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SYNTHESES AND ^{31}P NMR STUDIES OF SOME CHLOROCARBONYLRHODIUM(I) COMPLEXES CONTAINING 1,3-DI-t-BUTYL-2,4-DIHALOGENOCYCLODIPHOSPHAZANES $(PXN^tBu)_2$ (X = Cl, F) AND RELATED LIGANDS

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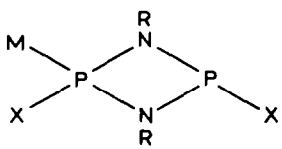
Summary

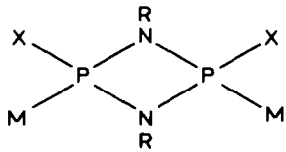
Syntheses of the chlorocarbonylrhodium complexes $[[RhCl(CO)_2]_2(PFN^tBu)_2]$, *trans*-$[RhCl(CO)(PFN^tBu)_2)_2]$, $[RhCl(CO)(PFN^tBu)_2]_x$, $[RhCl(CO)(PF(NMe_2)_2)]_2$ and *trans*-$[RhCl(CO)(PF(NMe_2)_2)_2]$ are described together with the structurally related $[RhCl(PFN^tBu)_2]_x$, $[RhCl(PClN^iPr)_2]_x$ and $[RhCl((PXN^tBu)_2)_2]_2$ (X = F, Cl). ^{31}P NMR spectroscopic studies establish the different types of coordination mode of the dihalogenocyclodiphosphazane ring in its complexes.

Introduction

The novel four-membered cyclo dihalogenodiphosphazane compounds $[PXNR]_2$ (X = halogen) exhibit different coordination behaviour in their transition metal complexes [1]. To date we have shown by NMR spectroscopy and single crystal X-ray studies [2,3] the existence of bonding modes **a** and **b** (M = Pt, Rh) and in the



(a)



(b)

system involving $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ and $[PXN^tBu]_2$ (X = Cl, F), we have established a ready interconversion of the two types of structure **a** and **b**.

In the present paper we report studies involving carbonylrhodium complexes with the cyclodihalogenodiphosphazane rings and related aminohalogenophosphine ligands.

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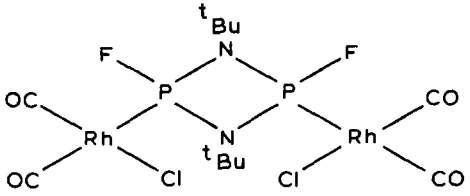
Results and discussion

When a toluene solution of $[RhCl(CO)_2]_2$ was treated with a single equivalent of $[PFN^tBu]_2$ in toluene under an atmosphere of carbon monoxide the orange-yellow complex $[Rh_2Cl_2(CO)_4(PFN^tBu)_2]$ (I) was immediately formed. The structure assigned is analogous to that we established both by NMR and crystallographically for $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})_2(PFN^tBu)_2]$ and the formulation is supported by the ob-



(Proposed structure of I)

servation of strong bands in the $\nu(C{\equiv}O)$ stretching region at 2096 and 1996 cm^{-1} and by the $^{31}P\{^1H\}$ NMR spectrum shown in Fig. 1. The spectrum which represents the A part of an MXAA'X'M' spin system ($M = {}^{103}Rh$, $X = {}^{19}F$, $A = {}^{31}P$, exhibits the expected mirror symmetry indicative of the single phosphorus environment of the bridging cyclodiphosphazane ligand, and although a full analysis was not carried out approximate coupling constant data are listed in Table 1. Complex I is unstable in the absence of CO and although evaporation of solvent from a solution of I under a CO atmosphere led to the isolation of the solid complex it proved impossible to dry

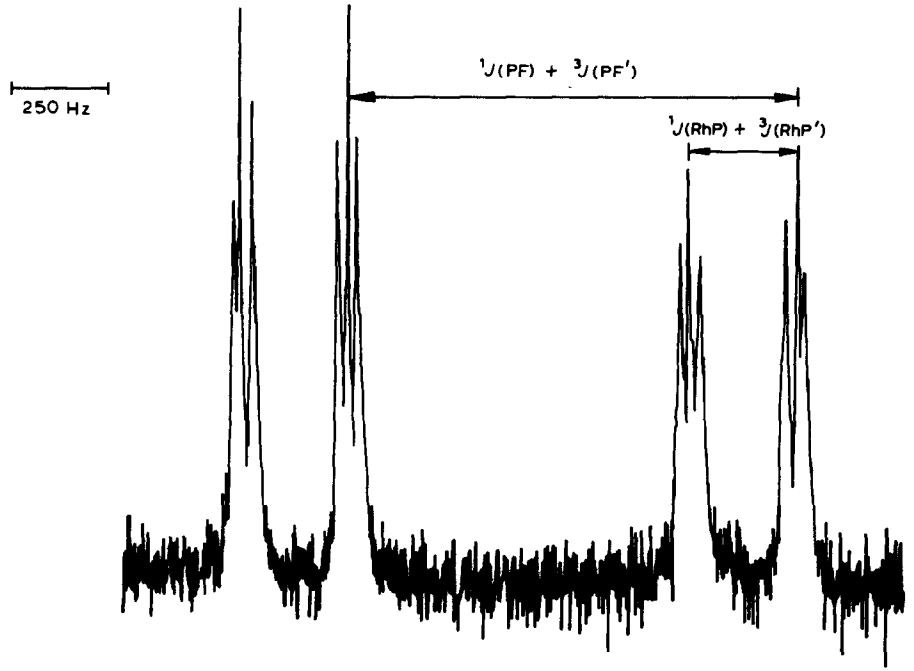


Fig. 1. The $^{31}P\{^1H\}$ NMR spectrum of complex I.

TABLE 1

$^{31}P\{^1H\}$ NMR DATA FOR COMPLEXES I–IV, VIII, IX

Complex	$\delta(P)$ [a]	$^1J(PF)+^3J(PF')$ * (or $^1J(PF)$) [b]	$^1J(RhP)+^3J(RhP')$* (or $^1J(RhP)$) [b]	$^2J(PRhP')$ [b]	other J [b] (Hz)
I [c]	+6.8	1195*	289*	–	–
II	−1.2	1178	–	–	
	−4.9	1149*	187	745	all <15
III	−4.3	1050	246	–	–
IV	−5.6	−1067	177	693	$^3J(PF)$+59 $^4J(FF')$ 6
VIII	−2.3	1197	260	–	<10
IX	−33.8	–	–		
	−14.5	–	295		<20

[a] Relative to $P(OMe)_3$; highfield shifts quoted +. [b] Hz. [c] Not fully analysed.

it without decomposition, furthermore the complex could only be redissolved in CO saturated toluene to regenerate I.

Treatment of I with three equivalents of $[PFN^tBu]_2$ led rapidly to the formation of the stable complex *trans*-$[RhCl(CO)\{(PFN^tBu)_2\}_2]$ (II), characterised by elemental analysis, IR, (ν(C≡O) 2012 cm^{-1}), and $^{31}P\{^1H\}$ NMR spectroscopy (Fig. 2).

The $^{31}P\{H\}$NMR spectrum of II consists of two sets of resonances, one of which is essentially a simple doublet ($^1J(P_2F)$) for the uncoordinated phosphorus atom while the other appears as a mirrored pattern doubleted due to the coupling

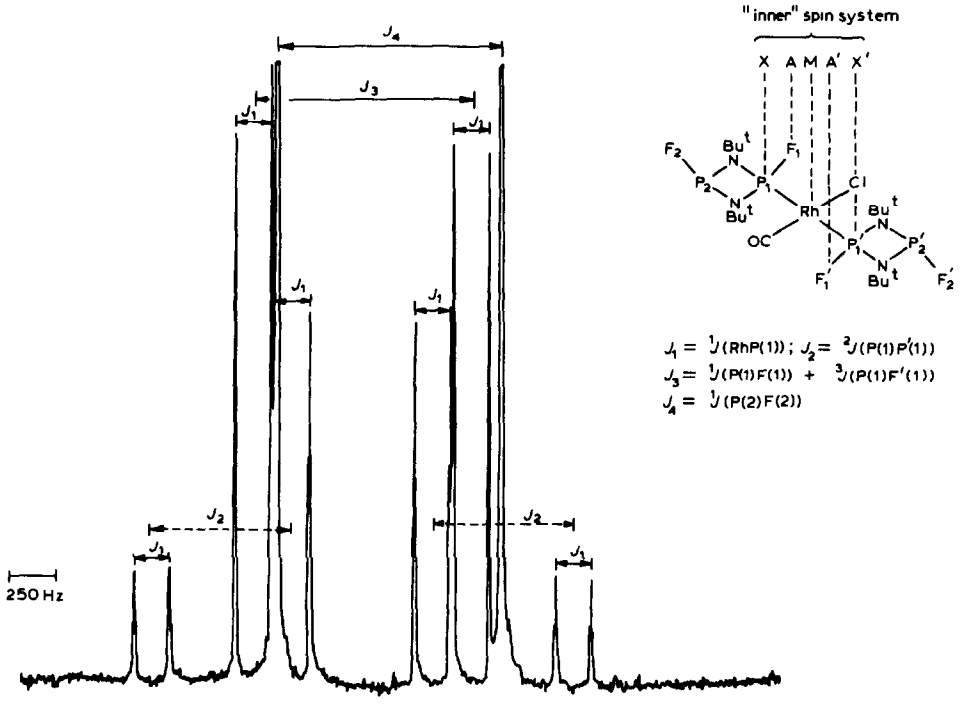
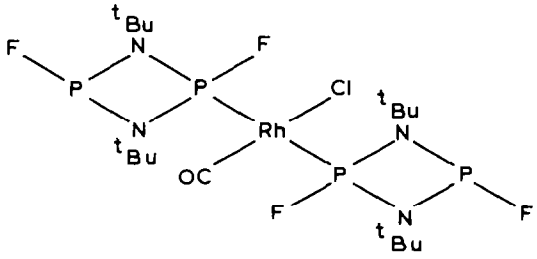


Fig. 2. The $^{31}P\{^1H\}$ NMR spectrum of complex II.



(II)

^1J(RhP(1)). The spin system associated with the complex is strictly [YBXAA'X'B'Y']M, however cross-ring couplings between the chemically shifted A and B ^{31}P nuclei are sufficiently small to allow approximate analysis of the "inner" system as [XAA'X']M. The parameters resulting from spectrum analysis using this treatment appear in Table 1, and the large value of ^2J(PP') (745 Hz) proves conclusively that in II the monodentate P-donor $(PFN^tBu)_2$ ligands occupy mutually *trans*-positions.

Further support for the structural assignment of II comes from analogous reactions between a 1/1 mixture of $PF(NMe_2)_2$ and $[RhCl(CO)_2]_2$ under an atmosphere of carbon monoxide to give the pale yellow complex $[RhCl(CO)(PF(NMe_2)_2]_2$ (III) (ν(CO) 2015 cm^{-1}) whose $^{31}P\{^1H\}$ NMR spectrum shown in Fig. 3 shows the expected simple doublet of doublet patterns. Treatment of $[RhCl(CO)_2]_2$ with $PF(NMe_2)_2$ under CO with stoichiometry Rh/L = 1/2 gives a product (ν(CO) 2000 cm^{-1}) whose $^{31}P\{^1H\}$ NMR spectrum (Fig. 4) is strikingly similar to that of II (except for the lack of resonances due to non coordinated ^{31}P

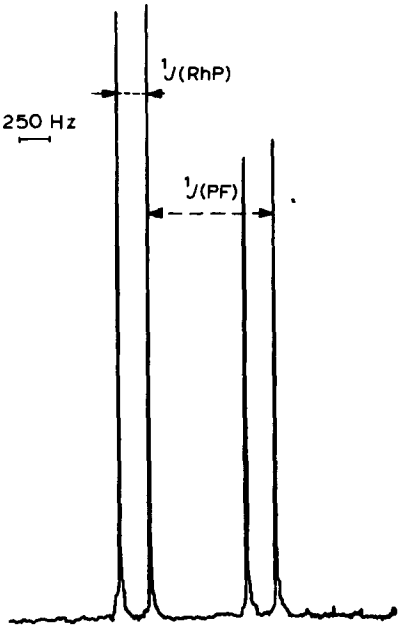


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of complex III.

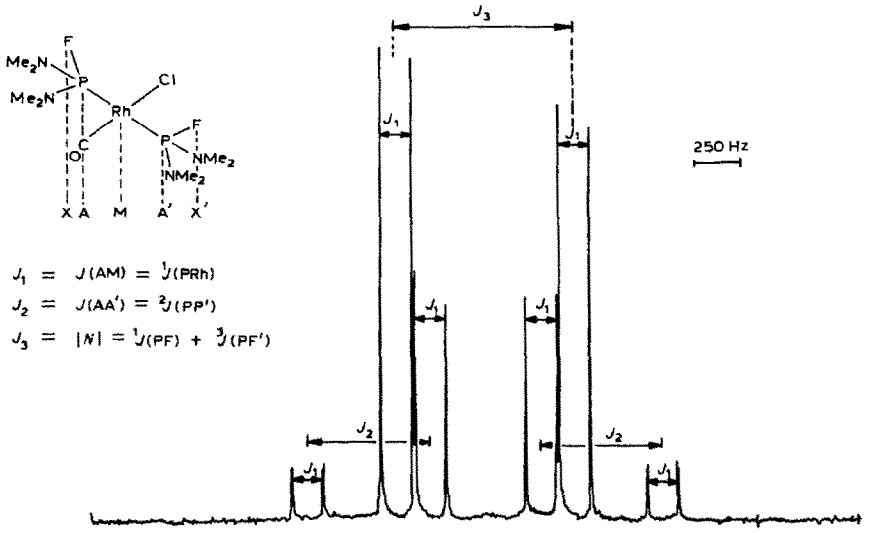
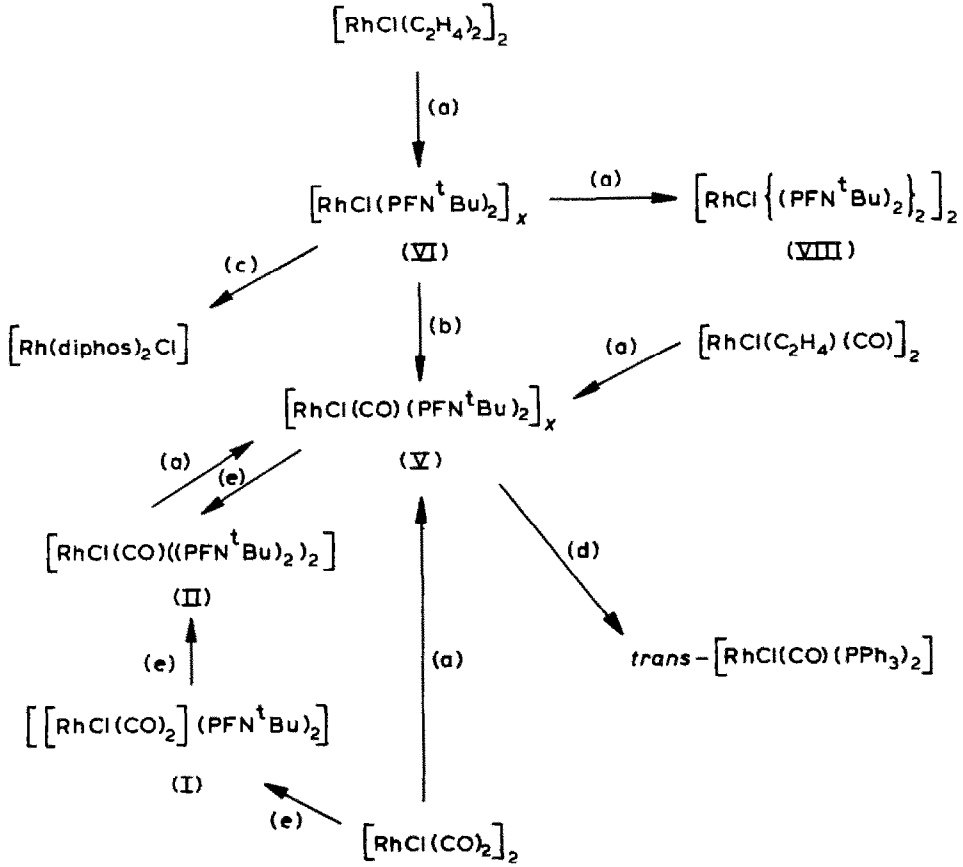


Fig. 4. The $^{31}P\{^1H\}$ NMR spectrum of complex IV.



SCHEME 1. (a) $(PFN^tBu)_2$; (b) CO; (c) diphos; (d) PPh_3; (e) $(PFN^tBu)_2 + CO$.

nuclei) suggestive of the formation of complex *trans*-[RhCl(CO){PF(NMe$_2$)$_2$}$_2$] (IV). The NMR spin system for IV is of the XAA'X'M type and has been fully analysed (Table 1). The ^2J(PP') coupling constant (693 Hz) is characteristic of the *trans*-disposition of the fluorophosphine ligands and the small value of ^4J(FF') (6 Hz) contrasts with that found for *cis*-[RhCl(PF(NMe$_2$)$_2$]$_2$ [2].

The formation of complexes I and II contrasts markedly with the interaction between either [RhCl(CO)$_2$]$_2$ or I with [PFN^{t}Bu]$_2$ in the absence of carbon monoxide, when the reaction product is the highly insoluble lemon yellow derivative formulated as [RhCl(CO)(PFN^{t}Bu)$_2$]$_x$ (V) (ν(C≡O) 2024 cm^{-1}) which can also be obtained by ethylene displacement from [RhCl(CO)(C$_2$H$_4$)]$_2$ (see Scheme 1) or more effectively by other synthetic routes (vide infra).

The products of the reaction between the [PXNR]$_2$ rings and [RhCl(C$_2$H$_4$)$_2$]$_2$ appear to depend on the molar ratios of the reacting species thus [RhCl(C$_2$H$_4$)$_2$]$_2$ and [PXNR]$_2$ (X = F, R = ^{t}Bu; X = Cl, R = ^{i}Pr) in a molar ratio Rh/ring of $< 1/2$ readily afford the orange insoluble complexes [RhCl(PFN^{t}Bu)$_2$]$_x$ (VI) and [RhCl(PClN^{i}Pr)$_2$]$_x$ (VII), respectively, whereas we find evidence for both [RhCl{(PFN^{t}Bu)$_2$}$_2$]$_2$ (VIII) and [RhCl{(PClN^{t}Bu)$_2$}$_2$]$_2$ (IX) from reactions of [RhClL$_2$] with [PClN^{t}Bu]$_2$ (L = C$_2$H$_4$, C$_6$H$_{10}$, C$_8$H$_{14}$; L$_2$ = C$_4$H$_6$) using Rh/ring ratios of 1/2. The insolubility of complexes VI → IX makes characterisation difficult, however the ^{31}P{^{1}H} NMR spectra of VIII synthesised in an NMR tube experiment (Fig. 5) is consistent with the formulation of the product, containing only two sets of resonances. The highfield set corresponds to the expected phosphorus directly bonded to rhodium (^1J(RhP) 295 Hz) while the lowfield resonance may be assigned to the uncoordinated phosphorus of the ring. Cross ring coupling ^2J(PNP') is also observed but steady precipitation of the complex causes some broadening of the lines. A single crystal crystallographic study of VIII was attempted but the compound decomposed in the X-ray beam.

The proposed formulation of [RhCl(PFN^{t}Bu)$_2$]$_x$ (VI) was confirmed by an almost quantitative reaction with 1,2-bis(diphenylphosphino)ethane, (diphos), to yield the known complex Rh(diphos)$_2$Cl [4] and some free ring compound whose isolation suggests the difluorocyclodiphosphazane is intact in VI. Likewise VI reacts readily with CO to give an almost quantitative yield of [RhCl(CO)(PFN^{t}Bu)$_2$]$_x$ (V) identical with that obtained by the methods outlined earlier. The latter reacts further

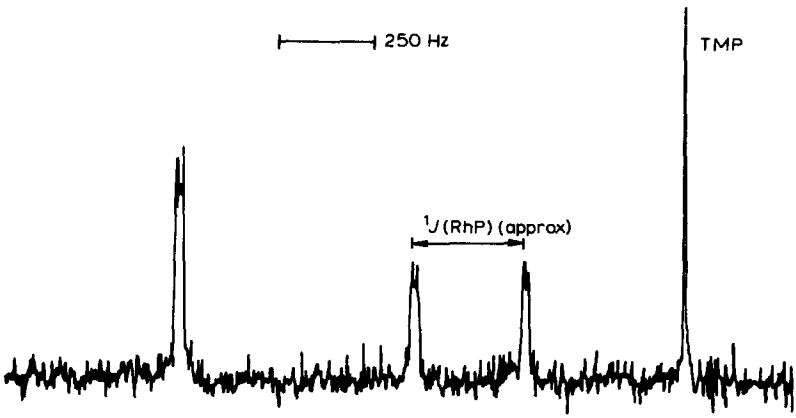
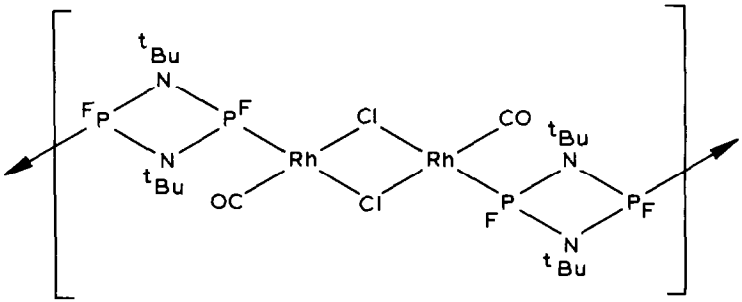


Fig. 5. ^{31}P{^{1}H} NMR spectrum of complex VIII.

with PPh_3 to give *trans*-$RhCl(CO)(PPh_3)_2$ in almost quantitative yield (See Scheme 1).

Interestingly although V cannot be converted to II by further addition of $[PFN^tBu]_2$ slow conversion does occur in the presence of carbon monoxide perhaps via a labile mononuclear dicarbonyl complex.

On the basis of the above data we propose a structure for V which involves a polymeric system involving dinuclear μ-chloro-bridged units since this would account for the insolubility of the complex and a similar structure could also obtain for the insoluble $[RhCl(PFN^tBu)_2]_x$ (VI).



(Proposed structure for VI)

Subsequent to the work reported above Jenkins and Willey [5] described an analogous complex to VI containing the $[PClN^tBu]_2$ ring (ν(C≡O) 2020 cm^{-1}) but proposed an alternative dimeric structure similar to that known in 'A' frame complexes containing bridging dppm ligands [6,7]. However the $^{31}P\{^1H\}$ NMR data quoted by Jenkins and Willey (singlets at +6.26 and −11.51 rel. H_3PO_4) are not consistent with such a structure since: (i) their ^{31}P chemical shift data do not fall in the range we have observed for a variety of rhodium complexes of $[PXN^tBu]_2$ [1,2]. (ii) no values for the directly bonded ^1J(RhP) coupling constant are reported and, (iii) the ^{31}P NMR shift data are more consistent with those of ring oxidation (or hydrolysis) products containing pentavalent phosphorus.

Alternative monomeric structures for V and VI containing the ring coordinated either (a) by both P and N or (b) acting as a chelate ligand via both phosphorus atoms must be considered unlikely on steric grounds and furthermore would not account for the insolubility of the complex. Very recently Kuhn and Winter while confirming our recent results on the establishment of monodentate and bridging modes of bonding for the $[PClN^tBu]_2$ ring in $[NiCl(C_5H_5)(PClN^tBu)_2]$ and $[Ni_2Cl_2(C_5H_5)_2)PClN^tBu)_2]$, respectively, have suggested chelating behaviour in the ionic complex $[Ni(C_5H_5)(PClN^tBu)_2][BF_4]$, however, there are no supportive ^{31}P NMR data [8].

Very recently Scherer et al. have established the bridging mode of bonding for the $[PRN^tBu]_2$ ring in a dirhenium carbonyl complex $[Re_2Br_2(CO)_6(RPN^tBu)_2]$ [9].

Experimental

Experimental procedures were as reported in ref. 2.

Reaction of $[PFN^tBu]_2$ with $[RhCl(CO)_2]_2$

All reactions were carefully monitored by ^{31}P NMR spectroscopy. Slow addition

of $[PFN^tBu]_2$ (0.0881 g, 0.3638 mmol) in toluene (1 cm^3) to a clear red solution of freshly prepared $[RhCl(CO)_2]_2$ (0.1414 g, 0.3638 mmol) in toluene (1 cm^3) under an atmosphere of carbon monoxide led to the quantitative formation of bis(chlorodicarbonyl)(1,3-di-t-butyl-2,4-difluorocyclodiphosphazanedirhodium(I) (I) as established by $^{31}P\{^1H\}$ NMR spectroscopy of the clear yellow solution. On evaporation of the solvent under a stream of carbon monoxide, the complex was deposited as a lemon yellow powder (0.2029 g, 88.4%). The latter could be redissolved in toluene saturated with carbon monoxide, giving an identical $^{31}P\{^1H\}$NMR spectrum, but any attempt at placing samples of solid I under vacuum or at washing (cold n-pentane) led to decomposition. (Found: C, 21.51; H, 3.89; N, 4.50. $C_{12}H_{18}N_2O_4F_2P_2Cl_2Rh_2$ calcd.: C, 22.84; H, 2.88; N, 4.44%). Infrared spectrum: ν(CO) 2096vs, 1996vs, 1395w, 1245m, 1185m, 1061s, 1052m, 930m, 905vs, 832s, 801s, 690m, 601m, 470s, 275s cm^{-1} (Nujol mull).

Reaction between di-μ-chlorotetra(ethylene)dirhodium(I) and 1,3-diisopropyl-2,4-dichlorocyclodiphosphazane

1,3-Diisopropyl-2,4-dichlorocyclodiphosphazane (2.297 g, 9.30 mmol) was added to di-μ-chlorotetraethylenedirhodium(I) (1.186 g, 3.05 mmol) suspended in ether (50 cm^3). The evolution of bubbles of ethylene gas indicated an immediate reaction. Stirring of the mixture was continued for 2 h, after which the suspension was filtered and the product washed with fresh ether and dried under vacuum to give μ-dichlorobis(1,3-diisopropyl-2,4-dichlorocyclodiphosphazanedirhodium(I) (VII) (2.244 g, 2.91 mmol, 95.4% based on $[RhCl(C_2H_4)_2]_2$). There was no change on heating up to 230°C. (Found: C, 19.36; H, 4.37; N, 7.26. $C_{12}H_{28}Cl_6N_4P_4Rh_2$ calcd.: C, 18.70; H, 3.66; N, 7.27%). IR spectrum: 1205w, sh, 1166s, 1148s, 1132s, 1018m, 960s, 928w, 892vs, 870m,sh, 808w, 675w, 658w, 638w, 574m, 518s, 470m, 438m cm^{-1} (Nujol mull).

Reaction between di-μ-chlorotetraethylenedirhodium (I) and 1,3-di-t-butyl-2,4-difluorocyclodiphosphazane

To $[RhCl(C_2H_4)_2]_2$ (1.069 g, 2.75 mmol) in ether (50 cm^3) was added $[PFN^tBu]_2$ (2.047 g, 8.45 mmol). An immediate reaction occurred, as evidenced by the instantaneous formation of bubbles of ethylene gas. The suspension was stirred for 4.5 h, filtered and the product washed with benzene and dried under vacuum to give di-μ-chlorobis(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)dirhodium(I), $Rh(Cl(PFN^tBu)_2)_x$ (VI) (1.348 g, 1.77 mmol, 64.4% based on $[RhCl(C_2H_4)_2]_2$) as a bright orange powder. The insolubility of the product prevented further purification. Decomposition occurs above 275°C. (Found: C, 25.41; H, 4.98; N, 7.07. $C_{16}H_{36}Cl_2F_4N_4P_4Rh_2$ calcd.: C, 25.26; H, 4.73; N, 7.36%). IR spectrum: 1398m, 1370s, 1250m, 1232w, 1210s, 1145w, 1058s, 1048s, 935m, 980vs, br, 832vs, 818s, 695m, 660m, 610m, 558w, 448m cm^{-1} (Nujoll mull).

Reaction between di-μ-chlorobis(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)dirhodium(I) (VI) and 1,2-bis(diphenylphosphino)ethane

Di-μ-chlorobis(1,3-di-t-butyl-2,4-difluorocyclodiphosphazanedirhodium(I) (0.1700 g, 0.92 mmol) and 1,2-bis(diphenylphosphino)ethane (1.994 g, 5.01 mmol) in toluene (50 cm^3) were stirred at 60°C for 2 h to give a yellow opaque mixture. The solvent was removed under vacuum and the residue was dissolved in chloroform (50 cm^3)

and the solution filtered. The yellow product was washed with fresh benzene and dried under vacuum to give $Rh(diphos)_2Cl$ (1.655 g, 1.77 mmol, 96.2% based on 0.92 mmol of starting material). M.p. 214–215°C (lit. [4] 215°C) (Found: C, 66.32; H, 5.20. $C_{52}H_{48}ClP_4Rh$ calcd.: C, 66.78; H, 5.18%).

Preparation of chloro(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)(carbonyl)-rhodium(I) (V)

(a) Reaction of di-μ-chlorobis(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)-dirhodium(I) (VI) with carbon monoxide. Di-μ-chlorobis(1,3-di-t-butyl-2,4-difluorodiphosphazane)dirhodium(I) (VI) (1.195 g, 1.57 mmol) was suspended in dry acetone (50 cm^3) and carbon monoxide gas was bubbled through the mixture for 1 h. Evaporation of the solvent afforded a buff coloured powder (1.200 g, 2.94 mmol) formulated as chloro(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)(carbonyl)rhodium(I), $RhCl(CO)(PFN^tBu)_2$, (V), (93.6% based on 1.57 mmol of starting material). On heating above 155°C the compound decomposes. Chloroform and ether may be used as alternative solvents for this reaction (Found: C, 26.49; H, 4.50; N, 6.69. $C_9H_{18}ClF_2N_2OP_2Rh$ calcd.: C, 26.48; H, 4.43; N, 6.85%). Infrared spectrum: 2024vs, 1397m, 1250ms, 1235m, 1190s, 1151w, 1060vs,br, 1045s,sh, 930m, 905vs,br, 835ms, 810m, 728w, 700m, 610w, 570m, 548w, 472ms, 400m, 320m,sh, 272 cm^{-1}, (Nujoll mull).

(b) Complex I (0.1003 g, 0.159 mmol) dissolved in toluene (1 cm^3) under carbon monoxide was converted quantitatively to V on treatment with $[PFN^tBu]_2$ (0.0385 g, 0.159 mmol). The complex (0.1216 g, 92.8%) precipitated as a yellow powder when a slight vacuum was applied to the reaction mixture to remove the CO.

(c) Complex V was also prepared by addition of two equivalents of $[PFN^tBu]_2$ to a n-hexane suspension of $[RhCl(CO)(C_2H_4)]_2$.

Reaction of chloro(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)(carbonyl)rhodium(I) (V) and triphenylphosphine

Chloro(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)(carbonyl)rhodium(I) (V) (0.589 g, 1.44 mmol) and triphenylphosphine (1.923 g, 733 mmol) were refluxed in toluene (50 cm^3) for 3 h. The hot solution was filtered to remove some insoluble black material (0.018 g) which is probably a metallic impurity in the starting material. The filtrate was evaporated to dryness and the resulting residue dissolved in warm chloroform (20 cm^3) and the product was *trans*-$RhCl(CO)(PPh_3)_2$ (0.958 g, 1.39 mmol, 96.5%) (Found: C, 64.29; H, 4.63. $C_{37}H_{30}ClOPRh$ calcd.: C, 64.32; H, 4.38%) which was recrystallised by the dropwise addition of ethanol to the chloroform solution, m.p. 189–191°C (lit. [10] 189–190.5°), ν(CO) 1965 cm^{-1} (Nujol mull) (lit. [11] 1961 cm^{-1} (Nujol mull)).

Preparation of trans-[RhCl(CO)((PFN^{t}Bu)$_2$)$_2$] (II)

A toluene suspension of $[RhCl(CO)(PFN^tBu)_2]_x$ (V) (0.2101 g, 0.1470 mmol) under dinitrogen was treated with $(PFN^tBu)_2$ (0.0712 g, 0.2940 mmol) and the mixture stirred for 24 h. Unreacted V (0.1173 g) was recovered by filtration. V (0.110 g, 0.1346 mmol) was again placed in suspension in toluene (1 cm^3) and carbon monoxide was bubbled through the mixture during the addition of $(PFN^tBu)_2$ (0.0652 g, 0.2692 mmol). The complex V slowly dissolved and the resulting yellow solution was established by $^{31}P\{^1H\}$ NMR spectroscopy to contain only *trans*-

$[RhCl(CO)[(PFN^tBu)_2)_2]$ (II) isolated as yellow crystals (0.1374 g, 78.4%) (ν(CO) 2012 cm^{-1}; toluene solution) by evaporation in vacuo. (Found, C, 31.32; H, 5.61; N, 8.44. $C_{19}H_{36}ON_4P_4F_4ClRh$ calcd.: C, 31.38; H, 5.58; N, 8.61%).

Reactions of $PF(NMe_2)_2$ with $[RhCl(CO)_2]_2$

A solution of $[RhCl(CO)_2]_2$ (0.0496 g, 0.1275 mmol) in toluene (1 cm^3) saturated with carbon monoxide was treated with portions of $PF(NMe_2)_2$ (0.0352 g, 0.2552 mmol). The observed $^{31}P\{^1H\}$NMR spectrum of the clear yellow solution obtained at a $Rh/PF(NMe_2)_2$ ratio 1/1 indicated the formation of bis(μ-chlorocarbonyldimethylaminofluorophosphine)dirhodium(I) (III). (ν(CO) 2015 cm^{-1}); toluene solution.

A reaction analogous to that described above was carried out under dinitrogen atmosphere and using a $Rh/PF(NME_2)_2$ ratio 1/2. The observed $^{31}P\{^1H\}$ NMR spectrum of the clear yellow solution indicated the formation of *trans*-{(chlorocarbonylbis(bisdimethylaminofluorophosphine)}rhodium(I) (IV), ν(CO) 2000 cm^{-1} (toluene solution).

Both reactions described above appeared to be quantitative on the basis of $^{31}P\{^1H\}$ NMR spectroscopy and no attempt was made to recrystallise the very soluble complexes or to determine isolated yields of the small samples prepared.

Preparations and reactions of $(RhCl(PXN^tBu)_2]_2$ (VIII, X = F; IX, X = Cl)

Complex VIII. The addition of $(PFN^tBu)_2$ (0.2272 g, 0.9380 mmol) in toluene (1 cm^3) to freshly prepared $[RhCl(C_8H_{14})_2]_2$ (0.1156 g, 0.2345 mmol) dissolved in toluene (0.5 cm^3) was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Despite rapid precipitation of the product which prevented full spectroscopic characterisation owing to line-broadening, the spectrum was consistent with the formation of a complex tentatively assigned as bis{(μ-chloro)bis(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)}dirhodium(I) (VIII). The yellow powder (0.2223 g, 76.1%) was separated by filtration, washed with n-pentane and dried in vacuo. Further purification was prevented by its insolubility in all common solvents. (Found: C, 33.56; H, 6.61; N, 8.98. $C_{32}H_{72}N_8F_8P_8Cl_2Rh_2$ calcd.: C, 30.86; H, 5.83; N, 8.99%. IR spectrum: 1396s, 1249s, 1230s, 1209vs,br, 1045vs,br, 1031s,sh, 930s, 900vs,br, 819s, 797s,br, 759m, 720vs, 670s, 651s, 638s, 596m, 553m, 540m, 495m, 440ms, 391w, 378m, 366m, 345vw, 335vw, 210vw, 301w, 255w cm^{-1} (Nujol mull).

A product having identical appearance and IR spectrum was obtained in analogous reactions of $[RhClL_2]_2$ ($L = C_2H_4$, $L_2 = C_4H_6$, C_6H_{10}) with $(PFN^tBu)_2$ in toluene using a Rh/ring ratio 1/2.

Complex IX. Freshly prepared dry $[Rh(Cl)C_4H_6]_2$ (0.2736 g, 0.6001 mmol) was added to a solution of $[PClN^tBu]_2$ (0.6603 g, 2.400 mmol) in toluene (20 cm^3) and the mixture was stirred at 40°C. Within ca. 2 min, all material had dissolved with effervescence forming a clear deep-red solution from which deep red-orange crystals were soon deposited. The solvent was removed by syringe and the product washed several times with n-pentane and dried in vacuo at room temperature. The complex bis{(μ-chloro)bis(1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane)}dirhodium(I) (IX) (0.7684 g, 93%) was sparingly soluble in dichloromethane but insoluble in benzene, toluene, tetrahydrofuran and acetonitrile. The $^{31}P\{^1H\}$ NMR spectrum is reported in the text. (Found: C, 28.16; H, 5.39; N, 8.29. $C_{32}H_{72}N_8P_8Cl_{10}Rh_2$ calcd.: C, 27.91; H, 5.27; N, 8.14%). Infrared spectrum: 1396m, 1366ms, 1300w, 1256m,sh, 1245sh,

1225s, 1199vs, 1136vw, 1069m, 1042s, 1030ms, 930m, 887vs,br, 810vw, 722vw, 641m, 629m, 586w-m, 560vs, 533m, 520m, 453m, 435w-m, 410m, 367w, 341w, 310w, 241w, 225w cm^{-1} (Nujol mull).

An identical product was obtained from analogous reactions in toluene at 25–60°C using $[RhClL_2]$ ($L = C_2H_4$, C_8H_{14}, C_6H_{10}). In all cases, increasing the $Rh/(PClN^tBu)_2$ stoicheiometry from 1/2 to > 1/3 did not lead to the isolation of trisubstitution products, instead IX was invariably obtained. IX can also be prepared by refluxing $[RhCl(C_8H_{12})_2]_2$ with a large excess of $[PClN^tBu)_2$ in toluene.

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