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Pentamethylcyclopentadienylrhodium Complexes with Tripod Tetradentate Ligands and Bidentate 'Mixed 'Ligands

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The synthesis and properties of the complexes $[\{Rh(C_5Me_5)\}_3Cl_5L]Y$ [Y = Cl, BF₄, or PF₆], obtained from $[Rh_2(C_5Me_5)_2Cl_4]$ and the appropriate tripodal tetradentate ligands, L = N(CH_2CH_2PPh_2)_3 or P(CH_2CH_2PPh_2)_3, are reported. These monoligand trimetallic compounds contain two Rh(C_5Me_5)Cl_2 units each bound to a terminal phosphorus atom of the tripod ligand and a Rh(C_5Me_5)Cl group linked to the third terminal phosphorus and to the apical donor atom, nitrogen for N(CH_2CH_2PPh_2)_3, phosphorus for P(CH_2CH_2PPh_2)_3. The Rh(C_5Me_5)Cl group linked to the tributylammonium chloride to give $[\{Rh(C_5Me_5)Cl_2S_3(N(CH_2CH_2PPh_2)_3]\}$. The influence of steric factors in the substitution reaction has been investigated by synthesising and characterising the complexes $[Rh(C_5Me_5)Cl_3(N(CH_2)_nPR_2)]BPh_4$ (n = 2, R = Ph or C_6H_{11} , R' = H, Me, or Et; n = 3, R = Ph, R' = H, Me, or Et; R = C_6H_{11} , R' = H or Me). The bidentate mixed ligands R'_2N(CH_2)_nPPh_2 (n = 2, R' = Et; n = 3, R' = Me or Et) give complexes of formula $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$, in which the ligands are monodentate through the phosphorus atom. The crystal structure of $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$, in which the ligands are monodentate through the phosphorus atom. The crystal structure of $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$ (n = 2, R' = Et; n = 3, R' = Me) exist as nalysis. The complexes $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$ (n = 2, R' = Et; n = 3, R' = Me or Et) give complexes of formula $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$, in which the ligands are monodentate through the phosphorus atom. The crystal structure of $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$ (n = 2, R' = Et; n = 3, R' = Me) exist as nalysis. The complexes $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$ (n = 2, R' = Et; n = 3, R' = Me or Et) give complexes of formula $[Rh(C_5Me_5)Cl[R'_2N(CH_2)_nPPh_2]_2]BPh_4$ (n = 2, R' = Et; n = 3, R' = Me) exist as nalysis. The c

OPEN chain and tripodal tetradentate ligands having tertiary Group 5 atoms as donors generally give monoligand monometallic compounds with transition-metal halides and pseudohalides.¹ The geometry and reactivity of these complexes are mainly determined by the nature and the ' cone angle ' of the donor atoms.²

Only one or at most two donor atoms of the four available bind to a metal if it is strongly linked to a π group like cyclopentadienyl.³ The dangling donor atoms in these systems should be ready to bind to other metal units giving oligomeric compounds in which the ligands act as holding centres for several metal units.

We now describe the preparation and properties of some monoligand trinuclear complexes obtained by reacting the tripod ligands tris(2-diphenylphosphinoethyl)amine, N(CH₂CH₂PPh₂)₃, and tris(2-diphenylphosphinoethyl)phosphine, P(CH2CH2PPh2)3, with di-uchloro-bis[chloro(pentamethylcyclopentadienyl)rhodium], $[Rh_2(C_5Me_5)_2Cl_4]$. This complex has a stable metal-ring bond and two halogen bridges which may be cleaved by a variety of ligands L (= PPh₃, C_5H_5N , or ptoluidine) to give $[Rh(C_5Me_5)Cl_2L]$ derivatives.⁴ To ascertain some properties of the complexes with N-(CH₂CH₂PPh₂)₃ a series of compounds obtained from $[Rh_2(C_5Me_5)_2Cl_4]$ and the 'mixed' bidentate ligands $\mathbf{R'_2N(CH_2)_nPR_2}$ (n = 2 or 3; $\mathbf{R'} = \mathbf{H}$, Me, or Et; R = Ph or C_6H_{11}) have been synthesised and characterised.

RESULTS AND DISCUSSION

The reaction of 3 moles of $[Rh_2(C_5Me_5)_2Cl_4]$ with 2 moles of the tripod ligand $N(CH_2CH_2PPh_2)_3$ or $P(CH_2-CH_2PPh_2)_3$ in dichloromethane affords, after addition of tetrabutylammonium tetrafluoroborate or hexafluorophosphate in ethanol, complexes of formula [{Rh(C_5-Me_5)}_3Cl_5L]Y [L = $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2P-1)_3$]

 $Ph_{2}a_{3}$; $Y = BF_{4}$ or PF_{6}]. The analytical data (Table 1) of the complexes, which crystallise with one molecule of ethanol, are in good agreement with the proposed formula. The complexes behave as 1:1 electrolytes in nitroethane (Table 1).⁵

The ¹H and ³¹P n.m.r. spectra of the complexes (Table 2) are not affected by the nature of the anion $(BF_4 \text{ or } PF_6)$ and do not vary with temperature. The ¹H n.m.r. spectra of the N(CH₂CH₂PPh₂)₃ derivatives (Table 2) show a multiplet due to the phenyl resonances at δ 7.42 and three doublets of intensity 1:1:1 in the methyl region, at 8 1.34, 1.24, and 1.07 p.p.m. Each doublet is due to the coupling of 15 equivalent methyl protons with one phosphorus atom of the ligand $[J(H-P) \approx 4 \text{ Hz}]$. The intensity ratio of the signals of the phenyl groups to the hydrogen atoms of the C_5Me_5 rings is 2:3, as expected for a monoligand trimetallic compound. The ³¹P-{¹H} n.m.r. spectra exhibit three doublets, of relative intensity 1:1:1, at δ 49.59, 27.79, and 24.42 (Table 2). Proton n.m.r. spectra of the $P(CH_2CH_2PPh_2)_3$ derivatives show a multiplet due to the phenyl resonances of the ligand at δ 7.48 and an unresolved multiplet in the methyl region, at 1.33, due to the 45 methyl protons of the pentamethylcyclopentadienyl rings which couple to the four phosphorus atoms of the ligand. The ³¹P-{¹H} n.m.r. spectra do not show any resonance due to unco-ordinated phosphorus atoms at high field; two groups of resonances at δ 68.4 and 30.6 (Table 2) are found for co-ordinated phosphorus atoms. No assignment could be made due to the complexity of the pattern.

The X-ray powder diagrams clearly show that the $N(CH_2CH_2PPh_2)_3$ and $P(CH_2CH_2PPh_2)_3$ derivatives with the same anion are isomorphous.

The above results are consistent with the assumption that the cations contain three inequivalent rhodium-

TABLE	1			
Analytical and conductivity	data	for	the	complexes

	$\Lambda_{M} ^{a} / \Omega^{-1} \mathrm{cm}^{2}$		Analysis (%) b			
Compound	mol ⁻¹	C	н	N	Other	
$[{Rh(C_{5}Me_{5})}_{3}Cl_{5}{N(CH_{2}CH_{2}PPh_{2})}_{3}]Cl \cdot C_{2}H_{5}OH$	49 °	54.3 (54.6)	5.8 (5.8)	1.0(0.9)	Cl, 12.9 (13.1)	
$[{\rm Rh}({\rm C_5Me_5})]_{3}{\rm Cl_6}[{\rm N}({\rm CH_2CH_2PPh_2})_{3}] \cdot {\rm C_2H_5OH}$	18	54.4 (54.6)	5.9 (5 .8)	1.0 (0.9)	P, 5.5 (5.7); Cl, 13.0 (13.1)	
$[\{Rh(C_{5}Me_{5})\}_{3}Cl_{5}\{N(CH_{2}CH_{2}PPh_{2})_{3}\}]BF_{4}\cdot C_{5}H_{5}OH$	90	53.1 (53.0)	5.6 (5.6)	1.0 (0.8)	Cl, 10.2 (10.6)	
$[{\rm Rh}(C_5{\rm Me}_5)]_{3}{\rm Cl}_{5}\{{\rm N}({\rm CH}_{2}{\rm CH}_{2}{\rm PPh}_{2})_{3}\}]{\rm PF}_{6}{\rm \cdot}C_{2}{\rm H}_{5}{\rm OH}$	89	51.2(51.2)	5.5 (5.4)	0.9 (0.8)	P, 7.2 (7.1); Cl, 9.9 (10.2)	
$[{\rm Rh}({\rm C}_{5}{\rm Me}_{5})]_{3}{\rm Cl}_{5}\{{\rm P}({\rm CH}_{2}{\rm CH}_{2}{\rm PPh}_{2})_{3}\}]{\rm Cl}\cdot{\rm C}_{2}{\rm H}_{5}{\rm OH}$	70	53.9 (54.1)	5.7 (5.7)	• •	Cl, 12.9 (13.0)	
$[{\rm Rh}({\rm C}_{5}{\rm Me}_{5})]_{3}{\rm Cl}_{5}\{{\rm P}({\rm CH}_{2}{\rm CH}_{2}{\rm PPh}_{2})_{3}\}]{\rm BF}_{4}{\rm \cdot C}_{2}{\rm H}_{5}{\rm OH}$	90	52.6 (52.4)	5.7 (5.5)			
$[\{Rh(C_{5}Me_{5})\}_{3}Cl_{5}\{P(CH_{2}CH_{2}PPh_{2})_{3}\}]PF_{6}\cdot C_{2}H_{5}OH$	89	50.3 (50.7)	5.5 (5.4)		P, 8.8 (8.8); Cl, 10.1 (10.1)	
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_2PPh_2\}]BPh_4$	52	70.0 (70.1)	6.3(6.2)	1.5(1.7)	P, 3.7 (3.8)	
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_2PPh_2\}]BPh_4$	50	70.4 (70.6)	6.6 (6.5)	1.4 (1.6)		
$[Rh(C_{5}Me_{5})Cl{Et_{2}N(CH_{2})_{2}PPh_{2}}]BPh_{4}$	54	71.0 (71.1)	7.0 (6.8)	1.5 (1.6)		
$[Rh(C_5Me_5)Cl{H_2N(CH_2)_3PPh_2}]BPh_4$	54	70.4 (70.4)	6.5 (6.4)	1.8 (1.7)		
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_3PPh_2\}]BPh_4$	52	71.0 (70.9)	6.8 (6.6)	1.5 (1.6)		
$[Rh(C_5Me_5)Cl{Et_2N(CH_2)_3PPh_2}]BPh_4$	51	71.2 (71.3)	6.9 (7.1)	1.5(1.6)		
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_2P(C_6H_{11})_2\}]BPh_4$	51	69.1 (69.1)	7.7 (7.6)	1.6 (1.5)		
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_2P(C_6H_{11})_2\}]BPh_4$	50	69.5 (69.6)	7.9 (7.8)	1.6 (1.6)		
$[Rh(C_5Me_5)Cl{Et_2N(CH_2)_2P(C_6H_{11})_2}]BPh_4$	49	69.9 (70.1)	8.1 (8.0)	1.5 (1.6)	P, 3.4 (3.5)	
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_3P(C_6H_{11})_2\}]BPh_4$	50	69.3(69.4)	7.8 (7.7)	1.5(1.6)		
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_3P(C_6H_{11})_2\}]BPh_4$	50	69.7 (69.9)	8.0 (7.9)	1.5 (1.6)	Cl, 4.1 (4.0)	
$[Rh(C_5Me_5)Cl{Et_2N(CH_2)_2PPh_2}]BPh_4$	51	72.2 (72.2)	7.3 (7.2)	2.3(2.4)	P, 5.3 (5.3); Cl. 3.0 (3.0)	
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_3PPh_2\}_2]BPh_4$	54	71.8 (71.9)	7.1 (7.0)	2.4(2.5)		
[Rh(C ₅ Me ₅)Cl{Et ₂ N(CH ₂) ₃ PPh ₂ }]BPh ₄	49	72.4 (72.6)	7.5 (7.4)	2.1(2.3)		
[Rh(C ₅ Me ₅)Br{Et ₂ N(CH ₂) ₂ PPh ₂ }]BPh ₄	51	69.4 (69.6)	7.0 (6.9)	2.4(2.3)	Br, 6.4 (6.4)	
$[\mathbf{Rh}(\mathbf{C_{5}Me_{5}})I\{\mathbf{Et_{2}N}(\mathbf{CH_{2}})_{2}\mathbf{PPh_{2}}\}_{2}]\mathbf{BPh_{4}}$	50	67.0 (67.0)	6.8 (6.7)	2.3(2.2)	I, 9.8 (10.1)	

^a Molar conductance of ca. 10⁻³ mol dm⁻³ solution in nitroethane at 20 °C. ^b Calculated values in parentheses. ^c Measured at equilibrium (see text).

 $TABLE \ 2$ Proton and ${}^{31}P{-}{}^{1}H{}^{1}$ n.m.r. spectral data of the complexes ${}^{\alpha}$

$Compound \\ [{Rh(C_5Me_5)}_3Cl_5{N(CH_2CH_2PPh_2)_3}]Cl \cdot C_2H_5OH$	³¹ P-{ ¹ H} N.m.r. (δ /p.p.m.) ^b 49.64 (d) (148.0), 27.86 (d) (143.6), 24.53 (d) (144.1), 22.64 (d) (143.1)	ΔP ° 69.20, 47.42, 44.09.	C ₅ Me ₅ ¹ H N.m.r. (8/p.p.m.) ^d 1.30 (m)
$\label{eq:constraint} \begin{array}{l} [\{ Rh(C_{5}Me_{6})\}_{3}Cl_{6}\{N(CH_{2}CH_{2}PPh_{2})_{3}\}]\cdot C_{2}H_{5}OH\\ [\{ Rh(C_{5}Me_{6})\}_{3}Cl_{5}\{N(CH_{2}CH_{2}PPh_{2})_{3}\}]BF_{4}\cdot C_{2}H_{5}OH \end{array}$	22.75 (d) (143.1) 49.59 (d) (148.5), 27.79 (d) (143.8), 24.42 (d) (144.3)	42.20 42.31 69.15, 47.35,	1.33 (d) (3.7) 1.34 (d) (3.7), 1.24 (d) (3.7),
$[\{\mathrm{Rh}(\mathrm{C}_{\mathfrak{b}}\mathrm{Me}_{\mathfrak{b}})\}_{\mathfrak{z}}\mathrm{Cl}_{\mathfrak{b}}\{\mathrm{N}(\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{PPh}_{\mathfrak{z}})_{\mathfrak{z}}\}]\mathrm{PF}_{\mathfrak{b}}\cdot\mathrm{C}_{2}\mathrm{H}_{\mathfrak{b}}\mathrm{OH}$	49.57 (d) (148.3), 27.74 (d) (143.6), 24.37 (d) (144.1)	43.98 69.13, 47.30, 43.93	1.07 (d) (3.6) 1.34 (d) (3.7), 1.24 (d) (3.7), 1.07 (d) (3.6)
$[\{Rh(C_5Me_{\delta})\}_3Cl_{\delta}\{P(CH_2CH_2PPh_2)_{\delta}\}]Cl \cdot C_2H_5OH$ $[\{Rh(C_5Me_{\delta})\}_3Cl_{\delta}\{P(CH_2CH_2PPh_2)_{\delta}\}]BF_4 \cdot C_2H_5OH$ $[\{Rh(C_Me_{\delta})\}_CL_{\delta}\{P(CH_{\delta}CH_{\delta}PPh_{\delta})_{\delta}\}]FF_{\delta} \cdot C_{\delta}H_{\delta}OH$	68.4 (m), 30.6 (m) 68.4 (m) 68.4 (m)	10100	1.33 (m) 1.33 (m) 1.33 (m)
$[Rh(C_{b}Me_{b})C]{H_{2}N(CH_{2})_{2}PPh_{2}}]BPh_{4}$ $[Rh(C_{b}Me_{b})C]{Me_{2}N(CH_{2})_{2}PPh_{2}}]BPh_{4}$ $[Rh(C_{b}Me_{b})C]{Me_{2}N(CH_{2})_{2}PPh_{2}}]BPh_{4}$	54.25 (d) (141.9) 52.20 (d) (146.1) 52 67 (d) (147.5)	75.85 72.15 71.84	1.20 (d) (3.4) 1.19 (d) (3.2) 1.19 (d) (3.3)
$[Rh(C_{4}Me_{5})C[\{H_{2}N(CH_{2})_{3}PPh_{4}]]BPh_{4}$ $[Rh(C_{6}Me_{5})C[\{Me_{2}N(CH_{2})_{3}PPh_{4}]]BPh_{4}$ $[Rh(C_{6}Me_{5})C[\{E_{4}N(CH_{3})_{3}PPh_{4}]]BPh_{4}$	28.09 (d) (138.7) 29.87 (d) (146.7) 29.64 (d) (147.1)	44.03 45.53 45.42	1.17 (d) (3.5) 1.17 (d) (3.4) 1.18 (d) (3.6)
$[Rh(C_sMe_s)Cl{H_2N(CH_2)_2P(C_sH_{11})_2}]BPh_4[Rh(C_sMe_s)Cl{Me_2N(CH_2)_2P(C_sH_{11})_2}]BPh_4[Rh(C_sMe_s)Cl{E_sN(CH_2)_2P(C_sH_{11})_2}]BPh_4$ [Rh(C_sMe_s)Cl{E_sN(CH_2)_2P(C_sH_{11})_2}]BPh_4	59.80 (d) (137.2) 59.31 (d) (138.2) 59.23 (d) (138.5)	66.43 66.61 66.05	1.38 (d) (3.1) 1.37 (d) (3.0) 1.39 (d) (3.0)
$ [Rh(C_{5}Me_{3})Cl{H_{2}N(CH_{2})_{3}P(C_{6}H_{11})_{2}}]BPh_{4} [Rh(C_{5}Me_{3})Cl{Me_{2}N(CH_{2})_{3}P(C_{6}H_{11})_{2}}]BPh_{4} [Rh(C_{5}Me_{3})Cl{Et_{2}N(CH_{2})_{2}PPh_{2}}]BPh_{4} [Rh(C_{5}Me_{3})Cl{Et_{2}N(CH_{2})_{2}PPh_{2}}]BPh_{4} $	29.38 (d) (132.0) 29.12 (d) (135.4) 22.48 (d) (136.1) (br) *	33.45 33.60 42.04	1.35 (d) (2.9) 1.36 (d) (3.0) 1.00 (t) (3.4)
	30.89 (d) (133.7) , f 29.28 (d) (133.7) , f 23.50 (d) (135.5) , f 21.90 (d) (135.4) f	50.45, 48.84, 43.06,	0.97 (m)
$[\mathrm{Rh}(\mathrm{C}_{5}\mathrm{Me}_{5})\mathrm{Cl}\{\mathrm{Me}_{2}\mathrm{N}(\mathrm{CH}_{2})_{3}\mathrm{PPh}_{3}\}_{2}]\mathrm{BPh}_{4}$	23.21 (d) (134.3) (br) ϵ 25.55 (d) (133.1), f 23.87 (d) (133.1), f 20.45 (d) (135.1) (f 18.87 (d) (135.0) (f	41.46 42.77 45.01, 43.43	1.00 (t) (3.4) 0.98 (m)
[Rh/C Me)Cl/Ft N/CH) PPh.}.]BPh.	23.26 (d) (135.1) (br)	40.01, 38.43 42.82	1.01 (t) (3.4)
$[Rh(C_5Me_5)Br{Et_2N(CH_2)_2Ph_2}_2]BPh_4$ [Rh(C_5Me_5)I{Et_2N(CH_2)_2Ph_2}_2]BPh_4	20.49 (d) (128.1) (br) 19.24 (d) (125.1) (br)	40.05 38.80	$\begin{array}{c} 1.04 (t) (3.4) \\ 1.12 (t) (3.2) \end{array}$

• Measured in CDCl_3 at room temperature unless otherwise indicated; d = doublet, t = triplet, m = multiplet, br = broad. • J(P-Rh) in Hz are given in parentheses. • $\Delta P = \delta P_{\text{co-ord.}} - \delta P_{\text{free ligand.}}$ • J(H-P) in Hz are given in parentheses. • Room temperature. • A t - 50 °C. pentamethylcyclopentadienyl units each bound to a terminal phosphorus atom of the tetradentate ligand. Two of the metal atoms must then complete their coordination spheres with two chloride ions while the third $Rh(C_5Me_5)$ moiety must be bound to one chloride and to the central donor atom of the ligand, *i.e.* to a nitrogen or phosphorus atom, depending on whether the ligand is $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$. If this interpretation is correct, the low-field resonances in the ³¹P spectra of both the $N(CH_2CH_2PPh_2)_3$ and $P(CH_2CH_2P-Ph_2)_3$ derivatives should be assigned to the cationic fragment, *i.e.* the one containing the metal atom linked to one chloride.

The proposed structure is confirmed by preliminary results of an X-ray analysis on the compound [{Rh- C_5Me_5]}₃Cl₅L]PF₆ [L = N(CH₂CH₂PPh₂)₃].⁶ The magnetic inequivalence of the phosphorus atoms of the Rh-(C₅Me₅)Cl₂ groups, giving the high-field doublets in the ³¹P spectra, is probably due to the bulk of the RhCl-(C₅Me₅) groups attached to P_a and P_b (see Scheme). This forces a *trans*-geometry on them and also severely restricts rotation about the N P_a and N P_b bonds.

The reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with tripod ligands in



a 3:2 ratio, in methylene chloride in the absence of PF_{6}^{-} or BF_{4}^{-} , yields, upon addition of ligroin, complexes of formula $[{Rh(C_5Me_5)}_3Cl_5L]Cl [L = N(CH_2-CH_2PPh_2)_3 \text{ or } P(CH_2CH_2PPh_2)_3]$. The $P(CH_2CH_2P-CH_2Ph_2)_3$ $Ph_2)_3$ derivative behaves as a 1:1 electrolyte and both its ¹H and ³¹P n.m.r. spectra are identical to the spectra of the tetrafluoroborate and hexafluorophosphate derivatives (Table 2), indicating that the monoligand trimetallic cation maintains the same geometry also in the presence of co-ordinating anions. The N(CH₂CH₂P- Ph_2)₃ derivative behaves as a 1 : 1 electrolyte only for a short time after it is dissolved in methylene chloride or nitroethane. The conductivity decreases within 3-4 min to a value which is intermediate between that of a 1:1 electrolyte and that of a non-ionic species. Thereafter the conductivity does not decrease any more. This behaviour indicates that a transformation takes place in which a neutral species is formed at the expense of the ionic complex; after few minutes an equilibrium between the two species is reached. The ¹H n.m.r. spectrum of this solution shows a multiplet due to the phenyl resonances at δ 7.45 and an unresolved multiplet at δ 1.33 in the methyl region; the intensity ratio is 2:3 indicating that only monoligand trimetallic species are still present in solution. The ³¹P n.m.r. spectrum of the same solution shows four doublets at δ 49.64, 27.86, 24.53, and 22.64 (Table 2). The three low-field doublets are the same as those shown by the $[{Rh(C_5Me_5)}_3Cl_5L]^+$ cation $[L = N(CH_2CH_2PPh_2)_3]$, the values of the coupling constants are also in agreement. By adding tetrabutylammonium chloride to this solution the three resonances due to the cationic species disappear, and the intensity of the fourth doublet increases until this is the only resonance in the spectrum.

A non-ionic complex of formula $[{Rh(C_5Me_5)Cl_2}_{sL}]$ $[L = N(CH_2CH_2PPh_2)_3]$ (Table 1) was isolated from the above solution after addition of NBu₄Cl. Its spectral properties (Table 2), in the presence of NBu₄Cl, are identical to those of the species which is believed to be present in the above solution after the decrease in conductivity. The above results clearly indicate that the nitrogen atom of the N(CH₂CH₂PPh₂)₃ ligand bound to the $Rh(C_5Me_5)Cl$ unit may be displaced by chloride according to the Scheme. It must be emphasized that as nitrogen is replaced by chloride the three $Rh(C_5Me_5)Cl_2$ units become equivalent. The n.m.r. spectra show that, by contrast with the above $[{Rh(C_5Me_5)}_3Cl_5L]Cl$ compound, the analogous P(CH₂CH₂PPh₂)₃ derivative retains its geometry in solution even after addition of a large excess of tetrabutylammonium chloride.

Such a difference in the co-ordinating ability of the apical donor atoms of the $N(CH_2CH_2PPh_2)_3$ and $P(CH_2-CH_2PPh_2)_3$ ligands has been found elsewhere. Several mononuclear $N(CH_2CH_2PPh_2)_3$ complexes in which the nitrogen atom of the tripod ligand is far from the metal have been characterised,⁷ whereas no $P(CH_2CH_2PPh_2)_3$ metal derivative with the apical donor unco-ordinated has been reported so far. Related behaviour is exhibited by potentially bidentate ' mixed ' ligands having

the same donor atoms and similar steric requirements to those of the chelating chain of the $N(CH_2CH_2PPh_2)_3$ ligand in the present compounds. When the former ligands behave as monodentate in palladium(II) and platinum(II) complexes, the nitrogen atom (never the phosphorus one) is unco-ordinated.⁸ Furthermore, amine ligands have been found to bind poorly to the metal in the Rh(C₅Me₅) system.⁹ However, the replacement of co-ordinated nitrogen by chloride is most unusual.

In order to understand the nature of the factors which control this substitution reaction complexes of formula $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPR_2\}]BPh_4$ have been synthesised and their properties investigated. The various $R'_2N(CH_2)_nPR_2$ ligands employed differ from each other both in the 'cone angle' of the nitrogen and/or the phosphorus donor, and in the length of the aliphatic chain.

The reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with the ligands $R'_2N(CH_2)_nPR_2$ (n = 2, R = Ph or C_6H_{11} , R' = H, Me, or Et; n = 3, R = Ph, R' = H, Me, or Et; $R = C_6H_{11}$, R' = H or Me) in a 1:2 ratio afforded, after addition of sodium tetraphenylborate in ethanol, complexes having the formula $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_n-PR_2\}]BPh_4$. Analytical data for the complexes, which behave as 1:1 electrolytes in nitroethane solution, are reported in Table 1.

The ¹H n.m.r. spectra of all these complexes show a doublet at *ca.* δ 1.17—1.39, Table 2, in the region of the hydrogens of the pentamethylcyclopentadienyl group, with a coupling constant of *ca.* 3.4 Hz. For each of the compounds the intensity ratio of the doublet due to the pentamethylcyclopentadienyl to the resonances arising from the other hydrogens present agrees with those expected for the proposed formula.

The ³¹P n.m.r. spectra of the complexes each show a doublet with a coupling constant in the expected range for J(P-Rh) in these systems. The complexes formed by R'2N(CH2)2PR2 ligands, having five-membered chelate rings, exhibit chemical shifts comparable to that ascribed to the Rh(C₅Me₅)Cl(PCH₂CH₂N) unit in the N(CH₂CH₂PPh₂)₃ trimetallic complex. From these data we deduce that both nitrogen and phosphorus are bound to the metal. The ³¹P spectra of the complexes with R'₂N(CH₂)₃PR₂ ligands, which form six-membered rings, are more shielded. This supports the assignment of the same type of co-ordination to both sets of complexes. In fact the difference in co-ordination chemical shift on going from the R'2N(CH2)2PR2 to the R'2N-(CH₂)₃PR₂ derivatives is of the same order as found for the 'ring contribution' on going from five- to sixmembered rings formed by polyphosphines, alkenylphosphines, or in orthometallated complexes.¹⁰

If tetrabutylammonium chloride is added to $[Rh(C_5-Me_5)Cl{Et_2N(CH_2)_2PPh_2}]BPh_4$ dissolved in nitroethane the conductivity of the solution does not change up to the point where one equivalent has been added; further addition of tetrabutylammonium chloride produces proportional increases in the conductivity. Phosphorus-31 n.m.r. spectra measured during the addition of the chlor-

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ide show both the resonances of the starting compound and a new doublet at & 25.65 [J(P-Rh) = 144.5 Hz]; the relative intensity of the latter signals increases with the amount of added chloride. At the equivalence point the doublet characteristic of the species having both nitrogen and phosphorus bound to the metal has been replaced by the doublet at & 25.65, J(P-Rh) 144.5 Hz. Conductometric measurements and n.m.r. spectra therefore indicate that the following reaction takes place. We



conclude that the nitrogen atom of the bidentate ligand can be easily replaced by chloride. Analogous behaviour, according to the n.m.r. spectra, is exhibited by other cationic complexes having one 'mixed ' bidentate ligand. The process is similar to that already described for the trimetallic $N(CH_2CH_2PPh_2)_3$ derivatives (Scheme). It therefore appears that the steric hindrance of the bulky groups attached to the nitrogen atom in the trimetallic complexes does not play a significant role in the process of nitrogen displacement.

Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with an excess of the bidentate ligand (e.g. in a 1:4 ratio) generally yields the complexes described above. However, when the R'_2N - $(CH_2)_nPPh_2$ ligands with n = 2, R' = Et, or with n = 3, R' = Me or Et, are employed, the reaction yields, after addition of sodium tetraphenylborate, complexes of formula $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPPh_2\}_2]BPh_4$. These behave as 1:1 electrolytes in nitroethane solution (Table 1). The ¹H and ³¹P n.m.r. spectra of these derivatives (Table 2) vary with temperature. At room temperature the ³¹P spectra show a broad doublet. The ¹H spectra exhibit R' (R' = Me or Et) resonances at the same frequencies as in the spectra of the free ligand; they also show a triplet in the region of C_5Me_5 resonances.

These complexes may therefore be assigned a structure in which the two potentially bidentate ligands act as monodentate through the phosphorus atom, while the $-(CH_2)_n NR'_2$ portion of each ligand is dangling. This hypothesis is confirmed by the results of an X-ray structural investigation performed on the compound $[Rh(C_5Me_5)Cl{Et_2N(CH_2)_2Ph_2}_2]BPh_4$ (see below).

At ca. +50 °C the broad doublet in the ³¹P n.m.r. spectra becomes a sharp doublet; on the other hand the ¹H spectra do not change appreciably. At low temperature, ca. -50 °C, ³¹P spectra of the [Rh(C₅Me₅)Cl{R'₂N-(CH₂)_nPPh₂}]BPh₄ (n = 2, R' = Et, n = 3, R' = Me) derivatives show four doublets grouped in pairs having different relative intensities (Table 2). In both compounds the doublets at lower field have J(P-Rh) 133 Hz and the other two doublets have J(P-Rh) 135 Hz. At low temperature (ca. -50 °C) both the signals of the R' groups and those of the C_5Me_5 ring in the ¹H spectra become broad multiplets. The bromo- and iododerivatives $[Rh(C_5Me_5)X{Et_2N(CH_2)_2PPh_2}_2]BPh_4$ (X = Br or I), obtained by refluxing the chloro-derivative with a large excess of sodium halide (Table 1), give n.m.r. spectra which vary with temperature in the same way as found for the chloro-derivative.

The two pairs of doublets that are present at ca. -50

chlorine atom, in the six-co-ordinate geometry which is usually referred to as a 'three-legged piano stool' (Figure). Selected distances and angles are reported in Table 3.

Individual rhodium-carbon distances range from Rh-C(4) = 2.217(7) to Rh-C(2) = 2.279(6) Å, the average value being 2.245(38) Å. The metal atom lies 1.88 Å away from the best plane through the atoms of the



View of the cationic part of [Rh(C₅Me₅)Cl{Et₂N(CH₂)₂PPh₂}]BPh₄

°C in the ³¹P spectra are probably due to rotamers; in each of these the phosphorus atoms are magnetically equivalent. The existence of rotamers at low temperature in the solutions of the above compounds arises mainly from the steric hindrance of the bulky substituent groups on the phosphorus atoms. This is shown by the results of the structural investigation performed on the compound $[Rh(C_5Me_5)Cl{Et_2N(CH_2)_2PPh_2}_2]BPh_4$. Furthermore, indirect but convincing evidence for such crowding is also provided by the fact that no compound with two bidentate ligands bearing the $-P(C_6H_{11})_2$ group, which has the largest 'cone angle' among those here employed, could be obtained. Finally, the lack of effect of the halogen size on the ³¹P n.m.r. spectra of the $[Rh(C_5Me_5)X{Et_2N(CH_2)_2PPh_2}_2]BPh_4 (X = Cl, Br, or I)$ complexes on cooling indicates that the important steric hindrances involve groups further removed from the metal.

The structure of $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]$ -BPh₄ consists of discrete complex cations and BPh₄ anions. The metal atom in the cation is co-ordinated by the atoms of the cyclopentadienyl ring, by the two phosphorus atoms of the tertiary phosphines, and by the C_5Me_5 ring. This distance is comparable to that, of 1.890 Å, found in the compound $[Rh(C_5Me_5)H(PPh_3)_2]$ -PF₆¹¹ but is longer than those observed in several related complexes.^{4,12} The C-C distances in the cyclopentadienyl ring, 1.41—1.45 Å, deviate only little from their mean value of 1.432(17) Å, which is close to that expected (1.43 Å).

The mean of the C(ring)-C(Me) bond distances [1.501(12) Å] agrees with the accepted $C(sp^2)-C(sp^3)$ distance of 1.51 Å.¹³ The methyl groups of the η^5 -C₅Me₅ ligand are bent away from the metal atom; their distances from the best plane through the five atoms in the ring range from 0.11 to 0.33 Å, the mean deviation being 0.22 Å. Such deformations are probably imposed by steric repulsions due to the substituent groups on the phosphines. However, electronic effects of the sort discussed by Hoffmann and co-workers 14 for bending of peripheral substituents on cyclopolyene rings could also be of importance. As may be qualitatively appreciated by inspection of the Figure, there are numerous short approaches affecting the peripheral carbon atoms in the complex cation. Also, the limited vibrational motion of the η^5 -C₅Me₅ ligand and the absence of disorder in the

TABLE 3

Selected bond distances (Å) and angles (°) in the co-ordination sphere of $[Rh(C_6Me_5)Cl{Et_2N(CH_2)_2PPh_2}_2]BPh_4$ with estimated standard deviations in parentheses

Rh-Cl Rh-P(1) Rh-P(2) Rh-C(1)	2.393(2) 2.358(2) 2.338(2) 2.222(6)	Rh-C(2) Rh-C(3) Rh-C(4) Rh-C(5)	2.279(6) 2.240(7) 2.217(7) 2.266(6)
$\begin{array}{c} \text{C(1)}-\text{Rh}-\text{P(1)}\\ \text{C(1)}-\text{Rh}-\text{P(2)}\\ \text{C(1)}-\text{Rh}-\text{C(1)}\\ \text{C(1)}-\text{Rh}-\text{C(1)}\\ \text{C(1)}-\text{Rh}-\text{C(2)}\\ \text{C(1)}-\text{Rh}-\text{C(3)}\\ \text{C(1)}-\text{Rh}-\text{C(3)}\\ \text{C(1)}-\text{Rh}-\text{C(4)}\\ \text{P(1)}-\text{Rh}-\text{C(1)}\\ \text{P(1)}-\text{Rh}-\text{C(2)}\\ \text{P(1)}-\text{Rh}-\text{C(2)}\\ \text{P(1)}-\text{Rh}-\text{C(3)}\\ \end{array}$	$\begin{array}{c} 88.2(1)\\ 88.0(1)\\ 151.3(2)\\ 119.9(2)\\ 89.3(2)\\ 91.8(2)\\ 125.6(2)\\ 96.3(1)\\ 109.5(2)\\ 98.0(2)\\ 118.7(2) \end{array}$	$\begin{array}{c} P(2)-Rh-C(2)\\ P(2)-Rh-C(3)\\ P(2)-Rh-C(4)\\ P(2)-Rh-C(5)\\ C(1)-Rh-C(5)\\ C(1)-Rh-C(3)\\ C(1)-Rh-C(4)\\ C(1)-Rh-C(5)\\ C(2)-Rh-C(3)\\ C(2)-Rh-C(4)\\ C(2)-Rh-C(4)\\ C(2)-Rh-C(5)\\ \end{array}$	$\begin{array}{c} 1.200(6)\\ 147.9(2)\\ 144.9(2)\\ 107.0(2)\\ 91.4(2)\\ 37.5(2)\\ 62.6(3)\\ 62.9(3)\\ 37.2(3)\\ 36.4(3)\\ 62.0(3)\\ 61.3(2)\end{array}$
P(1)-Rh-C(4) P(1)-Rh-C(5) P(2)-Rh-C(1)	$156.6(2) \\ 145.5(2) \\ 110.4(2)$	C(3)-Rh-C(4) C(3)-Rh-C(5) C(4)-Rh-C(5)	$37.9(2) \\ 61.8(2) \\ 36.9(3)$

arrangement of the $-(CH_2)_2NEt_2$ chains are indicative of a relatively crowded structure.

EXPERIMENTAL

All the solvents were reagent grade and were used without further purification. Conductivities, infrared spectra, and X-ray powder diagrams were obtained as previously described.¹⁵ Proton and ³¹P n.m.r. spectra were measured on a Varian EM390 (at 90 MHz) and a Varian CFT20 (at 32.19 MHz) spectrometer, respectively. Phosphorus-31 positive chemical shifts are downfield relative to H_3PO_4 at 0.0 p.p.m. Changes in chemical shifts on co-ordination are reported in p.p.m. relative to the corresponding phosphorus in the free ligand. tional distillation under reduced pressure. The pure ligands are air stable. Boiling points, analytical data (calculated values in parentheses), and spectroscopic data of the new ligands are reported in Table 4.

The complexes were prepared under a protective atmosphere of nitrogen; however, none of the isolated complexes showed any signs of instability toward air. Typical preparations are illustrated below. Analytical and spectroscopic data are collected in Tables 1 and 2 respectively.

Preparations.—[{Rh(C_5Me_5)}_3Cl_5L]Y [L = N(CH_2CH_2P-Ph_2)_3 or P(CH_2CH_2PPh_2)_3; Y = BF₄ or PF₆]. A solution of the appropriate ligand (0.33 mmol) in dichloromethane (10 cm³) was added to [Rh₂(C_5Me_5)₂Cl₄] (0.5 mmol) dissolved in dichloromethane (15 cm³) and the mixture was refluxed (30 min). After cooling, a solution of NBu₄Y (Y = BF₄ or PF₆) (0.7 mmol) in ethanol was added to the reaction mixture. The orange crystals of the complexes obtained by concentrating the resulting solution were filtered off and dried *in vacuo*. The complexes were recrystallised from dichloromethane and ethanol. All the complexes crystal-lised with one molecule of ethanol [v(OH) ca. 3 350 cm⁻¹].

 $\label{eq:charge} \begin{array}{l} [\{Rh(C_5Me_5)\}_3Cl_5L]Cl \ [\ L = N(CH_2CH_2PPh_2)_3 \ or \ P(CH_2-CH_2PPh_2)_3]. \end{array}$ These complexes were prepared by the procedure described above using ligroin as precipitating solvent. The compounds were recrystallised from ethanol and ligroin.

 $[{Rh(C_5Me_5)Cl_2}_3{N(CH_2CH_2PPh_2)_3}]$. A solution of N-Bu₄Cl (1 mmol) in ethanol (10 cm³) was added to the complex $[{Rh(C_5Me_5)}_3Cl_5{N(CH_2CH_2PPh_2)_3}]Cl (1 mmol)$ dissolved in ethanol (15 cm³). Ligroin was added to the resulting solution. The crystalline compound obtained by concentrating the solution was filtered off, washed with water, and dried *in vacuo*.

 $[Rh(C_5Me_5)Cl_2\{R'_2N(CH_2)_nPR_2\}].$ (n = 2, R = Ph, R' = H; n = 3, R = Ph, R' = H or Me). A solution of the appropriate ligand (1 mmol) in dichloromethane (10

TABLE 4										
Boiling points,	analytical,	and ³¹ P-{	¹ H}	n.m.r. s	spectroscor	oic data	ı of	the	ligands	;

	Bp /ºC		Analysis (%) ^ø		³¹ P-{ ¹ H} N.m.r
Ligand	(1 mmHg) ^a	С	H	N	in C^2HCl_3
$H_{a}N(CH_{a})_{a}P(C_{a}H_{11})_{a}$	147-148	69.6 (69.7)	11.9 (11.7)	5.6 (5.8)	-6.63
$Me_{2}N(CH_{2})_{2}P(C_{6}H_{11})_{2}$	146148	71.1 (71.3)	12.2 (12.0)	5.0 (5.2)	-7.30
$Et_{2}N(CH_{2})_{2}P(C_{6}H_{11})_{2}$	157-159	72.5 (72.7)	12.3(11.2)	4.5 (4.7)	-6.82
H ₂ N(CH ₂) ₃ PPh ₂	143 - 145	74.0 (74.1)	7.7 (7.5)	5.6 (5.8)	-15.94
$H_{2}N(CH_{2})_{3}P(C_{6}H_{11})_{2}$	142-143	70.6 (70.6)	11.9 (11.8)	5.3 (5.5)	-4.07
$Me_2N(CH_2)_3P(C_6H_{11})_2$	150-151	71.7 (72.0)	12.3 (12.1)	4.7 (4.9)	4.48
_					

• 1 mmHg = (101 325/760) N m⁻². • Calculated values are given in parentheses.

The ligand tris(2-diphenylphosphinoethyl)phosphine, P(CH₂CH₂PPh₂)₃, was purchased from the Pressure Chemical Co. Di- μ -chloro-bis[chloro(pentamethylcyclopentadienyl)rhodium]⁴ and the ligands tris(2-diphenylphosphinoethyl)amine, N(CH₂CH₂PPh₂)₃,¹⁶ 2-aminoethyldiphenylphosphine, H₂N(CH₂)₂PPh₂,¹⁷ 2-dimethylaminoethyldiphenylphosphine, Me₂N(CH₂)₂PPh₂,¹⁸ 2-dimethylaminoethyldiphenylphosphine, Et₂N(CH₂)₂PPh₂, and 3diethylaminopropyldiphenylphosphine, Et₂N(CH₂)₃PPh₂, were prepared as already described. The other ligands R'₂N(CH₂)_nPR₂ (n = 2, R = C₆H₁₁, R' = H, Me, or Et; n = 3, R = Ph and R' = H; R = C₆H₁₁ and R' = H or Me) were prepared in analogous fashion from the appropriate chlorides and lithium dicyclohexylphosphide or potassium diphenylphosphide. All the ligands have been obtained in good yield (75-80%) after purification by fraccm³) was added to $[Rh_2(C_5Me_5)_2Cl_4]$ (0.5 mmol) in dichloromethane (15 cm³) and the mixture was refluxed for 20 min. Orange-yellow crystals of the complexes were obtained by allowing the solvent to evaporate at 35—40 °C. These complexes were recrystallised from acetone and ethanol.

 $[Rh(C_6Me_5)Cl\{R'_2N(CH_2)_nPR_2\}]BPh_4$ $(n = 2, R = Ph \text{ or } C_6H_{11}, R' = H, Me, \text{ or Et}; n = 3, R = Ph, R' = H, Me, \text{ or Et}; R = C_6H_{11}, R' = H \text{ or } Me).$ The complexes were prepared by the above procedure and by adding a solution of sodium tetraphenylborate in ethanol.

 $[Rh(C_5Me_5)Cl{R'_2N(CH_2)_nPR_2}_2]BPh_4$ (n = 2 or 3; R = Ph; R' = Me or Et). These complexes were prepared by the procedure described above, but reacting the ligand and the rhodium complex in a 4:1 ratio.

 $[Rh(C_5Me_5)X{Et_2N(CH_2)_2PPh_3]_2}]BPh_4$ (X = Br or I) The complexes were prepared by refluxing the chloro_ derivative (1 mmol) in acetone (30 cm^3) with the appropriate sodium halide (20 mmol) for 5 h. The complexes were recrystallised from acetone and ethanol.

X-Ray Data Collection.—Crystals of $[Rh(C_5Me_5)Cl-{Et_2N(CH_2)_2PPh_2}_2]BPh_4$ were deposited as pale orange platelets from an acetone-ethanol mixture. Intensities were recorded on a Philips PW 1100 automated diffractometer using graphite monochromated Mo- K_{α} radiation, and a crystal dimensions ca. $0.25 \times 0.33 \times 0.08$ mm. Unit-cell dimensions were determined from the angular measurements of 24 strong reflections with $20 < 2\theta < 30^{\circ}$. Data were collected in the range $4 < 2\theta < 48^{\circ}$, by the θ —20 scan technique, with a symmetric scan range of 0.90 +0.30 tan θ and a scan speed of 3.0° min⁻¹ in 2 θ . Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three

TABLE 5

Atomic co-ordinates for non-hydrogen atoms of $[Rh(C_6Me_6)-Cl{Et_2N(CH_2)_2PPh_2}]BPh_4$ (×10⁴, except Rh × 10⁵) with estimated standard deviations in parentheses *

Atom	~		
TTO III		y 0.077(1)	A
Rh	27 453(4)	8 877(4)	35 680(4)
Cl	4 135(1)	101(1)	3 918(1)
P(1)	2 915(1)	1 027(1)	2 112(1)
P(2)	3 627(1)	$2\ 284(1)$	4 706(1)
NÌÚ	5 141(4)	1 266(5)	1 294(5)
N(2)	4 752(4)	3 259(5)	7 735(4)
còñ	1 268(4)	976(5)	3 361(5)
$\tilde{c}(\tilde{z})$	1 336(5)	42(5)	2 760(5)
Ca	1 966(5)	-403(5)	$\frac{2}{3} \frac{100}{422}(5)$
	9 965(5)	220(5)	4 456(5)
	2 203(5)	1 049(5)	4 419(6)
	576(5)	1 040(0)	4412(0)
	070(0) 710(5)	1 028(0)	3 010(0)
$\mathcal{C}(n)$	/10(5)	-432(0)	1 000(0)
C(8)	2 221(6)	-1397(5)	3 102(0)
C(9)	2 843(6)		5 406(6)
C(10)	1 722(5)	1 805(5)	5 293(6)
$C(\Pi)$	4 107(4)	1 195(5)	2 226(5)
C(12)	4 223(5)	989(5)	$1\ 201(5)$
C(13)	5 289(7)	2 309(6)	1 593(7)
C(14)	6 118(8)	2 601(9)	1 396(9)
C(15)	5 912(6)	850(8)	1 955(8)
C(16)	5 805(9)	-204(9)	1 604(9)
C(17)	4 170(5)	2 134(5)	5 984(5)
C(18)	4 951(5)	2 872(6)	6 828(5)
C(19)	4 766(7)	2 519(7)	8 225(7)
C(20)	4 192(8)	2 779(9)	8 917(9)
C(21)	5 452(7)	4 074(8)	8 483(7)
C(22)	5 303(9)	4 926(8)	8 112(9)
C(23)	$2\ 314(5)$	1934(5)	1 584(5)
$\tilde{C}(24)$	1 353(5)	1 877(5)	1 185(6)
$\tilde{C}(25)$	870(6)	2 594(6)	862(6)
C(26)	1 369(6)	3 389(6)	960(7)
C(27)	2 307(6)	3 443(6)	1 333(6)
C(28)	2 795(5)	2721(5)	1 653(5)
C/20)	2 496/4)	- 60(4)	1047(5)
C(20)	2 400(4)	801(5)	1 948(5)
C(21)	2 104(0)	-1746(5)	450(6)
C(31)	2 455(5)	-1740(6)	538(6)
C(32)	1 799(6)		- 555(0) 745(6)
C(33)	1 720(0)	930(0)	-745(0)
C(34)	1 965(5)	-73(0)	4 917(5)
C(35)	Z 907(4)	3 293(4)	4 817(8)
C(36)	2 360(5)	3 490(9)	3 934(3)
C(37)	1 841(5)	4 227(5)	3 009(0)
C(38)	1 910(5)	4 833(0)	4 905(6)
C(39)	2 489(5)	4 675(5)	5 781(6)
C(40)	3 023(5)	3 909(5)	5 757(5)
C(41)	4 629(4)	2 718(4)	4 576(5)
C(42)	4 645(5)	3 543(5)	4 328(5)
C(43)	5 449(5)	3 880(5)	4 301(6)
C(44)	6 233(5)	3 410(5)	4 514(6)
C(45)	6 217(5)	2 596(5)	4 760(5)
C(46)	5 431(5)	2 250(5)	4 794(5)

	TABLE 5	(continued)	
Atom	x	y	Z
C(47)	927(5)	4 018(5)	7 586(5)
C(48)	1 835(5)	3 931(5)	7 657(5)
C(49)	2 527(6)	4 694(6)	8 195(6)
C(50)	2 320(6)	5 547(6)	8 666(7)
C(51)	1 431(6)	5 669(6)	8 581(7)
C(52)	738(6)	4 916(6)	8 056(6)
C(53)	525(5)	$2\ 153(5)$	7 108(5)
C(34)	181(5)	$1\ 282(5)$	6 382(5)
C(55)	564(6)	444(6)	6 516(6)
C(56)	1 286(7)	463(7)	7 359(7)
C(57)	1 656(7)	1 301(7)	8 127(7)
C(58)	1 271(6)	2 128(6)	8 005(6)
C(59)	-689(4)	3 392(4)	7 463(5)
C(60)	-1541(5)	3 720(5)	7 008(5)
C(61)	-2155(5)	3 988(5)	7 503(6)
C(62)	-1910(5)	3 933(5)	8 491(6)
C(63)	-1053(6)	3 619(6)	8 981(6)
C(64)	-462(5)	3 324(5)	8 456(6)
C(65)	-360(4)	3 088(4)	5 735(5)
C(66)	-1 196(5)	2 526(5)	5 050(5)
C(67)	-1602(5)	2 477(5)	4 106(6)
C(68)	-1214(5)	3 023(5)	3 637(6)
C(69)	-392(5)	3 593(5)	4 283(5)
C(70)	25(5)	3 612(5)	5 320(5)
B	99(5)	3 147(5)	6 955(6)

* Atoms C(1)—C(10) belong to the pentamethylcyclopentadienyl group; C(11)—C(16) and, respectively, C(17)— C(22) to the aliphatic chains of the two phosphine groups; C(23)—C(34) and C(35)—C(46) to the phosphine phenyl groups; C(47)—C(70) to the tetraphenylborate phenyl groups.

reflections well separated in reciprocal space were monitored periodically throughout data collection and showed only random variations ($< \pm 3\%$) in the mean values. Corrections for Lorentz, polarisation, and X-ray absorption effects were applied. The 5 710 unique reflections having $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

Crystal data. $C_{70}H_{83}BClN_2P_2Rh$, M = 1.163.57, Triclinic, space group PI, a = 15.694(6), b = 15.023(6), c = 14.924(5) Å, $\alpha = 107.40(5)$, $\beta = 112.75(5)$, $\gamma = 87.88(5)^\circ$, U = 3.084.02 Å³, F(000) = 1.228, $D_c = 1.253$ g cm⁻³, Z = 2, Mo- K_{α} radiation, $\lambda = 0.710$ 69 Å, μ (Mo- K_{α}) = 4.07 cm⁻¹.

Structure solution and refinement. The structure was solved by the heavy-atom methods and refined by blockedcascade least-squares (blocks of ca. 280 parameters) with weights $w = 1/\sigma^2(F)$. The non-hydrogen atoms were assigned anisotropic thermal parameters, except for the phenyl carbon atoms and the boron atom, which were refined isotropically. The C₅Me₅ hydrogen atoms were included in CH_3 rigid groups (C-H = 1.00 Å) whose positional and orientational parameters were refined; such hydrogens were assigned an overall temperature factor, which refined to 0.11 Å². All the other hydrogen atoms were placed in idealised positions, each with a thermal parameter ca. 20%larger than that of the respective carbon atom. Convergence was reached at $R \ 0.054$ ($R' \ 0.055$) and the final difference map showed no significant peaks, except in the proximity of the metal atom, where residues of ca. 1 e Å⁻³ were observed. Scattering factors and anomalous dispersion corrections were taken from ref. 19. All computations were accomplished using the SHELX 76 20 and the 'X-RAY '76' 21 systems of programs implemented on a SEL 32/70 computer by Dr. C. Mealli. Molecular illustrations were obtained using ORTEP-II.22 Fractional co-ordinates of non-hydrogen atoms are listed in Table 5. Thermal parameters, hydrogen-atom positions, bond distances and angles of the C₅Me₅ ring, and observed and calculated structure

factors are listed in Supplementary Publication No. SUP 23282 (40 pp.).*

* For details see Notices to Authors No. 7, J. Chem. Soc., Dalton Trans., 1981, Index issue.

We thank Professor L. Sacconi for his interest and encouragement and NATO for the award of a co-operative grant.

[1/1719 Received, 5th November, 1981]

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