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SYNTHESES AND ^{31}P NMR STUDIES OF SOME CYCLOOCTA-1,5-DIENERHODIUM(I) COMPLEXES CONTAINING COORDINATED 1,3-DI-t-BUTYL-2,4-DIHALOGENOCYCLODIPHOSPHAZANES, $[PXN^tBu]_2$ (X = Cl, F) AND RELATED LIGANDS. CRYSTAL AND MOLECULAR STRUCTURE OF BIS{(CHLORO)(CYCLOOCTA-1,5-DIENE)}{1,3-DI-t-BUTYL-2,4-DIFLUOROCYCLODIPHOSPHAZANE}DIRHODIUM(I) *

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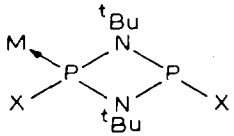
Summary

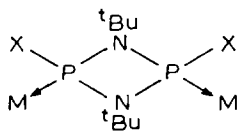
Syntheses of several cycloocta-1,5-dienerhodium(I) complexes containing coordinated 1,3-di-t-butyl-2,4-dihalogenocyclodiphosphazanes $(PXN^tBu)_2$ (X = Cl, F) and related ligands are described. ^{31}P NMR spectroscopic studies have established two different types of coordination mode of the ring system and their interconversion. A single crystal structure determination on $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})_2(PFN^tBu)_2]$ confirms the proposed structure.

Introduction

There are a variety of possible coordination modes for the novel four membered cyclodihalogenodiphosphazane ring systems $[PXNR]_2$, (X = halogen) in their metal complexes. Previously [1] we briefly reported syntheses and NMR spectroscopic studies on platinum(II) and some rhodium(I) derivatives of $[PXN^tBu]_2$ (X = F, Cl) which suggested the bonding modes (a) and (b) shown below, both involving



(a)



(b)

* Dedicated to Professor H.J. Emeléus on his 80th birthday on 22nd June 1983. John Nixon was an ICI Fellow with Professor Emeléus at Cambridge 1962–1964.

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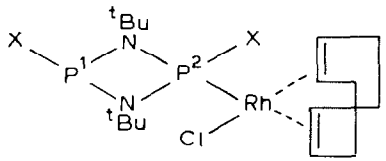
coordination to the metal only via phosphorus.

We now report full details of our spectroscopic studies on some cycloocta-1,5-dienerhodium(I) complexes containing 1,3-ditertiary 2,4-dihalogenocyclodiphosphazane ligands which reveal the ready interconversion of the two types of structure (a) and (b).

Results and discussion

$[RhCl(\eta^4\text{-}C_8H_{12})]_2$ reacts with two equivalents of $[PXN^tBu]_2$, (X = F, Cl), to afford the yellow-orange complexes $[RhCl(\eta^4\text{-}C_8H_{12})(PClN^tBu)_2]$ (I) and $[RhCl(\eta^4\text{-}C_8H_{12})(PFN^tBu)_2]$ (II), respectively. The unsymmetrical near first-order $^{31}P\text{-}\{^1H\}$ NMR spectra of I and II (Fig. 1a and 1b) indicate clearly that only a single phosphorus atom of the $(PXN^tBu)_2$ ring system is directly coordinated to the metal as shown below since each spectrum shows two sets of chemically shifted ^{31}P resonances only one of which exhibits a large doublet splitting ($^1J(P_2Rh)$) due to coupling with the ^{103}Rh nucleus (100% abundant $I = \frac{1}{2}$)



(I , X = Cl ;
II , X = F)

In the case of I the only additional splitting is due to $^2J(P(1)P(2))$ cross ring coupling whereas in II each resonance exhibits further fine structure arising from $^1J(PF)$ and $^3J(PF)$ couplings. Since the $^{31}P\text{-}\{^1H\}$ NMR spectrum of II deviates slightly from first order the calculated spectrum was obtained using PANIC 80 spectral simulation which is a version of the LAOCOON programme [2]. Chemical shift and coupling constant data for I and II are listed in Table 1. Prior to this work a few analogous triorganophosphine or $(RO)_3P$ complexes were known [3,4] and some cationic derivatives $[Rh(\eta^4\text{-}C_8H_{12})L_x]^+$ [5,6] have been described.

A study of the interaction of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ with a number of simple alkylaminohalophosphines was carried out, the course of the reaction being monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. PCl_2NMe_2 reacts with $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ in a 1/1 ratio in CH_2Cl_2 at ambient temperature to give $[RhCl(\eta^4\text{-}C_8H_{12})(PCl_2\text{-}NMe_2)]$ (III); however, intermolecular ligand exchange prevented measurement of $^1J(RhP)$. In contrast $^{31}P\text{-}\{^1H\}$ data were readily obtained for the complexes $[RhCl(\eta^4\text{-}C_8H_{12})(PCl(NMe_2)_2)]$ (IV), and $[RhCl(\eta^4\text{-}C_8H_{12})(P(NC_5H_{10})_3)]$ (V), containing bulkier ligands (Table 1). A mixture of $[RhCl(\eta^4\text{-}C_8H_{12})(PF(NMe_2)_2)]$ (VI) and the dimeric complex $[RhCl\{PF(NMe_2)_2\}]_2$ (VII) resulted from the reaction of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ with $PF(NMe_2)_2$ even when the rhodium/ligand ratio was very much greater than 1/1. The $^{31}P\text{-}\{^1H\}$ NMR spectrum (Fig. 2) of the reaction products showed a single doublet of doublets pattern for VI and lines typical of an $[XA]_2M$ spin system (X = ^{31}P, A = ^{19}F, M = ^{103}Rh) for VII which was fully analysed (Table 2).

Careful attempts to obtain $[RhCl(\eta^4\text{-}C_8H_{12})(PF_2NMe_2)]$ were unsuccessful, instead the known dimeric $[RhCl(PF_2NMe_2)]_2$ complex [7–10] was formed even in the

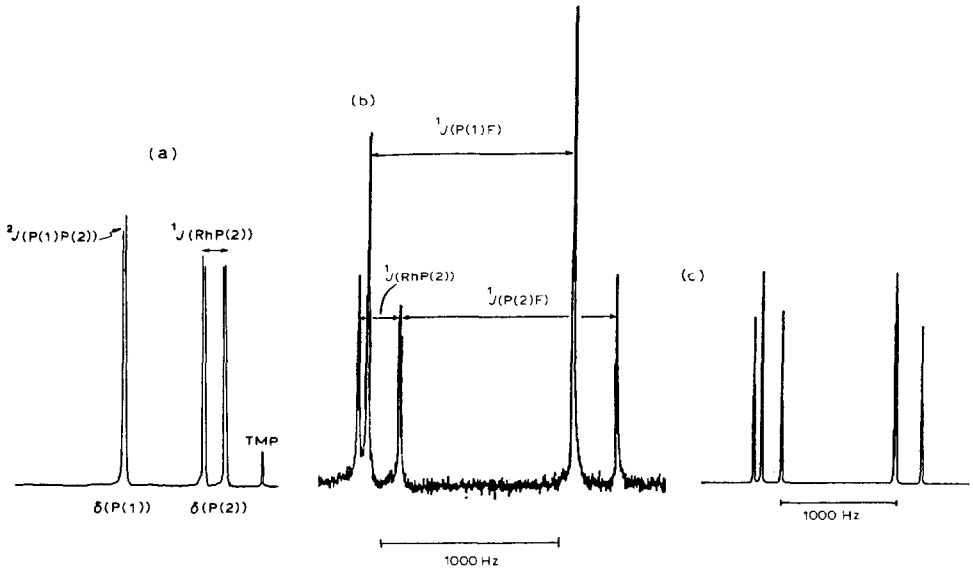


Fig. 1. (a) ^{31}P-{^1H} NMR spectrum of [RhCl(η^4-C_8H_{12})(PClN^{t}Bu)]$_2$ (I); (b) ^{31}P-{^1H} NMR spectrum of [RhCl(η^4-C_8H_{12})(PFN^{t}Bu)] (II), (c) simulated spectrum of II.

presence of a large excess of [RhCl(η^4-C_8H_{12})]$_2$, and although spectroscopic data were obtained for [RhCl(η^4-C_8H_{12})(PF_2NH^tBu)] (VIII) no evidence was obtained for stable alkylaminohalophosphine $(R_2N)_nPX_{3-n}$ complexes of the type [Rh_2Cl_2(η^4-C_8H_{12})L_2] analogous to [Rh_2Cl_2(η^4-C_8H_{12})($P(OPh)_3$)$_2$] [11] which has been characterised in the solid state.

Interestingly under carefully controlled conditions the new dinuclear complexes containing bridging $(RNPX)_2$ ligands [{RhCl(η^4-C_8H_{12})}$_2$$\mu$-(PClN^{t}Bu)$_2$] (IX) and [{RhCl($\eta^4$-$C_8H_{12}$)}$_2$$\mu$-(PFN^{t}Bu)$_2$] (X) could be prepared quantitatively by slow

TABLE 1

^{31}P NMR DATA FOR COMPLEXES [RhCl(η^4-C_8H_{12})L]

Complex	L	δ(P)(L) [a]	δ(P)(Complex) [a]	Δ [b]	^1J(RhP) [c]
I	[PClN^{t}Bu]$_2$	−67.3	−13.8(P(2)) [d] −40.3(P(1))	+53.5	245
II	[PFN^{t}Bu]$_2$	−24.8 [e]	+2.5(P(2)) [f] +0.2(P(1)) [f]	+27.3	242
III	PCl_2NMe_2	−25.1	+3.1	+28.2	− [g]
IV	$PCl(NMe_2)_2$	−17.1	−19.1	−1.4	232
V	$P(NC_5H_{10})_3$	+23.6	+35.7	+12.1	195
VI	$PF(NMe_2)_2$	−10.0	−4.5 [h]	+5.50	230
VIII	PF_2NH^tBu	−8.0	+11.0 [i]	+19.0	266

[a] In ppm (rel. $P(OMe)_3 = 0$ highfield +ve). [b] Coordination shift δ(P)(L) − δ(P)(complex). [c] In Hz. [d] ^2J(P(1)P(2)) 32 Hz. [e] ^1J(PF) −1190 Hz; ^2J(PP′) 30.7 Hz; ^3J(PF′) 25.5 Hz; ^4J(FF′) 93.0 Hz. [f] ^1J(PF) 1217 Hz; ^1J(P(1)F) 1162 Hz; ^3J(P(2)F) > 5 < 10 Hz; ^2J(P(1)P(2)) > 5 < 10 Hz, ^3J(P(1)F′) < 5 Hz. [g] Intermolecular ligand exchange. [h] ^1J(PF) 1061 Hz. [i] ^1J(PF) 1165 Hz, ^2J(PH) 32 Hz.

TABLE 2

^{31}P-{^{1}H} NMR DATA FOR $[RhClL_2]_2$ COMPLEXES

L	$\delta(P)(L)$ [c]	$\delta(P)$ [c]	Δ [d]	$^{1}J(PF)$ [e]	$^{1}J(RhP)$ [e,f]	$^{2}J(PP')$ [e]	$^{3}J(PF')$ [e]	$^{4}J(FF')$ [e]	Refs.
PF_3	+37.00	+30.20	−6.80	−1329	−344.0 341.0	−65.2 63.5	+19.1	+4.4	7,24
$PF_2(NMe_2)$	−2.00	−2.05	−0.05	(1108) [a] (1106) [a]	304.0 302.0	[b]	[b] 49.0	[b]	This work, 7,8
$(PF_2)_2NMe$	−0.50	+5.55	+6.05	(1200) [a]	303	104+	[b]	[b]	25
$PF(NMe_2)_2$	−10.00	−14.35	−4.35	−1025	286	41.2	46.0	18.0	This work

[a] $^{1}J(PF)+^{3}J(PF')$. [b] Full analysis not carried out. [c] ppm rel. to $P(OMe)_3$. [d] $\delta(P)(L)-\delta(P')$. [e] Hz.

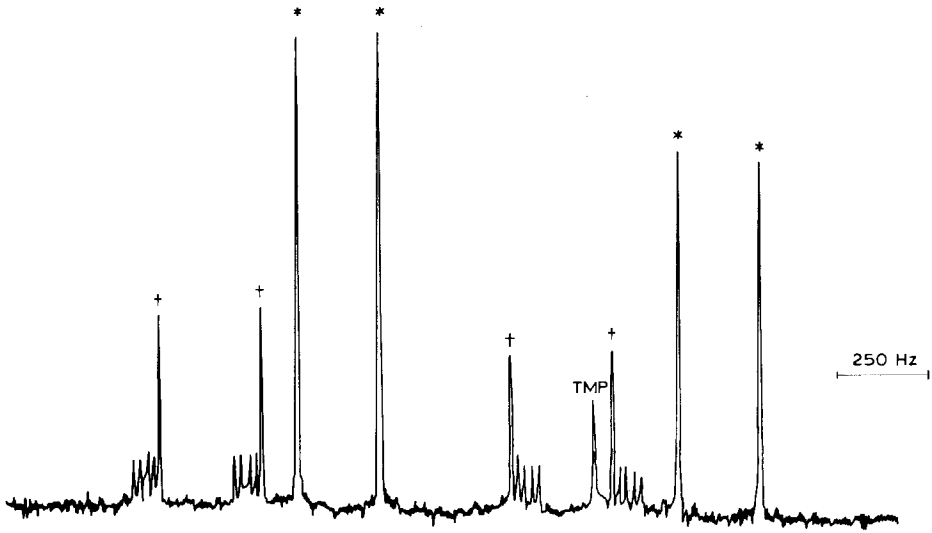
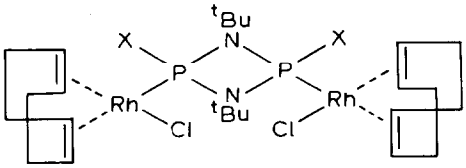


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of a mixture of $[RhCl(\eta^4\text{-}C_8H_{12})PF(NMe_2)_2]$ (VI) (*) and $[RhCl(PF(NMe_2)_2)_2]_2$ (VII) (†).

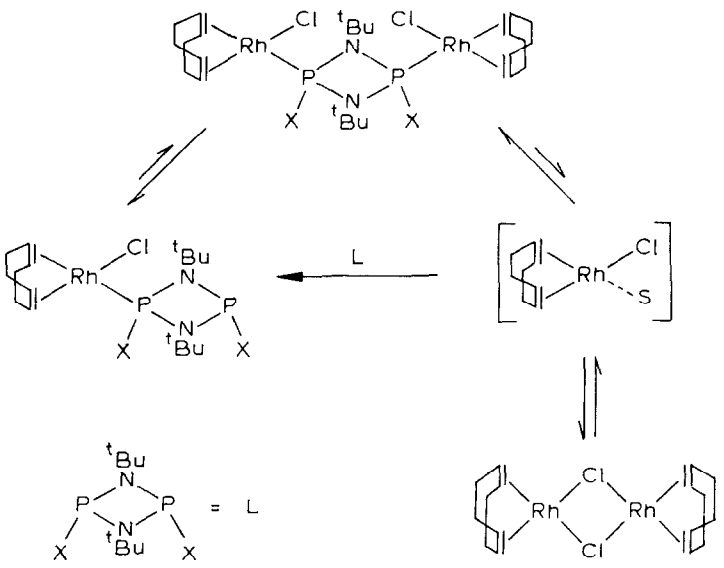
mixing of solutions of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ (one equivalent) and $(PXN^tBu)_2$ (X = F, Cl) (one equivalent). The complexes were characterised by elemental analysis, $^{31}P\{^1H\}$ NMR spectroscopy and IR spectroscopy and in the case of X by a single crystal X-ray structure determination.



(IX, X = Cl ;
X, X = F)

The interconversion of the mononuclear compounds I and II and the corresponding dinuclear complexes IX and X was demonstrated by progressive addition of the cyclodiphosphazane ligands to solutions of the dinuclear complexes, the reactions being monitored by ^{31}P NMR spectroscopy and the results confirmed by subsequent isolation of the mononuclear species. Further investigation showed that the mononuclear complexes I and II could be reconverted to IX and X, respectively, on addition of solutions of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ in the correct stoichiometry. Modification of the mixed solvent ratio and concentration of solutions of IX and X led to disproportionation of the dinuclear complexes to the mononuclear compounds which remained in solution and caused precipitation of the yellow $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ as evidenced by a careful ^{31}P NMR and IR study of solutions and solid, respectively. These interesting interconversions are summarised in Scheme 1, and are likely to involve an intermediate containing coordinated solvent although no evidence was obtained for such a species.

SCHEME 1



The ^{31}P NMR spectra of analytically pure samples of IX and X dissolved in CH_2Cl_2/toluene are shown in Fig. 3 and 4, respectively, and reveal some unusual features. Complex IX should exhibit lines characteristic of the A part of an $[MA]_2$ spectrum ($M = {}^{103}Rh$, $A = {}^{31}P$) whereas (X) should show lines typical of an $(XMA)_2$ spin system ($X = {}^{19}F$). The observed spectrum of IX is complicated by the appearance of the monomeric complex I arising from the disproportionation reaction mentioned above but shows three doublet patterns (A, B, C) containing further fine structure (from coupling ^1J(RhP) and ^3J(RhP)) rather than one such pattern ex-

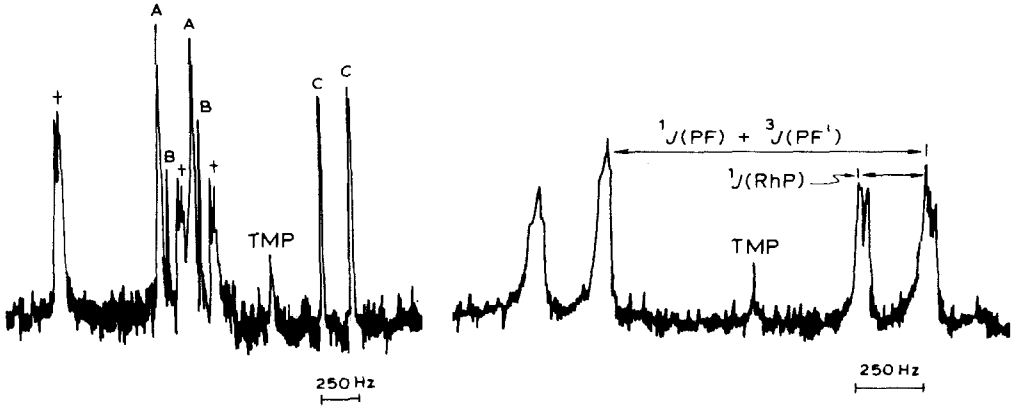


Fig. 3. ^{31}P-{^1H} NMR spectrum of $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})_2(\mu\text{-}PClN^tBu)]$ (IX) († are resonances of complex I and A, B and C represent isomers of IX see text).

Fig. 4. ^{31}P-{^1H} NMR spectrum of $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})(\mu\text{-}PFN^tBu)]$ (X).

TABLE 3

$^{31}P\{^{1}H\}$ NMR DATA FOR $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})_2(\mu\text{-}PXN^tBu)]$

Complex	X	$\delta(P)$ [a]	$^1J(RhP)$ [b]	$^1J(PF)$ [b]	Other J [b,e]
IX	Cl	−17.8 [f]	254 [c]		$^2J(PP') \simeq 23$
		−16.3 [g]	239		$^2J(PP') \simeq 15$
		+13.0 [h]	236		$^2J(PP') \simeq 17$
X	F	−2.3	260	1197 [d]	<10

[a] Relative to $P(OMe)_3$; highfield shifts quoted +. [b] Hz; [c] $^1J(RhP)+{}^3J(RhP')$. [d] $J(PF)+{}^3J(PF')$. [e] Spin systems generally complicated (see text) and not fully analysed; estimates are marked 'e'. [f] Isomer A. [g] Isomer B. [h] Isomer C (see Fig. 3).

pected for IX suggesting the existence of conformational isomers. Slow evaporation of the solution of IX led to recovery of the pure complex and on redissolving the sample the same ^{31}P NMR spectrum was obtained (Table 3).

The simplicity of the ^{31}P NMR spectrum of X indicates only one chemical environment for phosphorus which is consistent with the bridging mode of bonding for the cyclodiphosphazane ligand; observation of four groups of resonances resulting from dominant couplings of $^1J(PF)$ and $^2J(RhP)$. The presence of additional lines is expected in view of the complicated spin system, however the lack of a mirror plane of symmetry in the spectrum suggests that isomers having slightly differing chemical shifts may be present in solution.

The situation has been clarified by a single crystal X-ray structure determination of X which confirms (i) the bridging nature of the cyclodiphosphazane ligand and (ii) coordination through the phosphorus atoms and also reveals that a single

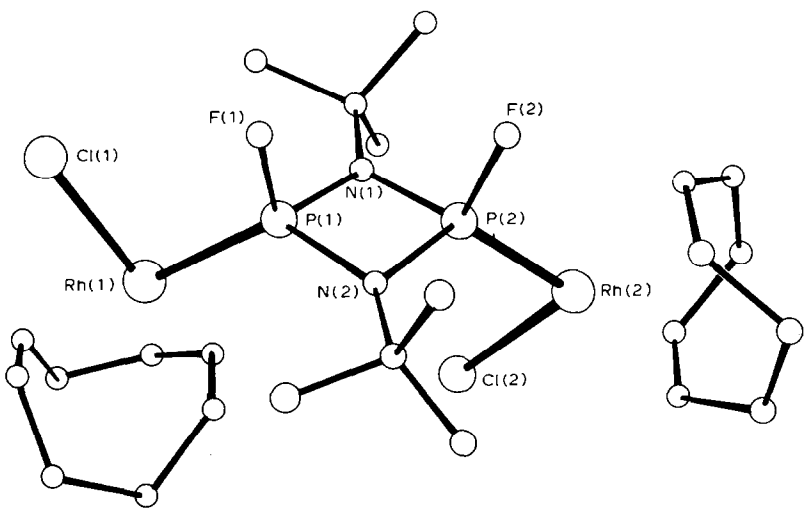


Fig. 5. Molecular structure of $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})_2(\mu\text{-}PFN^tBu)]$. Selected bond length data are: Rh(1)–P(1) 2.219(8); Rh(1)–Cl(1) 2.347(8); Rh(2)–P(2) 2.197(7); Rh(2)–Cl(2) 2.344(8); P(1)–F(1) 1.567(15); P(2)–F(2) 1.608(15); P(1)–N(1) 1.695(21); P(1)–N(2) 1.655(19); P(2)–F(2) 1.608(15); P(2)–N(1) 1.667(20); P(2)–N(2) 1.661(21) Å.

asymmetrical structure is observed in the solid state and the preferred structure is one which minimises the interhalogen repulsions (Fig. 5). Details of the structural features of interest in this complex will be reported in full elsewhere along with the crystal and molecular structure of the related complexes *cis*-$[PtCl_2(PMe_2Ph)(PClN^tBu)_2]$, *cis*-$[PtCl_2(PEt_3)(PFN^tBu)_2]$ and *cis*-$[PtCl_2[(PFN^tBu)_2]_2]$ [12,13].

Crystal data: $C_{24}H_{42}N_2F_2P_2Cl_2Rh_2$, orthorhombic, space group I_{ba2}, a 22.368(3), b 21.009(2), c 12.638(2) Å, $Z = 8$. The structure was determined by routine heavy atom methods and refined by least squares to $R = 0.059$ for 1234 reflections measured on a Hilger and Watts four circle diffractometer.

Experimental

All manipulations were carried out under an atmosphere of dry nitrogen gas or in vacuo. Solvents were dried and distilled under dinitrogen and freeze-thaw degassed before use. $^{31}P-\{^1H\}$ NMR spectra were obtained using a Jeol PFT 100 Fourier transform spectrometer operating at 40.49 MHz. Chemical shifts are quoted relative to TMP ($P(OMe)_3$) (highfield-positive) IR spectra were obtained on a Perkin–Elmer 457 grating spectrometer and frequencies are quoted to ± 1 cm^{-1}. Elemental analyses were obtained by Mr. and Mrs. A.G. Olney of this laboratory.

Alkylaminochlorophosphines PCl_2NMe_2 [14] and $PCl(NMe_2)_2$ [15] were synthesised from freshly distilled PCl_3 using literature procedures. $P(NC_5H_{10})_3$ [16] was similarly prepared and alkylaminofluorophosphines PF_2NMe_2 [17], PF_2NH^tBu [18] and $PF(NMe_2)_2$ [17] were prepared from their chloro analogues by treatment with freshly sublimed SbF_3. Purity of all the alkylaminohalophosphines was checked by physical and spectroscopic methods prior to use.

Preparation of $(PClN^tBu)_2$

This compound was prepared using a modification of the method of Keat et al. [19]: t-butylamine (62.9 g, 0.860 mol) was added dropwise to an efficiently stirred solution of phosphorus trichloride (39.4 g, 0.257 mol) in diethyl ether (600 cm^3) at −78°C. On completion of the addition, the mixture was allowed to warm to room temperature and stirred overnight. Solid amine hydrochloride was removed by filtration and carefully washed with diethyl ether (200 cm^3), the washings being added to the filtrate. The solvent was removed by room-temperature evaporation under reduced pressure. Traces of diethyl ether and a considerable quantity of $PCl_2\{N(H)Bu^t\}$ were finally removed at 35–75°C/0.1 mmHg. Distillation at 95°C/0.1 mmHg followed either by sublimation (50–70°C/0.05–0.001 mmHg) or recrystallisation from light petroleum (b.p. 40–60°C) gave 1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane in yields varying from 35–49%. The product was completely free from 1,3-di-t-butyl-2-chloro-4-t-butyl-aminocyclodiphosphazane and was characterised by melting point (42–43°C; lit. 42–44°C and 40–42°C [19] and $^{31}P-\{^1H\}$ NMR spectroscopy. IR spectra (not previously reported (2966s, 2928m, 2900sh, 2865w, 1457m, 1395m, 1367s, 1276sh, 1242sh, 1227sh, 1203vs,br, 1102vw, 1063sh, 1045vs, 1028vs, 934s, 906vs,br, 801w, 618w, 582w, 536m cm^{-1} (CH_2Cl_2 solution). Additional weak bands were observed in Nujol mulls at 2703, 2591, 2496, 2072 cm^{-1} with spectra identical in the range 2000–600 cm^{-1} to those obtained in solution, and

bands at 582vs, 536m, 496ms, 450m,sh, 440ms, 396ms, 356w,sh, 350w, and 326w cm^{-1}.

Synthesis of $(PFN^tBu)_2$

Small amounts of $(PClN^tBu)_2$ were fluorinated in high yield using antimony trifluoride in the absence of solvent, but on a larger scale $(PClN^tBu)_2$ was dissolved in diethyl ether and treated at room temperature with an excess of antimony trifluoride. Evaporation of solvent at 0°C/10 mmHg followed by repeated fractionation through traps at 20, −78 and −196°C led to the collection of 2,3-di-t-butyl-2,4-difluorocyclodiphosphazane at −78°C. Yields were generally in excess of 75%. The previously reported boiling point (23.5°C/4 mmHg) [20] is in error; it was found that $(PFN^tBu)_2$ boils in the range 60—70°C/2 mmHg and this has very recently been confirmed by Keat et al. [21]. The IR spectrum does not appear to have been reported in the literature: 2976vs, 2940m, 2915sh, 2880m, 1474m, 1465sh, 1403m, 1376s, 1257s, 1236sh, 1222vs,br, 1050vs,br, 945vs, 924vs, 820w, 811w, 763vs, 727vs, 652m, 602m, 555vw, 495wm, 450m, 400wm, 370m, 323vw cm^{-1} (liquid film).

$[RhCl(\eta^4\text{-}C_8H_{12})]_2$ was prepared by an improved version [18] of the literature methods [22,23].

Preparations of $[RhCl(\eta^4\text{-}C_8H_{12})(PXN^tBu)_2]$ *(X = Cl (I) and X = F (II))*

Solutions of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ in toluene were added rapidly, with stirring, to two equivalents of $(PXN^tBu)_2$ (X = F, Cl) dissolved in toluene. The reaction mixtures were stirred for a further 30 minutes and the solvent then stripped away under reduced pressure. The crude products were washed with n-pentane at −78°C and recrystallised from methylcyclohexane. $^{31}P\text{-}\{^1H\}$ NMR spectra were consistent with the quantitative formation of chloro(cycloocta-1,5-diene)(1,3-di-t-butyl-2,4-difluorocyclodiphosphazane)rhodium(I) and chloro(cycloocta-1,5-diene)(1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane)rhodium(I). Yields obtained after recrystallisation of the complexes are given in Table 4, together with experimental, microanalytical and infrared spectroscopic data.

Reactions of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ *with* $L = PCl_2NMe_2$, $PCl(NMe_2)_2$, $P(NC_5H_{10})_3$, $PF(NMe_2)_2$, PF_2NH^tBu *and* PF_2NMe_2

The progressive addition of ligands L to $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ in toluene or dichloromethane was monitored using $^{31}P\text{-}\{^1H\}$ NMR spectroscopy to a maximum Rh/L ratio = 1/1. The results are presented in Table 1.

General procedure. A 5 cm^3 0.2 *M* solution of $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ in dry, freeze-thaw outgassed $C_5D_5CD_3$ was prepared and aliquots (0.1 mmol) syringed under nitrogen atmosphere into 8 mm NMR tubes, each equipped with a rubber septum. Freshly purified ligands $L = PCl_2NMe_2$, $PCl(NMe_2)_2$, $P(NC_5H_{10})_3$, $PF(NMe_2)_2$, PF_2NH^tBu and PF_2NMe_2 were weighed as 0.2 mmol aliquots using conventional Schlenck-tube or vacuum-line techniques and toluene or dichloromethane was condensed on to the weighed samples to a total volume in each case not exceeding 0.5 cm^3. Addition of increments of the ligand solutions to the $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ solutions was accomplished using a 500 μl syringe flushed prior to use with nitrogen gas. Temperature was monitored in the spectrometer at 30°C during all reactions. The following complexes analogous to $[RhX(\eta^4\text{-}C_8H_{12})\text{-}\{PXN^tBu\}_2]$ (X = Cl, (I); X = F (II)) were identified in solution: [chloro(cycloocta-

TABLE 4

PREPARATIONS, ELEMENTAL ANALYSES AND INFRARED SPECTRA OF I AND II

X	$(PXN^tBu)_2$	$[RhCl(\eta^4\text{-}C_8H_{12})]_2$	$[RhCl(\eta^4\text{-}C_8H_{12})(PXN^tBu)_2]$
Cl	0.1894 g, 0.6885 mmol	0.1696 g, 0.3440 mmol	I 0.2761 g, 0.5293 mmol, 79.9% deep-orange crystals from methylcyclohexane
F	0.1040 g, 0.4924 mmol	0.1058 g, 0.2146 mmol	II 0.1729 g, 0.3538 mmol, 82.4% lemon-yellow crystals from methyl-cyclohexane

$[RhCl(\eta^4\text{-}C_8H_{12})(P\ Cl\ N^tBu)_2]$, (I): (Found: C, 36.90; H, 5.87; N, 5.25. $C_{16}H_{30}N_2P_2Cl_3Rh$ calcd.: C, 36.84; H, 5.80; N, 5.37%). IR spectrum: 1435m,sh, 1405m, 1395m, 1380s, 1370s, 1355w, 1228m, 1310w, 1295w, 1250s, 1230s, 1222s, 1195v,sh, 1082m, 1061m, 1050s, 1035m,sh, 1005w, 993w, 964w, 945w,sh, 930m, 900vs,br, 875m,sh, 812w, 783w, 756w, 720w, 685vw, 636s, 537s, 510s, 454ms, 415w, 395w, 362w, 345, 333w, 290w cm^{-1} (Nujol mull).

$[RhCl(\eta^4\text{-}C_8H_{12})(PFN^tBu)_2]$ (II): (Found: C, 39.27; H, 6.26; N, 5.73. $C_{16}H_{30}N_2F_2P_2ClRh$ calcd.: C, 39.32; H, 6.19; N, 5.73%). IR spectrum: 1425m,sh, 1415w,sh, 1388m, 1371s, 1332w, 1305w, 1240s, 1224s, 1195vs,br, 1140w,sh, 1040vs,br, 993w,sh, 960w,sh, 926s,sh, 905vs, 858w, 812m,sh, 795m,sh, 773s, 739s, 720s,sh, 657m, 637m, 596w, 536w, 495w, 443m, 422w, 390w,sh, 385m, 276w cm^{-1} (Nujol mull).

1,5-diene)(dimethylaminodichlorophosphine)rhodium(I)] (III): [chloro(cycloocta-1,5-diene)(bis(dimethylamino)chlorophosphine)rhodium(I)] (IV): [chloro(cycloocta-1,5-diene)(tripiperidylphosphine)rhodium(I)] (V): [chloro(cycloocta-1,5-diene)-(bis(dimethylamino)fluorophosphine)rhodium(I)] (VI) and [chloro(cycloocta-1,5-diene)(t-butylaminodifluorophosphine)rhodium(I) (VIII). The following complexes were identified in solution: bis{(μ-chloro)bis(bis(dimethylamino)fluorophosphine)}-dirhodium(I) (VII) and bis{(μ-chloro)bis(dimethylaminodifluorophosphine)}di-rhodium(I). The latter complex has previously been prepared by different routes [7–10].

It was not possible to recrystallise the complexes $[RhCl(\eta^4\text{-}C_8H_{12})L]$ L = $PX(NMe_2)_2$ (X = F, Cl); PF_2NH^tBu without decomposition, presumably involving loss of olefin. Similar problems were encountered by Grim et al. [3], who prepared a series of analogous complexes (L = alkyl- or arylphosphine) and also noted that the odour of free cycloocta-1,5-diene remained even after repeated washing of the samples. Microanalytical data with errors up to 1.5% on carbon were quoted. In this light, analyses for III (Found: C, 30.05; H, 4.89; N, 3.14. $C_{10}H_{18}NPCl_3Rh$ calcd.: C, 30.60; H, 4.62; N, 3.57%) and for V (Found: C, 31.62; H, 7.82; N, 7.66. $C_{23}H_{42}N_3PClRh$ calcd.: C, 32.13; H, 7.99; N, 7.93%) provide reasonable support for the proposed formulations but contrast with the excellent analytical results for complexes I and II.

Preparations and reactions of $[\{RhCl(\eta^4\text{-}C_8H_{12})\}_2(PXNBu^t)_2]$ *(X = Cl (IX) and X = F (X))*

Exactly 0.5 cm^3 of a toluene solution of $\{PFNBu^t\}_2$ 15 cm^3, 0.3277 *M*) was

removed by microsyringe and added portionwise to a solution of $\{RhCl(\eta^4\text{-}C_8H_{12})\}_2$ (0.08078 g, 0.1638 mmol) in dichloromethane (0.5 cm^3), the reaction being monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The clear yellow solution was evaporated and recrystallisation from chloroform/methylcyclohexane/n-hexane (1/1/1) yielded bis{(chloro)(cycloocta-1,5-diene)}{1,3-di-t-butyl-2,4-difluorocyclodiphosphazane}dirhodium(I) (X) (0.0925 g, 76.9%) as orange-yellow plates. (Found: C, 38.22; H, 5.84; N, 3.69. $C_{24}H_{42}N_2F_2P_2Cl_2Rh_2$ calcd.: C, 39.21; H, 5.76; N, 3.81%). The identity of the complex was confirmed by means of a single-crystal X-ray diffraction study (see text). IR spectrum: 1398w, 1371m, 1339w, 1315vw, 1248ms, 1228m, 1195s, 1050vs, 1006w, 974w, 938m, 907vs, 860m, 824ms, 805vs, 794s, 765m, 757ms, 728vw, 688ms, 607vw, 563w, 506vw, 479m, 464s, 423w, 391s, 351vw, 287s cm^{-1} (Nujol mull).

A sample of X (0.0501 g, 0.0681 mmol) was dissolved in dichloromethane (ca. 0.5 cm^{-3}) and was treated with a toluene solution containing 0.0688 mmol of $(PFN^tBu)_2$. Monitoring by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy revealed the presence of the mononuclear complex $[RhCl(\eta^4\text{-}C_8H_{12})(PFN^tBu)_2]$ (II) as the sole product of the reaction, and this was confirmed in a repeat experiment in which the complex was isolated.

It was also established by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy that on treatment of the solution of II with $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ (0.0336 g, 0.0681 mmol) in dichloromethane (0.3 cm^3), reconversion of the mononuclear complex to the dinuclear product X occurred.

In subsequent experiments it was shown that the isolation of X in the solid state is jeopardised unless at least 20% toluene is present in the reaction solution. When removal of solvent in vacuo is attempted, and insufficient toluene is present, disproportionation of X to II and $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ occurs. The former complex remains in solution and the latter precipitates as a yellow powder identified by IR spectroscopy.

Using procedures identical to those described above, the reaction of $(PClN^tBu)_2$ (0.1158 g, 0.4209 mmol) with $[RhCl(\eta^4\text{-}C_8H_{12})]$ (0.2076 g, 0.4209 mmol) in dichloromethane (0.5 cm^3) led to the formation of bis{(chloro)(cyclo-octa-1,5-diene)}{1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane}dirhodium(I) (IX), (yield 0.2813 g, 0.3663 mmol, 87% as an orange microcrystalline powder. (Found: C, 37.51; H, 5.62; N, 3.76. $C_{24}H_{42}N_2P_2Cl_4Rh_2$ calcd.: C, 37.53; H, 5.51; N, 3.65%). IR spectrum: 1392w, 1365m, 1287m, 1260m, 1244m, 1235m, 1221w, 1195vs, 1060vs, 1046vs, 1035s, 995m, 968m, 933m, 893vs, 869s, 812m, 785m, 760m, 735vw, 722w, 683w, 595vw, 555vs, 484w, 466m, 447m, 423m, 390vw, 360m, 335w, 297m, 240w cm^{-1} (Nujol mull). Disproportionation of this derivative to $[RhCl(\eta^4\text{-}C_8H_{12})(PClN^tBu)_2]$ (I) and $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ appeared on the basis of an NMR spectroscopic study to occur more easily than in the case of analogous fluoro complex, and recrystallisations of IX could not easily be achieved. It was however demonstrated that crystalline samples of IX could be redissolved in dichloromethane/toluene (1/1) giving $^{31}P\text{-}\{^1H\}$ NMR spectra identical to those of the freshly-prepared complex, and that unchanged IX could be quantitatively recovered by evaporation of such solutions to dryness. Quantitative conversion to $[RhCl(\eta^4\text{-}C_8H_{12})(PClN^tBu)_2]$ (I) occurred on treatment of IX (0.1171 g, 0.1524 mmol) in dichloromethane (0.5 cm^3) with $(PClN^tBu)_2$ (0.0419 g, 0.1524 mmol) as demonstrated by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy (isolated yield 0.1296 g, 81.5%).

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