Fluorophosphine Complexes of Rhodium(I). Part III.[1] Ligand-exchange Studies in Some Dimethylaminodifluorophosphinerhodium(I) Complexes

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

Di-μ-chloro-tetrakis(ethylene)dirhodium reacts with an excess of dimethylaminodifluorophosphine at room temperature affording the monomeric complex $RhCl(PF_2NMe_2)_3$. When $[RhCl(C_2H_4)_2]_2$ and Me_2NPF_2 react in a 1 : 4 molar ratio the product is the dimeric complex $[RhCl(PF_2NMe_2)_2]_2$. Both complexes exist as discrete entities in solution, and addition of PF_2NMe_2 to $[RhCl(PF_2NMe_2)_2]_2$ quantitatively affords $RhCl(PF_2NMe_2)_3$. The dimer is readily regenerated by pyrolysis of $RhCl(PF_2NMe_2)_3$ *in vacuo*. $[RhCl(PF_2NMe_2)_2]_2$ reacts with potassium amalgam in the presence of PF_2NMe_2 to yield $K[(PF_2NMe_2)_4Rh]$ and undergoes bridge cleavage with triphenylphosphine without loss of PF_2NMe_2 to afford $RhCl(PF_2NMe_2)_2(PPh_3)$. The latter has been assigned a *cis*-stereochemistry on the basis of its ^{19}F n.m.r. spectrum. The easy phosphine exchange processes occurring in these complexes have been established by ^{19}F and ^{1}H n.m.r. studies. The monosubstituted complex $RhCl(PF_2NMe_2)(PPh_3)_2$ is the product from the reaction between a 1 : 1 molar ratio of $RhCl(Ph_3P)_3$ and PF_2NMe_2. Both $RhCl(PF_2NMe_2)_3$ and $[RhCl(PF_2NMe_2)_2]_2$ act as catalysts for the decarbonylation of benzaldehyde.

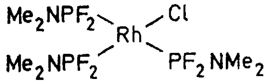
IN previous papers[1-4] we described low pressure synthetic routes to several trifluorophosphine complexes of rhodium(I). We have extended this work to the more basic dimethylaminodifluorophosphine,[5] PF_2NMe_2, and find interesting differences in behaviour compared with the parent trifluorophosphine.

RESULTS AND DISCUSSION

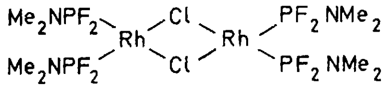
Di-μ-chloro-tetrakis(ethylene)dirhodium(I) reacts with an excess of dimethylaminodifluorophosphine at room temperature to give the yellow crystalline complex, (I), chlorotris(dimethylaminodifluorophosphine)rhodium(I).

$$[RhCl(C_2H_4)_2]_2 + 6PF_2NMe_2 \longrightarrow 2RhCl(PF_2NMe_2)_3 + 4C_2H_4$$

The complex melts with the decomposition over a very broad temperature range (110—139°), and is soluble in aromatic and chlorinated hydrocarbons, but almost completely insoluble in aliphatic hydrocarbons.



(I)



(II)

Solution molecular weight measurements indicate that $RhCl(PF_2NMe_2)_3$ is monomeric and the similarity of the i.r. spectra of the complex in the solid state and in benzene also suggests that there is no significant dissociation of the complex in solution.

When $[RhCl(C_2H_4)_2]_2$ and PF_2NMe_2 react in a 1 : 4 molar ratio a different yellow complex (II) is obtained which has been identified as di-μ-chloro-tetrakis-(dimethylaminodifluorophosphine)dirhodium(I), $[RhCl(PF_2NMe_2)_2]_2$. Compound (II), which melts sharply at 112—113° without decomposition, can be sublimed at 160° under high vacuum and in contrast to (I) is very soluble in aliphatic hydrocarbons. The dimeric structure is suggested by the observation of a parent ion at *m/e* 729 in the mass spectrum and a molecular weight measurement indicates that the dimeric structure is also retained in dichloromethane solution.

The i.r. spectra of $[RhCl(PF_2NMe_2)_2]_2$ in benzene is distinctly different from that of the monomeric $[RhCl(PF_2NMe_2)_3]$ complex, particularly in the 450—750 cm⁻¹ region, indicating that both (I) and (II) exist as discrete entities in solution.

The dimer (II) reacts with an excess of PF_2NMe_2 at room temperature to afford (I) and the reaction is easily reversed by heating (I) at 110° under high vacuum.

$$\underset{\text{(II)}}{[RhCl(PF_2NMe_2)_2]_2} \underset{\text{heat}}{\overset{+PF_2NMe_2}{\rightleftharpoons}} \underset{\text{(I)}}{RhCl(PF_2NMe_2)_3}$$

Dimethylaminodifluorophosphine therefore differs from CO,[6] PF_3,[1,2,7] and CCl_3PF_2 [2] in forming a $RhClL_3$ complex in addition to the dimeric $[RhClL_2]_2$ compound, and its behaviour is more like that reported previously for phosphites [8] or tris(dialkylamino)phosphines.[10]

Although neither CO nor PF_3 form $RhClL_3$ complexes, the latter does afford the yellow complex $RhCl(PF_3)_4$ [1,7] which is stable at room temperature only under a pressure of PF_3.*

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* Since completion of this work we have learned that there is also evidence for the formation of an unstable $RhCl(PF_2NMe_2)_4$ complex (M. A. Bennett, personal communication).

[1] Part II, D. A. Clement and J. F. Nixon, *J.C.S. Dalton*, 1972, 2553.

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

[3] D. A. Clement, J. F. Nixon, and B. Wilkins, *J. Organometallic Chem.*, 1972, **37**, C43.

[4] J. F. Nixon and A. A. Pinkerton, *J. Organometallic Chem.*, 1972, **37**, C47.

[5] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 345.

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

[7] M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, 1971, **10**, 2387.

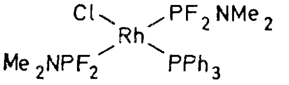
[8] L. Vallarino, *J. Chem. Soc.*, 1957, 2473.

[9] L. M. Haines, *Inorg. Chem.*, 1970, **9**, 1517.

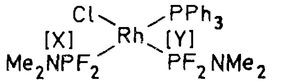
[10] Y. Chevallier, R. Stern, and L. Sajus, *Tetrahedron Letters*, 1969, **15**, 1199.

The reaction between triphenylphosphine and $[RhCl(PF_3)_2]_2$ is known to afford *trans*-$RhCl(PPh_3)_2(PF_3)$.[2,11,12] The corresponding reaction with $[RhCl(PF_2NMe_2)_2]_2$, however, does not lead to the displacement of PF_2NMe_2 but instead the yellow air stable crystalline complex chlorobis(dimethylaminodifluorophosphine)triphenylphosphinerhodium(I), (III), is formed, even when a large excess of Ph_3P is used.

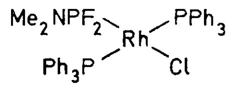
The most symmetrical structure (IIIa) is considered unlikely since this would place the stronger π-accepting fluorophosphine ligands in mutually *trans*-positions to each other. Support for the alternative *cis*-structure (IIIb) comes from the ^{19}F n.m.r. spectrum which shows *two* non-equivalent fluorine environments (*vide infra*).



(IIIa)



(IIIb)



(IV)

The *cis*-stereochemistry of an analogous diethylaminodifluorophosphine complex $RhCl(PF_2NEt_2)_2(PPh_3)$ reported after this work was completed has been established by an *X*-ray study.[13]

Dimethylaminodifluorophosphine reacts with $RhCl(PPh_3)_3$ in a 1 : 1 molar ratio to afford (IV) chloro(dimethylaminodifluorophosphine)bis(triphenylphosphine)rhodium(I), $RhCl(PF_2NMe_2)(PPh_3)_2$, which has a similar i.r. spectrum to $RhCl(PF_2NMe_2)_2(PPh_3)$ and by analogy with the related $RhCl(PF_3)(PPh_3)_2$ compound[2] is tentatively assigned a *trans*-configuration.

An unstable *cis*-dicarbonyl analogue of (IIIb) has been reported and was originally believed to isomerise rapidly to the more stable complex *trans*-$[RhCl(CO)_2PPh_3]$.[14-16] The work has recently been questioned and the *trans*-complex reformulated as $[RhCl(CO)(PPh_3)]_2$.[17,18] We find no evidence for the *trans*-isomer (IIIa) and interestingly (IIIb) does not undergo further reaction with triphenylphosphine to form (IV).

Both (I) and (II) react with potassium amalgam in the presence of excess PF_2NMe_2 to afford the white solid complex potassium tetrakis(dimethylaminodifluorophosphine)rhodium(−1), $K[Rh(PF_2NMe_2)_4]$, which is sparingly soluble in benzene and diethyl ether.

$$[RhCl(PF_2NMe_2)_2]_2 \xrightarrow[PF_2NMe_2]{K\text{-}Hg} K[(PF_2NMe_2)_4Rh]$$

The ^{19}F n.m.r. spectrum, though very broad, shows a very large downfield shift from the free ligand resonance which is similar to that observed in $Rh(NO)(PF_3)_3$ in which the rhodium is also formally in the (−1) oxidation state.[19-21] The analogous PF_3 complex $K[Rh(PF_3)_4]$ is converted to the hydride $HRh(PF_3)_4$ by the action of mineral acids.[5] However, the ready cleavage of the P–N bond of complexed PF_2NMe_2 [5] precludes a similar synthesis of $HRh(PF_2NMe_2)_4$.

N.M.R. Studies.—The ready exchange of ligands noted previously in square planar Rh^I systems [1-3,10,11] is also observed in complexes containing dimethylaminodifluorophosphine ligands.

$[RhCl(PF_2NMe_2)_2]_2$ *and* $RhCl(PF_2NMe_2)_3$.—The ^1H n.m.r. spectrum of $[RhCl(PF_2NMe_2)_3]$ in $CDCl_3$ [Figure 1(b)] consists of a slightly broadened triplet at τ 7·11 but no signals could be observed in the ^{19}F n.m.r. spectrum of the same solution and numerous unsuccessful attempts were made to observe the ^{19}F n.m.r. spectrum of this complex in other solvents.

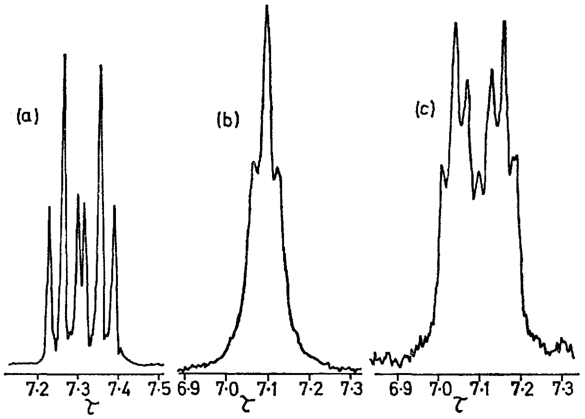


FIGURE 1 ^1H N.m.r. spectra at 100 MHz; (a), PF_2NMe_2 as neat liquid; (b), $RhCl(PF_2NMe_2)_3$ in $CDCl_3$ solution; (c), $[RhCl(PF_2NMe_2)_2]_2$ in $CDCl_3$ solution

The ^1H n.m.r. spectra of $[RhCl(PF_2NMe_2)_2]_2$ in $CDCl_3$ [Figure 1(c)] shows a distinctly different pattern to either that of $RhCl(PF_2NMe_2)_3$ or the free ligand PF_2NMe_2 [Figure 1(a)] and is very similar to the ^1H n.m.r. spectrum of *cis*-$Mo(PF_2NMe_2)(CO)_4$ [22] previously reported.

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[11] D. A. Clement, J. F. Nixon, and M. D. Sexton, *Chem. Comm.*, 1969, 1509.

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

[13] M. A. Bennett, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Chem. Comm.*, 1971, 762.

[14] G. Deganello, P. Uguagliati, B. Crociani, and V. Belluco, *J. Chem. Soc.* (*A*), 1969, 2726.

[15] P. Uguagliati, G. Deganello, L. Busetto, and V. Belluco, *Inorg. Chem.*, 1969, **8**, 1625.

[16] P. Uguagliati, A. Palazzi, G. Deganello, and V. Belluco, *Inorg. Chem.*, 1970, **9**, 724.

[17] R. Poilblanc and J. Gallay, *J. Organometallic Chem.*, 1971, **27**, C53.

[18] D. F. Steele and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 877.

[19] D. M. Bridges, D. W. H. Rankin, D. A. Clement, and J. F. Nixon, *Acta Cryst.*, 1972, **B28**, 1130.

[20] D. A. Clement, J. F. Nixon, and B. Wilkins, unpublished results.

[21] Th. Kruck and W. Lang, unpublished results quoted by Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

[22] C. G. Barlow, J. F. Nixon, and J. R. Swain, *J. Chem. Soc.* (*A*), 1969, 1082.

The ^{19}F n.m.r. spectrum of $[RhCl(PF_2NMe_2)_2]_2$ (Figure 2) shows a widely spaced doublet pattern of lines as expected for the X part of an $[X_2A]_2$ spin system[22-24] (X = fluorine, A = phosphorus) each line being further split by coupling with the rhodium and hydrogen nuclei. A full analysis was not attempted, but some coupling constants evaluated from the spectrum are listed in Table 1.

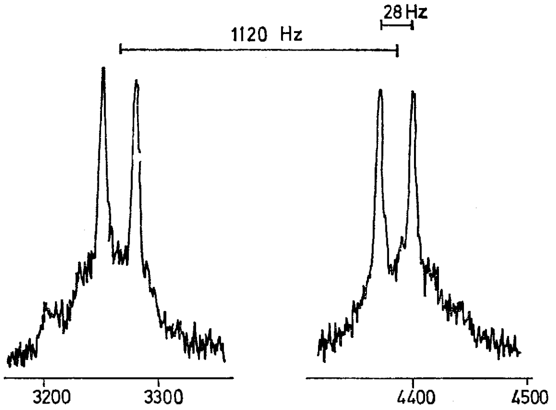

FIGURE 2 ^{19}F N.m.r. spectrum at 94·1 MHz of $[RhCl(PF_2NMe_2)_2]_2$ in chloroform solution (scale relative to CCl_3F)

TABLE 1

N.m.r. parameters for PF_2NMe_2 complexes of rhodium(I)

Compound	$^1J_{(PF)}$ [a]	$^1J_{(PF)} + {}^3J_{(PF)}$ [a]	$^2J_{(RhF)}$ [a]	ϕ_F [b]	τ	Solvent
PF_2NMe_2	1196			65·3	7·32	Neat
$RhCl(PF_2NMe_2)_3$ (I)					7·11	$CDCl_3$
$[RhCl(PF_2NMe_2)_2]_2$ (II)		1120	28·0	40·6	7·11	$CHCl_3$
cis-$RhCl(PF_2NMe_2)_2PPh_3$ (III)	1100 1125			25·4 46·5	*ca.* 7·2	$CHCl_3$
(III) + PPh_3	1148			38·9	*ca.* 7·3	$CHCl_3$
(III) + PF_2NMe_2	1164			41·1		$CDCl_3$
$RhCl(PF_2NMe_2)(PPh_3)_2$ (IV)					7·78	$CDCl_3$
$K[Rh(PF_2NMe_2)_4]$	1098		*ca.* 31·0	23·2	7·3	Benzene

[a] In Hz. [b] In p.p.m. (rel. CCl_3F).

The effect of the stepwise addition of PF_2NMe_2 to $[RhCl(PF_2NMe_2)_2]_2$ at room temperature was studied by ^{19}F and ^1H n.m.r. spectroscopy. Addition of trace amounts of PF_2NMe_2 immediately leads to considerable broadening of the ^{19}F n.m.r. spectrum and subsequent addition causes further broadening (Figure 3) and ultimately the complete loss of rhodium–fluorine coupling. As the amount of PF_2NMe_2 added approaches one molar equivalent per rhodium atom the broad doublet resonance reduces in intensity and finally disappears at the stoicheiometry corresponding equation (1).

$$[RhCl(PF_2NMe_2)_2]_2 + 2PF_2NMe_2 \longrightarrow 2RhCl(PF_2NMe_2)_3 \quad (1)$$

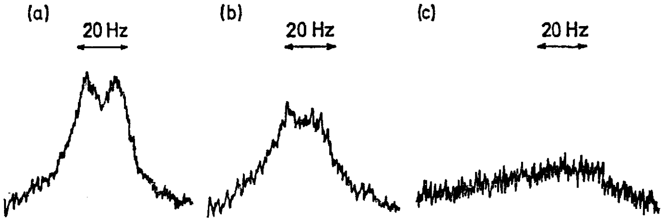

FIGURE 3 ^{19}F N.m.r. spectrum at 94·1 MHz of a benzene solution of $[RhCl(PF_2NMe_2)_2]_2$ in the presence of increasing concentrations of PF_2NMe_2; (a) with a trace of PF_2NMe_2; (b), with more PF_2NMe_2; (c), with an approximately stoicheiometric quantity of PF_2NMe_2 for equation (1), only one half of the spectrum is shown.

Further addition of PF_2NMe_2 initially gives rise to no further signals in the ^{19}F n.m.r. spectrum, but at a ratio of $PF_2NMe_2 : [RhCl(PF_2NMe_2)_2]$ of *ca.* 10 : 1, a doublet of broad singlets appears at higher field and at still higher ratios (15—20 : 1) the spectrum of the free ligand PF_2NMe_2 is observed.

The effect on the ^1H n.m.r. spectrum of $[RhCl(PF_2NMe_2)_2]_2$ on addition of PF_2NMe_2 is shown in Figure 4. The well resolved fine structure of the starting dimer [Figure 4(A)] is immediately lost on addition of a trace of free PF_2NMe_2 forming a poorly resolved doublet (B) which subsequently collapses (C), (D) to a broad singlet (E) on addition of more ligand. The singlet narrows (F) as the ratio of $PF_2NMe_2 : [RhCl(PF_2NMe_2)_2]$ approaches 0·5 and then broadens again (G) eventually showing the triplet pattern (H) characteristic of $RhCl(PF_2NMe_2)_3$ [Figure 1(b)]. Continued addition of ligand results in spectra (I), (J), (K), and ultimately (L), which is that of the free ligand. Spectra similar in appearance to (I), (J), (K), and (L) are obtained when PF_2NMe_2 is added to a solution of $RhCl(PF_2NMe_2)_3$.

These observations are consistent with a ready intermolecular exchange of PF_2NMe_2 ligands at the rhodium atom similar to that already reported[1,2,10,11] for certain square planar Rh^I–trifluorophosphine complexes. The pronounced broadening in the ^{19}F n.m.r. spectrum of the exchanging system reflects the large shift difference between the ^{19}F chemical shift of free and co-ordinated PF_2NMe_2 molecules. The corresponding shift difference in the ^1H n.m.r. spectrum is small.

cis-$RhCl(PF_2NMe_2)_2(PPh_3)$ (III).—The ^{19}F n.m.r. spectrum of a pure sample of $RhCl(PF_2NMe_2)_2(PPh_3)$ in chloroform solution [Figure 5(a)] establishes its *cis*-stereochemistry (IIIb). The spectrum contains two sets of broad doublets XX′ and YY′ of equal intensity

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[23] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087.

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

indicating that the two fluorophosphine ligands are in different environments thus ruling out the *trans*-structure (IIIa). If the PF_2NMe_2 ligands *trans*- and *cis*- to Ph_3P are labelled X and Y respectively the parameters obtained from the ^{19}F n.m.r. spectra are $^1J_{PF_X}$ 1100 Hz, ϕ_{P_X} 25·4 p.p.m., and $^1J_{PF_Y}$ 1125 Hz, ϕ_{F_Y} 46·5 p.p.m. The apparent triplet pattern of the X resonance may be due to $^2J_{RhF}$ and $^3J_{PF}$ being approximately equal.

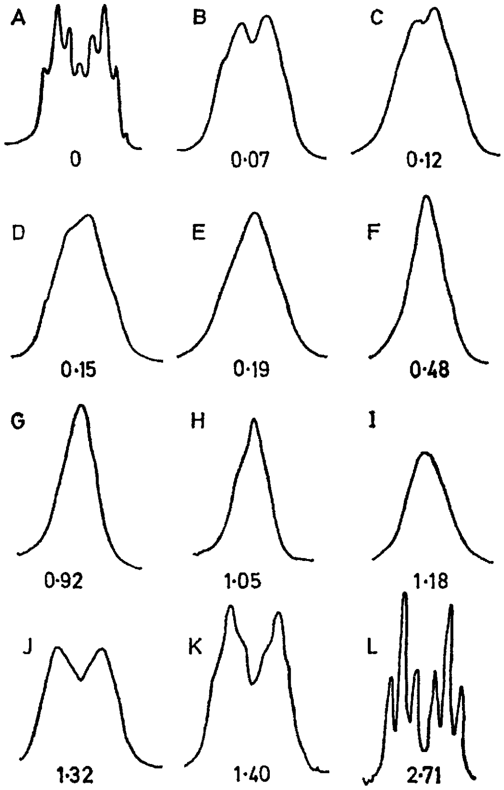

FIGURE 4 ^1H N.m.r. spectra at 60 MHz of a benzene solution of $[RhCl(PF_2NMe_2)_2]_2$ in the presence of increasing concentrations of PF_2NMe_2; the ratio of $PF_2NMe_2 : RhCl(PF_2NMe_2)_2$ is indicated below each spectrum

Addition of a small amount of triphenylphosphine to the solution immediately causes a collapse of the spectrum to a single broad doublet [Figure 5(b)] probably indicative of an intermolecular ligand exchange process between free and co-ordinated triphenylphosphine similar to that described previously for *trans*-$RhCl(PF_3)(PPh_3)_2$.[2,11]

The ^{19}F fluorine chemical shift in the exchanging system (Table 1) is, as expected, almost the mean of the original chemical shifts of the two fluorophosphine ligands in the starting *cis*-complex. The exchange process presumably involves an intermediate five-co-ordinate rhodium(I) complex.

Addition of PF_2NMe_2 to (IIIb) also causes a collapse of the ^{19}F n.m.r. spectrum this time to a very broad doublet centred at ϕ_F 41·1 p.p.m., which is intermediate between the shift values of the free and co-ordinated ligand.

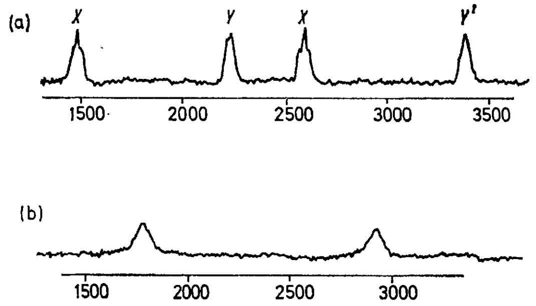

FIGURE 5 ^{19}F N.m.r. spectra (at 56·4 MHz) in chloroform solution of (a) *cis*-$RhCl(PF_2NMe_2)_2(PPh_3)$, (b) *cis*-$RhCl(PF_2NMe_2)_2(PPh_3)$ with a trace of PPh_3 (scales relative to CCl_3F)

The ^1H n.m.r. spectrum of (IIIb) shows a broad complex pattern centred at τ 7·2 for the methyl protons and a well resolved resonance at τ 2·6 for the phenyl protons. Addition of Ph_3P causes the methyl resonance to narrow appreciably while the phenyl resonance collapses to a broad singlet.

Decarbonylation Studies.—In view of the known decarbonylation of aldehydes and acid chlorides by $RhCl(PPh_3)_3$[25] the interaction between $[RhCl(CO)_2]_2$ and the dimethylaminodifluorophosphinerhodium complexes (I) and (II) and benzaldehyde was studied. All the complexes were found to decarbonylate benzaldehyde catalytically to benzene and in a quantitative experiment the order of catalytic efficiency at 160° was found to be $RhCl(PF_2NMe_2)_3 > [RhCl(PF_2NMe_2)_2]_2 > [RhCl(CO)_2]_2$. The results are summarised in Table 2.

TABLE 2

The catalytic decarbonylation of benzaldehyde at 160°

Catalyst	Wt. (g)	(mmol)	Benzaldehyde g	Benzaldehyde mmol	Benzene formed g	Benzene formed mmol	% catalysis[a]	No. of cycles per rhodium
$RhCl(PF_2NMe_2)_3$	1·105	2·31	21·77	205·4	3·59	46·0	2000	20·0
$[RhCl(PF_2NMe_2)_2]_2$	1·138	1·56	19·43	183·3	3·34	42·8	2740	13·7
$[RhCl(CO)_2]_2$	0·903	2·32	21·16	199·6	3·51	45·0	1940	9·7

[a] Calculated on the basis of 100% yield for 1 stoicheiometric reaction.

By analogy with our previous studies[1] on the $[RhCl(PF_3)_2]_2$–carbon monoxide system, dimeric intermediates of the type $Rh_2Cl_2(CO)_x(PF_2NMe_2)_{4-x}$ are expected during the decarbonylation by (I) and (II). The higher catalytic activity found for $RhCl(PF_2NMe_2)_3$

$$xC_6H_5CHO + [RhCl(PF_2NMe_2)_2]_2 \rightleftharpoons xC_6H_6 + [Rh_2Cl_2(CO)_x(PF_2NMe_2)_{4-x}] + xPF_2NMe_2$$

compared with $[RhCl(PF_2NMe_2)_2]_2$ may reflect the

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[25] K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 99.

ability of the excess PF_2NMe_2 present in the system continuously to displace carbon monoxide from these intermediates.

EXPERIMENTAL

Reactions were normally carried out in sealed evacuated Pyrex glass ampoules using normal high vacuum techniques. Solvents were all rigorously dried before use. Dimethylaminodifluorophosphine,[26] $[RhCl(C_2H_4)_2]$,[27] and $RhCl(PPh_3)_3$ [28] were obtained by literature methods. N.m.r. spectra were recorded as described previously.[2] I.r. spectra were recorded on either a Perkin-Elmer PF 337 spectrometer (4000—400 cm^{-1}) or a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}). Elemental analyses for C, H, and N were carried out by Mr. and Mrs. A. G. Olney of this laboratory.

Reaction between $[RhCl(C_2H_4)_2]_2$ *and an excess of* PF_2NMe_2.—In a typical reaction $[RhCl(C_2H_4)_2]_2$ (0·928 g, 2·66 mmol) and PF_2NMe_2 (1·882 g, 16·80 mmol) were sealed off in a glass ampoule. On warming the mixture from −196° to room temperature, effervescence occurred and the contents of the ampoule solidified. After 14 h the ampoule was opened and ethylene and unreacted PF_2NMe_2 (0·065 g, 0·58 mol) recovered indicating that the combining ratio of $[RhCl(C_2H_4)_2]_2$ to PF_2NMe_2 was 6·1 : 1. The solid product was extracted with toluene and the yellow solution concentrated. Addition of light petroleum afforded yellow, air stable crystals of *chlorotris(dimethylaminodifluorophosphine)rhodium*(I) (1·595 g, 3·33 mmol) 63%, m.p. 110—139° (extensive decomposition), *M* 479 (osmometric in CH_2Cl_2) calc. 477·5 (Found: C, 15·3; H, 3·9; N, 8·7. $C_6H_{18}ClF_6N_3P_3Rh$ requires C, 15·1; H, 3·8; N, 8·8%). I.r. spectrum 2948m, 2933m, 2906m, 2855w, 2810w, 1450m, 1414w, 1312s, 1250vw, 1185s, 1071m, 995vs, 867s, 830vs, 813s,sh, 787m,sh, 715vs, 658m,br, 543m, 526m, 512vs, 425m, 387w, 350vw, 336w cm^{-1} (benzene solution).

Reaction between $[RhCl(C_2H_4)_2]_2$ *and* PF_2NMe_2 *in a* 1 : 4 *Molar Ratio*.—A mixture of $[RhCl(C_2H_4)_2]_2$ (0·365 g, 0·94 mmol) and PF_2NMe_2 (0·365 g, 3·23 mmol) in toluene (5 ml) was heated at 60° for 72 h in a sealed evacuated glass ampoule. After removal of the displaced ethylene and the solvent the yellowish solid was extracted with light petroleum $[RhCl(PF_2NMe_2)_3$ is insoluble in petroleum] and concentration followed by cooling the solution to −78° afforded yellow needles of *di-μ-chloro-tetrakis(dimethylaminodifluorophosphine)dirhodium* (0·474 g, 0·65 mmol), 80% based on PF_2NMe_2 used, m.p. 113° (Found: C, 13·5; H, 3·3; N, 7·5. $C_4H_{12}ClF_4N_2P_2Rh$ requires C, 13·2; H, 3·3; N, 7·7%). The mass spectrum shows a parent ion at *m/e* 729. *M* (osmometric in CH_2Cl_2) 672. I.r. spectra: 2970w,sh, 2943m, 2930m, 2902m, 2854w, 2820w, 2810w, 1450m, 1413w, 1309s, 1187s, 1070m, 992vs, 846s, 827vs, 795s, 732s, 716s, 660m,br, 543s, 527s, 426m, 454w (benzene solution); 1308s, 1181s, 1145w,sh, 1066m, 994s, 865s, 820s, 807s, 793s, 735s, 718s, 544m, 526m, 423m cm^{-1} (Nujol mull).

Reaction between $[RhCl(PF_2NMe_2)_2]_2$ *and an Excess of* PF_2NMe_2.—A mixture of $[RhCl(PF_2NMe_2)_2]_2$ (0·440 g, 0·60 mmol) and PF_2NMe_2 (0·311 g, 2·75 mmol) was heated at 60° for 2 h in a sealed glass ampoule. The ampoule was opened after standing for 2 weeks at room temperature and the excess of PF_2NMe_2 was pumped away together with a small amount of PF_3 (0·011 g, 0·13 mmol). The yellow solid product was extracted with toluene, concentrated and on addition of light petroleum deposited yellow crystals of *chlorotris(dimethylaminodifluorophosphine)rhodium* (0·574 g, 1·14 mmol) 95% yield based on starting $[RhCl(PF_2NMe_2)_2]_2$ (Found: C, 15·3; H, 4·0; N, 8·8. $C_6H_{18}ClF_6N_3P_3Rh$ requires C, 15·1; H, 3·8; N, 8·8%). The complex had an identical i.r. spectrum to a sample made directly from $[RhCl(C_2H_4)_2]_2$.

Pyrolysis of $RhCl(PF_2NMe_2)_3$ *in Vacuo*.—A sample of $RhCl(PF_2NMe_2)_3$ (0·345 g, 0·72 mmol) was placed in a glass tube and slowly heated *in vacuo* to 120°. The solid melted to an orange oil and the volatile products (0·068 g, 0·60 mmol) of PF_2NMe_2 and a trace of PF_3 were collected in the high vacuum system. A small amount (0·025 g, 0·05 mmol) of $RhCl(PF_2NMe_2)_3$ sublimed up the tube. The stoicheiometry of the reaction is very close to that expected from the equation:

$$\begin{array}{lll} RhCl(PF_2NMe_2)_3 \longrightarrow & \tfrac{1}{2}[RhCl(PF_2NMe_2)_2]_2 + & PF_2NMe_2 \\ (0{\cdot}72 - 0{\cdot}05) & & \\ 0{\cdot}67\ \text{mmol} & 0{\cdot}33\ \text{mmol} & 0{\cdot}60\ \text{mmol} \end{array}$$

The orange liquid complex solidified on cooling to afford yellow crystals of $[RhCl(PF_2NMe_2)]_2$ (0·241 g, 0·33 mmol), 96%, (Found: C, 13·4; H, 3·4; N, 7·6. $C_4H_{12}ClF_4N_2P_2$ requires C, 13·2; H, 3·3; N, 7·7%).

Reaction between $[RhCl(PF_2NMe_2)_2]_2$ *and* Ph_3P.—A solution of $[RhCl(PF_2NMe_2)_2]_2$ (0·247 g, 0·34 mmol) and triphenylphosphine (0·167 g, 0·64 mmol) in dry toluene (1 ml) deposited a yellow precipitate after a few minutes at room temperature. The solid product was filtered and washed with ice-cold toluene (1 ml) to afford cis-*chlorobis(dimethylaminodifluorophosphine)triphenylphosphinerhodium*(I), *cis*-$RhCl(PF_2NMe_2)_2(PPh_3)$, (0·322 g, 0·51 mmol) 75%, m.p. 115—140° (dec.) (Found: C, 42·5; H, 4·4; N, 4·5. $C_{22}H_{27}ClF_4P_3Rh$ requires C, 42·1; H, 4·3; N, 4·5%). I.r. spectrum: 3079vw, 3060vw, 3040vw, 3007 vw, 2980vw, 2953w, 2934vw,sh, 2902w, 2854w, 2822w, 1480m, 1452m, 1442m, 1437, 1313w, 1310s, 1189s, 1148w, 1096s, 1090m, 1070w, 1025w, 992s, 839s, 817s, 800s, 770s, 757s, 744s, 729w, 715s, 694s, 617vw, 542m, 517s, 508s, 493m, 454w, 431m, 428w, 386w cm^{-1} (hexachlorobutadiene and Nujol mulls). The same product was obtained using a larger amount of triphenylphosphine.

Reaction between $RhCl(PPh_3)_3$ *and* PF_2NMe_2.—$RhCl(PPh_3)_3$ (2·569 g, 2·78 mmol) and PF_2NMe_2 (0·339 g, 3·00 mmol) were shaken at room temperature in toluene for 14 h. The resulting yellow solution was diluted with light petroleum to yield yellow crystals of *chlorobis(triphenylphosphine)(dimethylaminodifluorophosphine)rhodium*(I), $RhCl(PF_2NMe_2)(PPh_3)_2$ (1·934 g, 2·49 mmol), 89%, m.p. 143—146° (Found: C, 58·6; H, 4·5; N, 2·0. $C_{38}H_{36}FClNP_3Rh$ requires C, 58·8; H, 4·6; N, 1·8%). I.r. spectrum 3052w, 3858w, 3830vw, 2800vw, 1480m, 1435s, 1302m, 1188m, 1153w, 1090s, 1067w, 1025w, 989s, 817s, 786s, 755w, 751w, 744m, 738s, 720s, 697m, 691s cm^{-1} (hexachlorobutadiene and Nujol mulls).

Reaction between $[RhCl(PF_2NMe_2)_2]_2$ *and Potassium Amalgam and* PF_2NMe_2.—$[RhCl(PF_2NMe_2)_2]_2$ (0·801 g, 1·10 mmol) and PF_2NMe_2 (2·093 g, 28·7 mmol) were heated at 60° for 26 h in an ampoule containing potassium amalgam

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[28] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

(10·7 g, *ca.* 1%). The colour of the solution changed from yellow to dark brown and a precipitate formed. The excess of PF_2NMe_2 (1·395 g, 19·19 mmol) and a trace (0·009 g, 0·1 mmol) of PF_3 were removed *in vacuo*, the solid products extracted under nitrogen with 50 ml portions of ether, and the resulting pale yellow solutions evaporated to dryness to afford the off-white *potassium tetrakis(dimethylaminodifluorophosphine)rhodium*(−1) salt (0·385 g, 0·65 mmol), 29% (Found: C, 16·4; H, 4·1; N, 8·7. $C_8H_{20}F_8P_4RhK$ requires C, 16·2; H, 4·1; N, 9·4%). I.r. spectrum: 3001m, 2930s, 3898s, 2835s, 1484m, 1455s, 1415m, 1297s, 1184s, 1069m, 980s, 819m, 748s,sh, 763s, 746s, 721m,sh, 696s, 674m, 523w, 504s cm^{-1} (hexachlorobutadiene and Nujol mulls).

Catalytic Decarbonylation of Benzaldehyde.—The following procedure was used for the rhodium complexes listed in Table 2. A freshly distilled sample of benzaldehyde was weighed into a 50 ml round bottomed flask fitted with a reflux condenser, the system purged with oxygen-free, dry nitrogen and a weighed amount of the rhodium complex added. The flask was heated to 100° for 20 h and g.l.c. analysis of the products using a Pye 104 model 64 chromatograph showed that very little benzene had been formed. The temperature was increased to 160° and after 65 h the products were analysed by g.l.c. The data are in Table 2.

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