Fluorophosphine Complexes of Ruthenium and Osmium. Part 2.[1] Reactions of Dihydrido-complexes with Protic Species †

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The complexes $[MH_2(PF_3)_2(PPh_3)_2]$ (M = Ru or Os) react with HCl gas to give $[MCl_2(PF_3)_2(PPh_3)_2]$ or the intermediate $[MCl(H)(PF_3)_2(PPh_3)_2]$ (only for M = Os) depending on the conditions. The complex $[RuH_2(PF_3)_2(PPh_3)_2]$ and HBr gives $[RuBr_2(PF_3)_2(PPh_3)_2]$; $[RuCl(H)(PF_3)_2(PPh_3)_2]$ is obtained by treatment of $[RuH(PF_3)_2(PPh_3)_2][BF_4]$ {formed by HBF_4 addition to $[RuH_2(PF_3)_2(PPh_3)_2]$} with $[NEt_4]Cl$ or by the reaction between $[Ru(PF_3)_3(PPh_3)_2]$ and Bu^tCl. The complexes $[RuH_2(L)(PPh_3)_3]$ [L = PF_3 or $PF_2(NMe_2)$] react with trifluoroacetic acid to form $[Ru(O_2CCF_3)_2L(PPh_3)_2]$, while $[RuH_2L_2(PPh_3)_2]$ give $[RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2]$ and $[Ru(O_2CCF_3)_2\{PF_2(NMe_2)\}_2(PPh_3)]$ respectively; $[RuH_2(PF_3)_2(PPh_3)_2]$ or $[RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2]$ react with CF_3CO_2H under more vigorous conditions to yield a complex containing the $PF_2(O_2CCF_3)$ ligand. Fluorine-19 and ^{31}P n.m.r. spectra of all these complexes enable their stereochemistry to be established, and in the trifluoroacetato-derivatives provide evidence for an intramolecular exchange process between uni- and bi-dentate trifluoroacetate ligands.

TREATMENT of transition-metal hydrides with protic species has provided ready syntheses of nitrato-, halogeno-,[2] and carboxylato-complexes.[3] Robinson and his co-workers[3,4] have reported triphenylphosphine and carbonyl-containing ruthenium(II) and osmium(II) complexes containing both uni- and bi-dentate carboxylate ligands which undergo rapid exchange of co-ordination sites. Wilkinson *et al.*[5] have prepared a series of complexes of the type $[RuH(O_2CR)(PPh_3)_3]$ (R = CF_3 or Me) by treatment of $[RuCl_2(PPh_3)_3]$ with the sodium salt of the appropriate carboxylic acid. Here we report reactions of ruthenium and osmium dihydrido-complexes containing fluorophosphine ligands with hydrogen chloride, tetrafluoroboric acid, and trifluoroacetic acid, and synthetic routes to chlorohydrido-complexes of the type $[MCl(H)(PF_3)_2(PPh_3)_2]$ (M = Ru or Os) and $[OsCl(H)(PF_3)(PPh_3)_3]$ which are related to the well known olefin-hydrogenation catalyst $[RuCl(H)(PPh_3)_3]$.

RESULTS AND DISCUSSION

Treatment of *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$[1] with dry hydrogen chloride gas affords *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ which has been obtained by other methods discussed elsewhere.[6] The rather unstable $[RuBr_2(PF_3)_2(PPh_3)_2]$ is readily obtained in a similar manner using gaseous hydrogen bromide. No evidence was found for the formation of the intermediate complex $[RuCl(H)(PF_3)_2(PPh_3)_2]$ (1), although this can be made by an indirect route (see below). Treatment of $[RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2]$[1] with HCl gas affords a low yield of $[RuCl_2(PF_3)_2(PPh_3)_2]$, suggesting that P–N bond cleavage is occurring and the resulting unstable chlorodifluorophosphine complex subsequently undergoes disproportionation, *e.g.* as in equation (1). The other product from this reaction was not identified. The complex $[OsH_2(PF_3)_2(PPh_3)_2]$ reacts with slightly more than a 2 : 1 mol ratio of hydrogen chloride at 75 °C to give a high yield of the colourless crystalline complex $[OsCl(H)(PF_3)_2(PPh_3)_2]$ (2), and with a large excess to yield $[OsCl_2(PF_3)_2(PPh_3)_2]$.[6]

$$[RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2] \xrightarrow[-H_2]{HCl} [RuCl_2(PF_3)(PClF_2)(PPh_3)_2] \longrightarrow [RuCl_2(PF_3)_2(PPh_3)_2] \quad (1)$$

Tetrafluoroboric acid reacts rapidly with $[RuH_2(PF_3)_2(PPh_3)_2]$ at room temperature with evolution of dihydrogen and formation of the colourless crystalline

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† No reprints available.

[1] Part 1, R. A. Head and J. F. Nixon, preceding paper.

[2] M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741; J. R. Sanders, *J.C.S. Dalton*, 1973, 743.

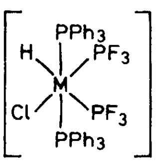
[3] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912.

[4] A. Dobson, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1975, 370.

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

[6] R. A. Head and J. F. Nixon, following paper.

ionic complex $[RuH(PF_3)_2(PPh_3)_2][BF_4]$ (3). Treatment of (3) with tetraethylammonium chloride readily affords



(1) M = Ru
(2) M = Os

complex (1), together with the new complex $[Ru(PF_3)_3(PPh_3)_2]$. The formation of the ruthenium(0) complex is unexpected, although a similar reduction has been reported by Knox and Stone,[7] who obtained $[Ru(CO)_3(PPh_3)_2]$ and $[Ru(SiMe_3)_2(CO)_2(PPh_3)_2]$ from the reaction of $[Ru_2(SiMe_3)_2(CO)_8]$ with PPh_3.

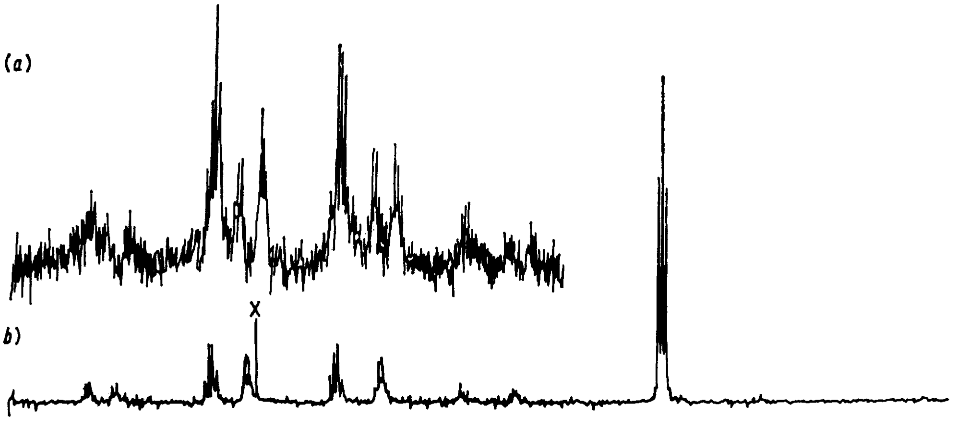


FIGURE 1 Phosphorus-31 n.m.r. spectrum of *cis*-$[RuCl(H)(PF_3)_2(PPh_3)_2]$: (*a*) proton undecoupled, (*b*) decoupled; X = $P(OMe)_3$, width 10 000 Hz

Treatment of $[Ru(PF_3)_3(PPh_3)_2]$ with HCl at 100 °C gives $[RuCl_2(PF_3)_2(PPh_3)_2]$; however, using t-butyl chloride leads to the formation of (1) in good yield. The mechanism of the latter reaction probably involves an initial oxidative addition followed by β-hydrogen elimination,[8] although the expected 2-methylpropene was not isolated.

TABLE 1

Phosphorus-31 n.m.r. chemical-shift and coupling-constant data [a]

Complex	δ(PF) [b]	δ(PPh$_3$) [b]	^2J(PMP′) [c]	^2J(F*PMP*F) [c]
(1) *cis*-$[RuCl(H)(PF_3)_2(PPh_3)_2]$	14.0 *trans* H) 4.2 (*trans* Cl)	101.2	36.0 36.6	41.0
(2) *cis*-$[OsCl(H)(PF_3)_2(PPh_3)_2]$	43.3 (*trans* H) 51.1 (*trans* Cl)	137.9	38.5 61.1	
(3) $[RuH(PF_3)_2(PPh_3)_2][BF_4]$	10.3 (*trans* H) 0.2	95.9	30.5 48.8	34.2
(4) $[Ru(O_2CCF_3)_2(PF_3)(PPh_3)_2]$	8.9	97.8	70.8	
(5) $[Ru(O_2CCF_3)_2\{PF_2(NMe_2)\}(PPh_3)_2]$	−7.8 −27.7 [d]	91.4 93.7	69.4 63.5	
(6) *cis*-$[RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2]$ [e]	13.9 (*trans* H) 0.0 (*trans* CF_3CO_2)	95.6	30.5 46.4	31.7
(7) $[Ru(O_2CCF_3)_2\{PF_2(NMe_2)_2\}(PPh_3)]$	13.4	102.5	46.5	
(8) $[Ru(O_2CCF_3)\{PF_2(O_2CCF_3)\}(PF_3)(PPh_3)_2]^+$	4.7 (PF_3) 38.3 [$PF_2(O_2CCF_3)$]	106.0	46.4 39.1	112.3

[a] In CH_2Cl_2. [b] P.p.m. upfield from $P(OMe)_3$. [c] In Hz. [d] Second isomer of uncertain structure. [e] $^2J(HRuPF_{trans})$ 222.2, $^2J(HRuPF_{cis})$ 29.3 Hz.

By analogy with structures established earlier[1] for $[MH_2(PF_3)_2(PPh_3)_2]$ (M = Ru or Os), complexes (1) and (2) are expected to have the following structure and this is confirmed by n.m.r. studies. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (1) (Figure 1) shows a high-field triplet pattern arising from coincidental overlap of two doublets and which is assigned to the resonance of two equivalent PPh_3 ligands coupled to two non-equivalent PF_3 ligands [^2J(PRuP′)] (Table 1). The resonances of the two PF_3 ligands appear at low field as quartets [^1J(PF)] of doublets [^2J(PRuP′)] of triplets [^2J(PRuP′)]. Further fine structure arises presumably from coupling to the fluorine nuclei of the adjacent ligand. The assignment of the resonance of the PF_3 *trans* to hydride is established from the proton-decoupled ^{31}P n.m.r. spectrum (also shown in Figure 1), which shows that the PF_3 resonance at highest field exhibits the expected further large doublet splitting. The ^{19}F n.m.r. spectrum of (1) (Figure 2) confirms the above stereochemical assignment, exhibiting two widely spaced doublets [^1J(PF)] (Table 2). The resonance of the PF_3 *trans* to hydride occurs at highest field and is split further into a doublet, while the lower-field resonance occurs as a doublet of doublets arising from coupling to the *cis*-hydride [^3J(FPRuH)] and to the phosphorus of the other PF_3 ligand [^3J(FPRuP)]. The ^1H n.m.r. spectrum of (1) gives the expected number of lines (Table 3).

The cation in the tetrafluoroborate (3) could be either

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[7] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559.

[8] R. J. Cross, *Inorg. Chim. Acta*, 1969, **3**, 75.

TABLE 2

Fluorine-19 n.m.r. chemical-shift and coupling-constant data [a]

Complex	ϕ(F) [b]	ϕ(CF_3) [b]	^1J(PF) [c]	^3J(*F*PM*H*) [c]	^3J(*F*PM*P*F) [c]
(1)	13.2 (*trans* H) 4.2		1 350 1 244	36.0 4.9	*ca.* 1.0 5.0
(2)	7.4 (*trans* H) 10.3		1 346 1 254	37.0 15.9	3.5 10.9
(3)	13.3 (*trans* H) 1.1		1 281 1 211	28.0 3.0	*ca.* 1.0 2.0
(4)	8.6	75.5	1 283		
(5)	7.8 13.8 [d]	77.0 76.5	1 177 1 096		
(6)	13.4 (*trans* H) 1.8 (*trans* CF_3CO_2)	74.7 76.3	1 351 1 244	36.0 10.5	
(7)	−1.7	76.5	1 189 [e]		
(8)	5.9 (PF_3) −3.9 [$PF_2(O_2CCF_3)$]	78.1 (CF_3CO_2) 77.2 [f] [$PF_2(O_2CCF_3)$]	1 276 1 206		

[a] $CDCl_3$. [b] P.p.m. upfield of CCl_3F. [c] In Hz. [d] Second isomer of uncertain structure. [e] ^1J(PF) + ^3J(*F*PRuP′). ϕ(F) of free ligand 76.5 p.p.m.

five- or six-co-ordinate in solution, depending on the involvement of a solvent molecule. The ^{31}P and ^{19}F n.m.r. spectra of (3) are very similar in appearance to those of the six-co-ordinate complexes (1) and (2), suggesting that there is solvent co-ordination in solution. This is supported by the fact that solutions of (3) are colourless, while five-co-ordinate d^6 complexes are generally highly coloured.[9] In the solid state the tetrafluoroborate ion may be weakly bonded to the metal atom as in the related [RuCl(NH=NPh)(CO)$(PPh_3)_2(BF_4)$] complex.[10,11]

TABLE 3

High-field ^1H n.m.r. chemical-shift and coupling-constant data [a]

Complex	τ	$^2J(HMP_{trans})$ [b]	$^2J(HMP_{cis})$ [b]
(1)	14.5	222.0	34.0
(2)	16.7	178.0	26.0
(3)	15.0	214.0	34.2

[a] In $CDCl_3$. [b] In Hz.

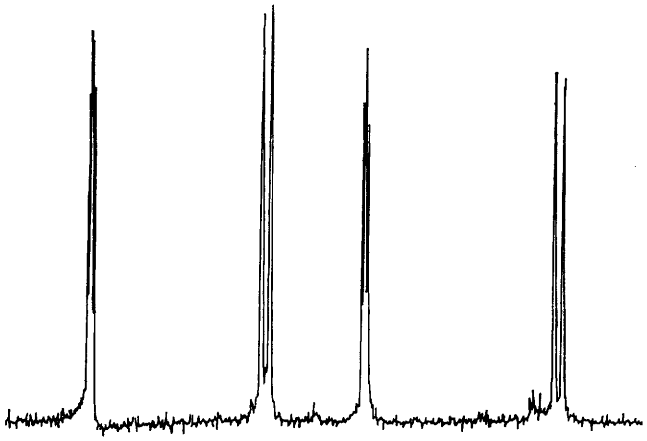
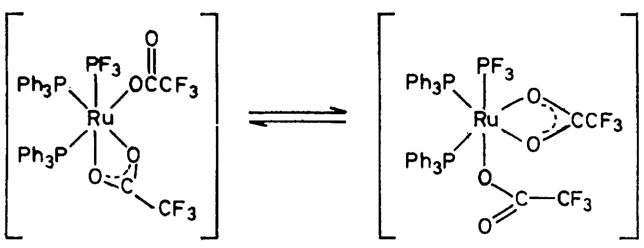


FIGURE 2 Fluorine-19 n.m.r. spectrum of *cis*-[RuCl(H)$(PF_3)_2(PPh_3)_2$]. Width 5 000 Hz

The complexes [$RuH_2L(PPh_3)_3$] [L = PF_3 or $PF_2(NMe_2)$] react readily with trifluoroacetic acid at room temperature with H_2 evolution to give good yields of the yellow crystalline [$Ru(O_2CCF_3)_2(PF_3)(PPh_3)_2$] (4) and [$Ru(O_2CCF_3)_2\{PF_2(NMe_2)\}(PPh_3)_2$] (5), while [$RuH_2L_2(PPh_3)_2$] afford colourless [$Ru(O_2CCF_3)H(PF_3)_2(PPh_3)_2$] (6) and yellow [$Ru(O_2CCF_3)_2\{PF_2(NMe_2)\}_2(PPh_3)$] (7), respectively. The formation of (7) rather than [$Ru(O_2CCF_3)_2\{PF_2(NMe_2)\}_2(PPh_3)_2$], which would be analogous to the related dicarbonyl complexes [$M(O_2CR)_2(CO)_2(PPh_3)_2$] (M = Ru or Os; R = CF_3, H, or alkyl),[3,4,12–14] presumably results from the larger stereochemical requirements of the $PF_2(NMe_2)$ ligand, and as discussed elsewhere [6] [$RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2$] readily undergoes triphenylphosphine dissociation in solution.

The stereochemistry of (4) is readily established by n.m.r. spectroscopic data. The ^{19}F n.m.r. spectrum of (4) at −33 °C (Figure 3) exhibits a low-field doublet [^1J(PF)] for the PF_3 ligand and two pairs of lines at high field assigned to trifluoroacetato-groups. As the temperature is increased the PF_3 resonance remains unchanged, but the trifluoroacetato-resonances broaden and then coalesce to a single line at room temperature. This behaviour is indicative of the presence of two isomers (4a) and (4b) containing mutually *cis*-PPh_3 ligands in which there is a dynamic equilibrium between the uni- and bi-dentate trifluoroacetate ligands. The most intense pairs of lines are assigned to isomer (4a), while the larger chemical-shift difference of the weaker



(4a) (4b)

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

[10] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1973, 2713.

[11] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Chem. Comm.*, 1973, 176.

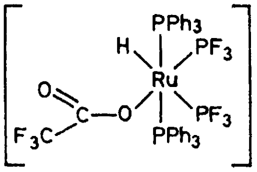
[12] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1969, 1889.

[13] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1969, 2645.

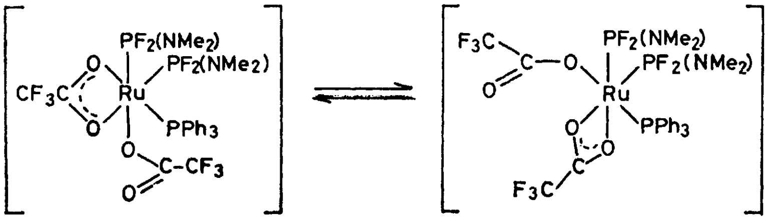
[14] B. F. G. Johnson, R. D. Johnston, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1971, 689.

pair of lines assigned to (4b) probably results from the presence of PF_3 *trans* to the unidentate trifluoroacetate ligand. The related carbonyl complex has been assigned a similar structure on the basis of its reaction with alcohols.[4]

The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (4) at room temperature confirms the above assignments, exhibiting a low-field quartet [^1J(PF)] of triplets [^2J(PRuP′)] for the PF_3 ligand and a high-field doublet for the PPh_3 groups. The magnitude of ^2J(PRuP′) (Table 1) is characteristic of phosphine ligands occupying mutually *cis* positions. The similarity of the ^{19}F and ^{31}P n.m.r. spectra of (7) suggests that it has a similar structure to (4), while n.m.r. studies also indicate a rapid intramolecular exchange between uni- and bi-dentate trifluoroacetato-groups in (7a) and (7b), *viz.*:



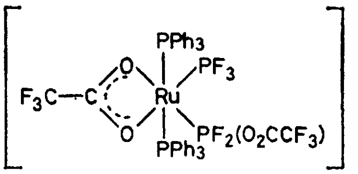
(6)



(7a) (7b)

The ^{31}P-$\{^1H\}$ n.m.r. spectrum [Figure 4(*a*)] of the monohydrido-complex (6) exhibits a high-field doublet of doublets arising from two chemically equivalent PPh_3 ligands which are coupled to two non-equivalent PF_3 groups [^2J(PRuP′)], and two low-field quartets [^1J(PF)] of doublets of triplets for the PF_3 resonances resulting from coupling with the adjacent PF_3 and two equivalent PPh_3 ligands (see Table 1). These data can only be interpreted in terms of the structure shown, which is similar to that determined for the related dihydrido- and dichloro-complexes. In the proton-undecoupled ^{31}P n.m.r. spectrum of (6) [Figure 4(*b*)] the PF_3 resonance at highest field exhibits a further widely spaced doublet pattern and can be assigned as being *trans* to the hydride ligand. Fluorine-19 n.m.r. studies (Table 2) confirm the stereochemistry of (6), but surprisingly the trifluoroacetato-group gives rise to two resonances of similar intensity which remain virtually unchanged over the range 25—55 °C.

An unusual reaction occurs when $[RuH_2(PF_3)_2(PPh_3)_2]$ or (6) is heated under reflux with trifluoroacetic acid in benzene solution. The ^{31}P-$\{^1H\}$ n.m.r. spectrum (Figure 5) of the product (8) (Table 1) exhibits a widely spaced quartet [^1J(PF)] pattern for a PF_3 group and a 1 : 2 : 1 triplet pattern [^1J(PF)] which strongly suggests the presence of a co-ordinated $PF_2(O_2CCF_3)$ ligand. Both resonances are further split into triplets [^2J(PRuP′)] of doublets [^2J(FPRuP′F)]. The high-field PPh_3 resonance appears as a doublet of doublets, and the magnitude of [^2J(PRuP′)] indicates that the PPh_3 and both fluorophosphine ligands are in mutually *cis* positions. Since (8) is a conductor in nitromethane we propose that it contains the cation shown above; however, no positive identification could be made for the likely $[(CF_3CO_2)_2H]^-$ counter ion.[15] The presence of ligated $PF_2(O_2CCF_3)$ is further evidenced by the observation of a strong ν(CO) stretching band at 1 768 cm^{-1} in the i.r. spectrum. The free ligand, which has previously been prepared[16] from $PClF_2$ and silver(I) trifluoroacetate, exhibits a strong ν(CO) band at 1 809 cm^{-1}. The ^{19}F n.m.r. spectrum of (8) exhibits two equally intense high-field resonances for the CF_3 groups, the lower-field broader line being assigned to the $PF_2(O_2CCF_3)$ ligand. The expected two doublet patterns for the co-ordinated PF_3 and $PF_2(O_2CCF_3)$ ligands were readily assigned on the basis of the magnitude of ^1J(PF).



EXPERIMENTAL

General procedures were as described in Part 1 of this series.

Reactions.—*cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ *with hydrogen chloride.* An ampoule containing *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ (0.087 g, 0.108 mmol), HCl (0.008 5 g, 0.23 mmol), and benzene (5 cm^3) was sealed off and the mixture heated at 60 °C for 4 h giving a colourless solution. Removal of volatiles left an oil which on recrystallisation from dichloromethane–hexane gave colourless crystals of cis-*dichlorobis(trifluorophosphine)bis(triphenylphosphine)ruthenium*(II) (0.086 g, 0.098 mmol, 91%), m.p. 193 °C (decomp.) (Found: C, 48.9; H, 3.65. $C_{36}H_{30}Cl_2F_6P_4Ru$ requires C, 49.5; H, 3.4%).

An attempt to prepare $[RuCl(H)(PF_3)_2(PPh_3)_2]$ by the use of a 1 : 1 mol ratio of reagents gave only a lower yield of $[RuCl_2(PF_3)_2(PPh_3)_2]$.

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[15] C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.

[16] G. G. Flaskerud, K. E. Pullen, and J. M. Shreeve, *Inorg. Chem.*, 1969, **8**, 728.

cis-$[\mathrm{RuH_2(PF_3)_2(PPh_3)_2}]$ *with* HBr.—The *cis*-dibromo-complex was obtained in an analogous reaction with hydrogen bromide, the product being obtained as orange crystals (60%), m.p. 141 °C (decomp.), which were very light- and air-sensitive and an acceptable analysis was not obtained. Infrared spectrum in Nujol mull: 3 052w, 1 586w, 1 481w, 1 438m, 1 268w, 1 188w, 1 112m, 1 071w, 1 028w, 998w, 900vs, 881s, 875s, 861s, 842m, 762w, 749ms, 740m, 722m, 691ms, 617w, 550m, 524ms, 511mw, 507mw, 499ms, 427w, and 403w cm^{-1}. ϕ(F) 12.4 p.p.m.; ^1J(PF) 1 288, ^2J(FPRuPF) 67.0, ^3J(FPRuP′F) 2.5 Hz.

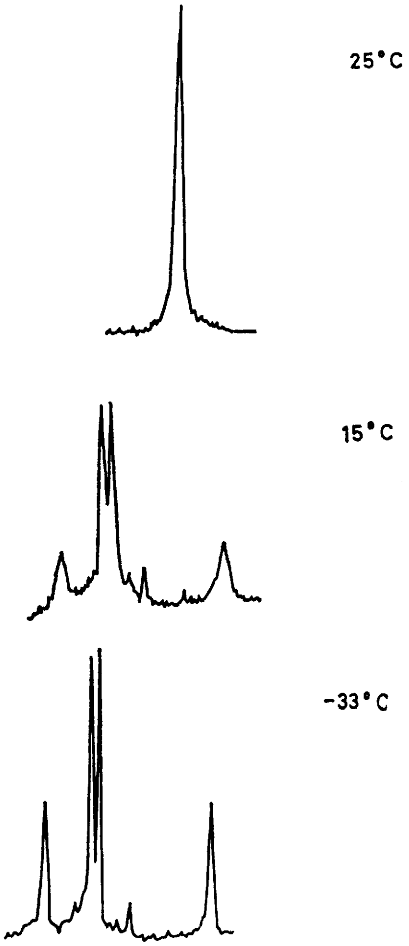

FIGURE 3 Variable-temperature ^{19}F n.m.r. spectrum of the CF_3 resonances of $[\mathrm{Ru(O_2CCF_3)_2(PF_3)(PPh_3)_2}]$

cis-$[\mathrm{RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2}]$ *with hydrogen chloride*. Similarly, a mixture of *cis*-$[\mathrm{RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2}]$ (0.178 g, 0.22 mmol), HCl (0.017 4 g, 0.47 mmol), and benzene (10 cm^3) gave an oil which, after washing with hexane, gave a solid (0.102 g) which was shown by ^{19}F n.m.r. spectroscopy to be a mixture of *cis*-$[\mathrm{RuCl_2(PF_3)_2(PPh_3)_2}]$ and an unidentified product.

cis-$[\mathrm{OsH_2(PF_3)_2(PPh_3)_2}]$ *with hydrogen chloride*. Similarly, a mixture of *cis*-$[\mathrm{OsH_2(PF_3)_2(PPh_3)_2}]$ (0.295 g, 0.33 mmol), HCl (0.026 g, 0.72 mmol), and benzene (15 cm^3) heated at 75 °C for 12 h gave colourless crystals of cis-*chlorohydridobis(trifluorophosphine)bis(triphenylphosphine)-osmium*(II) (2) (0.296 g, 0.32 mmol, 97%), m.p. 207—209 °C (Found: C, 43.5; H, 3.5. $C_{30}H_{31}ClF_6OsP_4$ requires C, 43.9; H, 3.3%). Infrared spectrum in Nujol: 3 060w, 2 031w, 1 591w, 1 489mw, 1 444vw, 1 441mw, 1 194w, 1 165w, 1 093m, 1 080w (sh), 1 032w, 1 006w, 905s, 880vs,br, 860vs, 945vs, 820vs, 752m, 711w (sh), 708s, 699s, 687w,

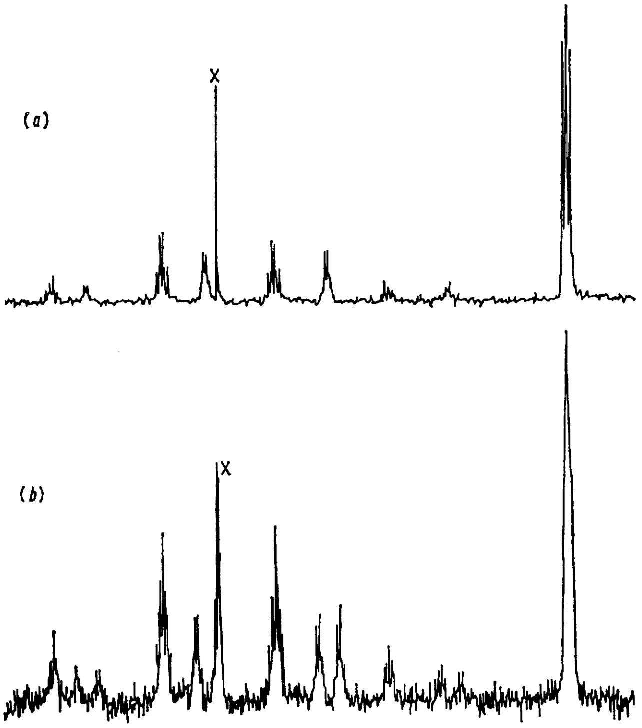

FIGURE 4 Phosphorus-31 n.m.r. spectra of $[\mathrm{RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2}]$: (*a*) proton decoupled; (*b*) undecoupled. X = P(OMe)$_3$, width 10 000 Hz

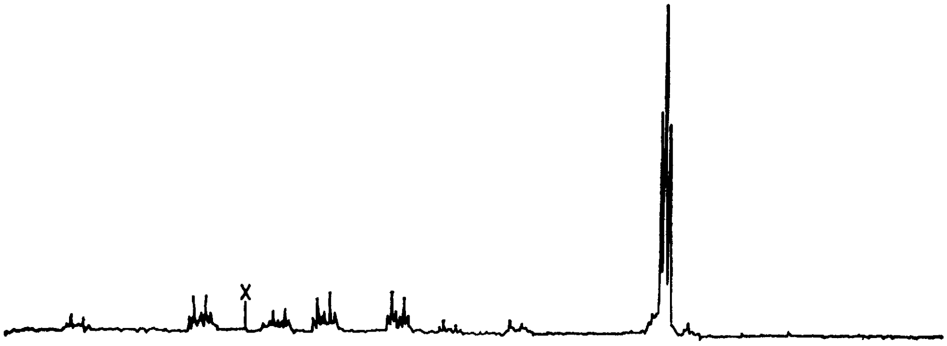

FIGURE 5 Proton-decoupled ^{31}P n.m.r. spectrum of $[\mathrm{Ru(O_2CCF_3)(PF_3)\{PF_2(O_2CCF_3)\}(PPh_3)_2}]^+$. X = P(OMe)$_3$, width 10 000 Hz

620w, 531vs,br, 510w (sh), 470w, 442w, 432mw, 419 mw, and 279w cm^{-1}.

cis-$[OsCl(H)(PF_3)_2(PPh_3)_2]$ *with hydrogen chloride*. Sufficient HCl to produce a pressure of 2 atm * was sealed in an ampoule with a solution of (2) (0.171 g, 0.18 mmol) in dichloromethane (10 cm^3) and the mixture shaken at room temperature for 36 h to give colourless crystals of cis-*dichlorobis(trifluorophosphine)bis(triphenylphosphine)osmium*(II) (0.138 g, 0.14 mmol, 80%) from CH_2Cl_2–hexane, m.p. >230 °C (decomp.) (Found: C, 45.4; H, 3.4. $C_{36}H_{30}Cl_2F_6OsP_4$ requires C, 45.0; H, 3.1%). Infrared spectrum in Nujol: 3 111w, 3 060w, 1 591w, 1 578w, 1 490mw, 1 441m, 1 200w, 1 166w, 1 098w (sh), 1 091m, 1 079w, 1 033w, 1 003w, 940vw, 932w, 921vs, 902vs, 877vs, 864w, 852w, 850m, 761m, 754m, 749s, 711w, 708m, 701vs, 695m, 689vw, 621w, 569mw, 542s, 531vs, 521mw, 509ms, 471m, 461w, 445w, 430w, 421w, 408ms, 326mw, and 271mw cm^{-1}.

Preparation of Hydridobis(trifluorophosphine)bis(triphenylphosphine)ruthenium(II) *Tetrafluoroborate* (3).—A solution of 53% HBF_4 in diethyl ether (0.5 cm^3) was added dropwise to a solution of *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ (0.300 g, 0.25 mmol) in benzene (10 cm^3). After the initial effervescence had ceased (*ca.* 5 min), the pale red solution was pumped to dryness, the resulting oily product was washed with hexane, and recrystallisation from dichloromethane–diethyl ether gave colourless *crystals* (0.188 g, 0.21 mmol, 85%), m.p. 169 °C (decomp.) (Found: C, 47.5; H, 3.9. $C_{36}H_{31}BF_{10}P_4Ru$ requires C, 48.6; H, 3.5%). Infrared spectrum in Nujol: 3 060w, 1 970w, 1 583vw, 1 570vw, 1 475m, 1 441m, 1 194w, 1 167w, 1 092m,br, 1 063s,br, 1 044w (sh), 1 032w (sh), 1 004w, 903m, 875vs,br, 860w, 843s, 759w (sh), 753m, 748m, 710w (sh), 707w (sh), 700s, 620w, 559w, 527vs,br, 518w, 509m (sh), 469w, 452s, 443w, 428m, 404m, 305w (sh), and 299w cm^{-1}. Conductivity measurements in $MeNO_2$ gave a molar conductance Λ of 81.75 S cm^2 mol^{-1}.

Reaction of $[RuH(PF_3)_2(PPh_3)_2][BF_4]$ *with Tetraethylammonium Chloride*.—Tetraethylammonium chloride (0.125 g, 1.3 mmol) was added to a solution of (3) (0.413 g, 0.46 mmol) in dichloromethane. After stirring the mixture for 30 min the solvent was removed to leave a pale yellow solid which was extracted with benzene (3 × 10 cm^3). The combined extracts were reduced to dryness giving a colourless oil which was washed with hexane (15 cm^3) and recrystallisation from dichloromethane–hexane gave large colourless crystals of cis-*chlorohydridobis(trifluorophosphine)bis(triphenylphosphine)ruthenium*(II) (1) (0.153 g, 0.18 mmol, 39% based on ruthenium salt), m.p. 164 °C (decomp.) (Found: C, 51.6; H, 3.8. $C_{36}H_{31}ClF_6P_4Ru$ requires C, 51.6; H, 3.7%). Infrared spectrum in Nujol: 3 060w, 1 930w, 1 590w, 1 574w, 1 488m, 1 198w (sh), 1 192w, 1 165w, 1 099w, 1 092m, 1 077w, 1 033w, 1 004w, 900w, 893vs, 880w, 873vs, 851vs, 844s, 835vs, 828w, 762w, 757w, 750s, 711v, 702s,br, 622w, 560m, 530vs, 520s, 515w, 467w, 459w, 440w, 431w, 418vw, 402w, 391vw, 380w, 343w, and 270w,br cm^{-1}. Further recrystallisation of the mother liquor gave colourless crystals (0.169 g) identified as a 2 : 1 mixture of *tris(trifluorophosphine)bis(triphenylphosphine)ruthenium*(0) [17] and (1).

Reaction of $[Ru(PF_3)_3(PPh_3)_2]$ *with Gaseous Hydrogen Chloride*.—The complex $[Ru(PF_3)_3(PPh_3)_2]$ (0.369 g, 0.42 mmol), HCl (0.036 g, 0.99 mmol), and benzene (10 cm^3) heated at 100 °C for 12 h gave, after removal of volatiles and recrystallisation from dichloromethane–hexane, colourless crystals of *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ (0.339 g, 0.39 mmol, 92.5%), m.p. 190—192 °C (decomp.) (Found: C, 50.1; H, 4.0. $C_{36}H_{30}Cl_2F_6P_4Ru$ requires C, 49.5; H, 3.4%). The i.r. and ^{19}F n.m.r. spectra were identical to those of known samples.

Reaction of $[Ru(PF_3)_3(PPh_3)_2]$ *with t-Butyl Chloride*.—A solution of $[Ru(PF_3)_3(PPh_3)_2]$ (0.320 g, 0.36 mmol) and t-butyl chloride (0.5 cm^3) in toluene (60 cm^3) was heated under reflux for 1.5 h and removal of solvent left a pale yellow oil which was washed with hexane (10 cm^3) and recrystallised from dichloromethane–hexane to give colourless crystals of (1) (0.273 g, 0.33 mmol, 90%), m.p. 163 °C (decomp.) (Found: C, 51.4; H, 3.9. $C_{36}H_{31}ClF_6P_4Ru$ requires C, 51.6; H, 3.7%). The i.r. spectrum was identical to the sample prepared previously.

Preparation of Bis(trifluoroacetato)(trifluorophosphine)bis(triphenylphosphine)ruthenium(II) (4).—Trifluoroacetic acid (1 cm^3) was added dropwise to a solution of *cis*-$[RuH_2(PF_3)(PPh_3)_3]$ (0.150 g, 0.15 mmol) in benzene (15 cm^3) and the mixture stirred for 5 min at room temperature. Removal of solvent left an oil which was washed with hexane (10 cm^3) and recrystallisation from dichloromethane–hexane gave large yellow *crystals* of (4) as the dichloromethane solvate (0.091 g, 0.097 mmol, 65%), m.p. 203—205 °C (Found: C, 48.5; H, 3.2. $C_{41}H_{32}Cl_2F_9O_4P_3Ru$ requires C, 48.05; H, 3.1%). Infrared spectrum in Nujol: 3 060w, 1 712w, 1 698w, 1 698m, 1 672vs, 1 653w (sh), 1 646w (sh), 1 597mw, 1 572w, 1 483m, 1 433m, 1 268w, 1 200vs,br, 1 150s,br, 1 091m, 1 027w, 1 001mw, 886vs, 877w (sh), 871w (sh), 863w (sh), 857w, 842w, 835w, 789w, 784w, 755w, 750m, 743w, 737w, 725m, 710w, 706w, 698s, 684w, 618w, 554m, 532w (sh), 525vs, 520w, 502w, 484w, 470w, 462w, 447w, and 420w cm^{-1}.

Preparation of [(Dimethylamino)difluorophosphine]bis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II) (5).—Trifluoroacetic acid (1.5 cm^3) was added dropwise to a solution of *cis*-$[RuH_2\{PF_2(NMe_2)\}(PPh_3)_3]$ (0.200 g, 0.20 mmol) in benzene (15 cm^3). Removal of the solvent left a yellow oil which was extracted with hexane using a Soxhlet apparatus to give yellow *crystals* (0.167 g, 0.17 mmol, 87%), m.p. 195 °C (decomp.) [Found: C, 51.8; H, 3.9; N, 1.0%; M (mass spectroscopy, $M^+ - PPh_3$) 704. $C_{42}H_{36}F_8NO_4P_3Ru$ requires C, 52.3; H, 3.7; N, 1.45%; M 703]. Infrared spectrum in Nujol: 3 062w, 1 782m, 1 656s, 1 602m, 1 487w, 1 440m, 1 316m, 1 205vs,br, 1 156s,br, 1 092m, 1 078w, 1 030vw, 1 008m, 999m, 871m, 857w, 858m, 833m, 824w, 789m, 783w, 754w, 748m, 737s, 729w, 726m, 705w, 697s, 688w, 619w, 551mw, 528s, 518w, 515w, 502w, 460w, 438w, 422w,br, and 392w cm^{-1}.

Preparation of Hydrido(trifluoroacetato)bis(trifluorophosphine)bis(triphenylphosphine)ruthenium(II) (6).—Trifluoroacetic acid (1.5 cm^3) was added dropwise to a solution of *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ (0.200 g, 0.25 mmol) in benzene (10 cm^3) After 1 h the solvent was removed leaving a yellow oil which was washed with hexane (10 cm^3) and recrystallisation from dichloromethane–hexane gave colourless *crystals* (0.211 g, 0.23 mmol, 92%), m.p. 170 °C (Found: C, 49.6; H, 3.4. $C_{37}H_{31}F_6O_2P_4Ru$ requires C, 49.8; H, 3.4%). Infrared spectrum in Nujol: 3 055w, 1 917m, 1 700m (sh), 1 686vs, 1 647w, 1 588w, 1 570w, 1 482m, 1 434m, 1 400w, 1 190vs, 1 171m, 1 160m, 1 140s, 1 090s, 1 085vw, 1 030w, 1 000m, 974w, 895vs, 875s, 863vs, 852vs,

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* Throughout this paper: 1 atm = 101 325 Pa.

[17] A. Al-Ohaly, R. A. Head, and J. F. Nixon, unpublished work.

834vs, 789ms, 758w (sh), 753w, 748s, 722m, 706s, 693s, 687w, 618w, 554s, 523vs, 510vs,br, 456w, 426w, and 403w cm^{-1}.

Reaction of $[RuH_2(PF_3)_2(PPh_3)_2]$ *with Trifluoroacetic Acid at* 80 °C.—A solution of *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ (0.313 g, 0.390 mmol) and trifluoroacetic acid (2 cm^3) in benzene (50 cm^3) was heated under reflux for 3 h to give a pale yellow oil which was washed with hexane (2 × 10 cm^3) and recrystallised from dichloromethane–hexane to give colourless crystals of product (8) (0.252 g), m.p. 200 °C (Found: C, 47.1; H, 3.1%). Infrared spectrum in Nujol: 3 070vw, 3 060w, 1 768s, 1 591m, 1 571w, 1 484mw, 1 434s, 1 304w, 1 328s, 1 209s, 1 198s, 1 155vs, 1 148vs, 1 094m, 1 031w, 1 000w, 975w, 930vw, 893s, 890s, 878vs, 870s, 853vs, 824vs, 818vs, 784w, 754m, 749w, 744m, 739w, 707w, 700s, 694s, 685w, 619vw, 565mw, 540w (sh), 532w (sh), 524vs, 510m, 458w, 453w, and 423w cm^{-1}.

Preparation of Bis[(dimethylamino)difluorophosphine]bis(trifluoroacetato)(triphenylphosphine)ruthenium(II) (7).—Trifluoroacetic acid (2 cm^2) was added dropwise to a solution of *cis*-$[RuH_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ (0.310 g, 0.37 mmol) in benzene (20 cm^3) and the mixture stirred at room temperature for 15 min. The resulting yellow oil was washed with hexane (10 cm^3) and recrystallised from dichloromethane–hexane to yield yellow *crystals* (0.235 g, 0.29 mmol, 77%), m.p. 184 °C (decomp.) (Found: C, 39.0; H, 3.2; N, 3.3. $C_{26}H_{27}F_{10}N_2O_4P_3Ru$ requires C, 38.2; H, 3.3; N, 3.4%). Infrared spectrum in Nujol: 3 060w, 1 697vs,br, 1 660w (sh), 1 611s, 1 580vw, 1 578vw, 1 491m, 1 445m, 1 429m, 1 318m, 1 210vs,br, 1 190vs, 1 160vs,br, 1 100ms, 1 082w, 1 012s, 1 006s, 940vw, 922vw, 893vw, 878s, 870s, 850vs, 810vs, 798m, 785m (sh), 780s, 765m, 757m, 740vs, 732m, 730vs, 725m, 714m, 709m, 702m, 688w, 620w, 568m, 533vs,br, 519m, 511vw (sh), 468m, 442w, 431mw, 425w, 362w (sh), 350mw, 340w, 328mw, 303mw, 295w (sh), and 284vw cm^{-1}.

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