Fluorophosphine Complexes of Rhodium(I). Part II.[1] Phosphine Exchange Studies

By **D. A. Clement** and **J. F. Nixon,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

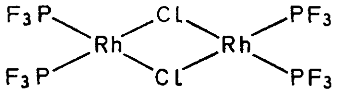
Trifluorophosphine readily displaces ethylene from $[RhCl(C_2H_4)_2]_2$ under mild conditions affording high yields of the red, volatile, dimeric complex $[RhCl(PF_3)_2]_2$, (I). The ^{19}F n.m.r. spectrum of (I) has been fully analysed as the X part of an $[X_3A]_2$ spin system (X = fluorine, A = phosphorus). A rapid intermolecular exchange between free and co-ordinated PF_3 has been observed in this system. The binuclear complex $[RhCl(C_2H_4)(PF_3)]_2$, (II), formed by mixing solutions containing equimolar amounts of $[RhCl(C_2H_4)_2]_2$ and $[RhCl(PF_3)_2]_2$ has been shown to have one ethylene and one trifluorophosphine group attached to each rhodium atom. Complex (I) reacts with an excess of carbon monoxide quantitatively forming $[RhCl(CO)_2]_2$, whereas triphenylphosphine cleaves the halogen bridge affording the square planar complex $RhCl(PF_3)(PPh_3)_2$, (III). Complex (III) has also been obtained directly from $RhCl(PPh_3)_3$ and trifluorophosphine. ^{19}F n.m.r. studies establish the *trans*-stereochemistry of (III) and indicate that the complex does not dissociate in solution. However (III) does undergo a ready intermolecular exchange of its co-ordinated PF_3 and PPh_3 ligands. Difluorotrichloromethylphosphine completely displaces ethylene or trifluorophosphine from $[RhCl(C_2H_4)_2]_2$ and $[RhCl(PF_3)_2]_2$ respectively affording $[RhCl(CCl_3PF_2)_2]_2$. $RhCl(PPh_3)_3$ reacts with CCl_3PF_2 to yield $RhCl(CCl_3PF_2)(PPh_3)_2$.

There has been considerable recent interest in the synthesis and properties of organophosphine–rhodium(I) complexes, and their potential as homogeneous catalysts.[2-4] In view of the known similarity between trifluorophosphine and carbon monoxide in transition metal complexes[5,6] we recently reported[1] the ready synthesis of $[RhCl(PF_3)_2]_2$ (I) from the well known carbonyl dimer $[RhCl(CO)_2]_2$, and we now present fuller details[7] of an alternative low pressure route to (I) from the $[RhCl(C_2H_4)_2]_2$ complex, and further synthetic and exchange studies on some of its derivatives.

RESULTS AND DISCUSSION

The Trifluorophosphine–Rhodium(I) *Complexes* $[RhCl(PF_3)_2]_2$ *and* $[RhCl(PF_3)(C_2H_4)]_2$.—Di-μ-chloro-tetrakis(ethylene)dirhodium(I), $[RhCl(C_2H_4)_2]_2$ readily reacts with an excess of trifluorophosphine in a sealed tube at 60° in the absence of solvent to afford an almost quantitative yield of the red, sublimable complex di-μ-chloro-tetrakis(trifluorophosphine)dirhodium(I), $[RhCl(PF_3)_2]_2$, (I).[1,8,9]

(I)



The ^{19}F n.m.r. spectrum of $[RhCl(PF_3)_2]_2$ [Figure 1(a)] has been fully analysed as the X part of an $[X_3A]_2$ spin system (X = fluorine, A = phosphorus) using the treatment of Harris and Woodman[10] and assuming $J_{XX'} = 0$. Each line in the spectrum is split further by the ^{103}Rh nucleus (100% abundance, $I = \frac{1}{2}$) into a 1 : 1 doublet ($^2J_{Rh-F}$ 31·5 Hz). Chemical shift and coupling constant data are summarised in the Table.

When a slight pressure of ethylene is held above a solution of $[RhCl(PF_3)_2]_2$ the fine structure in the ^{19}F n.m.r. spectrum disappears and the spectrum simplifies to two rather broad bands [Figure 1(b)] as the ethylene

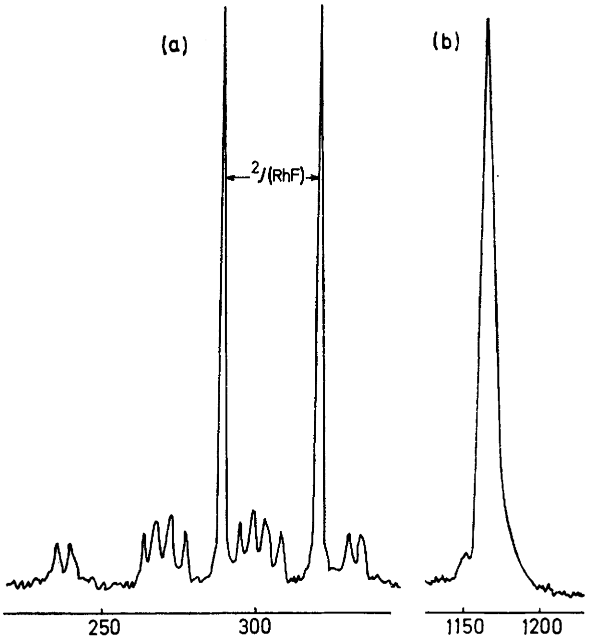


FIGURE 1 (a) The low field half of the ^{19}F n.m.r. spectrum (at 56·4 MHz) of $[RhCl(PF_3)_2]_2$ in benzene solution. An exact mirror image of this pattern occurs at high field; (b) the low field half of the ^{19}F n.m.r. spectrum (at 94·1 MHz) of $[RhCl(PF_3)_2]_2$ in benzene solution under a slight pressure of C_2H_4. An exact mirror image of this pattern occurs 1378 Hz to high field. (Figures are in Hz to high field of CCl_3F).

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[1] Part I, J. F. Nixon and J. R. Swain, *J.C.S. Dalton*, 1972, 1044.

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[3] D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2660 and references therein.

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

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

[6] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

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

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displaces PF_3 from the complex, thus inducing an intermolecular exchange process between co-ordinated and unco-ordinated PF_3 molecules noted previously.[1]

Ligand exchange has been reported in other rhodium(I) complexes [11-14] and is believed to be an important step in many homogeneous catalytic reactions.[2-4]

N.m.r. parameters for rhodium(I)–fluorophosphine complexes

	Complex	$^1J_{(PF)}$ [a]	$^3J_{(PF')}$ [a]	$^1J_{(PF)} + {}^3J_{(PF')}$ [a,b]	$^2J_{(PP')}$ [a]	$^2J_{(RhF)}$ [a]	ϕ_F [c]	Solvent
(I)	$[RhCl(PF_3)_2]_2$	1328	19	1309	63·5 ± 1	31·5	17·0	C_6H_6
	$[RhCl(PF_3)_2]_2 + PF_3$	1378					19·7	CCl_3F
	$[RhCl(PF_3)_2]_2 + C_2H_4$	1329					17·2	CCl_3F
(II)	$[RhCl(C_2H_4)(PF_3)]_2$ [d]	1332				27·0	24·6	Et_2O
(III)	*trans*-$RhCl(PF_3)(PPh_3)_2$	1286	7			32·0	15·2	C_6H_6
	trans-$RhCl(PF_3)(PPh_3)_2 + PPh_3$	1312				32·0	15·2	C_6H_6
	trans-$RhCl(PF_3)(PPh_3)_2 + PF_3$	1403					31·0	C_6H_6
(IV)	$[RhCl(CCl_3PF_2)_2]_2$			1220		21·0	56·5	$CHCl_3$

[a] In Hz. [b] $^1J_{(PF)}$ and $^3J_{(PF')}$ are of opposite sign. [c] In p.p.m. to high field of CCl_3F. [d] The ethylene proton resonance is at τ 6·20 (CCl_3H solution).

When equimolar quantities of $[RhCl(C_2H_4)_2]_2$ and $[RhCl(PF_3)_2]_2$ are shaken together in ether solution at room temperature the yellow complex $Rh_2Cl_2(PF_3)_2(C_2H_4)_2$ (II) can be obtained on careful removal of the solvent. N.m.r. studies indicate that in solution equilibrium (1) lies far to the right.

$$[RhCl(C_2H_4)_2]_2 + [RhCl(PF_3)_2]_2 \rightleftharpoons [Rh_2Cl_2(PF_3)_2(C_2H_4)_2] \quad (1)$$

The complex (II) does show some tendency to disproportionate to the parent dimers on prolonged heating under high vacuum.

The ^1H n.m.r. spectrum of (II) consists of a broad singlet at τ 6·20 which is downfield from that at τ 6·73 for $[RhCl(C_2H_4)_2]_2$.

The ^{19}F n.m.r. spectrum of (II) is similar to that observed for $Rh_2Cl_2(CO)_2(PF_3)_2$ [1] consisting of a widely spaced doublet of doublet pattern of lines arising from coupling with the rhodium and phosphorus nuclei. Thus the structure of $Rh_2Cl_2(PF_3)_2(C_2H_4)_2$ is either II(a) or II(b) *i.e.*, one in which a single PF_3 and ethylene molecule are bonded to each rhodium atom rather than structure II(c).

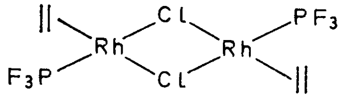
The related complexes $Rh_2Cl_2(CO)_2(C_2H_4)_2$ [15] and $Rh_2Cl_2(PPh_3)_2(C_2H_4)_2$ [16] have been described previously but their structures are unknown.

The ready exchange of co-ordinated and unco-ordinated ligands in these square planar rhodium(I)–trifluorophosphine complexes contrasts with the lack of intermolecular ligand exchange in the related $(\pi\text{-}C_5H_5)Rh(PF_3)_2$ [9,17] and $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$ [18] complexes and may reflect the formal attainment of the inert gas configuration in the latter complexes. It should be noted, however, that the dicarbonyl complex $(\pi\text{-}C_5H_5)Rh(CO)_2$ has been reported to undergo a bimolecular displacement reaction with both phosphites and phosphines,[19] while $(\pi\text{-}C_5H_5)Co(CO)_2$ rapidly undergoes carbon monoxide exchange with ^{14}CO.[20]

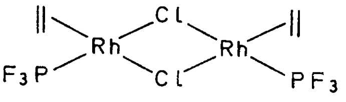
The $[RhCl(PF_3)_2]_2$ complex reacts with an excess of carbon monoxide in refluxing toluene solution affording essentially quantitative yields of $[RhCl(CO)_2]_2$.

$$[RhCl(PF_3)_2]_2 \xrightarrow{\text{excess CO}} [RhCl(CO)_2]_2 + 4PF_3$$

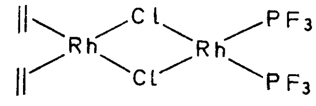
The intermediate binuclear complexes $[Rh_2Cl_2(CO)_x(PF_3)_{4-x}]$ involved in the reverse of this reaction have been discussed in detail elsewhere.[1]



(IIa)



(IIb)



(IIc)

The Complex trans-$RhCl(PF_3)(PPh_3)_2$.—When a toluene solution of $[RhCl(PF_3)_2]_2$ is heated with an excess of triphenylphosphine at 60° ligand substitution and halogen bridge cleavage occur to afford yellow crystals of the chlorobis(triphenylphosphine)trifluorophosphinerhodium(I) complex, $RhCl(PF_3)(PPh_3)_2$ (III). This reaction presumably proceeds *via* the intermediate $[RhCl(PF_3)(PPh_3)]_2$ complex and is analogous to the well known preparation of *trans*-$RhCl(CO)(PPh_3)_2$ from

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[14] D. R. Eaton and S. R. Suart, *J. Amer. Chem. Soc.*, 1968, **90**, 4170.

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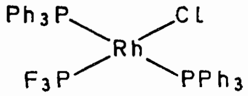
$[RhCl(CO)_2]_2$ and PPh_3.[21] A similar reaction has been briefly described previously[8] but was carried out on a mixture of $[RhCl(PF_3)_2]_2$ and $Rh_2(PF_3)_8$. High yields of complex (III) also result when a benzene solution of $RhCl(PPh_3)_3$ is shaken with PF_3 at room temperature,* but no further incorporation of PF_3 can be effected even when a large excess of trifluorophosphine is used.

The complex (III) is soluble in benzene or chloroform, but insoluble in aliphatic hydrocarbons. The *trans*-stereochemistry of (III) previously suggested by dipole moment measurements[8] has now been fully established by n.m.r. studies. The ^{19}F n.m.r. spectrum of a carefully purified sample of $RhCl(PF_3)(PPh_3)_2$ [Figure 2(a)] shows two widely spaced doublets of triplets arising from spin-coupling with phosphorus, rhodium, and the two equivalent phosphorus nuclei of the PPh_3 groups. Chemical shift and spin coupling data are listed in the Table.

(III)



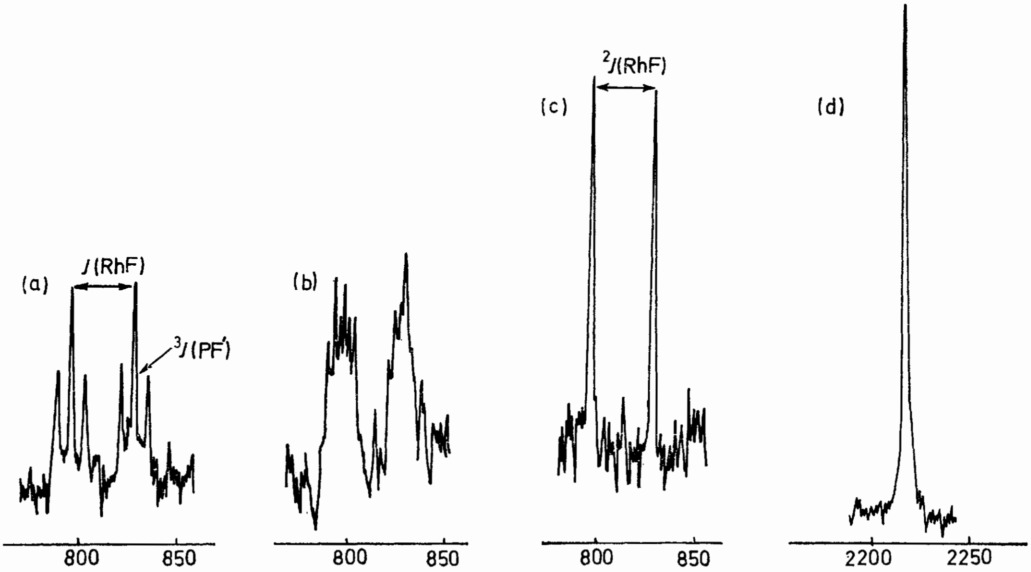


FIGURE 2 The low field halves of the ^{19}F n.m.r. spectra (at 94·1 MHz) of benzene solutions of (a), *trans*-$RhCl(PF_3)(PPh_3)_2$; (b), *trans*-$RhCl(PF_3)(PPh_3)_2$ + trace PPh_3; (c), *trans*-$RhCl(PF_3)(PPh_3)_2$ + PPh_3; (d), *trans*-$RhCl(PF_3)(PPh_3)_2$ + PF_3

The above n.m.r. data, together with previously reported solution molecular weight measurements,[8] clearly indicate that *trans*-$RhCl(PF_3)(PPh_3)_2$ like *trans*-$RhCl(CO)(PPh_3)_2$[22] is undissociated in solution. The analogous $RhCl(PPh_3)_3$ complex was originally reported to undergo significant dissociation in benzene and chloroform solutions[2] but later chemical,[23,24] and n.m.r. studies[14] indicate that there is no appreciable dissociation when oxygen is rigorously excluded from the system.

The ready intermolecular exchange of ligands in *trans*-$RhCl(PF_3)(PPh_3)_2$ has been established by ^{19}F n.m.r. spectroscopy. Thus addition of a very small amount of triphenylphosphine to a solution of *trans*-$RhCl(PF_3)(PPh_3)_2$ in an n.m.r. tube immediately causes the collapse of the triplet pattern in the ^{19}F n.m.r. spectrum to give a broadened doublet [Figure 2(b)] of doublets which sharpen [Figure 2(c)] on addition of further small quantities of PPh_3. This establishes that there is a ready exchange between free and co-ordinated PPh_3 molecules in this system. The retention of spin coupling between rhodium and fluorine on addition of the triphenylphosphine implies that the PF_3 ligand remains co-ordinated to the metal during the triphenylphosphine exchange process.

When a slight pressure of PF_3 is maintained above a solution of *trans*-$RhCl(PPh_3)_2(PF_3)$ the ^{19}F n.m.r. spectrum immediately collapses to a sharp doublet of singlets [Figure 2(d)] indicating loss of rhodium–fluorine coupling as the free and co-ordinated PF_3 molecules undergo intermolecular exchange. The observed fluorine chemical shift, ϕ_F, and coupling constant $^1J_{(PF)}$ depend on the pressure of PF_3 used and as the concentration of PF_3 increases the fluorine chemical shift moves slightly to higher field and there is a simultaneous increase in the magnitude of $^1J_{(PF)}$. N.m.r. data are listed in the Table.

The rapid exchange of ligands presumably involves five-co-ordinate intermediates (A) and (B) which are

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* This reaction has been briefly mentioned by M. A. Bennett and D. L. Milner, *Chem. Comm.*, 1967, 581, without any experimental details.

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analogous to $RhCl(PF_3)_4$. Recently we have synthesised the related five-co-ordinate hydrides $HRh(PF_3)(PPh_3)_3$ and $HRh(PF_3)_2(PPh_3)_2$.[25]

$$\mathrm{RhCl(PPh_3)_2(PF_3) + PPh_3 \rightleftharpoons RhCl(PPh_3)_3(PF_3)} \quad \text{(A)}$$

$$\mathrm{RhCl(PPh_3)_2(PF_3) + PF_3 \rightleftharpoons RhCl(PPh_3)_2(PF_3)_2} \quad \text{(B)}$$

The specific intermolecular exchange between co-ordinated and unco-ordinated triphenylphosphine molecules while the trifluorophosphine remains attached to the metal might be due to preferential loss of triphenylphosphine from the five-co-ordinate complex (A) on steric grounds. The previously mentioned ready formation of *trans*-$RhCl(PF_3)(PPh_3)_2$ from $RhCl(PPh_3)_3$ and PF_3 indicates that the equilibrium (2) lies well to the right.

$$\mathrm{RhCl(PPh_3)_3 + PF_3 \rightleftharpoons \mathit{trans}\text{-}RhCl(PPh_3)_2(PF_3) + PPh_3} \quad (2)$$

The five-co-ordinate intermediate (B) readily loses PF_3, leading to the observed rapid PF_3 exchange, rather rather than forming PPh_3 and $RhCl(PF_3)_2(PPh_3)$. The analogous dicarbonyl complex *cis*-$RhCl(CO)_2(PPh_3)$ exists only at temperatures below $-10°$ in the absence of excess triphenylphosphine.[26,27]

No evidence was found for a rhodium hydride species when a pressure of hydrogen gas was held above a solution of *trans*-$RhCl(PF_3)(PPh_3)_2$. Thus the behaviour of complex (III) is closer to that of the carbonyl complex *trans*-$RhCl(CO)(PPh_3)_2$ than $RhCl(PPh_3)_3$ for which a dihydrido-complex is known.

Difluorotrichloromethylphosphine–Rhodium(I) *Complexes*.—Difluorotrichloromethylphosphine, CCl_3PF_2,[28] behaves in a similar fashion to trifluorophosphine in its reaction with $[RhCl(C_2H_4)_2]_2$. An excess of CCl_3PF_2 affords an orange crystalline complex (IV) which is very soluble in aromatic hydrocarbons but sparingly soluble in aliphatic hydrocarbons. The melting point (118—119°) closely corresponds to that reported for a compound made from CCl_3PF_2 and $[RhCl(CO)_2]_2$ and assigned originally as $[RhCl(CCl_3PF_2)_3]$.[7,29] The ^{19}F n.m.r. spectrum of complex (IV), although not fully analysed because of overlapping lines, showed features quite characteristic of an $[X_2A]_2$ spin system[30-32] ($X =$ fluorine, $A =$ phosphorus) strongly suggesting that (IV) is in fact $[RhCl(CCl_3PF_2)_2]_2$. Complex (IV) has also been prepared by displacing trifluorophosphine from $[RhCl(PF_3)_2]_2$ at room temperature, the combining ratios of $[RhCl(PF_3)_2]_2 : CCl_3PF_2 : PF_3$ being 1 : 4·0 : 3·9 in close agreement with those expected from equation (3).

$$\mathrm{[RhCl(PF_3)_2]_2 + 4CCl_3PF_2 \longrightarrow [RhCl(CCl_3PF_2)_2]_2 + 4PF_3} \quad (3)$$

$RhCl(PPh_3)_3$ reacts with CCl_3PF_2 at room temperature affording the yellow crystalline chlorobis(triphenylphosphine)(difluorotrichloromethylphosphine)rhodium(I) complex, $RhCl(PPh_3)_2(CCl_3PF_2)$. By analogy with the trifluorophosphine derivative the compound probably has the *trans*-configuration.

EXPERIMENTAL

Reactions were usually carried out in sealed evacuated Pyrex glass ampoules using normal high vacuum techniques. Solvents were all rigorously dried before use. ^1H N.m.r. spectra were recorded on a Varian T60 instrument operating at 60 MHz, using tetramethylsilane as the internal standard. Fluorine n.m.r. spectra were obtained using the Varian HA100 spectrometer operating at 94·1 MHz or A60 operating at 56·4 MHz with CCl_3F or C_6F_6 as internal standard. In the latter case the chemical shifts were corrected to the CCl_3F scale by subtracting 16·30 p.p.m. from the observed value. I.r. spectra were recorded on either a Perkin-Elmer PF337 spectrometer (4000—400 cm^{-1}) or a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}). Elemental analyses for carbon and hydrogen were carried out by Mr. and Mrs. A. G. Olney of this Laboratory and analyses for other elements were performed by A. Bernhardt, Microanalytical Laboratory, Elbach über Engleskirchen, West Germany. Literature methods were used for the syntheses of PF_3,[33,34] CCl_3PF_2,[28] $[RhCl(C_2H_4)_2]_2$,[34] and $RhCl(PPh_3)_3$.[2]

Di-μ-chloro-tetrakis(trifluorophosphine)dirhodium.—In a typical experiment $[RhCl(C_2H_4)_2]_2$ (0·956 g, 2·46 mmol) was heated at 60° for 72 h with trifluorophosphine (1·503 g, 17·08 mmol) in a glass ampoule of approximate volume 80 ml. The product was a red liquid which on cooling deposited deep red crystals. After removal of the inseparable volatile mixture of PF_3 and C_2H_4, sublimation of the product *in vacuo* at room temperature afforded the red, air stable, crystalline $[RhCl(PF_3)_2]_2$ *complex*, (1·408 g, 2·24 mmol) m.p. 69—70, 91% yield based on $[RhCl(C_2H_4)_2]_2$ (Found: C, 0·0; H, 0·0; P, 19·45; Cl, 11·1. ClF_6P_2Rh requires C, 0·0; H, 0·0; P, 19·7; Cl, 11·3%). I.r. spectrum 967s, 915vs,br, 870s, 550s, 540s, 522s, 415w, 390w cm^{-1} (Nujol mull). The sample used in the n.m.r. studies was freshly sublimed before use.

Reaction between $[RhCl(PF_3)_2]_2$ *and Carbon Monoxide*.—A slow stream of carbon monoxide was bubbled through a refluxing solution of $[RhCl(PF_3)_2]_2$ (0·330 g, 0·52 mmol) in 10 ml dry toluene for 4 h. Evaporation of the solution afforded a red solid which was sublimed under high vacuum at 100° to yield $[RhCl(CO)_2]_2$ (0·197 g, 0·51 mmol), m.p. 129—130°, 98% (Found: C, 11·9; H, 0·0. Calc. for C_2ClO_2Rh; C, 12·5; H, 0·0%. I.r. spectrum 2108s, 2094s, 2038s cm^{-1} (Nujol mull).

Reaction between $[RhCl(PF_3)_2]_2$ and $[RhCl(C_2H_4)_2]_2$.—A solution of $[RhCl(C_2H_4)_2]_2$ (0·052 g, 0·13 mmol) in dry ether (2 ml) was added to $[RhCl(PF_3)_2]_2$ (0·081 g, 0·13 mmol) in a Schlenk flask and the mixture agitated until the solid

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[31] T. R. Johnson and J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 2518.

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[33] H. S. Booth and A. R. Bozarth, *J. Amer. Chem. Soc.*, 1939, **61**, 2927.

[34] R. Cramer, *Inorg. Chem.*, 1962, **1**, 722.

completely dissolved. After 10 min the ether was removed by passing a stream of dry nitrogen over the solution to minimise decomposition and afforded the dirty yellow solid complex $[RhCl(PF_3)(C_2H_4)]_2$ (0·131 g, 0·26 mmol) (Found: C, 12·5; H, 2·2. $C_2H_4ClF_3PRh$ requires C, 12·0; H, 2·0%). I.r. spectrum 1332vw, 1310w, 1220w, 1146w, 998w, 930m, 900s, 878s, 845w,sh, 538m, 522w, 499w cm^{-1} (Nujol mull).

Reaction between $[RhCl(PF_3)_2]_2$ *and Triphenylphosphine.*—A solution of $[RhCl(PF_3)_2]_2$ (0·110 g, 0·17 mmol) and triphenylphosphine (0·467 g, 1·78 mmol) in toluene (2 ml) was heated at 60° for 2 h. The ampoule was opened and the volatile products removed into the vacuum line to yield PF_3 (0·024 g, 0·27 mmol). The residue was extracted with chloroform and on dilution with light petroleum afforded yellow crystals of trans-*chlorotrifluorophosphinebistriphenylphosphine rhodium*(I), *trans*-$RhCl(PF_3)(PPh_3)_2$ (0·179 g, 0·24 mmol) 71% yield (Found: C, 56·0; H, 4·3. $C_{36}H_{30}ClF_3P_3Rh$ requires C, 57·6; H, 4·05%. I.r. spectrum: 3060w, 2955vw, 2924w, 2858vw, 1480m, 1436 (hexachlorobutadiene mull); 1300w, 1180m, 1094m, 1065vw, 1023m, 996w, 920w, 864vs, 855s, 848vs, 742s, 720m, 695s, 555m, 540s, 525vs, 514s, 501s cm^{-1} (Nujol mull).

Reaction between $RhCl(PPh_3)_3$ *and* PF_3.—A mixture of trifluorophosphine (0·366 g, 4·16 mmol) and chlorotris(triphenylphosphine)rhodium (2·980 g, 3·22 mmol) in dry benzene (10 ml) was shaken in an ampoule for 12 h at room temperature. The colour of the solution changed from a deep reddish brown to bright yellow. After removal of the solvent and a trace of PF_3 under vacuum the solid product was extracted with benzene, concentrated and addition of light petroleum afforded yellow crystals of *trans*-$RhCl(PF_3)(PPh_3)_2$ (1·809 g, 2·41 mmol), 75% based on $RhCl(PPh_3)_3$ (Found: C, 56·7; H, 4·1. $C_{36}H_{30}ClF_3P_3Rh$ requires C, 57·6; H, 4·05%). The product was identical with a sample obtained from $[RhCl(PF_3)_2]_2$ and triphenylphosphine.

In order to obtain high purity for the n.m.r. studies, *trans*-$RhCl(PF_3)(PPh_3)_2$ was taken up in the minimum volume of chloroform, and the solution diluted with an equal volume of light petroleum. The resulting yellow crystals were filtered immediately, washed with light petroleum and dried. Other methods of purification proved less efficient.

Reaction between $[RhCl(C_2H_4)_2]_2$ *and* CCl_3PF_2.—A mixture of difluorotrichloromethylphosphine (3·405 g, 18·16 mmol) and $[RhCl(C_2H_4)_2]_2$ (0·723 g, 1·86 mmol) were sealed off in a glass ampoule. Warming the mixture from −196° to room temperature led to a vigorous evolution of gas and orange crystals were deposited on the side of the ampoule. The ampoule was opened after 6 h and ethylene and unreacted difluorotrichloromethylphosphine (2·268 g, 12·10 mmol) were pumped into the high vacuum system. The solid residue was extracted with hexane and the resulting orange solution concentrated to yield orange crystals of *di-μ-dichloro-bis(difluorotrichloromethylphosphine)rhodium*(I), $[RhCl(CCl_3PF_2)_2]_2$ (1·165 g, 1·13 mmol) 61%, m.p. 118—119° (Found: C, 4·9; H, 0·0; P, 11·8; Cl, 41·8. $C_2Cl_7F_4P_2Rh$ requires C, 4·65; H, 0·0; P, 11·9; Cl, 41·9%; $[RhCl(CCl_3PF_2)_3]$ requires C, 5·13; H, 0·0; P, 13·0; Cl, 50·65%). I.r. spectrum: 916m,sh, 903s, 890s,sh, 883s, 870s, 855w, 845s, 776m cm^{-1} (Nujol mull).

Reaction between $[RhCl(PF_3)_2]_2$ *and* CCl_3PF_2.—A mixture of difluorotrichloromethylphosphine (2·238 g, 11·93 mmol) and $[RhCl(PF_3)_2]_2$ (0·464 g, 0·74 mmol) was sealed off in a glass ampoule and slowly warmed from −196° to room temperature. After 14 h orange crystals had deposited. The tube was opened, and unreacted difluorotrichloromethylphosphine (1·680 g, 8·96 mmol) was recovered, together with almost the calculated amount of trifluorophosphine (0·252 g, 2·87 mmol). (Calc. 2·96 mmol.) The involatile solid product (0·723 g, 0·70 mmol) was extracted with warm benzene affording an orange solution from which well formed orange crystals of $[RhCl(CCl_3PF_2)_2]_2$ (0·249 g, 0·24 mmol) 32%, m.p. 118—119° deposited. The product was identical with that described above.

Reaction between $RhCl(PPh_3)_3$ *and* CCl_3PF_2.—A mixture of $RhCl(PPh_3)_3$ (3·689 g, 3·98 mmol) and CCl_3PF_2 (0·645 g, 3·44 mmol) in toluene (8 ml) was shaken at room temperature in an evacuated glass ampoule for 14 h. The ampoule was opened and the contents diluted with light petroleum to afford the yellow solid *chlorodifluorotrichloromethylphosphinebis(triphenylphosphine)rhodium*(I), $RhCl(PF_2CCl_3)(PPh_3)_2$, (2·781 g, 3·16 mmol) 79% based on $RhCl(PPh_3)_3$, m.p. 163—168° (dec.) (Found: C, 52·7; H, 4·1. $C_{36}H_{30}Cl_4F_2P_3Rh$ requires C, 52·25; H, 3·55%). I.r. spectrum: 1187m, 1160m, 1026w, 996m, 875w,sh, 857m,br, 805m,br, 740s, 725s, 690s, 612vw, 538m, 514s, 494m, 470w cm^{-1} (Nujol mull). The complex could not be purified further by recrystallisation.

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