Fluorophosphine Complexes of Ruthenium and Osmium. Part 4.[1] Homobinuclear Trichloro-bridged Complexes of Ruthenium(II) †

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The reaction of $[RuCl_2(PPh_3)_3]$ with different mol ratios of PF_3 proceeds *via* the trichloro-bridged binuclear complexes $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PPh_3)_2]$ and $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$ to form the stable mononuclear complex *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$. Similar reactions occur with $PF_2(NMe_2)$. The binuclear complexes have been isolated and characterised by ^{19}F and ^{31}P n.m.r. spectroscopy. The *cis*-$[RuCl_2L_2(PPh_3)_2]$ complexes [L = PF_3 or $PF_2(NMe_2)$] react with $[RuCl_2(PPh_3)_2]$ to form the trichloro-bridged dimers $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$ and $[(Ph_3P)\{(Me_2N)F_2P\}_2RuCl_3RuCl(PPh_3)_2]$ respectively. Syntheses of $[(Ph_3P)_2(OC)RuCl_3RuCl(PF_3)(PPh_3)]$, $[(Ph_3P)_2(OC)RuCl_3RuCl(CO)(PPh_3)]$, and *cis*-$[RuCl_2(CO)(PF_3)(PPh_3)_2]$ are also reported. Possible mechanisms for the formation of the dimeric complexes are discussed and some reactions are reported.

As mentioned briefly in the previous paper,[1] attempts to synthesise monomeric complexes of Ru^{II} of the type $[RuCl_2L(PPh_3)_3]$ [L = PF_3 or $PF_2(NMe_2)$] either by treatment of the appropriate dihydrido-complex *cis*-$[RuH_2L(PPh_3)_3]$ with hydrogen chloride or $[RuCl_2(PPh_3)_3]$ with 1 equivalent of the appropriate fluorophosphine ligand led instead to the formation of the interesting dimeric trichloro-bridged complexes of formula $[(Ph_3P)_2LRuCl_3RuCl(L)(PPh_3)]$ [L = PF_3 or $PF_2(NMe_2)$]. The present paper is concerned with the synthesis of several structural types of binuclear ruthenium(II) trichloro-bridged complexes and a study of the mechanism involved in their formation. For a preliminary account see ref. 2.

Relatively few similar types of complex have been reported and their syntheses have involved several different routes, *e.g.* $[Ru_2Cl_3(PR_3)_6]Cl$ (PR_3 = PMe_2Ph, PEt_2Ph, $PMePh_2$, or $PEtPh_2$),[3] $[Ru_2Cl_3(AsEtPh_2)_6]Cl$,[4] $[Ru_2Cl_6(PBu_3)_4]$ and $[Ru_2Cl_5(PBu_3)_4]$,[5,6] $[(Ph_3P)_2(N_2)RuCl_3RuCl(PPh_3)_2]$,[7] $[(Ph_3P)_2(SC)RuCl_3RuCl(PPh_3)_2]$,[8] $[(Ph_3P)_2(OC)RuCl_3RuCl(PPh_3)_2]$,[9] $[Ru_2Cl_4(PEt_2Ph)_5]$,[10] $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$,[11,12] $[Ru_2Cl_3(SnCl_3)(CO)_5]$,[13] $[Os_2Cl_3(PR_3)_6]Cl$,[3,14,15] $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}$,[16] and $[Ir_2(C_5Me_5)_2H_3]^+$.[17]

RESULTS AND DISCUSSION

The product from the reaction of PF_3 with $[RuCl_2(PPh_3)_3]$ changes as the mol ratio of the reactants is varied. The reaction of a 2 : 1 mol ratio of PF_3 : $[RuCl_2(PPh_3)_3]$ proceeds *via* a series of colour changes in which the initial brown solution rapidly changes to purple, deep red, and yellow and subsequently affords colourless crystals of the monomeric complex *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$. A 1 : 1 mol ratio of reactants results in the formation of orange-yellow crystals of the binuclear complex $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$ (1), while a 1 : 2 mol ratio gives the deep red $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PPh_3)_2]$ (2). Attempts to isolate the purple intermediate were unsuccessful, and when mol ratios >1 : 2 are used only a correspondingly lower yield of (2) is obtained. Attempts to prepare the (dimethylamino)difluorophosphine analogue of (2) were unsuccessful, the reaction of $PF_2(NMe_2)$ with a two-fold excess of $[RuCl_2(PPh_3)_3]$ affording $[(Ph_3P)\{(Me_2N)F_2P\}RuCl_3RuCl\{PF_2(NMe_2)\}(PPh_3)]$ (3) and starting material. These binuclear complexes consist of two octahedra sharing a common face defined by the three bridging chlorides and structural assignments are based on detailed analysis of their ^{19}F and ^{31}P n.m.r. spectra (see below).

The proton-decoupled ^{31}P n.m.r. spectrum of (2) is shown in Figure 1 and the chemical-shift and coupling-constant data are recorded in Table 1. The low-field widely spaced quartet [$^1J(PF)$], which is readily assigned to the resonance of the PF_3 ligand, exhibits a further triplet pattern arising from a fortuitously overlapping doublet of doublets [$^2J(PRuP')$]. The two high-field AB patterns are assigned to the resonances of two pairs of chemically inequivalent PPh_3 groups indicating that

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† No reprints available.

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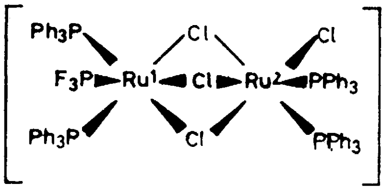
(2) has the structure shown above in which no two PPh_3 groups on Ru^1 or Ru^2 eclipse the same type of ligand. Each line of the highest-field AB pattern is further split into a doublet due to coupling to the PF_3 ligand [$^2J(PRuP')$], which confirms that this resonance arises from the PPh_3 groups co-ordinated to Ru^1. The ^{19}F n.m.r. spectra show the expected doublet [$^1J(PF)$] (Table 2). The stereochemical assignment of (2) is thus similar to the thiocarbonyl analogue $[(Ph_3P)_2(SC)RuCl_3RuCl(PPh_3)_2]$ whose structure has been recently established by *X*-ray crystallographic studies.[8]



(2)

Treatment of (2) with 1 equivalent of PF_3 affords complex (1), which can also be prepared by other routes summarised in the Scheme. Complex (1) can exist as the isomers (a)—(c), and the ^{31}P and ^{19}F n.m.r. spectra of (1) indicate that all three isomers are present in solution. Interestingly, their relative abundance remains similar, regardless of the preparative route. The ^{19}F n.m.r. spectrum of (1) (Figure 2 and Table 3) exhibits two intense doublets [$^1J(PF)$] assigned to the resonances of the PF_3 groups of isomer (a). The higher-field doublet is unequivocally assigned to the resonance of the PF_3 on Ru^2 since each line exhibits a further small doublet splitting arising from coupling to the adjacent PPh_3. The low-field resonance does not exhibit the expected triplet pattern arising from coupling to the two PPh_3 on Ru^1, although the lines are relatively broad. The remainder of the spectrum consists of three doublet patterns of relative intensity 1 : 1 : 2. The high-field doublet [$^1J(PF)$] of intensity 2 exhibits further coupling

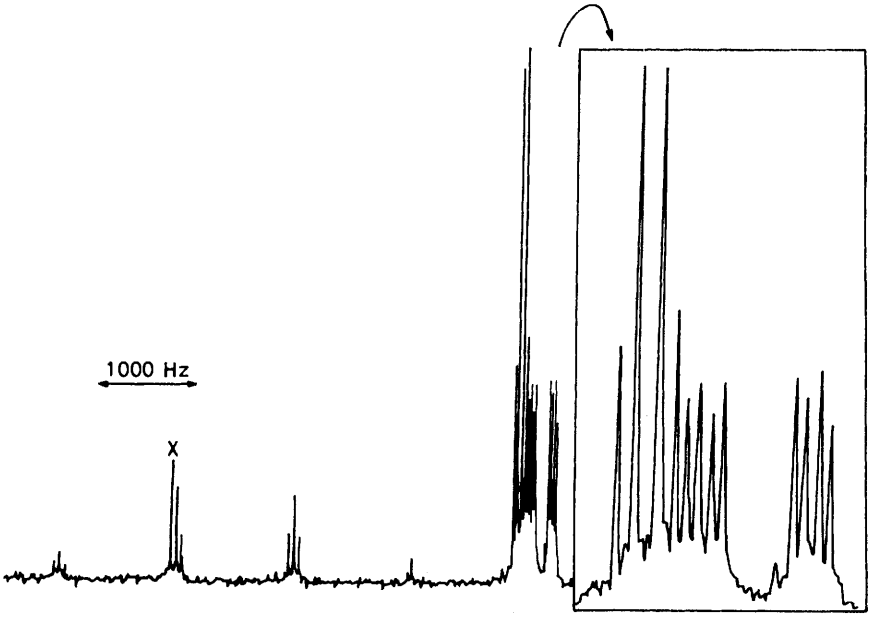


FIGURE 1 Proton-decoupled ^{31}P n.m.r. spectrum of $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PPh_3)_2]$. X = $P(OMe)_3$

TABLE 1

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

Complex	Ru¹			Ru²		
	δ(PF) [b]	δ(PPh) [b]	$^2J(PRuP')$ [c]	δ(PF) [b]	δ(PPh) [b]	$^2J(PRuP)$ [c]
(1) $[(Ph_3P)_2(F_3P)Ru^1Cl_3Ru^2Cl(PF_3)(PPh_3)]$ [d]	16.0	99.1	26.5	21.9	90.3	68.4
		96.7	58.6(PF)			
(2) $[(Ph_3P)_2(F_3P)Ru^1Cl_3Ru^2Cl(PPh_3)_2]$	17.2	103.0	24.4		95.0	36.6
		97.2	56.2(PF)		93.0	
(3) $[(Ph_3P)_2\{(Me_2N)F_2P\}Ru^1Cl_3Ru^2Cl\{PF_2(NMe_2)\}(PPh_3)]$ [d]	−20.1	98.9	53.7(PF)	−20.3	86.5	65.9
		98.9				
(4) $[(Ph_3P)_2(OC)Ru^1Cl_3Ru^2Cl(CO)(PPh_3)]$ [d]		100.3	28.1		118.2	
		98.2				
(5) $[(Ph_3P)_2(OC)Ru^1Cl_3Ru^2Cl(PF_3)(PPh_3)]$ [e]		100.1				
		96.7	24.4	22.2	89.6	70.8
		(102.2)	(24.4)	(21.6)	(92.5)	(70.8)
		(98.3)				
(6) $[(Ph_3P)\{(Me_2N)F_2P\}_2Ru^1Cl_3Ru^2Cl(PPh_3)_2]$ [d]	−20.0	102.8	45.2		92.1	
(8) $[RuCl_2(CO)(PF_3)(PPh_3)_2]$	14.2	125.4	39.6			

[a] In CH_2Cl_2. [b] P.p.m. relative to $P(OMe)_3$. [c] In Hz. [d] Major isomer. [e] Values for minor isomer are in parentheses.

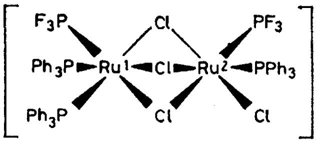
TABLE 2

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

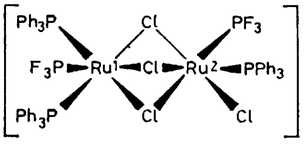
Complex	Ru¹ ϕ(F) [b]	Ru¹ ^1J(PF) [c]	Ru² ϕ(F) [b]	Ru² ^1J(PF) [c]	Ru² ^3J(FPRuP) [c]
(1a)	8.6	1 282	11.9	1 292	
(1b)	8.2	1 283	10.0	1 287	4.0
(1c)	6.7	1 283	10.0	1 287	4.0
(2)	8.5	1 284			
(3) [d]	18.8	1 138	27.2	1 157	4.5
	23.8	1 153	29.1	1 193	4.5
(4)			11.7	1 292	3.7
			10.3	1 293	4.9
(6) [d]	22.0	1 111			
	23.7	1 122			
	27.2	1 139			
	31.5	1 148			
	34.2	1 104			
	36.7	1 094			
(8)	12.6	1 305			

[a] In $CDCl_3$. [b] P.p.m. upfield of CCl_3F. [c] In Hz. [d] ^2J(FPF) *ca.* 25.0 Hz.

to PPh_3, confirming that this resonance is that of the PF_3 on Ru² from both (1b) and (1c). The similarity in chemical shift is a consequence of the PF_3 co-ordinated to Ru² eclipsing PPh_3 on Ru¹ in both isomers. In (1b) and (1c) the PF_3 co-ordinated to Ru¹ is eclipsed by PPh_3 and chloride respectively resulting in two distinct resonances.



(1a)



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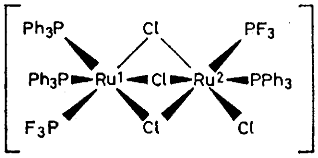
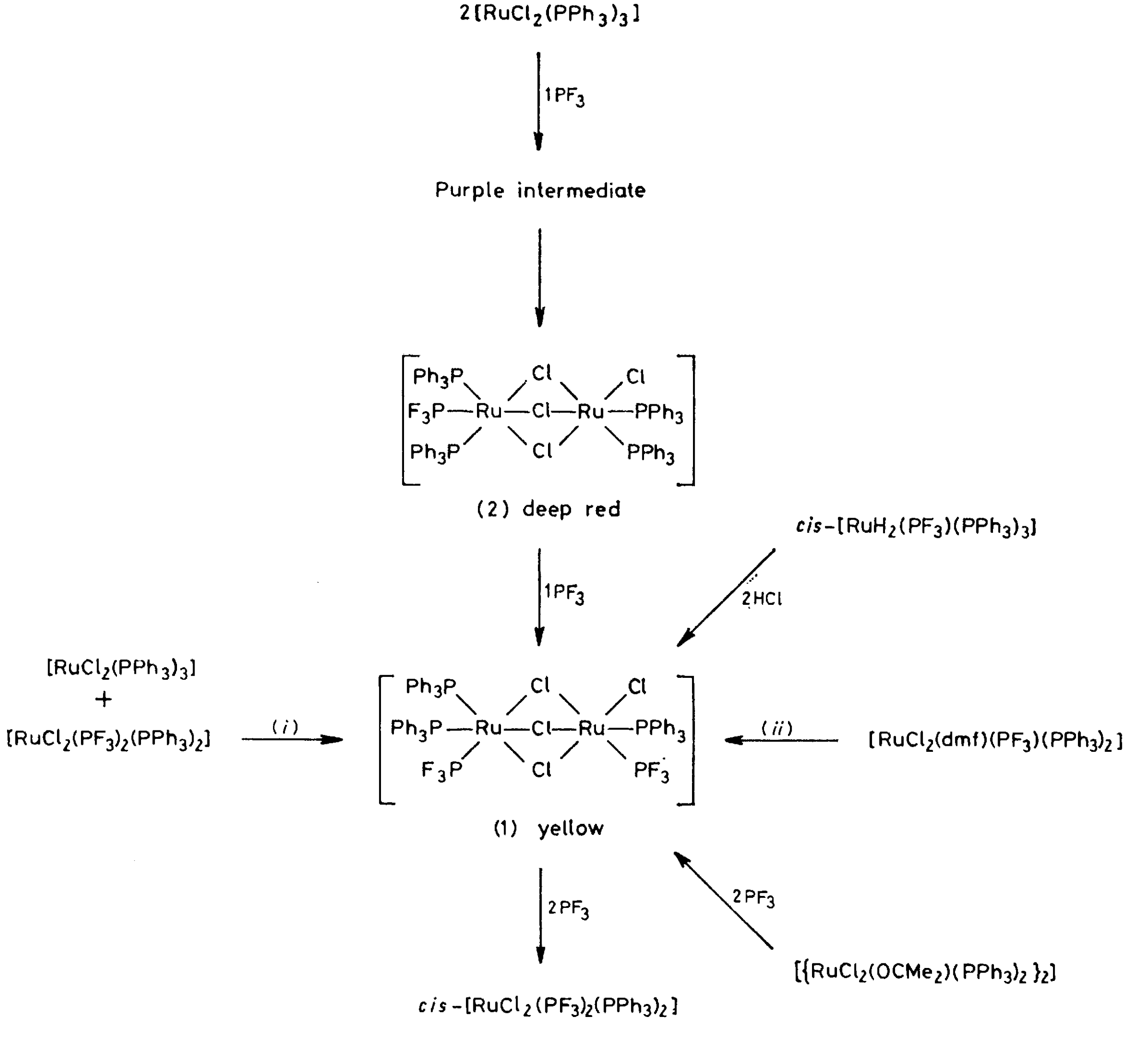


(1c)

The chemical shift of these lines has enabled a



SCHEME (*i*) Reflux in Me_2CO; (*ii*) thermal decomposition tentative assignment of each isomer to be made since the chemical-shift difference between the lowest-field pattern and the resonance of PF_3 on Ru^1 of isomer (1a) is identical to that between the two resonances observed for the PF_3 on Ru^2. The latter shift is the result of the eclipsing atoms changing from PF_3 to PPh_3 and the lowest-field pattern is therefore assigned to the resonance of the PF_3 on Ru^1 in isomer (1b), where the eclipsing ligand is PPh_3. The remaining lines are assigned to the PF_3 ligand co-ordinated to Ru^1 in isomer (1c). The isomers of (1) which have relative abundances of 74 (a), 15.5 (b), and 10.5% (c) respectively are not interconverted even on heating to 70 °C.

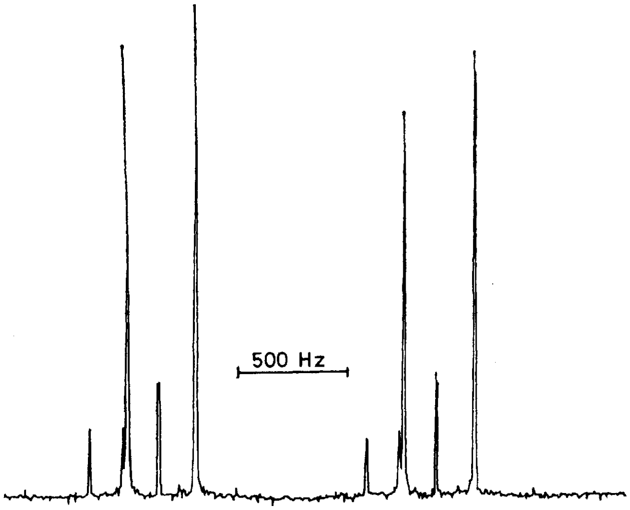


FIGURE 2 Fluorine-19 n.m.r. spectrum of $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$

The proton-decoupled ^{31}P n.m.r. spectrum of (1) shown in Figure 3 confirms the presence of all three isomers. The more intense lines are the expected spectrum of isomer (1a). Two PPh_3 resonances appear at high field and are assigned to the ligands on Ru^2 and Ru^1 respectively. The former resonance appears as a doublet from coupling to PF_3 [^2J(PRuP')], while the two PPh_3 groups on Ru^1 are chemically inequivalent and exhibit an AB pattern of lines, each line being further split into a doublet by coupling to PF_3 [^2J(PRuP')]. The unusual relative intensity of the lines in the latter resonance arise because isomers (1b) and (1c) exhibit similar overlapping patterns at slightly higher-field chemical shifts than (1a). The expected two widely spaced low-field quartets [^1J(PF)] are assigned to the resonances of the PF_3 ligands and the higher-field quartet exhibits a further 1 : 1 doublet splitting [^2J(PRuP')] which unambiguously identifies it as arising from the PF_3 on Ru^2, while the PF_3 on Ru^1 is identified by the appearance of a further triplet fine structure [^2J(PRuP')].

Complex (3), which is best prepared either by treatment of $[RuCl_2(PPh_3)_3]$ or $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ with 1 equivalent of $PF_2(NMe_2)$, or by decomposition of $[RuCl_2(dmf)\{PF_2(NMe_2)\}(PPh_3)_2]$ (dmf = dimethylformamide), also exists in all three possible isomeric forms. The ^{19}F n.m.r. spectrum (Figure 4) exhibits four major, widely spaced, doublet patterns [^1J(PF)], each line appearing as a further doublet [^2J(FPF')] indicating that the fluorine atoms on each $PF_2(NMe_2)$ ligand are anisochronic resulting from the presence of an asymmetric Ru^1 centre. Weaker lines are assigned to the presence of the other two isomers.

The new binuclear carbonyl complex $[(Ph_3P)_2(OC)RuCl_3RuCl(CO)(PPh_3)]$ (4) is made by treating *cis*-$[RuH_2(CO)(PPh_3)_3]$ with gaseous hydrogen chloride and its ^{31}P-$\{^1H\}$ n.m.r. spectrum indicates that two isomers are present in the ratio 3 : 1 (Table 1). The yellow binuclear complex $[(Ph_3P)_2(OC)RuCl_3RuCl(PF_3)(PPh_3)]$ (5) is readily obtained from the reaction of $[(Ph_3P)_2(OC)RuCl_3RuCl(PPh_3)_2]$ with 1 equivalent of PF_3. The proton-decoupled ^{31}P n.m.r. (Table 1) and ^{19}F n.m.r. spectra (Table 2) indicate that both the expected isomers of (5) are present, but in different concentrations. It seems likely that the major isomer of (5) has a similar stereochemistry to (1a).

An unexpected reaction occurs when $[RuCl_2(PPh_3)_3]$ and *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ are heated under reflux in acetone solution, and a good yield of (1) is obtained (see Scheme). In the absence of $[RuCl_2(PPh_3)_3]$, the *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ is recovered unchanged. An un-

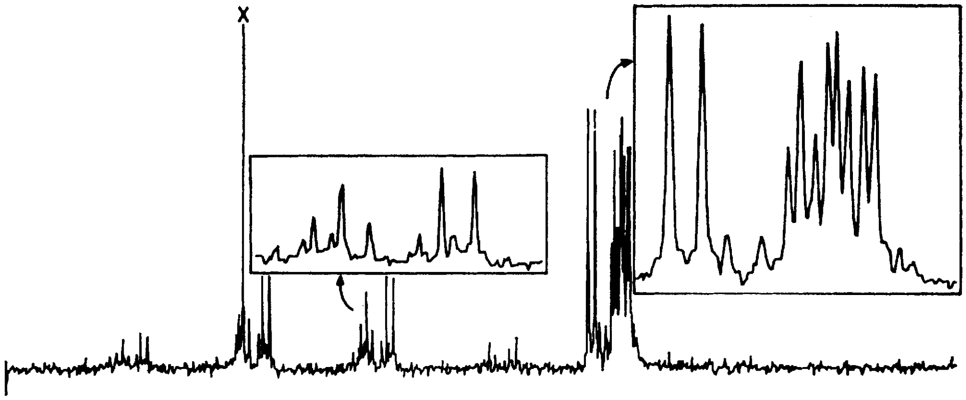


FIGURE 3 Proton-decoupled ^{31}P n.m.r. spectrum of $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$. X = $P(OMe)_3$, width 10 000 Hz

usual feature of the above reaction is the ready transfer of PF_3 from one ruthenium atom to the other. Trifluorophosphine is not known to act as a bridging group as is carbon monoxide, and since the reaction is carried out in an open system any unco-ordinated PF_3 would be expected to be readily lost on account of its volatility. Related ligand-transfer reactions are known involving involatile tertiary phosphines[18-21] but these could proceed *via* ligand dissociation and subsequent attack at another metal centre. Alkyl transfer between platinum and palladium[20] is assumed to involve an intermediate bridging ligand. No ligand transfer occurs during the formation of the deep red binuclear complex $[(Ph_3P)\{(Me_2N)F_2P\}_2RuCl_3RuCl(PPh_3)_2]$ (6) by heating an equimolar mixture of $[RuCl_2(PPh_3)_3]$ and $[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$, and this may reflect the ease of PPh_3 dissociation from the latter.

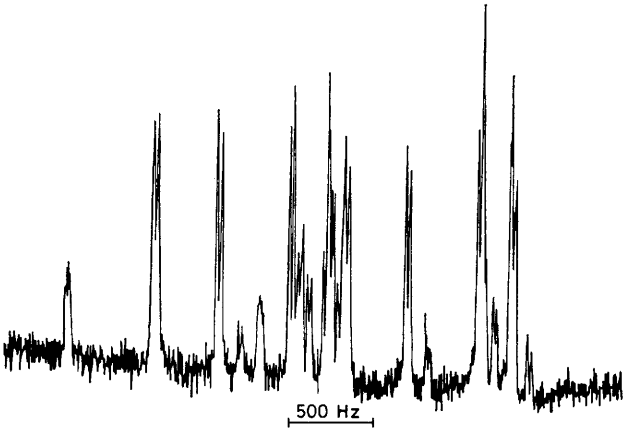
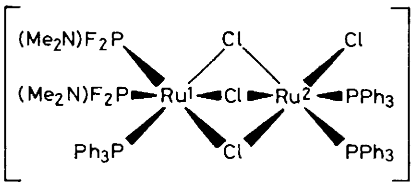
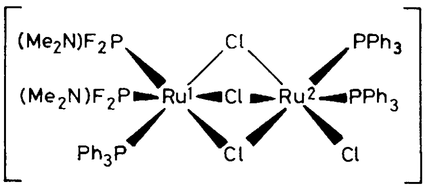


FIGURE 4 Fluorine-19 n.m.r. spectrum of $[(Ph_3P)_2\{(Me_2N)F_2P\}RuCl_3RuCl\{PF_2(NMe_2)\}(PPh_3)]$



(6a)



(6b)

Complex (6) can exist in the two possible isomeric structures shown above. The ^{19}F n.m.r. spectrum of (6) shown in Figure 5(*a*) contains six pairs of lines $[^1J(PF)]$ each line exhibiting a further doublet coupling $[^2J(FPF)]$ (see Table 2). The two fluorines on a $PF_2(NMe_2)$ group in each isomer are anisochronic and since there is chemical-shift equivalence between the fluorophosphines on (6b) but not on (6a) the latter isomer should give rise to four pairs of lines and the former only two as found.* The ratio of (a) : (b) is *ca.* 2 : 1 and this is also evident from the ^1H n.m.r. spectrum [Figure 5(*b*)]. On increasing the temperature the ^{19}F n.m.r. spectrum simplifies to two $^1J(PF)$ doublets at 75 °C with coincidence of inner lines, suggesting that there is rapid equilibration of the isomers. The ^1H n.m.r. spectrum shows a similar coalescence of the methyl resonances on increasing the temperature [Figure 5(*b*)].

In contrast to the two previous reactions, treatment of $[RuCl_2(PPh_3)_3]$ with *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ in acetone does not give the expected dimer $[(Ph_3P)_2(OC)RuCl_3RuCl(CO)(PPh_3)]$ but instead a red crystalline solid, (7), precipitates from the reaction mixture, and *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ is recovered in virtually quantitative yield. The instability of (7) has precluded assignment of a structure. A band at 1 653 cm^{-1} in the i.r. spectrum is typical of ν(CO) of co-ordinated acetone, while the reaction of (7) with PF_3 to give (1) and *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ suggests that it may have a similar structure to the red dimeric acetone complex reported by Gilbert and Wilkinson.[21]

Mechanistic Considerations.—Since completion of this study other workers[7,9,22] have proposed mechanisms for the formation of binuclear ruthenium(II) complexes containing triple halide bridges. In our study we find that no reaction occurs between $[RuCl_2(PPh_3)_3]$ and fluorophosphine ligands when air is rigorously excluded from the system. At the outset of our work the behaviour of $[RuCl_2(PPh_3)_3]$ in solution had not been described in detail, but subsequently two reports[23,24] established that PPh_3 dissociation occurs to produce the dichloro-bridged binuclear complex $[\{RuCl_2(PPh_3)_2\}_2]$, thus discounting an earlier proposal[25] of the existence of a mononuclear ' $RuCl_2(PPh_3)_2$ ' species. Similar dissociative behaviour has been established for $[RhCl(PR_3)_3]$ (R = Ph or C_6H_4Me-*p*).[26]

Since the extent of PPh_3 dissociation is known to be enhanced in the presence of air the reaction of $[RuCl_2(PPh_3)_3]$ with fluorophosphines, L, could conceivably

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* We thank a referee for pointing this out.

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proceed *via* a short-lived intermediate shown on p. 907 which then rapidly forms the first trichloro-bridged product (isolated for L = PF_3 and CO). Further reaction with the fluorophosphine would lead to replacement of PPh_3 on Ru^2, *e.g.* to give (1) or (3).

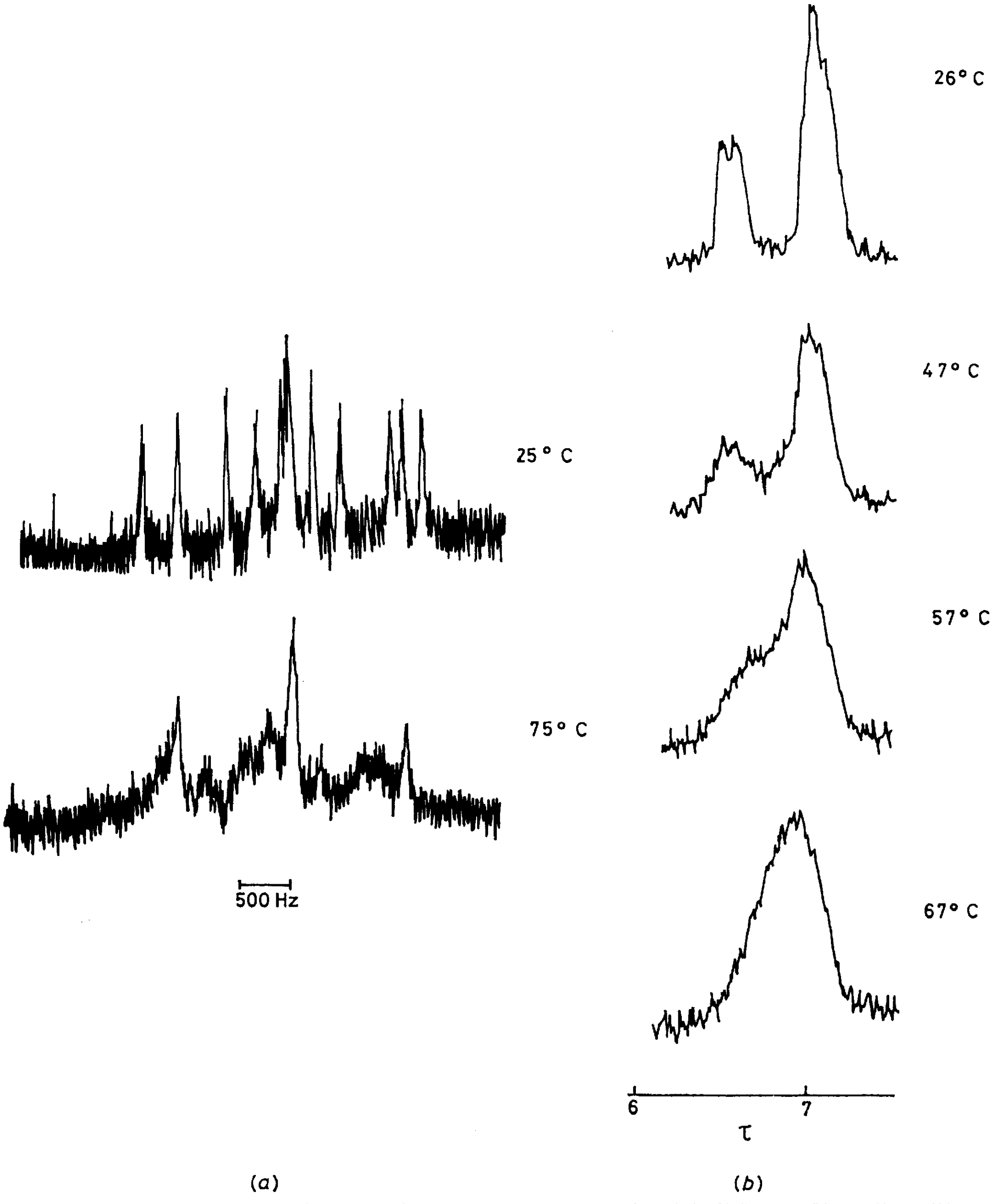

FIGURE 5 Variable-temperature ^{19}F (*a*) and ^{1}H (*b*) n.m.r. spectra of $[(Ph_3P)\{(Me_2N)F_2P\}_2RuCl_3RuCl(PPh_3)_2]$

An alternative synthesis of (1) *via* the thermal decomposition of the monomeric complex $[RuCl_2(dmf)(PF_3)(PPh_3)]$ could also involve a dichloro-bridged dimeric intermediate. The complex $[RuCl_2(PEtPh_2)_3]$ is also reported to dimerise in solution forming an unstable complex which then rearranges to $[(Ph_2EtP)_3RuCl_3RuCl(PEtPh_2)_2]$.[24] Similar behaviour has also been reported for $[\{RuCl_2L(PPh_3)_2\}_2]$ which affords $[(Ph_3P)_2LRuCl_3RuCl(L)(PPh_3)]$ (L = CS or CO),[8,22] while $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ rearranges to $[Rh_2(\eta\text{-}C_5Me_5)_2Cl_3][BPh_4]$ on treatment with sodium tetraphenylborate.[27]

Attempts to obtain a binuclear complex containing PF_3 which contains a double chloro-bridge by treatment of $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ [21] with 2 equivalents of PF_3 led instead to the production of the trichloro-bridged complex (1). A similar reaction occurred with $PF_2(NMe_2)$. The complex $[RuCl_2(dmf)\{PF_2(NMe_2)\}(PPh_3)_2]$, which dimerises to the trichloro-bridged complex faster than the trifluorophosphine analogue, only exhibits lines in the ^{31}P n.m.r. spectrum for the monomeric and trichloro-bridged dimeric complexes.[1]

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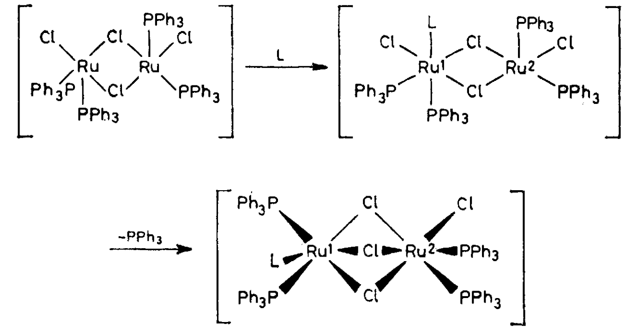
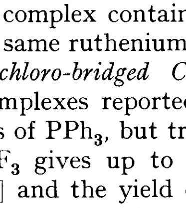
[27] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **30**, 127.

Support for an alternative mechanism involving a concerted reaction with phosphine elimination comes from the reaction of $[RuCl_2(PPh_3)_3]$ with $[RuBr_2(CO)(dmf)(PPh_3)_2]$ [9] in which both halogens initially on the carbonyl complex become bridging ligands. Likewise, $[RuCl_2(CO)(dmf)(PPh_3)]$ and $[RuBr_2(PPh_3)_3]$ afford $[(Ph_3P)_2(OC)RuBrCl_2RuBr(PPh_3)_2]$.[9] There is no evidence for a dimeric complex containing more than two PPh_3 ligands on the same ruthenium atom.

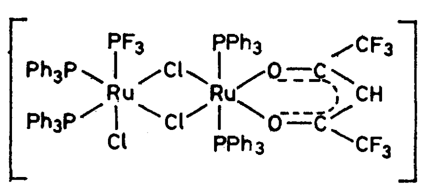


Reactions of Trichloro-bridged Complexes.—All the trichloro-bridged complexes reported are stable in the presence of an excess of PPh_3, but treatment of (1) with 2 equivalents of PF_3 gives up to 50% yields of *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ and the yield can be increased in the presence of PPh_3. A similar reaction occurs between (2) and $PF_2(NMe_2)$. Trifluorophosphine reacts readily with (4) in the presence of PPh_3 to afford high yields of the colourless crystalline monomeric complex $[RuCl_2(CO)(PF_3)(PPh_3)_2]$ (8). The high-field doublet in the $^{31}P-\{^1H\}$ n.m.r. spectrum of (8) is assigned to the resonance of two magnetically equivalent PPh_3 groups coupled to PF_3 [$^2J(PRuP')$], while the low-field PF_3 resonance occurs as the expected triplet [$^2J(PRuP')$] of quartets [$^1J(PF)$]. The magnitude of $^2J(PRuP')$ indicates that the PPh_3 ligands are both *cis* to the PF_3, and since a mutually *trans* arrangement of CO and PF_3 is unlikely we assign the structure shown below, which is analogous to that of *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ recently established by *X*-ray crystallography.[28]



(8)

A tetrahydrofuran (thf) solution of (2) reacts with an equimolar amount of thallium 1,1,1,5,5,5-hexafluoropentane-2,4-dionate to yield the salmon-pink complex (9), formulated as $[Ru_2Cl_3(PF_3)(PPh_3)_4(CF_3COCHOCCF_3)]$. The i.r. spectrum of (9) exhibits a strong band at 1 660 cm^{-1} assigned to ν(C=O) of a bidentate pentanedionate group, while strong bands at 1 208 and 1 150 cm^{-1} and 890, 879, and 845 cm^{-1} are assigned to ν(C–F) and ν(P–F) modes respectively. On the basis of the ^{19}F n.m.r. spectrum, which exhibits a low-field doublet [ϕ(F) 7.7 p.p.m., $^1J(PF)$ 1 270 Hz] for the PF_3 ligand and a high-field singlet [ϕ(F) 73.8 p.p.m.] of two equivalent CF_3 groups, (9) is tentatively assigned the following structure.



(9)

EXPERIMENTAL

General procedures were as described earlier.[1]

Preparation of Tri-μ-chloro-chlorobis(trifluorophosphine)-tris(triphenylphosphine)diruthenium(II) (1).—(*i*) *Reaction of* $[RuCl_2(PPh_3)_3]$ *with trifluorophosphine*. A mixture of $[RuCl_2(PPh_3)_3]$ (0.510 g, 0.53 mmol), trifluorophosphine (0.051 g, 0.58 mmol), and benzene (10 cm^3) was shaken in an ampoule and warmed from −196 °C to room temperature, when a rapid reaction occurred involving a series of colour changes from brown to violet to red and finally to pale yellow. After 4 h at room temperature, removal of solvent afforded a red oil which was washed with hexane (10 cm^3) and recrystallisation from dichloromethane–hexane gave orange-yellow *crystals* of $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$ (0.280 g, 0.21 mmol, 74%), m.p. 191—192 °C [Found: C, 49.6; H, 3.2%; *M* (osmometrically) 1 346. $C_{54}H_{45}Cl_4F_6P_5Ru_2$ requires C, 49.6; H, 2.5%; *M* 1 306]. Infrared spectrum in Nujol mull: 3 060w, 1 587w, 1 572, 1 484mw, 1 438m, 1 191w, 1 160w, 1 099w (sh), 1 090m, 1 076w, 1 030w, 1 002w, 892w (sh), 880vs, 870s (sh), 860w (sh), 759w (sh), 750m, 743w, 712w (sh), 703m, 697s, 690w (sh), 621w, 554vw (sh), 550ms, 529vs, 509w, 476w, and 459w cm^{-1}. Recrystallisation from thf–hexane gave yellow crystals of (1) as the 1 : 2 solvate (Found: C, 51.5; H, 4.4. $C_{62}H_{61}Cl_4F_6O_2P_5Ru_2$ requires C, 51.3; H, 4.2%).

(*ii*) *Reaction of* $[RuCl_2(PPh_3)_3]$ *with cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$. A solution of $[RuCl_2(PPh_3)_3]$ (0.195 g, 0.20 mmol) and *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$ (0.177 g, 0.20 mmol) in acetone (100 cm^3) heated for 6 h gave an oil which was washed with hexane (10 cm^3) and recrystallisation from dichloromethane–hexane gave yellow crystals of (1) (0.264 g, 0.18 mmol, 90%), m.p. 184 °C (Found: C, 49.8; H, 3.5%).

(*iii*) *Reaction of* $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ *with* PF_3. Similarly, $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$ (1.113 g, 0.74 mmol), PF_3 (0.149 g, 1.69 mmol), and benzene (20 cm^3) heated at 60 °C for 30 min gave a red oil which was purified as above to give (1) (0.423 g, 0.33 mol, 45%) (Found: C, 50.5, H, 4.7%) whose i.r. and ^{19}F n.m.r. spectra were identical with those of the previous sample. A small amount (0.103 g, 0.11 mmol, 8%) of $[RuCl_2(PF_3)_2(PPh_3)_2]$ was also obtained.

(*iv*) *Thermal decomposition of* $[RuCl_2(dmf)(PF_3)(PPh_3)_2]$. A solution of $[RuCl_2(dmf)(PF_3)(PPh_3)]$ (0.182 g, 0.21 mmol) in CH_2Cl_2 (50 cm^3) heated for 3 h gave (1) (0.079 g, 0.06 mmol, 57%) (Found: C, 49.1; H, 3.5; N, 0.0%) and a smaller amount (15%) of starting material.

Preparation of Tri-μ-chloro-chlorotrifluorophosphinetetrakis(triphenylphosphine)diruthenium(II) (2).—Similarly to the preparation of (1), $[RuCl_2(PPh_3)_3]$ (1.164 g, 1.22 mmol) and PF_3 (0.585 g, 0.66 mmol) gave deep red

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

crystals of $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PPh_3)_2]$ isolated as the 2 : 1 dichloromethane solvate (0.834 g, 0.55 mmol, 91%), m.p. 166 °C (decomp.) (Found: C, 56.9; H, 4.2. $C_{72.5}H_{61}Cl_5F_3P_5Ru_2$ requires C, 57.1; H, 4.0%). Infrared spectrum in Nujol: 3 056w, 1 587w, 1 572w, 1 483w, 1 433m, 1 318vw, 1 269w, 1 195 (sh), 1 191mw, 1 159w, 1 088s, 1 080w (sh), 1 030w, 1 001mw, 932w,br, 870vw, 863vs, 852w (sh), 848w (sh), 765w, 753w (sh), 750w, 741s, 735w (sh), 715w, 708w (sh), 698vs,br, 684w, 621w, 550w, 544vs, 527vs,br, 550ms, 466w, 440w, 524w (sh), 420mw, and 400w cm^{-1}. A small amount of (1) was also obtained from the mother liquor.

Preparation of Tri-μ-chloro-chlorobis[(dimethylamino)difluorophosphine]tris(triphenylphosphine)diruthenium(II) (3).—(*i*) *From* $[RuCl_2(PPh_3)_2]$. The complex $[RuCl_2(PPh_3)_3]$ (0.982 g, 1.03 mmol) and $PF_2(NMe_2)$ (0.116 g, 1.03 mmol) in benzene (25 cm^3) gave a red oil after 15 min at room temperature. After washing with hexane recrystallisation from CH_2Cl_2–hexane gave orange-yellow *crystals* of $[(Ph_3P)_2\{(Me_2N)F_2P\}RuCl_3RuCl\{PF_2(NMe_2)\}(PPh_3)_2]$ isolated as the 2 : 1 dichloromethane solvate (0.482 g, 0.36 mmol, 71%), m.p. 176 °C (Found: C, 50.0; H, 4.4; N, 2.0. $C_{58.5}H_{58}Cl_5F_4N_2P_5Ru_2$ requires C, 50.2; H, 4.15; N, 2.0%). Infrared spectrum in Nujol: 3 060w, 3 045w, 1 584w, 1 571w, 1 482w, 1 434mw, 1 296mw,br, 1 263w, 1 193w (sh), 1 188mw, 1 162w, 1 158w (sh), 1 090m, 1 071w, 1 029w, 1 000w (sh), 990vs, 930w, 863vw, 852w, 848w, 827w (sh), 815s, 789m, 777s, 759vw, 746s, 739m, 733vw, 720vs, 703w, (sh), 696vs, 648w (sh), 620w, 542s, 527vs, 523vs, 516w (sh), 502m (sh), 462m, 458w (sh), 452vw (sh), 430w, 417w, 370w, 340w, 335w, 325w, and 304mw cm^{-1}. A small amount (10%) of $[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ was also obtained.

(*ii*) *From* $[\{RuCl_2(OCMe_2)(PPh_3)_2\}_2]$. A mixture of $[\{RuCl_3(OCMe_2)(PPh_3)_2\}_2]$ (0.493 g, 0.33 mmol) and $PF_2(NMe_2)$ (0.075, 0.66 mmol) in benzene (20 cm^3) was heated in a sealed tube at 60 °C for 1 h to form orange crystals of the 2 : 1 CH_2Cl_2 solvate of (3) (0.371 g, 83%), m.p. 177 °C (Found: C, 50.5; H, 4.5; N, 2.1%) whose i.r. spectrum was as given above.

(*iii*) *From* $[RuCl_3(dmf)\{PF_2(NMe_2)\}(PPh_3)]$. A freshly prepared sample of $[RuCl_2(dmf)\{PF_2(NMe_2)\}(PPh_3)]$ (0.283 g, 0.32 mmol) was recrystallised from hot CH_2Cl_2 to give the 2 : 1 CH_2Cl_2 solvate of (3) (0.189 g, 87%), m.p. 177 °C (Found: C, 50.6; H, 4.6; N, 2.0%).

Preparation of Dicarbonyltri-μ-chloro-chlorotris(triphenylphosphine)diruthenium(II) (4).—A mixture of $[RuH_2(CO)(PPh_3)_3]$ (1.170 g, 1.27 mmol) and HCl gas (0.110 g, 3.0 mmol) in benzene (20 cm^3) was warmed slowly from −196 °C to room temperature to afford after recrystallisation from CH_2Cl_2–hexane yellow *crystals* of $[(Ph_3P)_2(OC)RuCl_3RuCl(CO)(PPh_3)]$ as the 2 : 1 dichloromethane solvate (0.712 g, 0.60 mmol, 94%), m.p. 214—216 °C (Found: C, 58.9; H, 4.4. $C_{56.5}H_{47}Cl_5O_2P_5Ru_2$ requires C, 58.85; H, 4.0%). Infrared spectrum in Nujol: 3 060w, 3 050w, 1 989w, 1 977vs, 1 950m, 1 586w, 1 570w, 1 484w, 1 436m, 1 264w, 1 196w, 1 191w, 1 162w, 1 100w (sh), 1 092m, 1 083w, 1 031w, 1 001w, 849vw, 756w (sh), 749w, 741s, 710w (sh), 698vs, 620w, 594vs (sh), 589m, 581m, 543m, 529vs, 523s, 509w (sh), 503w (sh), 500w, 465w, 458w, 445w, 437w, and 417w; ν(CO) at 1 979vs and 1949vs cm^{-1} in CH_2Cl_2.

Preparation of Carbonyltri-μ-chloro-chloro(trifluorophosphine)tris(triphenylphosphine)diruthenium(II) (5).—A mixture of $[(Ph_3P)_2(OC)RuCl_3RuCl(PPh_3)_2]$ (0.624 g, 0.42 mmol) and PF_3 (0.039 g, 0.43 mmol) in benzene (20 cm^3) was heated to 100 °C for 3 h to give yellow *needles* of $[(Ph_3P)_2(OC)RuCl_3RuCl(PF_3)(PPh_3)]$ (0.494 g, 0.40 mmol, 94%), m.p. 184 °C (Found: C, 53.2; H, 4.0. $C_{55}H_{45}Cl_5F_3OP_4Ru_2$ requires C, 53.0; H, 3.6%). Infrared spectrum in Nujol: 3 059w, 1 980vs, 1 586vw, 1 573w, 1 482w, 1 435mw, 1 315vw, 1 270vw, 1 264w, 1 190w, 1 162w, 1 092m, 1 082w (sh), 1 030m, 1 001w, 921w, 879vs, 862s, 856s, 852s, 755w (sh), 748s, 742s, 719w (sh), 705w (sh), 698vs, 689w, 620w, 591mw, 582mw, 553m, 541m, 530vs, 520s (sh), 506w (sh), 492w, 463w, 443w, 422w, and 400w; ν(CO) at 1 980vs,br cm^{-1} in CH_2Cl_2. A small amount (7%) of (8) was also obtained.

Preparation of cis-*Carbonyldichloro(trifluorophosphine)bis(triphenylphosphine)ruthenium*(II) (8).—A mixture of (4) (0.137 g, 0.12 mmol), PF_3 (0.030 g, 0.34 mmol), and dichloromethane (10 cm^3) shaken for 12 h at room temperature gave colourless *crystals* of (8) isolated as the 2 : 1 dichloromethane solvate (0.090 g, 0.11 mmol, 46%), m.p. 225 °C (darkens at 218 °C) (Found: C, 53.2; H, 3.8. $C_{37.5}H_{31}Cl_3F_3OP_3Ru$ requires C, 52.7; H, 3.6%). Infrared spectrum in Nujol: 3 060w, 2 022vs, 2 016w, 1 968vw, 1 589w, 1 575w, 1 486w, 1 439m, 1 320vw, 1 268vw, 1 188w, 1 163w, 1 112, 1 095m, 1 089w (sh), 1 075vw, 1 031w, 1 002w, 902vw, 887vs, 877vs, 870vs, 857w (sh), 759w, 751m, 740m, 710s, 703s, 690w (sh), 621w, 569s, 549w, 524vs, 509s, 500w, 460w, 439w, 435w, 424w, 400vw, 394w, 340w, 296w, and 260w,br cm^{-1}. The yield was improved by adding PPh_3 to the reaction mixture.

Preparation of Tri-μ-chloro-chlorobis[(dimethylamino)difluorophosphine]tris(triphenylphosphine)diruthenium(II) (6).—A solution of $[RuCl_2(PPh_3)_3]$ (0.315 g, 0.33 mmol) and $[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ (0.303 g, 0.33 mmol) in acetone (120 cm^3) was heated under reflux for 5.5 h. Removal of solvent left an oil which was washed with hexane (2 × 10 cm^3) and recrystallisation from dichloromethane–hexane gave deep red *crystals* of $[(Ph_3P)\{(Me_2N)F_2P\}_2RuCl_3RuCl(PPh_3)_2]$ (0.366 g, 0.27 mmol, 82%), m.p. 161 °C (Found: C, 51.6; H, 4.2; N, 2.2. $C_{58}H_{57}Cl_4F_4N_2P_5Ru_2$ requires C, 51.3; H, 4.2; N, 2.1%). Infrared spectrum in Nujol: 3 058w, 1 590w, 1 573w, 1 487w, 1 437w, 1 302m, 1 193w (sh), 1 184m, 1 168w (sh), 1 091s, 1 078w, 1 032w, 992vs, 934vw, 862s, 857s, 848s, 840m, 830s, 808w, 789w, 757s, 752s, 733w, 719s, 700vs, 689w (sh), 624w, 548vs, 529vs,br, 507w, 465w, 442w (sh), and 432mw cm^{-1}.

Reaction of $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$ *with Trifluorophosphine*.—A mixture of (1) (0.100 g, 0.08 mmol), dichloromethane (15 cm^3), and PF_3 (0.532 g, 6.65 mmol) shaken at room temperature for 18 h gave an oil which was recrystallised from dichloromethane–hexane to give colourless crystals of cis-*dichlorobis(trifluorophosphine)bis(triphenylphosphine)ruthenium*(II) (0.060 g, 0.07 mmol, 43%). The yield was increased by the addition of PPh_3 to the reaction mixture.

Reaction of $[RuCl_2(PPh_3)_3]$ *with cis*-$[RuCl_2(CO)_2(PPh_3)_2]$.—A solution of $[RuCl_2(PPh_3)_3]$ (0.391 g, 0.41 mmol) and *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ (0.307 g, 0 41 mmol) in acetone (100 cm^3) heated under reflux for 4.5 h afforded a red crystalline precipitate of the unidentified complex (7) (0.083 g), m.p. 135—136 °C (decomp.) (Found: C, 60.8; H, 5.0%). Infrared spectrum in Nujol: 3 060w, 1 715ms, 1 653m, 1 589w, 1 575w, 1 488w, 1 440w, 1 370w, 1 320w, 1 247w, 1 229w, 1 199w, 1 161w, 1 123w, 1 098m, 1 087w (sh), 1 032w, 1 005w, 978w, 931vw, 855w, 764mw, 756s, 750vs, 728w, 715w (sh), 711vs, 700vs, 689w, 621w, 588w, 550s, 544vs, 532vs, 521w (sh), 511w, 505m, 475w, 469w, 445w, 430mw, 327w, 295w, 272w, and 252w cm^{-1}. Phosphorus n.m.r. resonances at 85.0, 89.1, 92.5, and 100.6 p.p.m. relative to $P(OMe)_3$; *J*(PRuP′) 36.6 Hz. An almost quantitative recovery of $[RuCl_2(CO)_2(PPh_3)_2]$ was obtained from the acetone solution.

Preparation of Di-μ-chloro-chloro(1,1,1,5,5,5-*hexafluoropentane*-2,4-*dionato*)(*trifluorophosphine*)*tetrakis*(*triphenylphosphine*)*diruthenium*(II) (9).—A solution of thallium(I) 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (0.177 g, 0.43 mmol) in thf (10 cm^3) was added to a solution of (2) (0.632 g, 0.43 mmol) in thf (25 cm^3) and the mixture stirred for 1 h at room temperature to give a red oil which was washed with hexane. Recrystallisation from dichloromethane–hexane gave salmon-pink crystals of $[Ru_2Cl_3(CF_3COCHOCCF_3)(PF_3)(PPh_3)_4]$ (0.395 g, 0.24 mmol, 56%), m.p. 184 °C (decomp.) (Found: C, 56.8; H, 4.1. $C_{77}H_{61}Cl_3F_9O_2P_5Ru_2$ requires C, 56.5; H, 3.75%). Infrared spectrum in Nujol: 3 050w, 1 660vs, 1 651w (sh), 1 488w, 1 440m, 1 208s, 1 195w (sh), 1 168vw, 1 165w, 1 150mw, 1 093m, 1 080w, 1 031w, 1 004w, 980vs, 879s, 861w, 850w (sh), 845m, 839w, 832w, 775vw, 760w (sh), 735w (sh), 751m, 745m, 731mw, 725w, 710s, 700vs, 689w (sh), 621w, 554w, 545s, 533vs, 519s, 512w, 505w, 464w, 453w, 429w,br, 405vw, 333w, 329w, and 323 cm^{-1}.

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