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, BF_4, or PF_6], 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 in the $N(CH_2CH_2PPh_2)_3$ derivative undergoes substitution when treated with tetrabutylammonium chloride to give $[\{Rh(C_5Me_5)Cl_2\}_3\{N(CH_2CH_2PPh_2)_3\}]$. The influence of steric factors in the substitution reaction has been investigated by synthesising and characterising the complexes $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPR_2\}]BPh_4$ (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 $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$ has been determined by *X*-ray crystallographic analysis. The complexes $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPPh_2\}_2]BPh_4$ (n = 2, R' = Et; n = 3, R' = Me) exist as four rotamers due to restricted rotations of the bulky phosphine substituents about the Rh–P bonds, as shown by low-temperature ^{31}P n.m.r. spectroscopy.

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, $N(CH_2CH_2PPh_2)_3$, and tris(2-diphenylphosphinoethyl)phosphine, $P(CH_2CH_2PPh_2)_3$, with di-μ-chloro-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 (= PPh_3, C_5H_5N, or *p*-toluidine) to give $[Rh(C_5Me_5)Cl_2L]$ derivatives.[4] To ascertain some properties of the complexes with $N(CH_2CH_2PPh_2)_3$ a series of compounds obtained from $[Rh_2(C_5Me_5)_2Cl_4]$ and the ' mixed ' bidentate ligands $R'_2N(CH_2)_nPR_2$ (n = 2 or 3; R' = 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 $P(CH_2CH_2PPh_2)_3$ in dichloromethane affords, after addition of tetrabutylammonium tetrafluoroborate or hexafluorophosphate in ethanol, complexes of formula $[\{Rh(C_5Me_5)\}_3Cl_5L]Y$ [L = $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$; 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 ^{31}P n.m.r. spectra of the complexes (Table 2) are not affected by the nature of the anion (BF_4 or PF_6) and do not vary with temperature. The ^1H n.m.r. spectra of the $N(CH_2CH_2PPh_2)_3$ 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 δ 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 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 $^{31}P-\{^1H\}$ 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 $^{31}P-\{^1H\}$ 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

Compound	Λ_M [a]/ Ω^{-1} cm^2 mol^{-1}	Analysis (%) [b]			
		C	H	N	Other
$[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]Cl\cdot C_2H_5OH$	49 [c]	54.3 (54.6)	5.8 (5.8)	1.0 (0.9)	Cl, 12.9 (13.1)
$[\{Rh(C_5Me_5)\}_3Cl_6\{N(CH_2CH_2PPh_2)_3\}]\cdot C_2H_5OH$	18	54.4 (54.6)	5.9 (5.8)	1.0 (0.9)	P, 5.5 (5.7); Cl, 13.0 (13.1)
$[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]BF_4\cdot C_5H_5OH$	90	53.1 (53.0)	5.6 (5.6)	1.0 (0.8)	Cl, 10.2 (10.6)
$[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]PF_6\cdot C_2H_5OH$	89	51.2 (51.2)	5.5 (5.4)	0.9 (0.8)	P, 7.2 (7.1); Cl, 9.9 (10.2)
$[\{Rh(C_5Me_5)\}_3Cl_5\{P(CH_2CH_2PPh_2)_3\}]Cl\cdot C_2H_5OH$	70	53.9 (54.1)	5.7 (5.7)		Cl, 12.9 (13.0)
$[\{Rh(C_5Me_5)\}_3Cl_5\{P(CH_2CH_2PPh_2)_3\}]BF_4\cdot C_2H_5OH$	90	52.6 (52.4)	5.7 (5.5)		
$[\{Rh(C_5Me_5)\}_3Cl_5\{P(CH_2CH_2PPh_2)_3\}]PF_6\cdot C_2H_5OH$	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)	
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}]BPh_4$	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)
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$	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)	
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_3PPh_2\}_2]BPh_4$	49	72.4 (72.6)	7.5 (7.4)	2.1 (2.3)	
$[Rh(C_5Me_5)Br\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$	51	69.4 (69.6)	7.0 (6.9)	2.4 (2.3)	Br, 6.4 (6.4)
$[Rh(C_5Me_5)I\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$	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-$\{^1H\}$ n.m.r. spectral data of the complexes [a]

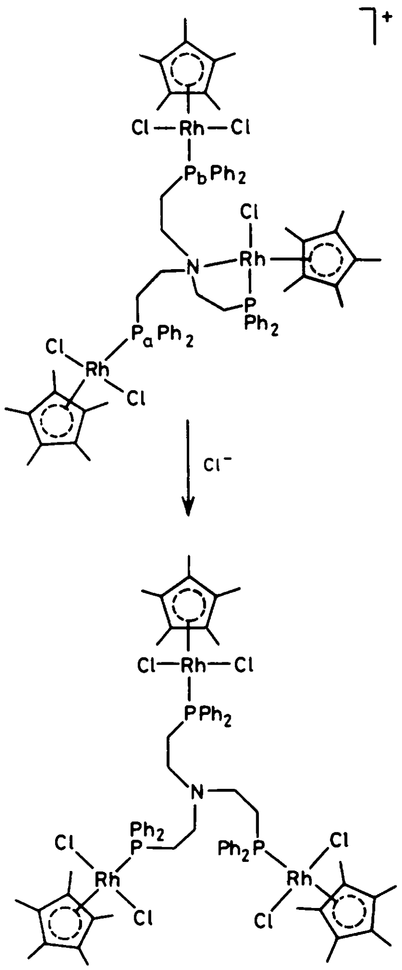
Compound	^{31}P-$\{^1H\}$ N.m.r. (δ/p.p.m.) [b]	ΔP [c]	C_5Me_5 ^1H N.m.r. (δ/p.p.m.) [d]
$[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]Cl\cdot C_2H_5OH$	49.64 (d) (148.0), 27.86 (d) (143.6), 24.53 (d) (144.1), 22.64 (d) (143.1)	69.20, 47.42, 44.09, 42.20	1.30 (m)
$[\{Rh(C_5Me_5)\}_3Cl_6\{N(CH_2CH_2PPh_2)_3\}]\cdot C_2H_5OH$	22.75 (d) (143.1)	42.31	1.33 (d) (3.7)
$[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]BF_4\cdot C_2H_5OH$	49.59 (d) (148.5), 27.79 (d) (143.8), 24.42 (d) (144.3)	69.15, 47.35, 43.98	1.34 (d) (3.7), 1.24 (d) (3.7), 1.07 (d) (3.6)
$[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]PF_6\cdot C_2H_5OH$	49.57 (d) (148.3), 27.74 (d) (143.6), 24.37 (d) (144.1)	69.13, 47.30, 43.93	1.34 (d) (3.7), 1.24 (d) (3.7), 1.07 (d) (3.6)
$[\{Rh(C_5Me_5)\}_3Cl_5\{P(CH_2CH_2PPh_2)_3\}]Cl\cdot C_2H_5OH$	68.4 (m), 30.6 (m)		1.33 (m)
$[\{Rh(C_5Me_5)\}_3Cl_5\{P(CH_2CH_2PPh_2)_3\}]BF_4\cdot C_2H_5OH$	68.4 (m)		1.33 (m)
$[\{Rh(C_5Me_5)\}_3Cl_5\{P(CH_2CH_2PPh_2)_3\}]PF_6\cdot C_2H_5OH$	68.4 (m)		1.33 (m)
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_2PPh_2\}]BPh_4$	54.25 (d) (141.9)	75.85	1.20 (d) (3.4)
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_2PPh_2\}]BPh_4$	52.20 (d) (146.1)	72.15	1.19 (d) (3.2)
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}]BPh_4$	52.67 (d) (147.5)	71.84	1.19 (d) (3.3)
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_3PPh_2\}]BPh_4$	28.09 (d) (138.7)	44.03	1.17 (d) (3.5)
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_3PPh_2\}]BPh_4$	29.87 (d) (146.7)	45.53	1.17 (d) (3.4)
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_3PPh_2\}]BPh_4$	29.64 (d) (147.1)	45.42	1.18 (d) (3.6)
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_2P(C_6H_{11})_2\}]BPh_4$	59.80 (d) (137.2)	66.43	1.38 (d) (3.1)
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_2P(C_6H_{11})_2\}]BPh_4$	59.31 (d) (138.2)	66.61	1.37 (d) (3.0)
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2P(C_6H_{11})_2\}]BPh_4$	59.23 (d) (138.5)	66.05	1.39 (d) (3.0)
$[Rh(C_5Me_5)Cl\{H_2N(CH_2)_3P(C_6H_{11})_2\}]BPh_4$	29.38 (d) (132.0)	33.45	1.35 (d) (2.9)
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_3P(C_6H_{11})_2\}]BPh_4$	29.12 (d) (135.4)	33.60	1.36 (d) (3.0)
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$	22.48 (d) (136.1) (br) [e] 30.89 (d) (133.7),[f] 29.28 (d) (133.7),[f] 23.50 (d) (135.5),[f] 21.90 (d) (135.4) [f]	42.04 50.45, 48.84, 43.06, 41.46	1.00 (t) (3.4) 0.97 (m)
$[Rh(C_5Me_5)Cl\{Me_2N(CH_2)_3PPh_2\}_2]BPh_4$	23.21 (d) (134.3) (br) [e] 25.55 (d) (133.1),[f] 23.87 (d) (133.1),[f] 20.45 (d) (135.1),[f] 18.87 (d) (135.0) [f]	42.77 45.01, 43.43, 40.01, 38.43	1.00 (t) (3.4) 0.98 (m)
$[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_3PPh_2\}_2]BPh_4$	23.26 (d) (135.1) (br)	42.82	1.01 (t) (3.4)
$[Rh(C_5Me_5)Br\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$	20.49 (d) (128.1) (br)	40.05	1.04 (t) (3.4)
$[Rh(C_5Me_5)I\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$	19.24 (d) (125.1) (br)	38.80	1.12 (t) (3.2)

[a] Measured in $CDCl_3$ at room temperature unless otherwise indicated; d = doublet, t = triplet, m = multiplet, br = broad. [b] *J*(P–Rh) in Hz are given in parentheses. [c] $\Delta P = \delta P_{co\text{-}ord.} - \delta P_{free\ ligand}$. [d] *J*(H–P) in Hz are given in parentheses. [e] Room temperature. [f] At −50 °C.

pentamethylcyclopentadienyl units each bound to a terminal phosphorus atom of the tetradentate ligand. Two of the metal atoms must then complete their co-ordination 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 ^{31}P spectra of both the $N(CH_2CH_2PPh_2)_3$ and $P(CH_2CH_2PPh_2)_3$ 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 $[\{Rh(C_5Me_5)\}_3Cl_5L]PF_6$ [$L = N(CH_2CH_2PPh_2)_3$].[6] The magnetic inequivalence of the phosphorus atoms of the $Rh(C_5Me_5)Cl_2$ groups, giving the high-field doublets in the ^{31}P spectra, is probably due to the bulk of the $RhCl(C_5Me_5)$ groups attached to P_a and P_b (see Scheme). This forces a *trans*-geometry on them and also severely restricts rotation about the $\overset{\frown}{N\;P_a}$ and $\overset{\frown}{N\;P_b}$ 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 $[\{Rh(C_5Me_5)\}_3Cl_5L]Cl$ [$L = N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$]. The $P(CH_2CH_2PPh_2)_3$ derivative behaves as a 1 : 1 electrolyte and both its ^1H and ^{31}P 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 $N(CH_2CH_2PPh_2)_3$ 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 ^{31}P 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.



SCHEME

A non-ionic complex of formula $[\{Rh(C_5Me_5)Cl_2\}_3L]$ [$L = N(CH_2CH_2PPh_2)_3$] (Table 1) was isolated from the above solution after addition of NBu_4Cl. Its spectral properties (Table 2), in the presence of NBu_4Cl, 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 $N(CH_2CH_2PPh_2)_3$ 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 $P(CH_2CH_2PPh_2)_3$ 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 $P(CH_2CH_2PPh_2)_3$ 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 $Rh(C_5Me_5)$ system.[9] However, the replacement of co-ordinated nitrogen by chloride is most unusual.

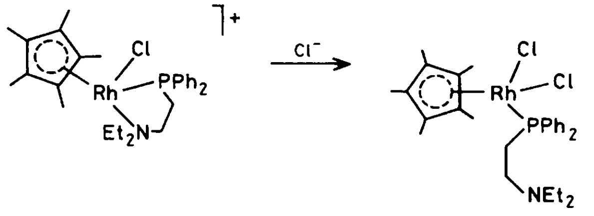
In order to understand the nature of the factors which control this substitution reaction complexes of formula $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPR_2\}]BPh_4$ have been synthesised and their properties investigated. The various $R'_2N(CH_2)_nPR_2$ ligands employed differ from each other both in the 'cone 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 $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPR_2\}]BPh_4$. 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 ^{31}P 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 $R'_2N(CH_2)_2PR_2$ ligands, having five-membered chelate rings, exhibit chemical shifts comparable to that ascribed to the $\overline{Rh(C_5Me_5)Cl(PCH_2CH_2N)}$ unit in the $N(CH_2CH_2PPh_2)_3$ trimetallic complex. From these data we deduce that both nitrogen and phosphorus are bound to the metal. The ^{31}P spectra of the complexes with $R'_2N(CH_2)_3PR_2$ 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 $R'_2N(CH_2)_2PR_2$ to the $R'_2N(CH_2)_3PR_2$ derivatives is of the same order as found for the 'ring contribution' on going from five- to six-membered rings formed by polyphosphines, alkenylphosphines, or in orthometallated complexes.[10]

If tetrabutylammonium chloride is added to $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}]BPh_4$ 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 chloride show both the resonances of the starting compound and a new doublet at δ 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 δ 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.

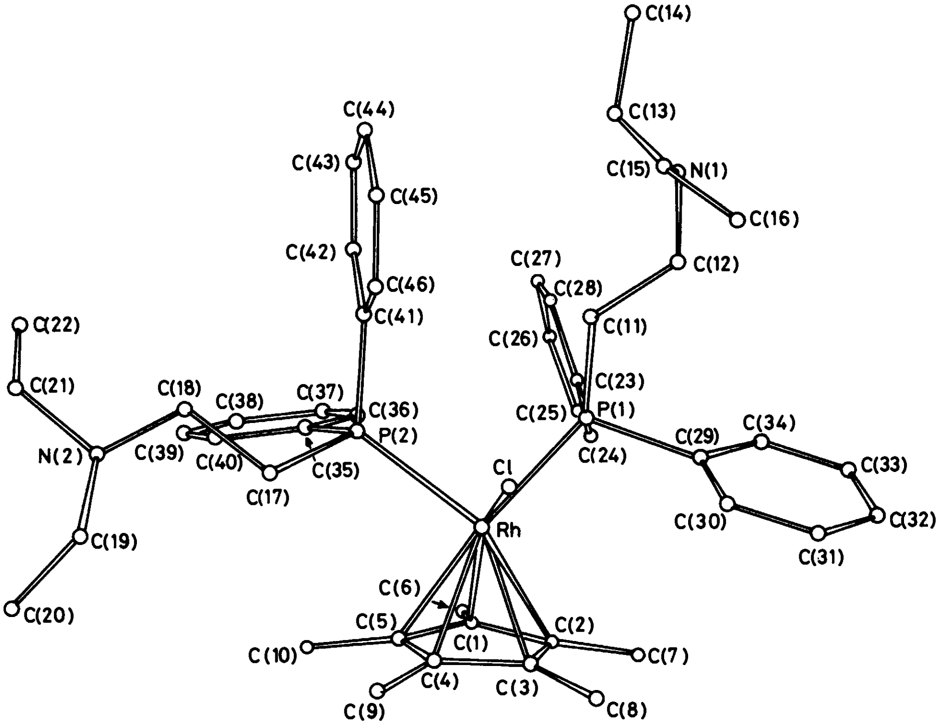


Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with an excess of the bidentate ligand (*e.g.* in a 1 : 4 ratio) generally yields the complexes described above. However, when the $R'_2N(CH_2)_nPPh_2$ ligands with $n = 2$, $R' = Et$, or with $n = 3$, $R' = Me$ or Et, are employed, the reaction yields, after addition 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 ^{31}P n.m.r. spectra of these derivatives (Table 2) vary with temperature. At room temperature the ^{31}P 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 $-(CH_2)_nNR'_2$ portion of each ligand is dangling. This hypothesis is confirmed by the results of an *X*-ray structural investigation performed on the compound $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$ (see below).

At *ca.* +50 °C the broad doublet in the ^{31}P 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, ^{31}P spectra of the $[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPPh_2\}_2]BPh_4$ ($n = 2$, $R' = Et$, $n = 3$, $R' = Me$) 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 iodo-derivatives $[Rh(C_5Me_5)X\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$ (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.



View of the cationic part of $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$

The two pairs of doublets that are present at *ca.* −50 °C in the ^{31}P 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 ^{31}P 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 $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]$-$BPh_4$ consists of discrete complex cations and BPh_4 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 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 C_5Me_5 ring. This distance is comparable to that, of 1.890 Å, found in the compound $[Rh(C_5Me_5)H(PPh_3)_2]$-PF_6 [11] 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-C_5Me_5 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-C_5Me_5 ligand and the absence of disorder in the

TABLE 3

Selected bond distances (Å) and angles (°) in the co-ordination sphere of $[Rh(C_5Me_5)Cl\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$ with estimated standard deviations in parentheses

Rh–Cl	2.393(2)	Rh–C(2)	2.279(6)
Rh–P(1)	2.358(2)	Rh–C(3)	2.240(7)
Rh–P(2)	2.338(2)	Rh–C(4)	2.217(7)
Rh–C(1)	2.222(6)	Rh–C(5)	2.266(6)
C(1)–Rh–P(1)	88.2(1)	P(2)–Rh–C(2)	147.9(2)
C(1)–Rh–P(2)	89.0(1)	P(2)–Rh–C(3)	144.9(2)
C(1)–Rh–C(1)	151.3(2)	P(2)–Rh–C(4)	107.0(2)
C(1)–Rh–C(2)	119.9(2)	P(2)–Rh–C(5)	91.4(2)
C(1)–Rh–C(3)	89.3(2)	C(1)–Rh–C(2)	37.5(2)
C(1)–Rh–C(4)	91.8(2)	C(1)–Rh–C(3)	62.6(3)
C(1)–Rh–C(5)	125.6(2)	C(1)–Rh–C(4)	62.9(3)
P(1)–Rh–P(2)	96.3(1)	C(1)–Rh–C(5)	37.2(3)
P(1)–Rh–C(1)	109.5(2)	C(2)–Rh–C(3)	36.4(3)
P(1)–Rh–C(2)	98.0(2)	C(2)–Rh–C(4)	62.0(3)
P(1)–Rh–C(3)	118.7(2)	C(2)–Rh–C(5)	61.3(2)
P(1)–Rh–C(4)	156.6(2)	C(3)–Rh–C(4)	37.9(2)
P(1)–Rh–C(5)	145.5(2)	C(3)–Rh–C(5)	61.8(2)
P(2)–Rh–C(1)	110.4(2)	C(4)–Rh–C(5)	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 ^{31}P 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.

TABLE 4

Boiling points, analytical, and ^{31}P-$\{^1H\}$ n.m.r. spectroscopic data of the ligands

Ligand	B.p./°C (1 mmHg) [a]	Analysis (%) [b]			^{31}P-$\{^1H\}$ N.m.r. (δ/p.p.m., in C^2HCl_3)
		C	H	N	
$H_2N(CH_2)_2P(C_6H_{11})_2$	147—148	69.6 (69.7)	11.9 (11.7)	5.6 (5.8)	−6.63
$Me_2N(CH_2)_2P(C_6H_{11})_2$	146—148	71.1 (71.3)	12.2 (12.0)	5.0 (5.2)	−7.30
$Et_2N(CH_2)_2P(C_6H_{11})_2$	157—159	72.5 (72.7)	12.3 (11.2)	4.5 (4.7)	−6.82
$H_2N(CH_2)_3PPh_2$	143—145	74.0 (74.1)	7.7 (7.5)	5.6 (5.8)	−15.94
$H_2N(CH_2)_3P(C_6H_{11})_2$	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

[a] 1 mmHg = (101 325/760) N m^{-2}. [b] Calculated values are given in parentheses.

The ligand tris(2-diphenylphosphinoethyl)phosphine, $P(CH_2CH_2PPh_2)_3$, was purchased from the Pressure Chemical Co. Di-μ-chloro-bis[chloro(pentamethylcyclopentadienyl)rhodium] [4] and the ligands tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$,[16] 2-aminoethyldiphenylphosphine, $H_2N(CH_2)_2PPh_2$,[17] 2-dimethylaminoethyldiphenylphosphine, $Me_2N(CH_2)_2PPh_2$,[18] 2-diethylaminoethyldiphenylphosphine, $Et_2N(CH_2)_2PPh_2$, and 3-diethylaminopropyldiphenylphosphine, $Et_2N(CH_2)_3PPh_2$, were prepared as already described. The other ligands $R'_2N(CH_2)_nPR_2$ ($n = 2$, R = C_6H_{11}, R′ = H, Me, or Et; $n = 3$, R = Ph and R′ = H; R = C_6H_{11} 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 fractional 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 = $N(CH_2CH_2PPh_2)_3$ *or* $P(CH_2CH_2PPh_2)_3$; Y = BF_4 *or* PF_6]. A solution of the appropriate ligand (0.33 mmol) in dichloromethane (10 cm^3) was added to $[Rh_2(C_5Me_5)_2Cl_4]$ (0.5 mmol) dissolved in dichloromethane (15 cm^3) and the mixture was refluxed (30 min). After cooling, a solution of NBu_4Y (Y = BF_4 or PF_6) (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 crystallised with one molecule of ethanol [ν(OH) *ca.* 3 350 cm^{-1}].

$[\{Rh(C_5Me_5)\}_3Cl_5L]Cl$ [L = $N(CH_2CH_2PPh_2)_3$ *or* $P(CH_2CH_2PPh_2)_3$]. 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 NBu_4Cl (1 mmol) in ethanol (10 cm^3) was added to the complex $[\{Rh(C_5Me_5)\}_3Cl_5\{N(CH_2CH_2PPh_2)_3\}]Cl$ (1 mmol) dissolved in ethanol (15 cm^3). 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 cm^3) was added to $[Rh_2(C_5Me_5)_2Cl_4]$ (0.5 mmol) in dichloromethane (15 cm^3) 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.

$[Rh(C_5Me_5)Cl\{R'_2N(CH_2)_nPR_2\}]BPh_4$ ($n = 2$, 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 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.

$[Rh(C_5Me_5)X\{Et_2N(CH_2)_2PPh_2\}_2]BPh_4$ (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 × 0.33 × 0.08 mm. Unit-cell dimensions were determined from the angular measurements of 24 strong reflections with $20 < 2\theta < 30°$. Data were collected in the range $4 < 2\theta < 48°$, by the θ—2θ scan technique, with a symmetric scan range of $0.90 + 0.30 \tan\theta$ and a scan speed of 3.0° min^{-1} in 2θ. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three 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.

TABLE 5

Atomic co-ordinates for non-hydrogen atoms of [Rh(C_5Me_5)-Cl{$Et_2N(CH_2)_2PPh_2$}$_2$]BPh_4 ($\times 10^4$, except Rh $\times 10^5$) with estimated standard deviations in parentheses *

Atom	*x*	*y*	*z*
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)
N(1)	5 141(4)	1 266(5)	1 294(5)
N(2)	4 752(4)	3 259(5)	7 735(4)
C(1)	1 268(4)	976(5)	3 361(5)
C(2)	1 336(5)	42(5)	2 760(5)
C(3)	1 966(5)	−403(5)	3 422(5)
C(4)	2 265(5)	229(5)	4 456(5)
C(5)	1 791(5)	1 048(5)	4 412(6)
C(6)	576(5)	1 628(6)	3 016(6)
C(7)	716(5)	−432(5)	1 656(6)
C(8)	2 221(6)	−1 397(5)	3 162(6)
C(9)	2 843(6)	−25(6)	5 406(6)
C(10)	1 722(5)	1 805(5)	5 293(6)
C(11)	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)	1 934(5)	1 584(5)
C(24)	1 353(5)	1 877(5)	1 185(6)
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)	2 721(5)	1 653(5)
C(29)	2 496(4)	−60(4)	1 047(5)
C(30)	2 764(5)	−891(5)	1 248(5)
C(31)	2 499(5)	−1 746(5)	450(6)
C(32)	1 984(6)	−1 749(6)	−538(6)
C(33)	1 728(6)	−930(6)	−745(6)
C(34)	1 985(5)	−73(5)	44(5)
C(35)	2 957(4)	3 293(4)	4 817(5)
C(36)	2 360(5)	3 456(5)	3 934(5)
C(37)	1 841(5)	4 227(5)	3 669(5)
C(38)	1 910(5)	4 833(5)	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)
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(54)	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)	−1 541(5)	3 720(5)	7 008(5)
C(61)	−2 155(5)	3 988(5)	7 503(6)
C(62)	−1 910(5)	3 933(5)	8 491(6)
C(63)	−1 053(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)	−1 602(5)	2 477(5)	4 106(6)
C(68)	−1 214(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.

Crystal data. $C_{70}H_{83}BClN_2P_2Rh$, $M = 1\,163.57$, Triclinic, space group $P\bar{1}$, $a = 15.694(6)$, $b = 15.023(6)$, $c = 14.924(5)$ Å, $\alpha = 107.40(5)$, $\beta = 112.75(5)$, $\gamma = 87.88(5)°$, $U = 3\,084.02$ Å^3, $F(000) = 1\,228$, $D_c = 1.253$ 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 blocked-cascade 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 C_5Me_5 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 Å^2. 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 C_5Me_5 ring, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23282 (40 pp.).*

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

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