The resulting trihydrido-complex still has a vacant site for alkene co-ordination allowing transfers then to proceed.

What appears to be this trihydrido-species has been isolated by using concentrated solutions containing an excess of PPh_3 in methanol and stirring in hydrogen extremely rapidly *via* a high-speed stirrer to increase the H_2 concentration. Addition of hexane gives an almost white salt that has broad and quite strong Ru–H stretches, *ca.* 2 000 cm^{-1}, PPh_3 and BF_4^- bands, and is probably $[RuH_3(PPh_3)_3][BF_4]$. In methanol, acetone, or dichloromethane, the salt dissolves both readily and immediately giving hydrogen and a red solution. The red solutions in methanol were clearly identical to those produced on direct protonation and they age to $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$.

EXPERIMENTAL

Apparatus.—^1H n.m.r. spectra were recorded on Perkin-Elmer R12A (60 MHz) and Varian HA100 (100 MHz) spectrometers. ^{31}P N.m.r. spectra were recorded at 40.505 MHz using a Varian XL100-12 spectrometer operating in Fourier transform mode. Perkin-Elmer model 257, 457, and 325 spectrometers were used to record i.r. spectra. G.l.c. measurements were made with a Perkin-Elmer F33 chromatograph with flame ionisation detector; peak areas were obtained with an Infotronics CRS-208 automatic digital integrator. Conductivities were measured for $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$ using recommended procedures[12] and using a Mullard conductivity-bridge type E7566/3 with a matching conductivity cell with nitromethane as solvent at 23 °C. This compound was then used as a standard.

Microanalyses (Table 2) were by the microanalytical laboratories of Imperial College, and Bernhardt, Mülheim, and Pascher, Bonn.

Materials and Procedure.—All preparations and other operations were normally carried out under oxygen-free argon, nitrogen, or hydrogen and solvents were degassed by purging for 5—10 min. Transfers were made by conventional techniques using thin steel tubing, syringe, serum cap, *etc.* The complex, $RuCl_2(PPh_3)_3$, was prepared[13] from Johnson, Matthey 'ruthenium trichloride trihydrate'. $RuH(CO_2Me)(PPh_3)_3$ and $Ru(CO_2Me)_2(PPh_3)_2$ were prepared from $RuCl_2(PPh_3)_3$ as previously.[1] $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$ were prepared from $RuCl_2(PPh_3)_3$ following the general procedure described by Harris *et al.*;[11b] however, good crystalline samples of $RuH_2(PPh_3)_4$ were obtained if after addition of the $NaBH_4$ the solution was heated slowly to reflux for *ca.* 10 min and then allowed to cool $RuHCl(PPh_3)_3$ was prepared as the benzene solvate from

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[9] B. R. James, L. D. Markham, B. C. Hui, and G. R. Rempel, *J.C.S. Dalton*, 1973, 2247.

[10] (*a*) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143; (*b*) G. W. Parshall, W. M. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **91**, 4990; G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139; R. A. Schunn, *Inorg. Chem.*, 1970, **9**, 2567; G. Strathdee and R. Given, *Canad. J. Chem.*, 1975, **53**, 106, 1402.

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[12] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81; R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

[13] P. S. Hallman, T. A. Stephenson, and G. Wilkinson, *Inorg. Synth.*, 1970, **12**, 238.

$RuCl_2(PPh_3)_3$ as previously [10a] or as the toluene solvate by the method previously applied to $RuCl_2(PPh_3)_4$.[14]

Hydrido(η^6-phenyldiphenylphosphine)bis(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—Suspensions of $RuH(CO_2Me)(PPh_3)_3$, $RuH_2(PPh_3)_4$, or $Ru(CO_2Me)_2(PPh_3)_2$ in methanol under Ar, N_2, or H_2 all react with large excesses of HBF_4(aq.) and PPh_3 to yield $[RuH\{(\eta^6\text{-}C_6H_5)PPh_2\}(PPh_3)_2][BF_4]$.

$RuH(CO_2Me)(PPh_3)_3$ (0.5 g, 0.53 mmol) and PPh_3 (0.5 g, 1.91 mmol) were added to 42% (aq.) HBF_4 (5 cm^3) in methanol (50 cm^3), which had been purged with hydrogen for *ca.* 5 min. The suspension was heated to reflux with rapid stirring then allowed to cool under H_2. The precipitated pale yellow crystalline *complex* was collected under N_2, washed with degassed methanol and ether, and dried *in vacuo*. The complex as isolated contains one methanol of solvation (0.35—0.40 g, 66—75%); Λ_M (10^{-3}M) = 80 Ω^{-1} cm^2 mol^{-1}.

TABLE 2

Analytical data for the ruthenium complexes.[a] Found (calcd.) %

	C	H	P	N	X
$[RuH\{(\eta^6\text{-}C_5H_5)PPh_2\}(PPh_3)_2][BF_4]\cdot MeOH$ [b]	65.7 (65.5)	5.1 (5.0)			
$[RuH(H_2O)_2(MeOH)(PPh_3)_2][BF_4]$	56.3 (56.8)	4.8 (5.0)	7.2 (7.9)		
$[Ru(CO_2Me)(H_2O)(PPh_3)_3][BF_4]$	63.6 (63.9)	4.9 (4.8)	8.7 (8.8)		6.4 (7.3)F
$[Ru(CO_2Me)(CO)(PPh_3)_3][BF_4]$	64.5 (64.5)	4.7 (4.5)	8.9 (8.8)		
$[Ru(CO_2Me)(MeCN)(PPh_3)_3][BF_4]$	63.9 (64.8)	5.1 (4.8)	8.6 (8.7)	1.6 (1.3)	
$RuH(CO_2C_{17}H_{35})(PPh_3)_3$	73.5 (73.8)	7.0 (6.9)	7.3 (7.9)		
$[Ru(H_2O)(MeCN)_2(PPh_3)_3][BF_4]_2$	58.3 (59.8)	4.5 (4.6)	7.6 (8.0)	2.8 (2.4)	13.5 (13.2)F
$[RuH(MeCN)_2(PPh_3)_3][BF_4]$	65.5 (65.8)	5.0 (4.9)	8.4 (8.8)	2.4 (2.6)	
$[RuH(MeCN)_2(PPh_3)_3]Cl$	68.6 (69.2)	5.5 (5.2)	8.6 (9.2)	3.1 (2.8)	3.8 (3.5)Cl
$[RuH(H_2O)(CO)_2(PPh_3)_2][BF_4]$	56.8 (57.9)	4.3 (4.2)	7.5 (7.9)		
$RuHCl(CO)_2(PPh_3)_2$	62.8 (63.6)	4.6 (4.3)	8.1 (8.6)		5.2 (4.9)Cl

[a] Carbon analyses of ruthenium compounds of these types tend to be slightly low, probably due to combustion difficulties, *cf.* ref. 9. [b] *X*-Ray diffraction studies [3] show that this complex appears to contain a loosely held MeOH molecule in the crystal lattice.

Diaquahydridomethanolbis(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—$RuH(CO_2Me)(PPh_3)_3$ (0.5 g, 0.53 mmol) was added to 42% (aq.) HBF_4 (5 cm^3) in methanol (15 cm^3) degassed with argon. The suspension was heated to reflux with rapid stirring then allowed to cool under argon. The precipitated bright yellow microcrystalline *complex* was collected, washed with degassed methanol and ether, and dried *in vacuo* (0.31—0.35 g, 74—83%). The i.r. spectrum (Nujol mull) includes absorptions at 3 640, 3 560 [ν(OH)], 2 060 and 2 020 cm^{-1} [ν(RuH)]. The ^1H n.m.r. spectrum (at 35 °C in $CDCl_3$) includes a hydride signal consisting of a doublet of doublets τ 18.8 (J_{HP_1} = 32 Hz, J_{HP_2} = 38 Hz).

Acetatoaquatris(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—$RuH(CO_2Me)(PPh_3)_3$ (0.5 g, 0.53 mmol) was added to 42% (aq.) HBF_4 (5 cm^3) in acetone (15 cm^3) degassed with argon. The suspension was heated to reflux, with rapid stirring, giving initially a deep red solution, which rapidly became lighter in colour. The resulting orange solution was reduced *in vacuo* to half its volume when the orange microcrystalline *complex* was precipitated. This was collected under argon, washed with degassed acetone and ether, and dried *in vacuo* (0.5 g, *ca.* 90%). The i.r. spectrum (Nujol mull, and KBr disc) includes absorptions at 3 585, 3 305, 3 195 [ν(OH)], and 1 498, 1 467 cm^{-1} [ν_{asym}(OCO) and ν_{sym}(OCO)]; Λ_M (10^{-3}M) = 78 Ω^{-1} cm^2 mol^{-1}.

Acetatocarbonyltris(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—This *complex* is precipitated as a yellow crystalline solid in high yield when CO is passed through a saturated methanolic solution of $[Ru(CO_2Me)(H_2O)(PPh_3)_3][BF_4]$ and the solution reduced to half its original volume (>85%). The i.r. spectrum (Nujol and hexachlorobutadiene mulls) includes an intense carbonyl absorption at 1 963 cm^{-1} and bands at 1 500 [ν_{asym}(OCO)] and 1 467 cm^{-1} [ν_{sym}(OCO)].

Acetatoacetonitriletris(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—The *complex* is obtained as an orange-yellow crystalline solid when $[Ru(CO_2Me)(H_2O)(PPh_3)_3][BF_4]$ is dissolved in the minimum amount of warm MeCN and the solution reduced to half its original volume and cooled to 0 °C (>85%). The i.r. spectrum (Nujol and hexachlorobutadiene mulls) includes absorptions at 2 285 and 2 250 [ν(CN)], 1 500 [ν_{asym}(OCO)], and 1 468 cm^{-1} [ν_{sym}(OCO)].

Bisacetonitrileaquatris(triphenylphosphine)ruthenium(II) *Bis(tetrafluoroborate).*— $[Ru(CO_2Me)(H_2O)(PPh_3)_3][BF_4]$ (0.25 g, 0.24 mmol) was dissolved in acetonitrile (15 cm^3) and 42% (aq.) HBF_4 (5 cm^3) was added; the orange solution immediately became pale lime-green and the pale yellow crystalline *complex* was precipitated. This was collected in air, washed (×2) with ether, and air dried (0.22 g, 80%). The i.r. spectrum (Nujol mull) includes bands at 3 625 and 3 557 [ν(OH)], 2 320 and 2 290 cm^{-1} [ν(CN)]; Λ_M (10^{-3}M) = 142 Ω^{-1} cm^2 mol^{-1}.

Bisacetonitrilehydridotris(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—*Method A.* $RuH(CO_2Me)(PPh_3)_3$ (0.5 g, 0.53 mmol) was added to solutions of acetonitrile (5 cm^3) in acetone (or methanol) (25 cm^3). The yellow suspension was vigorously stirred and heated to reflux. Addition of 42% (aq.) HBF_4 (2 cm^3) gave a pale yellow solution, from which on reduction to about half the volume the white microcrystalline *complex* was precipitated. The product was collected, washed with degassed ether (×2), and dried *in vacuo*; yield 0.30—0.34 g (52—59%).

Method B. $[Ru(H_2O)(MeCN)_2(PPh_3)_3]][BF_4]_2$ (0.5 g, 0.43 mmol) was dissolved in acetone (15 cm^3) purged with argon. Addition of $NaBH_4$ (0.1 g, 2.63 mmol) to the lime-green solution caused an immediate change to yellow. The solution was reduced to half volume and methanol (10 cm^3) was added to precipitate the white microcrystalline *complex*; this was collected under argon, washed (×2) with ether, and dried *in vacuo* (0.21 g, 46%). The i.r. spectrum (Nujol mull) includes a very strong absorption assigned to the Ru–H stretching mode at 1 960 cm^{-1} together with weak bands assigned to co-ordinated acetonitrile at 2 295 and 2 280 cm^{-1} [ν(CN)]. The ^1H n.m.r. spectrum in dichloromethane–

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[14] R. A. Schunn and E. R. Wonchoba, *Inorg. Synth.*, **1972**, **13**, 131.

acetonitrile includes a symmetrical quartet hydride signal at τ 23.5 (J_{HP} *ca.* 20 Hz).

Bisacetonitrilehydridotris(triphenylphosphine)ruthenium(II) *Chloride.*—$RuHCl(PPh_3)_3(C_7H_8)$ (0.5 g, 0.49 mmol) was dissolved in acetonitrile (15 cm^3). The lime-green solution was reduced to half volume to precipitate white microcrystals of the *complex* which were collected, washed with degassed ether (×2), and dried *in vacuo* (0.25 g, 52%). The i.r. spectrum was similar to that of the analogous tetrafluoroborate. The ^{1}H n.m.r. spectrum in methanol–acetonitrile includes a slightly exchange broadened (35 °C) symmetrical quartet hydride signal at τ 23.6 (J_{HP} 22 Hz).

Hydridostearatotris(triphenylphosphine)ruthenium(II).—$RuCl_2(PPh_3)_3$ (2 g, 2.09 mmol) and sodium stearate (5 g, 16.3 mmol) were added to methanol (250 cm^3) and the mixture was heated to reflux. The orange-yellow crystals of the *complex* which rapidly precipitated on cooling were collected and dried *in vacuo* (50%). The complex is moderately soluble in light petroleum (60—80 °C) and a petroleum wash resulted in some loss of yield. The i.r. spectrum (Nujol mull) includes a strong Ru–H stretching mode at 1 965 cm^{-1}. The ^{1}H n.m.r. spectrum in acetone includes a symmetrical quartet hydride signal τ 28.25 (J_{HP} 27 Hz).

Aquadicarbonylhydridobis(triphenylphosphine)ruthenium(II) *Tetrafluoroborate.*—$RuH(CO_2Me)(PPh_3)_3$ (0.5 g, 0.53 mmol) was added to 42% (aq.) HBF_4 (5 cm^3) in acetone (15 cm^3) under hydrogen. The suspension was heated to reflux, and carbon monoxide passed through the resulting red solution, which immediately became pale yellow. The solution was reduced to half volume, degassed ether (10 cm^3) was added, and the solution was stored at −20 °C for 24 h. The white crystalline *complex* was collected, washed with ether (×2), and dried *in vacuo* (0.14 g, 36%). The i.r. spectrum (Nujol mull) includes a broad hydroxyl stretching band centred at 3 420 cm^{-1} together with carbonyl bands at 2 070 and 1 990 cm^{-1}, the lower being the broader and the stronger. The ^{1}H n.m.r. in [$^2H_6$]acetone at 35 °C contains two distinct triplet hydride signals of approximate relative intensity 1 : 4 at τ 14.15 (J_{PH} 19 Hz) and τ 14.68 (J_{PH} 18 Hz), suggesting that the complex is a mixture of isomers.

Dicarbonylchlorohydridobis(triphenylphosphine)ruthenium(II).—$[RuH(H_2O)(CO)_2(PPh_3)_2][BF_4]$ (*ca.* 0.2 g) was dissolved in methanol (10 cm^3), LiCl (0.05 g) was added, and the colourless solution was heated under reflux under N_2 for a few minutes. The white crystalline *complex* precipitated on cooling, was collected, washed with degassed methanol and ether, and dried *in vacuo* (*ca.* 65%). The i.r. and ^{1}H n.m.r. spectra were in good agreement with those previously recorded by James *et al.*[9]

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