Fluorophosphine Complexes of Ruthenium and Osmium. Part 3.[1] Monomeric Ruthenium(II) and Osmium(II) Halogeno-complexes †

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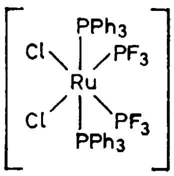
The complex $[RuCl_2(PPh_3)_3]$ or $[RuCl(H)(dma)(PPh_3)_2]$ (dma = $MeCONMe_2$) reacts with 2 mol of PF_3 to give *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$. The analogous complex *cis*-$[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ made from either $[RuCl_2(PPh_3)_3]$ or $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ undergoes ready dissociation of PPh_3 in solution to give $[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)]$. Trifluorophosphine or $PF_2(NMe_2)$ reacts with solutions of $[RuCl_2(PPh_3)_3]$ in dimethylformamide to give complexes of the type $[RuCl_3(dmf)L(PPh_3)_2]$ [L = PF_3 or $PF_2(NMe_2)$] which readily undergo dimerisation reactions to yield binuclear complexes $[(Ph_3P)_2LRuCl_3RuCl(L)(PPh_3)]$. Reduction of $[OsCl_3(PMe_2Ph)_3]$ with zinc in the presence of PF_3 affords *trans*-$[OsCl_2(PF_3)(PMe_2Ph)_3]$ which can be isomerised to the *cis* complex. The related *trans*- and *cis*-$[OsCl_2(PF_3)_2(PMe_2Ph)_2]$ are also described; the former complex exhibits a very large $^2J(PMP')$ coupling constant between the two PF_3 ligands. Structures of all the complexes reported have been elucidated by ^{19}F and ^{31}P n.m.r. spectroscopy.

THERE are only two reports[2,3] of trifluorophosphine complexes of iron(II) halides and no analogous ruthenium or osmium complexes are known. In this paper we describe synthetic routes to several types of mononuclear ruthenium and osmium dichloro-complexes containing fluorophosphine ligands.

RESULTS AND DISCUSSION

Although $[RuCl_2(PPh_3)_3]$ reacts with carbon monoxide to afford *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$,[4] passage of trifluorophosphine through a benzene solution of $[RuCl_2(PPh_3)_3]$ results in rapid decomposition. When, however, a 2 : 1 mol ratio of PF_3 and $[RuCl_2(PPh_3)_3]$ in benzene is slowly warmed from −196 °C to room temperature a series of colour changes is observed and colourless crystals of $[RuCl_2(PF_3)_2(PPh_3)_2]$ (1) are obtained in high yield. Previously we obtained (1) in low yield by heating triphenylphosphine with the red oil formed by treatment of $[RuCl_2(C_{10}H_{16})]$ with PF_3.[5] Alternative routes involve treatment of *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ or $[Ru(PF_3)_3(PPh_3)_2]$ with hydrogen chloride gas.[1]



(1)

The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (1) is shown in Figure 1 and chemical-shift and coupling-constant data are summarised in Table 1. The high-field triplet is assigned to the resonance of the chemical-shift equivalent PPh_3 ligands which are coupled to two trifluorophosphines [$^2J(PRuP')$]. The magnitude of $^2J(PRuP')$ is indicative of mutually *cis* PF_3 and PPh_3 ligands. The low-field PF_3 resonance appears as the A part of an

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† No reprints available.

[1] Part 2, A. R. Al-Ohaly, R. A. Head, and J. F. Nixon, *J.C.S. Dalton*, preceding paper.

[2] Th. Kruck and L. Knott, *Z. Naturforsch.*, 1973, **B28**, 34.

[3] Th. Kruck, R. Kobelt, and A. Prasch, *Z. Naturforsch.*, 1972, **B27**, 344.

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

[5] R. A. Head, J. F. Nixon, J. R. Swain, and C. M. Woodward, *J. Organometallic Chem.*, 1974, **76**, 393.

$[AX_3]_2$ spin system (A = P, X = F), each line appearing as a triplet due to coupling to the PPh_3 groups. The spectrum has been completely analysed using the LAME computer program and the calculated and experimental spectra are shown in Figure 1. The magnitude of the phosphorus–phosphorus coupling constant [^2J(PRuP')] between the two PF_3 ligands indicates they are mutually *cis*; hence (1) has the structure shown above, which is similar to that assigned to the analogous dihydrido-complex.[6] Analysis of the ^{19}F n.m.r. spectrum confirms the assignment (Table 2). Recently, a single-crystal *X*-ray study[7] of (1) confirms the stereochemical assignment and reveals that in the solid state there are some deviations from octahedral geometry caused by steric interactions of the phosphine ligands. Interestingly, whereas only one isomer of (1) has been detected in solution, all the five possible isomers of the related carbonyl complex $[RuCl_2(CO)_2(PPh_3)_2]$ have been reported by various workers, although

TABLE 1

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

Complex	δ(*P*F) [b]	δ(*P*Ph$_3$) [b]	^2J(F*P*M*P*Ph$_3$) [c]	^2J(F*P*M*P*'F) [c]
(1) *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$	16.3	125.5	40.0	69.0
(2) $[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$	−18.0	124.3	27.0	
(3) $[\{RuCl_2[PF_2(NMe_2)]_2(PPh_3)\}_n]$ [d]	−17.1	102.0	49.3	
(4) *cis*-$[RuCl_2(dmf)(PF_3)(PPh_3)_2]$	14.8	112.8	56.1	
(6) *cis*-$[OsCl_2(PF_3)_2(PPh_3)_2]$	68.1	157.6	24.5	62.0
(7) *trans*-$[OsCl_2(PF_3)(PMe_2Ph)_3]$ [e]	73.4	188.4(2)	39.0	
		187.6(1)	524.9	
(9) *trans*-$[OsCl_2(PF_3)_2(PMe_2Ph)_2]$ [f]	64.9	184.7	41.5	949.7

[a] In CH_2Cl_2. [b] P.p.m. upfield from $P(OMe)_3$. [c] In Hz. [d] See text. [e] ^2J(Ph*P*Os*P*Ph) 31.7 Hz. [f] *cis*-isomer, ^2J(F*P*Os*P*'F) 63.0 Hz.

TABLE 2

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

Complex	φ(F) [b]	^1J(PF) [c]	^3J(*F*PRu*P*'F) [c]
(1)	12.4	1 285	3.5
(2) [d]	21.8	1 079	
	22.2	1 137	
	32.3	1 131	
	33.3	1 116	
(4)	4.7	1 257	
(6)	18.4	1 234	2.0 (*cis*-*P*F$_3$)
(7)	25.4	1 267	46.0 (*trans*)
(8) *cis*-$[OsCl_2(PF_3)(PMe_2Ph)_3]$	13.1	1 208	6.0 (*cis*)
(9)	32.9	1 453	228.0 (*trans*)
(10) *cis*-$[OsCl_2(PF_3)_2(PMe_2Ph)_2]$	18.8	1 230	5.0 (*cis*) 4.0 (*cis*-*P*F$_3$)

[a] $CDCl_3$. [b] P.p.m. upfield from $CFCl_3$. [c] In Hz. [d] ^4J(FPRuP'F') 21 Hz.

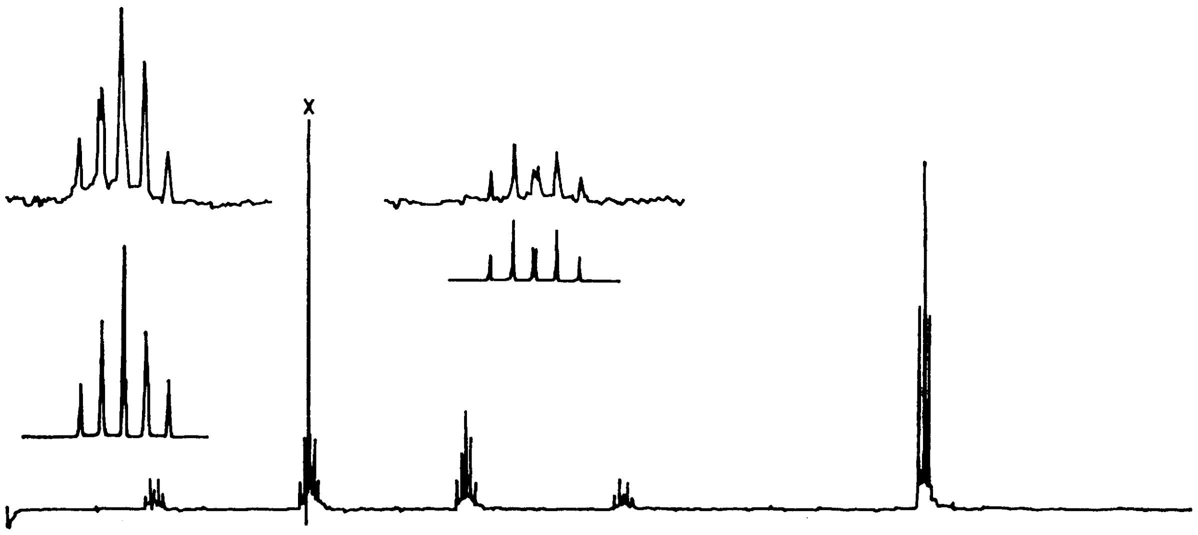


FIGURE 1 Proton-decoupled ^{31}P n.m.r. spectrum of *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$. X = $P(OMe)_3$, width 10 000 Hz. Comparison of recorded and computed patterns

[6] R. A. Head and J. F. Nixon, *J.C.S. Dalton*, 1978, 885.

[7] P. B. Hitchcock, J. F. Nixon, and J. Sinclair, *J. Organometallic Chem.*, 1975, **86**, C34.

there are contradictory data regarding values of ν(CO) for particular isomers.[4,8-13]

The complex $[\mathrm{RuCl_2(PPh_3)_3}]$ or $[\{\mathrm{RuCl_2(OCMe_2)(PPh_3)_2}\}_2]$ reacts with a 2 : 1 ratio of (dimethylamino)-difluorophosphine at room temperature to form the pale yellow crystalline complex $[\mathrm{RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2}]$ (2). The ^{31}P-{^{1}H} n.m.r. spectrum (Figure 2) of a freshly recrystallised sample of (2) always shows a resonance for free PPh$_3$ which is consistent with ligand

$$\underset{(2)}{n[\mathrm{RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2}]} \rightleftharpoons \underset{(3)}{[\{\mathrm{RuCl_2[PF_2(NMe_2)]_2(PPh_3)}\}_n]} + n\mathrm{PPh_3} \qquad (1)$$

dissociation in solution, *e.g.* as in equation (1). The high-field triplet resonance is assigned to co-ordinated PPh$_3$ coupled to two PF$_2$(NMe$_2$) ligands [^2J(PRuP′)]. The resonance of the fluorophosphine ligands occurs as a widely spaced [^1J(PF)] triplet exhibiting further complicated fine structure. The magnitude of ^2J(PRuP′) indicates that the ligands are in a mutually *cis* position. The weak triplet at 124.3 p.p.m. is assigned to the PPh$_3$ resonances of undissociated (2), since the signal is enhanced on addition of PPh$_3$ to the solution.

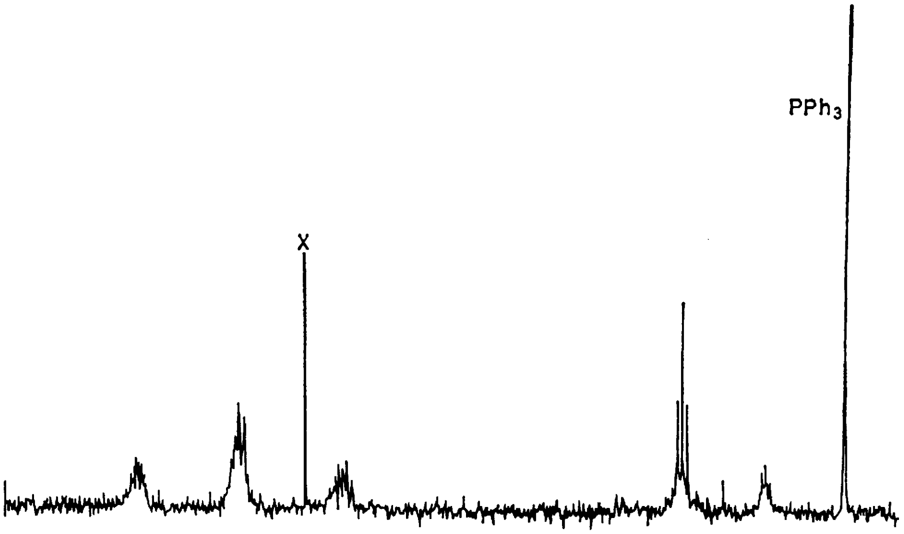
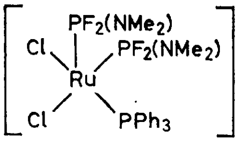


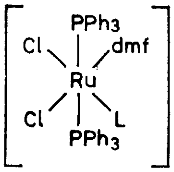
FIGURE 2 Proton-decoupled ^{31}P n.m.r. spectrum of $[\mathrm{RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2}]$. X = P(OMe)$_3$, width 10 000 Hz



(3)

The most likely structure of (3) is shown above, although the possibility of a dimeric dichloro-bridged complex similar to that known to exist in small concentrations in solutions of $[\mathrm{RuCl_2(PPh_3)_3}]$ cannot be discounted.[14] The ^{19}F n.m.r. spectrum of (3) exhibits four widely spaced doublets [^1J(PF)] (Table 2), since the two fluorine nuclei on each PF$_2$(NMe$_2$) ligand are anisochronic. The ^{1}H n.m.r. spectrum exhibits the expected resonances of the PPh$_3$ groups and two resonances centred at τ 7.72 and 8.02, assigned to the methyl groups of the PF$_2$(NMe$_2$) ligands. Each resonance appears as a doublet [^3J(PNCH) 10.5 Hz] of doublets [^4J(FPNCH) 3.0 Hz] of doublets [^4J(FPNCH) 3.0 Hz]. Attempts to isolate (3) from solution were unsuccessful, complex (2) being obtained.

James and his co-workers[11,15] have reported that treatment of $[\mathrm{RuCl_2(PPh_3)_3}]$ with H$_2$ in highly polar solvents such as dimethylacetamide (dma) or dimethylformamide (dmf) affords the violet complexes $[\mathrm{RuCl(H)(PPh_3)_3(solvent)}]$. We find that PF$_3$ reacts instantly at room temperature with $[\mathrm{RuCl(H)(dma)(PPh_3)_3}]$ to give (1), while $[\mathrm{RuCl_2(PPh_3)_3}]$ reacts with PF$_3$ or PF$_2$(NMe$_2$) in dmf to yield the yellow crystalline air-stable complexes $[\mathrm{RuCl_2(dmf)(PF_3)(PPh_3)_2}]$ (4) and $[\mathrm{RuCl_2(dmf)\{PF_2(NMe_2)\}(PPh_3)_2}]$ (5), respectively. The stereochemistry of (4), determined by ^{31}P and ^{19}F n.m.r. spectroscopy (Tables 1 and 2), is



(4) L = PF$_3$
(5) L = PF$_2$(NMe$_2$)

similar to that of (1); the n.m.r. spectra also reveal the presence of smaller amounts of another isomer, PPh$_3$,

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[8] J. Halpern, B. R. James, and A. L. W. Kemp, *J. Amer. Chem. Soc.*, 1966, **88**, 5142.

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

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

[11] B. R. James and L. D. Markham, *Inorg. Nuclear Chem. Letters*, 1971, 373.

[12] N. Ahmad, S. D. Robinson, and M. F. Utley, *J.C.S. Dalton*, 1972, 843.

[13] J. P. Collmann and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.

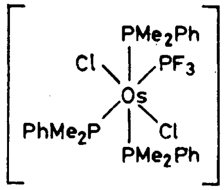
[14] P. R. Hoffman and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221.

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

and the interesting binuclear complex $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$.[16] The latter complex is discussed fully in the following paper. The rate of formation of the binuclear complex from (4) was ascertained by n.m.r. spectroscopy to be virtually complete after 48 h at room temperature. Complex (5) is even more unstable in solution and could not be recrystallised owing to the quantitative formation of $[(Ph_3P)_2\{(Me_2N)F_2P\}RuCl_3RuCl\{PF_2(NMe_2)\}(PPh_3)]$.[16]

The behaviour of these new dichlororuthenium(II) fluorophosphine complexes seems to be governed by the steric requirements of the attached ligands. Six-coordinate complexes are only stable when at least two phosphines have small cone angles. Thus the bis(trifluorophosphine) complex (1) is stable, whereas (2), containing the bulkier $PF_2(NMe_2)$ ligands, undergoes triphenylphosphine dissociation. Similarly, although the dihydrido-complexes $[RuH_2L(PPh_3)_3]$ [$L = PF_3$ or $PF_2(NMe_2)$] have been prepared,[6] attempts to obtain the analogous dichlorides lead to the formation of binuclear trichloro-bridged complexes.[16] It is noteworthy that $[RuCl_2(PPh_3)_3]$, which readily dissociates in solution,[14,17] has been shown by an *X*-ray study to be crowded.[18] Likewise it has been suggested that $[RuCl_2(PPh_3)_4]$ is actually $[RuCl_2(PPh_3)_3]$ containing a lattice PPh_3.[11,14]

As discussed elsewhere,[1] *cis*-$[OsH_2(PF_3)_2(PPh_3)_2]$ reacts with an equimolar amount of gaseous HCl to yield *cis*-$[OsCl(H)(PF_3)_2(PPh_3)_2]$ and with an excess to afford *cis*-$[OsCl_2(PF_3)_2(PPh_3)_2]$ (6), whose structure is similar to (1) on the basis of its ^{31}P and ^{19}F n.m.r. spectra (Tables 1 and 2). Chatt *et al.*[19] have prepared $[OsCl_2(CO)(PR_3)_3]$ and $[OsCl_2(CO)_2(PR_3)_2]$ ($PR_3 = PMe_2Ph$, PEt_2Ph, *etc.*) *via* zinc-amalgam reduction of $[OsCl_3(PR_3)_3]$ under an atmosphere of carbon monoxide. We find that the yellow complex $[OsCl_2(PF_3)(PMe_2Ph)_3]$ (7) is obtained in high yield from the reaction of $[OsCl_3(PMe_2Ph)_3]$ and granulated zinc under a PF_3 atmosphere. The observation of two methyl resonances in the ^1H n.m.r. spectrum of (7) (Table 3) as a virtually coupled triplet (intensity 12) characteristic of two mutually *trans* PMe_2Ph ligands and a higher-field doublet of doublets (intensity 6) arising from coupling with PMe_2Ph and a *trans*-PF_3 ligand indicates that (7) has the *trans* structure shown below, which is similar to the related carbonyl complex.[19]



(7)

TABLE 3

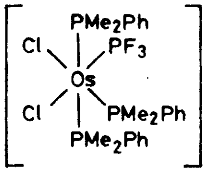
Methyl ^1H n.m.r. chemical-shift and coupling-constant data [a]

Complex	τ [b]	$^2J(PCH)$ [c]
(7) [d]	8.17(2) 8.77(1)	7.0 [e] 3.0
(8)	8.14(2) 8.73(1)	3.0 [e] 2.0
(9)	8.01	8.0 [e]
(10)	8.05	3.5 [e]

[a] In $CDCl_3$. [b] Relative to internal $SiMe_4$. [c] Hz. [d] $^4J(POsPCH_{trans})$ 9.0 Hz. [e] $^2J(PCH) + ^4J(POsPCH)$.

The proposed stereochemistry is supported by the ^{31}P-$\{^1H\}$ n.m.r. spectrum shown in Figure 3, which exhibits two high-field PMe_2Ph resonances in the ratio 2 : 1. The more intense signal is of the two chemical-shift equivalent ligands and appears as a doublet of doublets due to coupling to PF_3 and the unique PMe_2Ph ligand, while the resonance of the latter, which spans the above resonance, appears as a widely spaced doublet [$^2J(POsP')$] of triplets [$^2J(POsP)$] of quartets [$^3J(POsPF)$] and shows significant second-order features expected of an AB_2MX_3 system. The very large doublet coupling (524.9 Hz) indicates that the PF_3 and one of the PMe_2Ph groups are in mutually *trans* positions. The low-field PF_3 resonance appears as the expected quartet [$^1J(PF)$] of doublets [$^2J(POsP')$] of triplets [$^2J(POsP')$]. The ^{19}F n.m.r. spectrum of (7) further supports the formulation. Chemical-shift and coupling-constant data are listed in Table 2.

When a benzene solution of (7) is heated under reflux for 16 h the colour of the solution changes and colourless crystals of an isomeric complex (8) are obtained which is assigned the structure shown above on the basis of its ^{19}F and ^1H n.m.r. spectrum.



(8)

Prolonged reduction of $[OsCl_3(PMe_2Ph)_3]$ under a PF_3 atmosphere affords the pale yellow crystalline complex $[OsCl_2(PF_3)_2(PMe_2Ph)_2]$ (9). The ^1H n.m.r. spectrum exhibits a virtually coupled triplet pattern for the methyl resonances indicating that the two PMe_2Ph ligands occupy *trans* positions, while the ^{19}F n.m.r. spectrum shown in Figure 4 is that expected for the X part of an $[AX_3]_2$ spin system (A = P, X = F) and the very large value (949.7 Hz) for the $^2J(POsP')$ coupling constant indicates that the PF_3 ligands are also mutually *trans*. Thus (9) has the following structure and represents a rare example of a trifluorophosphine complex of a metal not in a zero oxidation state in which the PF_3 groups are in *trans* positions. The ^{31}P n.m.r. spectrum confirms the above assignment. A further interesting feature of the ^{19}F n.m.r. spectrum of (9) is that the magnitude of $^1J(PF)$ is greater than that for free PF_3. In a wide range of PF_3 complexes of metals in different oxidation states the magnitude of $^1J(PF)$ is invariably found to be

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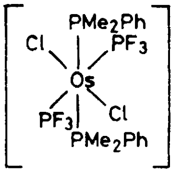
[16] R. A. Head and J. F. Nixon, *J.C.S. Dalton*, following paper.

[17] P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J.C.S. Dalton*, 1975, 1663.

[18] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

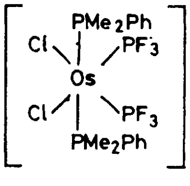
[19] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 1169.

less than for the free ligand.[20] Recently, Dean and Ibbott [21] have found that certain trifluorophosphine complexes of Ag^I and Hg^I have unusually large ^1J(PF) values and it has been suggested that these metals are good σ acceptors but poor π donors. This may also be


(9)

true of (9), where the *trans*-PF$_3$ ligands would compete strongly for any available osmium d_π electrons.

Although (9) is stable in the solid state under dry nitrogen, it decomposes slowly in solution. However, low yields of the colourless *cis* isomer (10) are obtained


(10)

when a benzene solution of (9) is heated under reflux for several hours. The stereochemistry of (10) was established by ^{1}H and ^{19}F n.m.r. spectroscopy. Analysis of the latter spectrum results in a much smaller value for ^2J(POsP') between the two PF$_3$ ligands (Table 2), indicative of their occupying mutually *cis* positions.

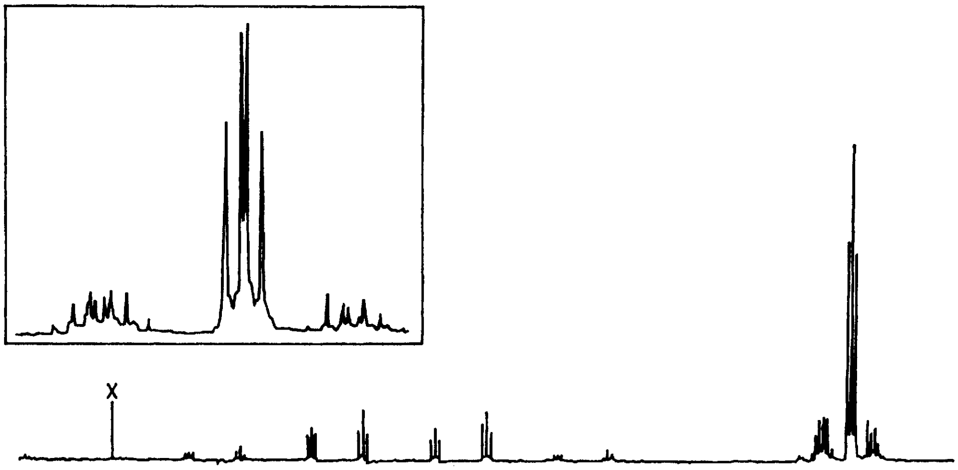


FIGURE 3 Proton-decoupled ^{31}P n.m.r. spectrum of *trans*-[OsCl$_2$(PF$_3$)(PMe$_2$Ph)$_3$]. X = P(OMe)$_3$, width 10 000 Hz (insert shows high-field resonance expanded)

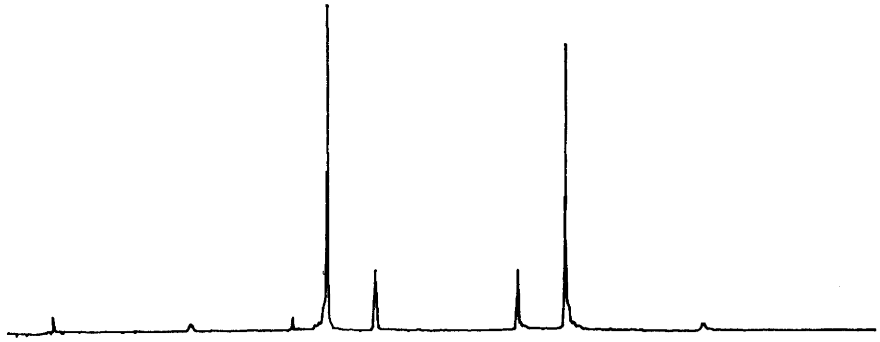


FIGURE 4 Fluorine-19 n.m.r. spectrum of *trans*-[OsCl$_2$(PF$_3$)$_2$(PMe$_2$Ph)$_2$]. Width 5 000 Hz

EXPERIMENTAL

General procedures were as described in earlier parts of this series.

Reaction of [RuCl$_2$(PPh$_3$)$_3$] *with Trifluorophosphine.*—Trifluorophosphine (0.097 g, 1.10 mmol), [RuCl$_2$(PPh$_3$)$_3$] (0.498 g, 0.52 mmol), and dichloromethane were sealed in an ampoule and the mixture allowed to warm to room temperature. A rapid reaction occurred, as indicated by a series of colour changes from brown to deep red to yellow and finally to colourless. The ampoule was shaken for 2 h and removal of solvent left an oil which, after washing with hexane and recrystallisation from dichloromethane–hexane, gave colourless crystals of *cis-dichlorobis(trifluorophosphine)bis(triphenylphosphine)ruthenium*(II) (1) (0.419 g, 0.48 mmol, 92%), m.p. 193 °C (Found: C, 49.3; H, 3.9. $C_{36}H_{30}Cl_2F_6P_4Ru$ requires C, 49.5; H, 3.4%). Infrared spectrum in Nujol mull: 3 100vw, 3 059w, 1 588vw, 1 574vw, 1 484w, 1 437mw, 1 320vw, 1 268vw, 1 198vw (sh), 1 192m, 1 162w, 1 096w (sh), 1 090s, 1 076vw, 1 030w, 1 000w, 979vw, 975vw (sh), 914s, 893vs, 881vs, 863s,

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[20] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

[21] P. A. W. Dean and D. G. Ibbott, *Canad. J. Chem.*, 1976, **54**, 177.

840ms, 756w (sh), 750vs, 725w, 707w (sh), 700vs, 685w, 671vw, 621w, 560m, 527vs,br, 504m, 468w, 458vw, 445w, 421w, 403w, 357w, 320w, 270w, 261w, and 251w cm^{-1}.

Reaction of $[RuCl_2(PPh_3)_3]$ *with (Dimethylamino)difluorophosphine.*—Similarly a mixture of $[RuCl_2(PPh_3)_3]$ (1.464 g, 1.53 mmol) and $PF_2(NMe_2)$ (0.346 g, 3.06 mmol) in benzene (25 cm^3) heated at 60 °C for 2 h gave pale yellow crystals of *dichlorobis[(dimethylamino)difluorophosphine]bis(triphenylphosphine)ruthenium*(II) (2) (1.013 g, 1.10 mmol, 72%), m.p. 164 °C (decomp.) (Found: C, 51.9; H, 4.85; N, 3.0. $C_{40}H_{42}Cl_2F_4N_2P_4Ru$ requires C, 52.1; H, 4.4; N, 3.0%). Infrared spectrum in Nujol: 3 120w, 3 067vw, 3 056vw, 3 040vw, 1 585vw, 1 570w, 1 483w, 1 441w, 1 433w, 1 299m, 1 191w, 1 177m, 1 163w, 1 120vw, 1 100mw, 1 088m, 1 084w (sh), 1 076w, 1 030w, 998w (sh), 991vs, 903w, 882mw, 869w, 852mw, 841w (sh), 837vs, 819s, 771mw, 764ms, 751ms, 746vs, 728w, 713s, 708m, 700s, 694w (sh), 683w (sh), 619w, 546w, 523vs, 500m, 462w, 458mw, 438w, and 419w cm^{-1}.

Reaction of $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ *with* $PF_2(NMe_2)$.—A mixture of $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ (0.552 g, 0.73 mmol), $PF_2(NMe_2)$ (0.130 g, 1.2 mmol), and benzene (20 cm^3), shaken at room temperature for 14 h, gave an oil which was washed with hexane (15 cm^3), and recrystallisation from dichloromethane–hexane gave pale yellow crystals of (2) (0.650 g, 0.70 mmol, 48%), m.p. 164 °C (decomp.) (Found: C, 51.3; H, 4.4; N, 3.0. $C_{40}H_{42}Cl_2F_4N_2P_4Ru$ requires C, 51.2; H, 4.4; N, 3.0%). The i.r. spectrum was identical to that of the product from the previous preparation.

Preparation of cis-*Dichloro(dimethylformamide)(trifluorophosphine)bis(triphenylphosphine)ruthenium*(II) (4).—Trifluorophosphine was passed slowly through a stirred suspension of $[RuCl_2(PPh_3)_3]$ (2.00 g, 2.09 mmol) in dimethylformamide (30 cm^3) at room temperature for 10 min. The solvent was removed from the deep yellow solution and the product washed with diethyl ether (5 × 10 cm^3) to give yellow crystals of (4) as the dimethylformamide solvate (1.697 g, 1.98 mmol, 95%), m.p. 170 °C (Found: C, 54.2; H, 5.15; N, 2.9. $C_{42}H_{44}Cl_2F_3N_2O_2P_3Ru$ requires C, 54.2; H, 4.7; N, 3.0%). Recrystallisation of the product from dichloromethane–hexane afforded yellow crystals of the dichloromethane solvate, m.p. 168—170 °C (Found: C, 50.8; H, 4.1; N, 1.55. $C_{40}H_{39}Cl_4F_3NOP_3Ru$ requires C, 50.8; H, 4.1; N, 1.5%). Infrared spectrum in Nujol: 3 050w, 1 638vs, 1 585vw, 1 511vw, 1 483mw, 1 434ms, 1 369mw, 1 268w, 1 194vw (sh), 1 189w, 1 160w, 1 112w, 1 089m, 1 030w, 1 000w, 970vw, 921vw, 900vw, 877s, 869s, 842w, 826ms, 757ms, 747ms, 740m, 703s, 695vs, 682w, 619w, 552m, 523vs, 519m (sh), 503m, 462mw, 441w, 419w, 415vw, 400w, 390vw, 344m, and 330vw cm^{-1}.

Preparation of cis-*Dichloro[(dimethylamino)difluorophosphine](dimethylformamide)bis(triphenylphosphine)ruthenium*(II) (5).—(Dimethylamino)difluorophosphine (0.452 g, 4.0 mmol) was condensed into a Schlenk tube containing $[RuCl_2(PPh_3)_3]$ (1.850 g, 1.93 mmol) and dmf (30 cm^3) and the mixture allowed to warm from −196 °C to room temperature. The resulting precipitate was filtered off, washed with diethyl ether (2 × 10 cm^3), and dried *in vacuo* to give lemon-yellow crystals of (5) (1.09 g, 1.27 mmol, 66%), m.p. 141—142 °C (decomp.) (Found: C, 55.7; H, 4.9; N, 2.85. $C_{42}H_{43}Cl_2F_2N_2OP_3Ru$ requires C, 55.8; H, 5.0; N, 3.2%). Infrared spectrum in Nujol: 3 100vw, 3 065vw, 3 059w, 1 632vs, 1 589w, 1 573w, 1 488mw, 1 439mw, 1 363m, 1 313w, 1 265w, 1 197m, 1 168w, 1 158w, 1 119m, 1 100ms, 1 091ms, 1 077w, 1 032w, 1 004vs, 880w, 870w, 860w, 851w, 839w, 801vs, 768m (sh), 760vs, 750m (sh), 730s, 725w (sh), 713s, 703vs, 620w, 550w, 545w, 531vs,br, 508s, 468m, 448w, 422w, 400w, 370w, 327w, 298w, and 285w cm^{-1}.

Reaction of $[RuCl(H)(dma)(PPh_3)_3]$ *with Trifluorophosphine.*—A solution of $[RuCl_2(PPh_3)_3]$ (0.943 g, 0.99 mmol) in dimethylacetamide (50 cm^3) was stirred for 12 h at room temperature under a dihydrogen atmosphere and PF_3 was bubbled through the solution. Removal of solvent left an orange oil which was washed with hexane (2 × 20 cm^3) and recrystallisation from dichloromethane–hexane gave colourless crystals of (1) (0.573 g, 0.66 mmol, 66%), m.p. 188 °C. The i.r. and ^{19}F n.m.r. spectra were identical to those of previously prepared samples.

Preparation of trans-*Dichlorotris(dimethylphenylphosphine)(trifluorophosphine)osmium*(II) (7).—A mixture of *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.436 g, 0.61 mmol), granulated zinc (3 g), and tetrahydrofuran (thf) (60 cm^3) was heated under reflux and PF_3 passed through the deep red solution which slowly became pale yellow. After 4 h the solution was filtered and removal of solvent left a yellow oil which, on recrystallisation from dichloromethane–hexane, gave yellow *crystals* (0.288 g, 0.38 mmol, 63%), m.p. 171 °C (decomp.) (Found: C, 37.4; H, 4.05. $C_{24}H_{33}Cl_2F_3OsP_4$ requires C, 37.7; H, 4.3%). Infrared spectrum in Nujol: 3 048w, 1 492vw, 1 436w, 1 303mw, 1 298w, 1 285mw, 1 200vw, 1 190vw, 1 164w, 1 102mw, 1 077w, 1 031w, 1 004vw, 959m, 950m, 942m, 931w, 920s, 908w, 891w, 885w, 881w, 870w (sh), 862vw, 857vs, 847vs, 841vs, 829vs, 750w, 745vs, 738m, 713w, 709s, 702s, 697ms, 678m, 621vs, 544ms, 508vw, 502w (sh), 497s, 442ms, 423m, 412w, and 398w cm^{-1}.

Isomerisation of trans-$[OsCl_2(PF_3)(PMe_2Ph)_3]$.—A solution of (7) (0.231 g, 0.30 mmol) in benzene (50 cm^3) was heated under reflux for 16 h affording a colourless solution which was pumped to dryness. Recrystallisation from dichloromethane–hexane gave white *platelets* of the *cis* isomer (8) (0.207 g, 0.27 mmol, 90%), m.p. 228 °C. Infrared spectrum in Nujol: 3 060w, 1 439w, 1 327w, 1 319w, 1 310w, 1 294w, 1 289w, 1 102w, 960w, 951mw, 948w, 936w, 929w, 918s, 909vs, 875vs,br, 864vs, 857w, 851w, 839w, 756ms, 749ms, 716ms, 703m, 687w, 681w, 559ms, 509w, 499m, 441w, 430mw, and 419 cm^{-1}.

Preparation of trans-*Dichlorobis(dimethylphenylphosphine)bis(trifluorophosphine)osmium*(II) (9).—Trifluorophosphine was passed slowly through a refluxing mixture of *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.800 g, 1.13 mmol) and granulated zinc (5 g) in thf (100 cm^3) for 5 h. The yellow solution was filtered and removal of solvent gave a pale red oil which was washed with hexane (10 cm^3). Recrystallisation from dichloromethane–hexane gave yellow *crystals* (0.510 g, 0.72 mmol, 63%), m.p. 149 °C (Found: C, 26.9; H, 3.1. $C_{16}H_{22}Cl_2F_6OsP_4$ requires C, 26.9; H, 3.1%). Infrared spectrum in Nujol: 3 059w, 1 576vw, 1 483w, 1 440w, 1 431w, 1 423w, 1 412vw, 1 306m, 1 295m, 1 192w, 1 164w, 1 115w, 1 105mw, 1 082w, 1 033w, 1 007w, 979w, 950s, 936w, 915vs,br, 901s, 894s, 883vs, 870s, 853vs,br, 759m, 752vs, 748m, 742w, 719m, 700ms, 683m, 621w, 551w, 505vs,br, 431ms, 418m, 404m, 344mw, 337w, 331w, 325mw, 318w, 311vw, and 264mw cm^{-1}.

Isomerisation of trans-$[OsCl_2(PF_3)_2(PMe_2Ph)_2]$.—A solution of (9) (0.168 g, 0.24 mmol) in benzene (50 cm^3) was heated under reflux for 6 h. The solution was reduced to dryness affording a pale green solid which was washed with hexane (10 cm^3). Recrystallisation from dichloromethane–hexane gave white *crystals* of the *cis* isomer (10) (0.109 g, 0.15 mmol, 64%) (Found: C, 27.1; H, 3.1. $C_{16}H_{22}Cl_2F_6OsP_4$ requires C, 26.9; H, 3.1%).

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