Trifluorophosphine Complexes of Rhodium(I): Syntheses and Ligand-exchange Studies

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The complexes $[RhX(CO)_2]_2$ (X = Cl, Br, or I) react with an excess of trifluorophosphine at room temperature to afford the red, volatile, crystalline di-μ-halogenotetrakis(trifluorophosphine)dirhodium(I) complexes, $[RhX(PF_3)_2]_2$, in almost quantitative yield. Binuclear mixed carbonyl trifluorophosphine complexes, $Rh_2Cl_2(PF_3)_x(CO)_{4-x}$ (x = 1, 2, or 3), are obtained by treatment of $[RhCl(CO)_2]_2$ with smaller amounts of PF_3, and are also produced as a result of ready intermolecular ligand-exchange reactions between $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$ in solution at room temperature. The complex $[RhCl(PF_3)(CO)]_2$ has one PF_3 group co-ordinated to each rhodium atom. The red complexes $[RhX(PF_3)_2]_2$ react further with PF_3 to yield yellow $RhX(PF_3)_4$ compounds which are stable at room temperature only under a pressure of PF_3. Fluorine-19 n.m.r. studies show that exchange between PF_3 or CO and the co-ordinated PF_3 ligands of $[RhCl(PF_3)_2]_2$ occurs easily.

The chemical and physical properties of fluorophosphine complexes of transition metals are usually very similar to those of the corresponding carbonyl complexes.[1,2] The presence of fluorine-19 and phosphorus-31 nuclei (both with $I = \frac{1}{2}$, 100% natural abundance) in fluorophosphine complexes, however, offers advantages in studying exchange processes by means of n.m.r. spectroscopy. Ready ligand exchange has frequently been observed for rhodium(I) complexes; for example, the well known carbonyl complex $[RhCl(CO)_2]_2$ undergoes immeasurably fast exchange with ^{14}CO [3] and $C^{18}O$,[4] while intermolecular ligand exchange has also been established in the structurally related complexes *trans*-$RhCl(CO)(PPh_3)_2$,[3,5] $RhCl(PPh_3)_3$,[6] and *trans*-$RhCl(PF_3)(PPh_3)_2$.[7]

There is considerable current interest in the function of organophosphine rhodium(I) complexes as homogeneous catalysts for several reactions where ready ligand exchange is believed to play an important role.[8-10] Such considerations led us to investigate convenient synthetic routes to rhodium(I) complexes containing fluorophosphine ligands.

RESULTS AND DISCUSSION

We recently briefly described the synthesis of the dark red sublimable complex di-μ-chloro-tetrakis(trifluorophosphine)dirhodium(I), $[RhCl(PF_3)_2]_2$, by displacement of ethylene from $[RhCl(C_2H_4)_2]_2$ under mild conditions.[7] Bennett *et al.* independently obtained $[RhCl(PF_3)_2]_2$ from the analogous cyclo-octene rhodium(I) complex.[11] The first reported synthesis of $[RhCl(PF_3)_2]_2$ involved the passage of PF_3 over a heated mixture of rhodium trichloride and copper powder, but gave only a very low yield of the product.[12]

A dimeric structure with chlorine bridges between the rhodium atoms was established for $[RhCl(PF_3)_2]_2$ by the observation of the parent-ion peak in the mass spectrum and peaks corresponding to $Rh_2Cl_2(PF_3)_3^+$, $Rh_2Cl_2(PF_3)_2^+$, $Rh_2Cl_2(PF_3)^+$, and $Rh_2Cl_2^+$. The solid-state structure of $[RhCl(PF_3)_2]_2$ is presumably similar to that found for $[RhCl(CO)_2]_2$ where the two essentially planar $(CO)_2RhCl$ groups intersect at an angle of 124°.[13]

We now find that when $[RhCl(CO)_2]_2$ reacts with a large excess of PF_3, the carbon monoxide is completely replaced by the phosphine under mild conditions to form $[RhCl(PF_3)_2]_2$ in almost quantitative yield. It has also been shown by us [7] and others [11] that carbon monoxide can completely displace PF_3 from $[RhCl(PF_3)_2]_2$ to yield $[RhCl(CO)_2]_2$, suggesting that these displacement reactions proceed *via* the intermediates $Rh_2Cl_2(PF_3)_x(CO)_{4-x}$ (x = 1—3), and this proved to be the case.

$$[RhCl(CO)_2]_2 \underset{CO}{\overset{PF_3}{\rightleftharpoons}} [RhCl(PF_3)_2]_2$$

When PF_3 and $[RhCl(CO)_2]_2$ in a 4 : 1 molar ratio react in a sealed tube at room temperature in the absence of solvent, a red solid sublimable product is obtained after removal of the unreacted PF_3 and the CO displaced. The mass spectrum of the product shows parent ions for the three binuclear complexes $[RhCl(PF_3)_2]_2$, $[Rh_2Cl_2(PF_3)_3(CO)]$, and $[RhCl(PF_3)(CO)]_2$ in the approximate ratio 11 : 13 : 5. In accord with this, the i.r. spectrum of the product exhibits three ν(CO) modes (2097m, 2058vs, and 2030m cm^{-1}) which differ from those observed for $[RhCl(CO)_2]_2$ (2106s, 2090vs, and 2033vs cm^{-1}) indicating that the reaction product is not simply a mixture of $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$. If each molecule of PF_3 absorbed displaces one CO from $[RhCl(CO)_2]_2$, the stoicheiometry of reaction shows that the composition of the product is $RhCl(PF_3)_{1.3}(CO)_{0.7}$ and elemental analyses are consistent with this formula. No evidence was found for

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[10] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1392, and references therein.

[11] M. A. Bennett and D. J. Patmore, *Chem. Comm.*, 1969, 1510; *Inorg. Chem.*, 1971, **10**, 2387.

[12] Th. Kruck, N. Derner, and W. Lang, *Z. Naturforsch.*, 1966, **21b**, 1020.

[13] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

the formation of the previously proposed monomeric complex *trans*-$RhCl(PF_3)_2(CO)$.[14]

The ^{19}F n.m.r. spectrum of the reaction product exhibits only two resonances (denoted A and B in Figure 1). It seems that in these binuclear complexes the resonance of the fluorine nuclei of PF_3 molecules attached to one rhodium atom is insensitive to the nature of the substituents on the other rhodium atom. Thus the resonance (A) which is observed for $[RhCl(PF_3)_2]_2$ may more generally be assigned to the moiety (*a*) (X = Cl), while the higher field doublet of doublets (B) can be assigned to species (*b*) (X = Cl), where the vacant sites are occupied by either PF_3 or CO molecules. The intensity ratio of (A) : (B) is *ca.* 6 : 7 as expected for a product of empirical formula $RhCl(PF_3)_{1\cdot 3}(CO)_{0\cdot 7}$, assuming that species containing two CO molecules bound to one rhodium atom are present to a negligible extent.

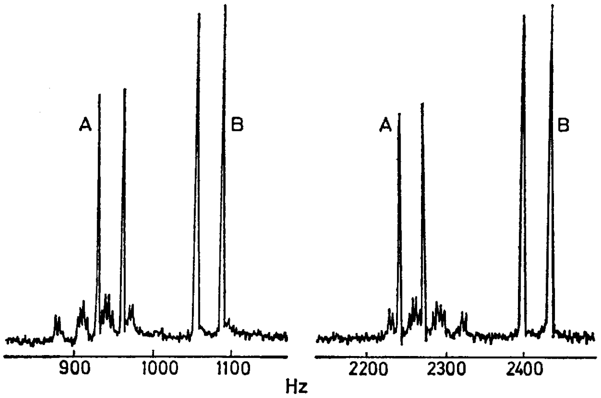
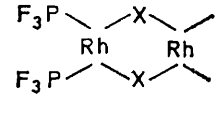
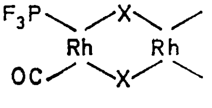


FIGURE 1 ^{19}F N.m.r. spectrum of the product of the reaction of PF_3 with $[RhCl(CO)_2]_2$ in 4 : 1 molar ratio



(*a*)



(*b*)

Resonance (A), which is observed for $[RhCl(PF_3)_2]_2$, represents the X spectrum of an $[X_3A]_2$ spin system (X = fluorine, A = phosphorus) of which each line is further split into a doublet by coupling to the ^{103}Rh nucleus. The fine structure arises from phosphorus–phosphorus coupling through the metal atom, and has commonly been observed for fluorophosphine complexes.[15,16] Detailed analysis of the ^{19}F n.m.r. spectrum of $[RhCl(PF_3)_2]_2$ is discussed elsewhere.[17] Resonance (B) is a doublet of doublets from coupling to phosphorus [^1J(PF) 1343 Hz] and rhodium [^2J(RhF) 34 Hz].

When PF_3 and $[RhCl(CO)_2]_2$ react in a 12 : 1 molar ratio, the mass spectrum of the red crystalline product establishes the presence of both the binuclear complexes $[RhCl(PF_3)_2]_2$ and $Rh_2Cl_2(PF_3)_3(CO)$. The stoicheiometry of the reaction and elemental analysis indicate that the product has the empirical formula $RhCl(PF_3)_{1\cdot 91}(CO)_{0\cdot 09}$. The i.r. spectrum shows one ν(CO) mode at 2055 cm^{-1} which is identical to that originally assigned to '*trans*-$RhCl(PF_3)_2(CO)$,'[14] strongly suggesting that the latter substance was incorrectly formulated and is in fact a mixture of the dimeric $[RhCl(PF_3)_2]_2$ and $Rh_2Cl_2(PF_3)_3(CO)$ complexes. The ^{19}F n.m.r. spectrum of the product exhibits the resonances (A) and (B) as in Figure 1, but the intensity ratio of (A) : (B) is, as expected, much greater than in Figure 1.

The reaction of PF_3 with $[RhCl(CO)_2]_2$, which simply results in successive replacement of the CO molecules by PF_3, should be contrasted with the behaviour observed for other phosphorus donor ligands. For example, triphenylphosphine reacts with $[RhCl(CO)_2]_2$ to yield the well known monomeric square planar *trans*-$RhCl(PPh_3)_2(CO)$, from which it is not possible to displace the CO molecule by reaction with excess triphenylphosphine.[18] The intermediate in this reaction has recently been shown to be $[RhCl(Ph_3P)(CO)]_2$.[19,20] Triaryl phosphites react similarly with $[RhCl(CO)_2]_2$ to form the monomeric complexes *trans*-$RhCl[P(OAr)_3]_2(CO)$, from which it is possible to displace the CO with excess of the phosphite, producing $RhCl[P(OAr)_3]_3$.[21]

Another convenient route to the mixed carbonyl trifluorophosphine complexes $Rh_2Cl_2(PF_3)_x(CO)_{4-x}$ (x = 1—3) is provided by ligand-exchange reactions which immediately occur when solutions of the parent dimeric complexes $[RhCl(PF_3)_2]_2$ and $[RhCl(CO)_2]_2$ are mixed at room temperature. Addition of $[RhCl(PF_3)_2]_2$ to a benzene solution of $[RhCl(CO)_2]_2$ causes the ν(CO) region of the i.r. spectrum to change in appearance as illustrated in Figure 2. For a 1 : 1 mixture of $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$ three ν(CO) modes are visible (2100s, 2055vs, 2032s) and it might be expected that the major species present in solution is $[RhCl(PF_3)(CO)]_2$.

From an equimolar mixture of $[RhCl(CO)_2]_2$ and the ethylene complex $[RhCl(C_2H_4)_2]_2$ in benzene, Powell and Shaw[22] were able to isolate $[RhCl(C_2H_4)(CO)]_2$ which exhibited only one ν(CO) mode at 2000 cm^{-1}. By analogy it might be expected that $[RhCl(PF_3)(CO)]_2$ would also exhibit one ν(CO) frequency and it seems that the observation of more than one mode is probably due to $[RhCl(PF_3)(CO)]_2$ always being in equilibrium with the species $Rh_2Cl_2(PF_3)_3(CO)$ and $Rh_2Cl_2(PF_3)(CO)_3$ and possibly with smaller amounts of $[RhCl(PF_3)_2]_2$ and $[RhCl(CO)_2]_2$. Further evidence for this equilibrium comes from the ambient-temperature mass spectrum of the product prepared by mixing solutions of $[RhCl(CO)_2]_2$

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[22] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 211.

and $[RhCl(PF_3)_2]_2$ in a 1 : 1 ratio, which establishes that although the major component is indeed $[RhCl(PF_3)(CO)]_2$, appreciable amounts of $Rh_2Cl_2(PF_3)_3(CO)$ and $Rh_2Cl_2(PF_3)(CO)_3$ are also present together with a very small amount of $[RhCl(PF_3)_2]_2$.

When $[RhCl(CO)_2]_2$ is added to a solution of $[RhCl(PF_3)_2]_2$, the resonance (A) in the ^{19}F n.m.r. spectrum diminishes in intensity and resonance (B) appears and grows in intensity with further addition of $[RhCl(CO)_2]_2$. When $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$ are mixed in a 1 : 1 ratio, resonance (B) is found to have much greater intensity than resonance (A), and the major species present in solution is probably $[RhCl(PF_3)(CO)]_2$. The lack of any fine structure around the doublet of doublets pattern (coupling to phosphorus and rhodium) of resonance (B) implies the absence of geminal phosphorus–phosphorus coupling and establishes that only one PF_3 molecule is bonded to each rhodium atom. Thus the molecule $[RhCl(PF_3)(CO)]_2$ may be represented by one of the structures (I) or (II):

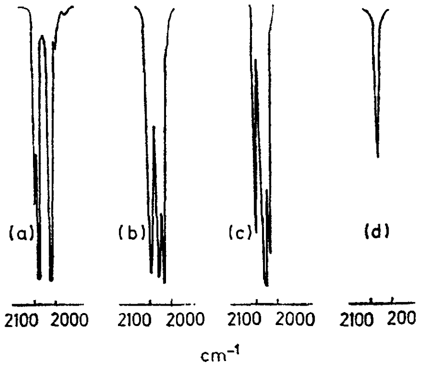
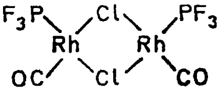
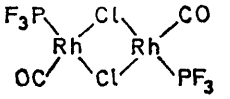


FIGURE 2 Infrared spectra in the carbonyl stretching region of benzene solutions of (a) $[RhCl(CO)_2]_2$, (b) $[RhCl(CO)_2]_2$ + a small amount of $[RhCl(PF_3)_2]_2$, (c) a 1 : 1 molar ratio of $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$, and (d) $[RhCl(PF_3)_2]_2$ + a small amount of $[RhCl(CO)_2]_2$



(I)



(II)

The ready interchange between CO and PF_3 in these complexes underlines the similarity of co-ordination ability of the two ligands, noted previously for many other systems.[1,2]

The reaction of PF_3 with other halogenodicarbonylrhodium dimers $[RhX(CO)_2]_2$ (X = Br or I) follows a similar path to that observed for the chloro complex, *i.e.*, when a sufficient excess of PF_3 is employed, the carbonyl groups are completely replaced:

$$[RhX(CO)_2]_2 \xrightarrow[\text{of PF}_3]{\text{excess}} [RhX(PF_3)_2]_2$$

The red volatile solid products which were identified by elemental analyses and mass spectroscopy are rather less stable than $[RhCl(PF_3)_2]_2$, especially in solution. The reaction of the readily accessible $[RhX(CO)_2]_2$ (X = Br or I) complexes with excess of PF_3 in a sealed tube in the absence of solvent thus provides a convenient high-yield synthesis of the complexes $[RhX(PF_3)_2]_2$. The ^{19}F n.m.r. spectra of the latter compounds are similar to that observed for $[RhCl(PF_3)_2]_2$, but rather less well resolved due to faster decomposition of the complexes in solution. Mass spectra exhibit parent-ion peaks and peaks corresponding to successive loss of all four trifluorophosphine ligands with retention of the halogen-bridged $[Rh_2X_2]$ structure.

When solutions of $[RhBr(PF_3)_2]_2$ or $[RhI(PF_3)_2]_2$ are mixed with the carbonyl complexes $[RhBr(CO)_2]_2$ or $[RhI(CO)_2]_2$ respectively, rapid ligand interchange occurs as for the case of the chloro-complexes described above. The ^{19}F n.m.r. spectra are analogous to that of the mixed chloro-complexes, but are somewhat broader due to the more rapid decomposition of the species formed in solution. The resonance of type (B) for the species (*b*) (X = Cl, Br, I) always occurs at higher field and has a larger value for $^2J(RhF)$ than the resonance [type (A)] of species (*a*). Relevant spectral parameters are listed in the Table.

^{19}F N.m.r. data for rhodium trifluorophosphine complexes (benzene solutions)

Complex	$^1J(PF)$/Hz	$^2J(RhF)$/Hz	$\phi(F)$ [a]
$[RhCl(PF_3)_2]_2$ (A) in Figure (1) *	1311 [b]	31·5	17·1
(B) in Figure (1) *	1343	34	18·6
$[RhBr(PF_3)_2]_2$	1309 [b]	31·5	15·9
$[RhBr(PF_3)_2]_2$ + $[RhBr(CO)_2]_2$ [c]	1343	33·5	17·9
$[RhI(PF_3)_2]_2$	1316 [b]	31	14·2
$[RhI(PF_3)_2]$ + $[RhI(CO)_2]_2$ [c]	1358	33	16·3

[a] In p.p.m. relative to CCl_3F internal standard. [b] $^1J(PF) + {}^3J(PF')$. [c] Resonance analogous to (B), see Figure (1).

* See text.

When the red complexes $[RhX(PF_3)_2]_2$ (X = Cl, Br, or I) are sealed off with a large excess of PF_3 (pressure *ca.* 8 atm.), yellow solids are formed which melt close to room temperature. These complexes are stable under high vacuum at −78°, but readily decompose on warming to room temperature, evolving PF_3 and regenerating the red $[RhX(PF_3)_2]_2$ compounds:

$$\underset{\text{red}}{[RhX(PF_3)_2]_2} + 2PF_3 \rightleftharpoons \underset{\text{yellow}}{RhX(PF_3)_4}$$
$$(X = Cl, Br, or I)$$

The yellow complexes which were found to contain two extra molecules of PF_3 per rhodium atom thus have the formula $RhX(PF_3)_4$, and are analogous to the rather unstable cobalt and iridium trifluorophosphine complexes $MI(PF_3)_4$ (M = Co or Ir) previously isolated by Kruck *et al.*[23,24] The great volatility of the latter compounds suggests that they are monomeric and thus bridge cleavage has probably occurred in the reaction

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[23] Th. Kruck and W. Lang, *Z. anorg. Chem.*, 1966, **343**, 181.

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of PF_3 with the $[RhX(PF_3)_2]_2$ dimers to produce monomeric $RhX(PF_3)_4$ complexes. Further evidence for a monomeric structure is provided by recent *X*-ray diffraction studies on the related ethylene complex $IrCl(C_2H_4)_4$ which established that this compound is not dimeric.[25] The latter compound is also somewhat analogous to the rhodium trifluorophosphine complexes $RhX(PF_3)_4$ in that it readily loses ethylene to yield the dimeric $[IrCl(C_2H_4)_2]_2$ complex.[25]

Ready intermolecular exchange occurs when an atmosphere of PF_3 is maintained above a solution of $[RhCl(PF_3)_2]_2$, as shown by the collapse of the ^{19}F n.m.r. spectrum to a sharp doublet [^1J(PF) 1330 Hz, ϕ(F) 17·2 p.p.m.] indicating loss of phosphorus–phosphorus and rhodium–fluorine coupling. Similarly, when an atmosphere of CO is maintained above a solution of $[RhCl(PF_3)_2]_2$ in an n.m.r. tube, the ^{19}F n.m.r. spectrum again collapses to a doublet [^1J(PF) 1330 Hz, ϕ(F) 17·9 p.p.m.] as the co-ordinated ligands undergo exchange with CO or with liberated PF_3.

Both these observations provide further illustrations of the extreme ease with which these rhodium(I) complexes undergo ligand-exchange processes.

EXPERIMENTAL

Fluorine-19 n.m.r. spectra were recorded on a Varian HA 100 operating at 94·1 MHz with CCl_3F as internal standard. I.r. spectra were recorded on a Perkin-Elmer PE 337 spectrometer and mass spectra on a Hitachi RMU-6E with the sample chamber at ambient temperature.

Elemental analyses were carried out by Mr. A. G. Olney of this department (for carbon and hydrogen) and by A. Bernhardt, Elbach über Engelskirchen, West Germany (for other elements). Solvents were dried by standard methods.

Except where stated, reactions were carried out in sealed evacuated Pyrex glass tubes using a standard high-vacuum system.

The reactions between PF_3 and $[RhX(CO)_2]_2$ (X = Cl, Br, or I) appeared to have reached equilibrium after a few minutes at room temperature, but the tubes were set aside for *ca.* 16 h before being opened.

None of the complexes formed is notably sensitive to air or moisture, but they were normally handled under nitrogen. Many of the complexes slowly decompose at room temperature (over a period of weeks) as evidenced by a darkening in colour, and samples were therefore kept at −20°.

Di-μ-chloro-tetra(carbonyl)dirhodium(I) was synthesised by the method of Powell and Shaw [22] and purified by sublimation at 80°, 10^{-3} mmHg. Di-μ-bromo-tetra(carbonyl)dirhodium(I) and di-μ-iodo-tetra(carbonyl)dirhodium(I) were synthesised as mentioned by Johnson *et al.*[4] by refluxing $[RhCl(CO)_2]_2$ in hexane with a very large excess of KX (X = Br or I). After the solids had been filtered off and solvent removed under vacuum, the crude products were obtained in yields of 70—80%. Samples for analysis were prepared by sublimation in high vacuum (30—40° for X = Br, 70° for X = I), but as considerable decomposition occurred during sublimation, the crude products were reacted with PF_3 without further purification (Found: C, 10·3. Calc. for $C_4Br_2O_4Rh_2$: C, 10·1%. Found: C, 8·3. Calc. for $C_4I_2O_4Rh_2$: C, 8·4%).

Reaction between Trifluorophosphine and Di-μ-chloro-tetra(carbonyl)dirhodium(I).—(a) *In a* 4 : 1 *molar ratio.* Trifluorophosphine (0·380 g, 4·31 mmol) and $[RhCl(CO)_2]_2$ (0·418 g, 1·07 mmol) were sealed off in a glass ampoule. After the ampoule had stood at room temperature for a few minutes, a red liquid containing some red solid had formed. The ampoule was opened, CO pumped away, and PF_3 (0·124 g, 1·53 mmol) recovered. The red, solid product was sublimed at room temperature under high vacuum to give 0·566 g product, m.p. 29—35°. I.r. spectrum: 2097m, 2058vs, 2030m, 932m, 900vs, 866m cm^{-1} (Nujol mull). The reaction stoicheiometry suggests the empirical formula $RhCl(PF_3)_{1\cdot3}(CO)_{0\cdot7}$ (Found: C, 2·7. $RhCl(PF_3)_{1\cdot3}(CO)_{0\cdot7}$ requires C, 3·1%). The mass spectrum shows the presence of $[RhCl(PF_3)_2]_2$, $[Rh_2Cl_2(PF_3)_3(CO)]$, and $[RhCl(PF_3)(CO)]_2$ in the approximate ratio 11 : 13 : 5.

(b) *A large excess of* PF_3. Trifluorophosphine (1·362 g, 15·48 mmol) and $[RhCl(CO)_2]_2$ (0·503 g, 1·29 mmol) were sealed off and warmed to room temperature affording a pale red liquid containing some red crystals. The CO displaced was pumped away and PF_3 (0·927 g, 10·53 mmol) recovered, indicating that the empirical formula of the product is $RhCl(PF_3)_{1\cdot9}(CO)_{0\cdot09}$. The red solid was sublimed at room temperature under high vacuum, yield 0·789 g, m.p. 66—67° [Found: C, 0·23. $RhCl(PF_3)_{1\cdot91}(CO)_{0\cdot09}$ requires C, 0·34%]. The mass spectrum indicated the presence of $[RhCl(PF_3)_2]_2$ as the major product, together with a lesser amount of $Rh_2Cl_2(PF_3)_3(CO)$. The i.r. spectrum showed a weak ν(CO) mode at 2055 cm^{-1} (Nujol mull).

In order to effect complete displacement of CO, the product (0·540 g) was sealed off again with PF_3 (1·055 g). The tube was opened as before to yield PF_3 (1·045 g) and, after sublimation at 25°, 10^{-3} mmHg, the red complex di-μ-chloro-tetrakis(trifluorophosphine)dirhodium(I) (0·529 g), m.p. 70° (Found: Cl, 11·2; P, 19·7. $Cl_2F_{12}P_4Rh_2$ requires Cl, 11·3; P, 19·7%).

Reaction between Trifluorophosphine and Di-μ-bromo-tetra(carbonyl)dirhodium(I).—In a similar manner, PF_3 (1·346 g, 15·3 mmol) and $[RhBr(CO)_2]_2$ (0·348 g, 0·73 mmol) were sealed off together and formed an orange liquid in the ampoule at room temperature. Carbon monoxide was pumped away, PF_3 (1·092 g, 12·4 mmol) recovered, and the red solid product sublimed at 25°, 10^{-4} mmHg to yield di-μ-bromo-tetrakis(trifluorophosphine)dirhodium(I) (0·474 g, 91%), m.p. 61·5—62° (Found: Br, 22·2; P, 17·1. $Br_2F_{12}P_4Rh_2$ requires Br, 22·3; P, 17·3%). I.r. spectrum: 940s, 920s, 912vs, 900sh, 870s, 720w, 540m, 516m cm^{-1} (Nujol mull).

Reaction between Trifluorophosphine and Di-μ-iodo-tetra(carbonyl)dirhodium(I).—Trifluorophosphine (1·401 g, 15·9 mmol) and $[RhI(CO)_2]_2$ (0·464 g, 0·81 mmol) produced a dark red liquid in the ampoule at room temperature. Carbon monoxide was pumped away, PF_3 (1·119 g, 12·7 mmol) recovered, and the red solid product (0·618 g) was found to exhibit a very weak ν(CO) mode at 2050 cm^{-1} and so some of the product (0·528 g) was resealed with a large excess of PF_3 (1·119 g) to displace the final trace of CO. The recovered PF_3 weighed 1·114 g and the crude red solid (0·497 g) was sublimed at 40°, 10^{-3} mmHg to afford the dark red di-μ-iodo-tetrakis(trifluorophosphine)dirhodium(I), (0·36 g), m.p. 62·5° (Found: I, 31·2; P, 15·2. $F_{12}I_2P_4Rh_2$ requires I, 31·3; P, 15·3%). I.r. spectrum: 933s, 913sh, 906vs, 892sh, 866s, 720w, 547sh, 538s, 523m, 513m cm^{-1} (Nujol mull).

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[25] A. Van der Ent and T. C. van Soest, *Chem. Comm.*, 1970, 225.

Reaction between Trifluorophosphine and Di-μ-chloro-tetrakis(trifluorophosphine)dirhodium(I).— Trifluorophosphine (0·677 g, 7·70 mmol) and $[RhCl(PF_3)_2]_2$ (0·295 g, 0·469 mmol) were sealed off in a glass ampoule (volume *ca.* 20 ml) so that the initial pressure of PF_3 was *ca.* 8 atmospheres at room temperature. A yellow solid was produced. The tube was held at −196°, opened to the vacuum system, and slowly warmed to −78°. Trifluorophosphine (0·514 g, 5·84 mmol) was recovered indicating that the combining ratio of $PF_3 : Rh$ is 1·95 : 1. When the ampoule was warmed to room temperature, the yellow solid decomposed, regenerating the red $[RhCl(PF_3)_2]_2$ and evolving PF_3 (0·161 g, 1·83 mmol). The yellow solid thus has the formula $RhCl(PF_3)_4$.

Reaction between Trifluorophosphine and Di-μ-bromo-tetrakis(trifluorophosphine)dirhodium(I).—Similarly, PF_3 (12·09 mmol) and $[RhBr(PF_3)_2]_2$ (0·42 mmol) formed a yellow solid which melted near room temperature. The tube was opened as above and on warming from −78° to room temperature PF_3 (1·66 mmol) was evolved and $[RhBr(PF_3)_2]_2$ regenerated. The number of molecules of PF_3 absorbed per rhodium atom was 1·97, *i.e.*, the yellow solid is $RhBr(PF_3)_4$.

Reaction between Trifluorophosphine and Di-μ-iodo-tetrakis(trifluorophosphine)dirhodium(I).—As above, PF_3 (9·31 mmol) and $[RhI(PF_3)_2]_2$ (0·30 mmol) afforded a dark red liquid product at room temperature. The ampoule was opened as before and the product in the tube at −78° was an orange-yellow solid. On warming to room temperature, PF_3 (1·15 mmol) was evolved and $[RhI(PF_3)_2]_2$ re-formed, showing that 1·96 molecules of PF_3 were absorbed per rhodium atom in the yellow solid, which thus has the formula $RhI(PF_3)_4$.

Synthesis of 'Di-μ-chloro-di(carbonyl)bis(trifluorophosphine)dirhodium(I)'.—To a solution of $[RhCl(PF_3)_2]_2$ (0·651 g, 1·03 mmol) in dry petroleum (b.p. 40—60°) was added $[RhCl(CO)_2]_2$ (0·401 g, 1·03 mmol) and the solution stirred for 1 h, filtered, and solvent removed in *vacuo* to afford a dark red, volatile solid (0·874 g), m.p. 40·5—41·5° (Found: C, 4·9. $C_2Cl_2F_6O_2P_2Rh_2$ requires C, 4·7%). I.r. spectrum: 2100s, 2060vs, 2037s, 933s, 918sh, 900vs, and 870s cm^{-1} (Nujol mull).

The mass spectrum of the product showed that the major component was $[RhCl(PF_3)(CO)]_2$ with smaller amounts of $Rh_2Cl_2(PF_3)_3(CO)$ and $Rh_2Cl_2(PF_3)(CO)_3$ and a very small amount of $[RhCl(PF_3)_2]_2$.

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