Synthesis of Trimethylphosphine Complexes of Rhodium and Ruthenium. *X*-Ray Crystal Structures of Tetrakis(trimethylphosphine)rhodium(I) Chloride and Chlorotris(trimethylphosphine)rhodium(I) †

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The synthesis and characterization of the following trimethylphosphine complexes of rhodium and ruthenium are reported; $[Rh(PMe_3)_4]Cl$, (A), $RhCl(PMe_3)_3$, (B), $[Rh(PMe_3)_3]X$, ($X = PF_6$, BPh_4), $[RhH_2(PMe_3)_4]Cl$, $RhCl(CO)(PMe_3)_2$, $[Rh(PMe_3)_3(CH_2Cl_2)]Cl$, $[RuCl(PMe_3)_2]_2$, $[RuCl(PMe_3)_4]BF_4$, *trans*-$RuCl_2(PMe_3)_4$, $[RuCl(PMe_3)_4]_2Cl_2$ and $RuHCl(PMe_3)_4$.

The crystal structures of (A) and (B) have been determined by single-crystal *X*-ray diffraction. Compound (A) is orthorhombic, space group *Ccmm* with $a = 12.366$, $b = 13.584$, $c = 12.554$ Å, and $Z = 4$; (B) is triclinic, space group $P\bar{1}$ with $a = 8.842$, $b = 8.982$, $c = 11.825$ Å, $\alpha = 98.74$, $\beta = 92.38$, $\gamma = 116.09°$, $Z = 2$. The structures were determined using 1 476 and 2 695 observed intensities measured on an automatic diffractometer and refined to *R* values of 0.030 and 0.023 for (A) and (B) respectively. The geometries of both the RhP_4^+ cation and RhP_3Cl molecule can be described as square planar, with considerable tetrahedral distortion as a result of steric crowding. Rh–P distances in (A) are 2.295 and 2.299(1) Å, whilst in (B) Rh–P bonds *trans* to each other are 2.295 and 2.296(1) Å, but *trans* to Cl 2.203 Å; Rh–Cl is 2.410 Å.

SINCE the discovery of chlorotris(triphenylphosphine)rhodium(I) and its ability to act as a hydrogenation catalyst for C–C multiple bonds,[1] innumerable studies have been made on tertiary phosphine complexes of rhodium and other elements. There is still relatively little information on alkylphosphine complexes of rhodium(I) other than the tricyclohexyl, $RhCl\{P(C_6H_{11})_3\}_2$,[2,3] the tributyl, $RhH(PBu^t{}_3)_2$,[3] the tri-isopropyl,[4] $RhCl(N_2)(PPr^i{}_3)_2$, and the phenyldi-t-butyl,[5] $RhH(N_2)(PPhBu^t{}_2)_2$, although during the course of this work the synthesis of $[Rh(PMe_3)_4]Cl$ from $[Rh(C_8H_{12})Cl]_2$ and excess of PMe_3 in benzene was reported.[6a]

Previously, Intille[7] had reported the synthesis of a number of alkylphosphine complexes including that of trimethylphosphine. In connection with our studies on alkyl trimethylphosphine complexes[8] we attempted to repeat the synthesis of $RhCl(PMe_3)_3$. In our hands, the complicated procedure, which involves reduction of $RhCl_3{\cdot}3H_2O$ in refluxing ethanol–benzene by ethylene, followed by addition of PMe_3 and work-up, did not lead to the compound described as a red powder (m.p. 205—210 °C). Instead, much rhodium metal deposited on the walls of the flask and only a small amount of a mixture of red, yellow, and white materials could be recovered. I.r. spectra of the products showed bands due to water.

We have now made authentic $RhCl(PMe_3)_3$ from $[Rh(PMe_3)_4]Cl$, which in turn can be obtained by phosphine exchange from $RhCl(PPh_3)_3$ in petroleum, and we conclude that the tris(trimethylphosphine) species has not previously been isolated pure.

Studies of alkylphosphine chloro-complexes of ruthenium[9] have so far not been extended to those of trimethylphosphine, although the cation $[RuH(PMe_3)_5]^+$ and some related compounds have been described.[10]

In this paper we report the synthesis and properties of trimethylphosphine complexes of both rhodium and ruthenium. Spectroscopic data are collected in Table 1, and analytical data in Table 2.

RESULTS AND DISCUSSION

Rhodium Complexes.—Tetrakis(trimethylphosphine)rhodium(I) *chloride and chlorotris(trimethylphosphine)rhodium*(I). The interaction of an excess of trimethylphosphine with $RhCl(PPh_3)_3$ in petroleum yields a yellow powder, which on crystallisation from boiling toluene yields large, orange, hygroscopic prisms of $[Rh(PMe_3)_4]Cl$ (A). If this species is heated in refluxing toluene under nitrogen (48 h), the tris-complex, $RhCl(PMe_3)_3$ (B), can be obtained as orange prisms in high yield. Although (A) can also be prepared from $[Rh(C_8H_{12})Cl]_2$ as noted above, $RhCl(PMe_3)_3$ was not isolated.[6a] Both complexes have been studied by *X*-ray diffraction.

The crystal structure of $[Rh(PMe_3)_4]Cl$ shows that the chloride anion is fully dissociated in the solid state, with the closest contact to Cl^- being $Cl \cdots C(12) = 3.90$ Å; $RhCl(PMe_3)_3$, however, exists as discrete molecules. Important molecular geometry parameters for both species are given in Tables 3 and 4. The structures of the cation in (A) and the molecule (B), together with the atom numbering scheme used, are given in Figures 1 and 2, respectively; packing diagrams are given as Figures 3 and 4.

The geometries of both the cation and molecule (B) can be described as square with tetrahedral distortions due to steric crowding. Thus the angles at the metal atom between *trans* ligands, which would be 180° in a square situation, are 148.29, 151.46° in (A) and 163.16, 163.99° in (B). It is clear that these distortions from the expected square geometry are due to intramolecular phosphine–phosphine (or to a smaller extent phosphine–chlorine) repulsions (Table 5). It is interesting to note

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† No reprints available.

the effect these have on the geometry of the phosphine ligands themselves. In both complexes, the Rh–P–C angles are significantly greater than tetrahedral, ranging from 112 to 127° in (A) and 112 to 122° in (B). On the other hand, the P–C–H angles at the methyl carbon atoms show a much smaller variation, ranging from 106 to 114°; the steric crowding does not, however, seem to have affected the Rh–P and Rh–Cl bond lengths, since these are similar to, or even smaller than, those found in related compounds. The molecular structure of (B) is very similar to that found in the two forms of the corresponding triphenylphosphine analogue in which Rh–P bond lengths are 2.214, 2.225 Å (*trans* to P), 2.321, 2.328 Å (*trans* to Cl), and Rh–Cl is 2.376, 2.404 Å.[11] The main differences are thus that the Rh–P bonds in (B) are systematically *ca.* 0.02 Å shorter in our compound whereas the Rh–Cl distances are the same within experimental error.

Although (A) is slightly soluble in aromatic hydrocarbons at room temperature it is far more soluble in

TABLE 1

^{1}H and ^{31}P{^{1}H} N.m.r. data

	Compound	δ [a]	Multiplicity (relative intensity)	Assignment	^{31}P{^{1}H} [b] δ	Multiplicity (relative intensity)	$^1J_{\text{Rh-P}}$/Hz
(A)	[Rh(PMe$_3$)$_4$]Cl	1.47	s	PMe$_3$ [c]	−14.5	d [c]	125.6
(B)	RhCl(PMe$_3$)$_3$	1.47	s	PMe$_3$ [c]	−0.38	td [$^2J_{\text{P-P}}$ 46.1 Hz [d]]	179.5
					−11.31	dd[$^2J_{\text{P-P}}$ 46.4 Hz]	130.6
(C)	[Rh(PMe$_3$)$_3$]PF$_6$	1.48	s	PMe$_3$ [c]	38.7	s [e] PF$_6$	
					−14.72	br s	
					−14.99	d (−25 °C)	132.5
(D)	[Rh(PMe$_3$)$_3$]BPh$_4$	7.55—6.80	br m (20)	BPh$_4^-$ [e]	−14.87	br d [e]	110
		1.55	m (27)	PMe$_3$			
(E)	[RhH$_2$(PMe$_3$)$_4$]Cl	1.55	m (36)	PMe$_3$ [e]	−11.08 [e]	td [e]	94.4
		−10.6	d q (2)	Rh–H		[$^2J_{\text{P-P}}$ 28.0 Hz]	
			[$^1J_{\text{Rh-H}}$ 135, $^2J_{\text{P-H}}$ 13.5 Hz]		−22.69	br, m	
(F)	RhCl(CO)(PMe$_3$)$_2$	1.38	m (18)	PMe$_3$	−10.22	d	114.7
(G)	[Rh(PMe$_3$)$_3$(CH$_2$Cl$_2$)]Cl	1.53	d (27)	PMe$_3$	16.39	d [e]	148.0
			[$^2J_{\text{P-H}}$ 11 Hz]				
		3.56	br s (2)	CH$_2$Cl$_2$			
(H)	Ru$_2$Cl$_2$(PMe$_3$)$_4$	1.20	m	PMe$_3$	−11.70	s	
(I)	[RuCl(PMe$_3$)$_4$]BF$_4$	1.40	m	PMe$_3$ [e]	23.50	s	
(J)	*trans*-RuCl$_2$(PMe$_3$)$_4$	1.25	m	PMe$_3$	−6.63	s	
(K)	[RuCl(PMe$_3$)$_4$]$_2$Cl$_2$	1.49	m	PMe$_3$ [e]	13.17	t[$J_{\text{P-P}}$ 33 Hz [e]]	
					−8.80	t[$J_{\text{P-P}}$ 33 Hz]	
(L)	RuHCl(PMe$_3$)$_4$	1.48	+ (18) [$^2J_{\text{P-H}}$ 3 Hz]	PMe$_3$ *trans*	−4.85	dd [$^2J_{\text{P-P}}$ 34, 25 Hz]	
		1.24	d (9) [$^2J_{\text{P-H}}$ 5 Hz]	PMe$_3$ *cis*	16.7	td [$^2J_{\text{P-P}}$ 34.2, 20.7 Hz]	
		1.09	d (9) [$^2J_{\text{P-H}}$ 8 Hz]	PMe$_3$ *cis*	−16.6	m	
		−8.50	d q (1) [$^2J_{\text{P-H}}$ 108, 29 Hz]	Ru–H			

[a] In C$_6$D$_6$ solvent referenced to SiMe$_4$ (δ 0.0) at 90 MHz and 35 °C. [b] In C$_6$D$_6$/[^{2}H]benzene (10%) and referenced to external 85% H$_3$PO$_4$ (δ 0.0) at 40.5 MHz. Peaks to high frequency (low field) of the reference are positive. [c] In D$_2$O. [d] [^{2}H$_8$]Toluene. [e] In CD$_3$NO$_2$.

TABLE 2

Analytical data

	Compound	Colour	Found (%)				M [a] (required)	Required (%)				Λ_M [b]
			C	H	P	Cl		C	H	P	P	
(A)	[Rh(PMe$_3$)$_4$]Cl	Orange	32.3	8.2	28.3	8.2		32.5	8.1	28.0	8.0	96
(B)	RhCl(PMe$_3$)$_3$	Orange	29.3	7.4	25.6	9.7	373 (367)	29.5	7.4	25.4	9.7	
(C)	[Rh(PMe$_3$)$_3$]PF$_6$	Yellow	21.6	5.4	25.5			22.7	5.7	26.1		106
(D)	[Rh(PMe$_3$)$_3$]BPh$_4$	Yellow	61.1	7.5	14.0	1.8 [c]		60.9	7.2	14.3	1.7	74
(E)	[RhH$_2$(PMe$_3$)$_4$]Cl	White	32.7	8.6	27.4	8.1		32.4	8.6	27.9	8.0	120
(F)	*trans*-RhCl(CO)(PMe$_3$)$_2$	Yellow	29.7	6.6	23.0	9.7	320 (335)	30.4	6.8	23.6	9.0	
(G)	[Rh(PMe$_3$)$_3$(CH$_2$Cl$_2$)]Cl	Yellow	26.7	6.2	20.1	24.6		26.6	6.4	20.6	23.6	108
(H)	Ru$_2$Cl$_2$(PMe$_3$)$_4$	Orange	26.4	6.6	22.6	12.5	530 (577)	25.0	6.2	21.5	12.3	
(I)	[RuCl(PMe$_3$)$_4$]BF$_4$	Yellow	27.5	6.6	23.4	6.6		27.3	6.8	23.5	6.8	92
(J)	*trans*-RuCl$_2$(PMe$_3$)$_4$	Orange	29.7	7.1	24.6	15.9	488 (476)	30.3	7.6	26.1	14.9	
(K)	[RuCl(PMe$_3$)$_4$]$_2$Cl$_2$	Yellow	28.8	6.8	23.7	14.9		30.3	7.6	26.1	14.9	150
(L)	RuHCl(PMe$_3$)$_4$	White	32.4	7.9			480 (442)	32.6	8.4			

[a] Cryoscopically in benzene. [b] In MeNO$_2$ at 25° C and 10^{-3} mol dm^{-3}, values in Ω^{-1} cm^2 mol^{-1}. [c] Boron.

TABLE 3

Intramolecular bond lengths and angles for $[Rh(PMe_3)_4]^+$

(*a*) Bond lengths (Å)

Rh–P(1)	2.295(1)	P(1)–C(12)	1.839(4)
Rh–P(2)	2.299(1)	P(2)–C(21)	1.816(3)
P(1)–C(11)	1.826(3)	P(2)–C(22)	1.829(5)

(*b*) Bond angles (°)

P(1)–Rh–P(2)	93.86(5)	C(11)–P(1)–C(11′)	98.6(2)
P(1)–Rh–P(1′) *	151.46(5)	C(11)–P(1)–C(12)	101.5(2)
P(2)–Rh–P(2′)	148.29(5)	C(21)–P(2)–C(21′)	99.0(2)
		C(21)–P(2)–C(22)	101.3(2)
Rh–P(1)–C(11)	112.8(1)		
Rh–P(1)–C(12)	125.7(2)		
Rh–P(2)–C(21)	112.3(1)		
Rh–P(2)–C(22)	126.7(2)		

The C–H distances range from 0.81(7) to 1.16(4) Å; average = 0.97 Å.

* The primed atoms are illustrated in Figure 1.

polar solvents such as water or nitromethane. Conductivity measurements indicate a 1 : 1 electrolyte in the latter solvents ($\Lambda_M = 96\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 10^{-3} mol dm^{-3}, 25 °C).

$RhCl(PMe_3)_3$ is much more soluble in aromatic hydrocarbons, in which it is monomeric, and the $^{31}P\{^1H\}$ n.m.r. spectrum (AX_2 triplet–doublet pattern, also split by ^{103}Rh) is in accord with the *X*-ray crystal structure (2) which shows square co-ordination for rhodium. This compound is also soluble in water although it dissolves much less readily than does $[Rh(PMe_3)_4]Cl$.

Both compounds are soluble in diethyl ether, tetrahydrofuran, methanol, and ethanol, although they slowly abstract CO from these solvents to give *trans*-$RhCl(CO)(PMe_3)_2$. The abstraction from alcohol doubtless is the reason for Intille's failure to obtain genuine $RhCl(PMe_3)_3$ and it seems likely that other alkylphosphine complexes prepared by similar procedures are dubious.

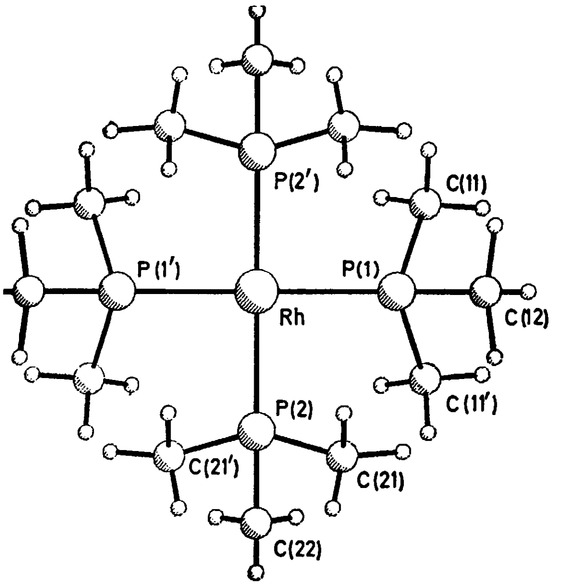


FIGURE 1 Structure of the $[Rh(PMe_3)_4]^+$ cation showing the numbering system of the non-hydrogen atoms. The primed atoms are related to the unprimed ones by *m* symmetry

Although phosphine and phosphite (L) complexes $[RhL_4]^+$ and $[RhL_5]^+$ were isolated as their BPh_4 salts from benzene solutions of $[Rh(C_8H_{12})Cl]_2$ containing an excess of L,[12] the $[Rh(PMe_3)_4]^+$ ion could not be isolated by precipitation from aqueous solutions as the BPh_4 or PF_6 salts. Instead, the tris-ion $[Rh(PMe_3)_3]^+$ is quantitatively precipitated from solution of either $[Rh(PMe_3)_4]Cl$ or $RhCl(PMe_3)_3$. It may be noted that the triphenylphosphine cation has recently been structurally characterised as its perchlorate, $[Rh(PPh_3)_3]ClO_4$.[13]

The ^1H n.m.r. spectrum of $[Rh(PMe_3)_4]Cl$ in D_2O or CD_3NO_2 is a sharp singlet while the $^{31}P\{^1H\}$ spectrum is a doublet ($J_{Rh\text{-}P}$ 125.6 Hz). In CD_3NO_2 the lines broaden only slightly on cooling. For the hexafluorophosphate

TABLE 4

Intramolecular bond lengths and angles for $RhCl(PMe_3)_3$

(*a*) Bond lengths (Å)

Rh–Cl	2.410(1)	P(1)–C(13)	1.833(3)
Rh–P(1)	2.295(1)	P(2)–C(21)	1.827(4)
Rh–P(2)	2.203(1)	P(2)–C(22)	1.818(3)
Rh–P(3)	2.296(1)	P(2)–C(23)	1.830(3)
		P(3)–C(31)	1.835(4)
P(1)–C(11)	1.828(4)	P(3)–C(32)	1.825(3)
P(1)–C(12)	1.821(3)	P(3)–C(33)	1.821(4)

(*b*) Bond angles (°)

Cl–Rh–P(1)	88.04(5)	Rh–P(2)–C(21)	118.6(1)
Cl–Ph–P(2)	163.16(5)	Rh–P(2)–C(22)	121.8(1)
Cl–Rh–P(3)	85.55(5)	Rh–P(2)–C(23)	113.9(1)
P(1)–Rh–P(2)	95.66(5)	C(21)–P(2)–C(22)	99.7(2)
P(2)–Rh–P(3)	94.70(5)	C(22)–P(2)–C(23)	102.0(2)
P(1)–Rh–P(3)	163.99(5)	C(21)–P(2)–C(23)	96.8(2)
Rh–P(1)–C(11)	118.3(1)	Rh–P(3)–C(31)	122.4(1)
Rh–P(1)–C(12)	120.4(1)	Rh–P(3)–C(32)	115.9(1)
Rh–P(1)–C(13)	112.9(1)	Rh–P(3)–C(33)	113.2(2)
C(11)–P(1)–C(12)	102.1(2)	C(31)–P(3)–C(32)	102.3(2)
C(11)–P(1)–C(13)	99.1(2)	C(31)–P(3)–C(33)	98.0(3)
C(12)–P(1)–C(13)	100.6(2)	C(32)–P(3)–C(33)	101.8(2)

The C–H distances range from 0.87(5) to 1.14(6) Å; average = 0.97 Å

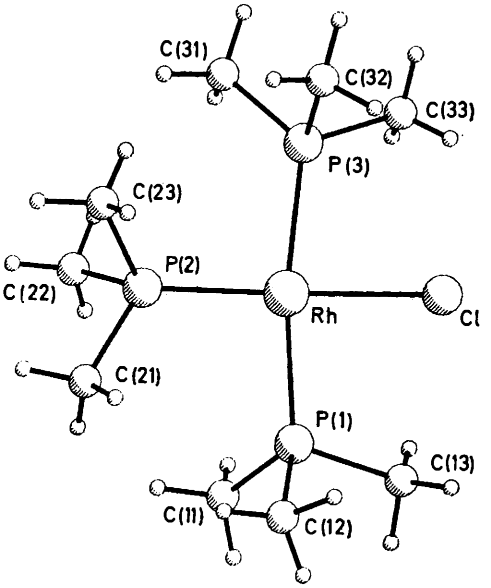


FIGURE 2 Structure of the $RhCl(PMe_3)_3$ molecule showing the numbering system of the non-hydrogen atoms

salt in CD_3NO_2 the ^1H and $^{31}P\{^1H\}$ spectra are both singlets at 35 °C; at −25 °C ^{103}Rh–^{31}P coupling can be observed, the $^{31}P\{^1H\}$ spectrum being a sharp doublet (J_{Rh-P} 132.5 Hz).

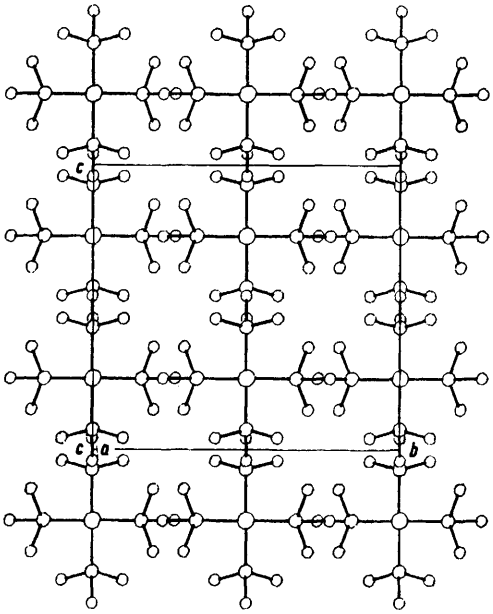


FIGURE 3 Packing diagram of $[Rh(PMe_3)_4]Cl$

The $^{31}P\{^1H\}$ n.m.r. spectra of ' aged ' toluene solutions showed the presence of both $[RhP_4]^+$, $[RhP_3]^+$ and free PMe_3 in accord with the suggestion that in solution the solvated ion $[Rh(PMe_3)_4(sol)_2]^+$ readily loses phosphine to give $[Rh(PMe_3)_3(sol)_2]^+$, which is then the major species in polar solvents (sol):

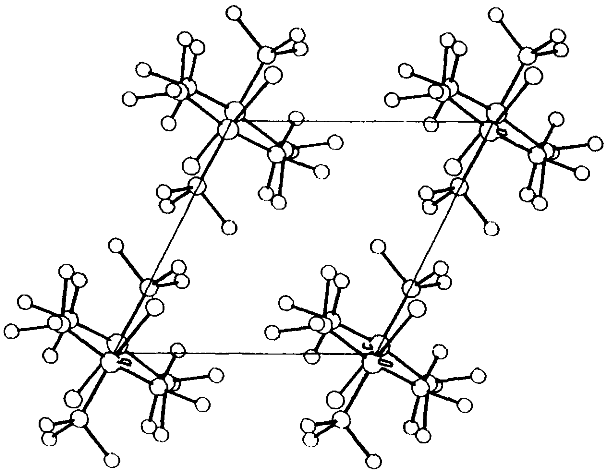


FIGURE 4 Packing diagram of $RhCl(PMe_3)_3$

$$[Rh(PMe_3)_4]Cl + 2sol \rightleftharpoons [Rh(PMe_3)_4(sol)_2]^+ + Cl^-$$

$$[Rh(PMe_3)_4(sol)_2]^+ \rightleftharpoons [Rh(PMe_3)_3(sol)_2]^+ + PMe_3$$

Although some rhodium(I) tetraphenylborates contain a π-bonded phenyl ring,[14,15] this is not the case for $[Rh(PMe_3)_3]BPh_4$, (D), either in the solid state or in solution. Thus the i.r. spectrum is characteristic of ionic BPh_4^- and shows two strong bands at 1 477 and 1 425 cm^{-1}, while the regions around *ca.* 1 460 and 1 390 cm^{-1}, diagnostic for π-$C_6H_5BPh_3$, are clear. The ^1H n.m.r. spectrum in CH_3NO_2 has only one broad multiplet (δ 7.1, area (20) due to BPh_4^- plus the PMe_3 multiplet (δ 1.55, area 27).

TABLE 5

Selected non-bonded contacts ⩽4.0 Å

(a) Intramolecular			
Compound (A)		Compound (B)	
C(11) ··· C(21^{II})	3.84	Cl ··· C(13^{I})	3.22
C(11) ··· C(22^{II})	3.71	Cl ··· C(32^{I})	3.78
C(12) ··· C(21^{I})	3.63	Cl ··· C(33^{I})	3.32
C(12) ··· C(21^{II})	3.63	C(11) ··· C(21^{I})	3.63
		C(12) ··· C(21^{I})	3.65
		C(23) ··· C(31^{I})	3.63

For compound (A) the roman numerals refer to the following symmetry operations

I x, y, z III $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$
II $x, y, \frac{1}{2} - z$ IV $1 - x, -y, -\frac{1}{2} + z$

(b) Intermolecular			
Compound (A)		Compound (B)	
C(11) ··· C(21^{III})	3.69	Cl ··· C(22^{II})	3.88
C(21) ··· C(21^{IV})	3.87	Cl ··· C(23^{II})	3.71
		Cl ··· C(12^{III})	3.82
Cl ··· C(12^{I})	3.90	C(22) ··· C(33^{IV})	3.67

For compound (B) the roman numerals refer to the following symmetry operations

I x, y, z III $-x, -y, -z$
II $-1 + x, y, z$ IV $-x, -y, 1 - z$

Reactions of $[Rh(PMe_3)_4]Cl$ *and* $RhCl(PMe_3)_3$. (1) *With hydrogen.* Interaction of $[Rh(PMe_3)_4]Cl$ with H_2 at 1 atm in tetrahydrofuran gives a white microcrystalline precipitate of the dihydrido-salt $[RhH_2(PMe_3)_4]Cl$ (E). This cation has previously been obtained as the PF_6^- and ClO_4^- salts from cationic diene complexes.[16]

The n.m.r. spectra are similar to those reported and in accord with the *cis*-dihydrido-configuration. The chloride is stable for weeks in the solid or in solution and hydrogen cannot be removed by pumping or flushing with nitrogen. It is very soluble in water. Compound (E) is also obtained from the tris-phosphine complex with H_2, although in lower yield. The additional phosphine can only come from $RhCl(PMe_3)_3$ and the supernatant contains some other yellow and red ' $RhCl(PMe_3)$ ' species which we have not characterised.

(2) *With carbon monoxide.* In toluene, CO and both $[Rh(PMe_3)_4]Cl$ or $RhCl(PMe_3)_3$ react rapidly to give *trans*-$RhCl(CO)(PMe_3)_2$ (F). Although briefly reported by Intille,[7] the nature of his starting ' $RhCl(PMe_3)_3$ ' is questionable; the ^1H n.m.r. spectrum at 60 MHz is reported to be a ' well defined 1 : 2 : 1 triplet ' δ 1.30, J_{P-H} 7.5 Hz. In $[^2H_8]$toluene at 60 and 90 MHz we find a very sharp multiplet of at least 13 lines, and the second-order spectrum is no doubt further complicated by ^{103}Rh coupling as described for $RhCl_3(PMe_3)_3$.[17] The $^{31}P\{^1H\}$ spectrum is a sharp doublet (J_{Rh-P} 114.7 Hz), confirming *trans*-PMe_3 stereochemistry. There is no evidence for ionic dissociation in nitromethane.

(3) *With chlorinated hydrocarbons.* On stirring [$Rh(PMe_3)_4$]Cl in neat CH_2Cl_2 at room temperature, pale yellow crystals of the solvate [$Rh(PMe_3)_3(CH_2Cl_2)$]Cl, (G), are deposited in high yield. However, in thf solution at room temperature, chlorine is abstracted from CCl_4, $CHCl_3$, and CH_2Cl_2 and *mer*-$RhCl_3(PMe_3)_3$[17] is formed, either from [$Rh(PMe_3)_4$]Cl or from $RhCl(PMe_3)_3$.

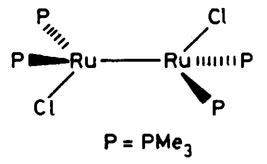
The compound (G) is insoluble in hydrocarbons but is very soluble in polar solvents, giving conducting solutions. The $^{31}P\{^1H\}$ n.m.r. spectrum is a sharp, temperature-independent doublet (+35 to −25 °C) and the large value for J_{Rh-P} of 148 Hz confirms that oxidation to Rh^{III} has not occurred and the complex contains Rh^I.

Ruthenium Compounds.—Bis[chlorobis(trimethylphosphine)ruthenium(I)](Ru–Ru) (H) *and chlorotetrakis(trimethylphosphine)ruthenium*(II) *tetrafluoroborate* (I). The reaction of $Ru_2(O_2CMe)_4Cl$ with 2.5 mol equiv. of $(2\text{-}MeOC_6H_4)_2Mg$ in the presence of PMe_3 has been reported.[18] Although a mixture of compounds was formed we were able to isolate a ruthenium(II) metallacycle $(Me_3P)_4\text{-}\overline{Ru\text{-}CH_2\text{-}OC}_6H_4$ in moderate yield, and also a diamagnetic crystalline complex $Ru_2Cl_2(PMe_3)_4$ (H) in low yield.

The interaction of trityl tetrafluoroborate in thf with the reaction mixture also produces [$RuCl(PMe_3)_4$]BF_4 (I). This pale yellow, diamagnetic, crystalline complex behaves as a 1 : 1 electrolyte in $MeNO_2$ and the $^{31}P\{^1H\}$ n.m.r. sharp singlet (28 °C) which broadens somewhat on cooling (−25 °C) suggests a fluxional five-co-ordinate structure in solution. The similar compound [$NiX(PMe_3)_4$]BF_4 has recently been described.[19]

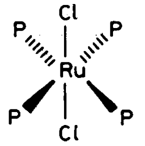
Despite the almost identical i.r. and ^1H n.m.r. spectra for $Ru_2Cl_2(PMe_3)_4$ and *trans*-$RuCl_2(PMe_3)_4$ the former is slightly darker orange in colour and the two compounds are clearly different on the basis of melting point, analytical, and ^{31}P n.m.r. data. (See Experimental section.)

Both compounds give temperature-independent singlets in the $^{31}P\{^1H\}$ spectrum, while molecular weight determinations on (H), and also its diamagnetism, suggest a dimeric structure (1), with a single Ru–Ru bond between two formally Ru^I atoms. The far-i.r. spectra are both virtually identical suggesting that (H) has terminal rather than bridging chlorides (ν_{Ru-Cl} = 315 cm^{-1}). Few well characterised Ru^I complexes have been reported.[20] So far, we have been unable to obtain any crystals suitable for an *X*-ray diffraction study.



P = PMe$_3$

(1)

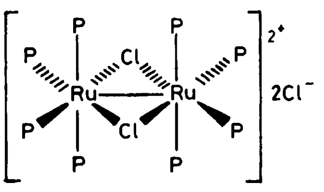


(2)

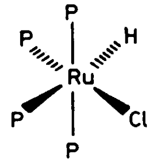
trans-*Dichlorotetrakis(trimethylphosphine)ruthenium*(II) (J). *trans*-$RuCl_2(PMe_3)_4$ can be readily prepared from $RuCl_2(PPh_3)_3$ and an excess of PMe_3 in petroleum,[21] and we have also obtained it in high yield from the interaction of $Ru_2(O_2CMe)_4Cl$ with an excess of sodium amalgam in thf in the presence of an excess of PMe_3 and LiCl. The $^{31}P\{^1H\}$ n.m.r. (temperature-independent singlet) indicates *trans*-chlorines as in (2).

Bis[μ-chloro-tetrakis(trimethylphosphine)ruthenium(II)] *dichloride* (K). Unlike most other complexes of the type $RuCl_2(PR_3)_{3\text{ or }4}$,[22] (J) does not readily form halide bridged species in polar solvents.[21,9]

However, under anaerobic conditions, benzene solutions of $RuCl_2(PMe_3)_4$ become pale yellow over several weeks at room temperature (or more rapidly under reflux) and pale yellow, diamagnetic crystals are formed. These are insoluble in aromatic hydrocarbons but are very soluble in polar solvents such as $MeNO_2$ and MeOH. Analytical, conductivity, and spectroscopic data show the compound to be the salt [$RuCl(PMe_3)_4$]$_2Cl_2$ (K). The $^{31}P\{^1H\}$ n.m.r. is an A_2X_2 (triplet–triplet) pattern indicating two *trans* and two *cis* phosphines on each ruthenium atom. A double chloride-bridged structure (3) which gives each ruthenium(II) atom a roughly octahedral six-co-ordinate environment seems reasonable as suggested for [$RuCl\{P(OEt)(Ph)_2\}_2$]$^{2+}$.[9] The far-i.r. region differs from that of (H) or (J) and a weak broad peak (220—240 cm^{-1}) can be assigned to the bridging chlorides.

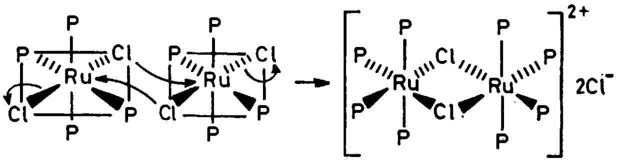


(3)



(4)

This dinuclear cationic compound could be formed as in the reaction:



The process involves only a movement of 90° for one phosphine on each metal; alternatively, the initial dissociation of Cl^- or PMe_3 could be involved in the mechanism.

cis-*Chlorohydridotetrakis(trimethylphosphine)ruthenium*(II) (L). Although the interaction of [$Rh(PMe_3)_4$]Cl with an excess of sodium amalgam in thf yields the mixed cluster $Hg_6Rh_4(PMe_3)_{12}$,[6b] the similar reaction with $RuCl_2(PMe_3)_4$ merely yields *cis*-$RuHCl(PMe_3)_4$ (L) in low yield. We have also isolated (L) in low yield from the reaction of $Ru_2(O_2CMe)_4Cl$ with 2.5 equiv. of Et_2Mg in the presence of excess of PMe_3. The compound is colourless, crystalline, and moderately air-sensitive and it is very difficult to separate cleanly from oily materials in both reactions. Analytically pure samples are difficult to obtain. The ^{1}H and ^{31}P{^{1}H} n.m.r. spectra clearly indicate *cis*-H and -Cl atoms (4).

EXPERIMENTAL

Microanalyses were by Butterworth, Pascher, and Imperial College laboratories.

Instruments.—N.m.r.: Perkin-Elmer R32 and R12B (^{1}H); Varian XL-100 (^{1}H, ^{31}P, Fourier-transform). I.r.: Perkin-Elmer P.E. 597, 457. Conductivity data were obtained on a Mullard Conductivity Bridge type E7566/3 with a matching conductivity cell.

All operations were performed under oxygen-free nitrogen or *in vacuo*. Tetrahydrofuran, toluene, and petroleum (b.p. 40—60 °C) were dried over sodium–benzophenone and distilled under nitrogen before use. Melting points were determined in sealed capillaries under nitrogen.

(1) *Tetrakis(trimethylphosphine)rhodium*(I) *Chloride* (A).—Trimethylphosphine (0.5 cm^3, 5 mmol) was added to a suspension of chlorotris(triphenylphosphine)rhodium(I) (0.3 g, 0.32 mmol) in petroleum (50 cm^3) and the mixture stirred rapidly (4 h) at room temperature. The lemon solid was collected, washed with petroleum (4 × 30 cm^3), and dried *in vacuo* (2 h). It was dissolved in boiling toluene (5 min) (50 cm^3) and the solution allowed to cool slowly to room temperature yielding orange *prisms*, which were washed with petroleum (2 × 10 cm^3) and dried *in vacuo*, yield 0.1 g (71%), m.p. 162—172 °C. The melting point is quite different from [Rh(PMe$_3$)$_4$]Cl previously reported[6a] (90 °C). Melting points of various samples as prepared above were always consistent; (A) is hygroscopic and dissolves in absorbed water at *ca.* 90 °C when the m.p. is taken in air. We cannot reconcile the low conductivity reported[6a] (62 Ω^{-1} cm^2 mol^{-1}). I.r. (Voltalef 3.S., B.D.H.) 2 980w, br, 2 900w, 1 435m, 1 425m; (Nujol) 1 300w, 1 290s, 1 285s, 1 270m, 950s, 870m, 850m, 730s, 720s, and 670s cm^{-1}. The compound is sensitive to oxygen both in solution and in the solid state and the i.r. spectra of exposed samples show the presence of OPMe$_3$($\nu_{P=O}$ at 1 152 cm^{-1}).

(2) *Chlorotris(trimethylphosphine)rhodium*(I) (B).—[Rh(PMe$_3$)$_4$]Cl (0.5 g, 1.1 mmol) was heated in refluxing toluene (25 cm^3) (48 h) under a slow stream of nitrogen. The solution was cooled and filtered, and on standing at −20 °C yielded orange *prisms*, which were collected, washed with petroleum (2 × 10 cm^3), and dried *in vacuo*, yield 0.4 g (99%); i.r. (Nujol) as for (A).

(3) *Tris(trimethylphosphine)rhodium*(I) *Hexafluorophosphate* (C).—Potassium hexafluorophosphate (0.1 g, 0.54 mmol) in water (20 cm^3) was slowly added to an aqueous solution of [Rh(PMe$_3$)$_4$]Cl (0.24 g, 0.54 mmol, in 20 cm^3). The solution was stirred (0.5 h) and the pale yellow powder collected, washed with water (2 × 30 cm^3) until traces of chloride were absent from the washings, and dried *in vacuo*, yield 0.22 g (85%), m.p. 90–150 °C (decomp.). I.r. (Voltalef) 2 980w, 2 910w, 1 420m; (Nujol) 1 455s, 1 422s, 1 365s, 1 304m, 1 286s, 940s,br, 872m,sh, 835s,b,r 730m, 715s, 662s, 550s, 350m, and 315w cm^{-1}. The compound is insoluble in H$_2$O, hydrocarbons, Et$_2$O, and tetrahydrofuran, but is soluble in MeNO$_2$.

(4) *Tris(trimethylphosphine)rhodium*(I) *Tetraphenylborate* (D).—Sodium tetraphenylborate (0.14 g, 0.4 mmol) in water (20 cm^3) was added to an aqueous solution of [Rh(PMe$_3$)$_4$]Cl (0.15 g, 0.34 mmol in 20 cm^3) and the pale yellow powder isolated as for (C), yield 0.2 g (91%), m.p. 120—180 °C (decomp.). I.r. (Voltalef) 3 050m, 2 995m, 2 910m 1 580m, 1 477s, 1 425s; (Nujol) 1 305m, 1 285m, 1 145w, 1 030w, 935s, 845m, 740s, 730s, 700s, 660m, 625w, 615w, 600m, 480w, 460w, and 355m cm^{-1}.

The compound is insoluble in H$_2$O, hydrocarbons, Et$_2$O, and thf, but is soluble in MeNO$_2$ and MeCN (moderately).

(5) cis-*Dihydridotetrakis(trimethylphosphine)rhodium*(III) *Chloride* (E).—Hydrogen gas was slowly bubbled through a solution of [Rh(PMe$_3$)$_4$]Cl (0.4 g, 0.9 mmol) in toluene (50 cm^3) with stirring (0.5 h). The white microcrystalline precipitate was filtered off, washed with petroleum (2 × 20 cm^3), and dried *in vacuo*, yield 0.34 g (85%), m.p. 163 °C (turns yellow at *ca.* 123 °C); i.r. (Voltalef) 2 980w, 2 910w, 1 930s; (Nujol) 1 930s, 1 425s, 950s, 870s, 805w, 765w, 730s, 675s, 570w, and 355w cm^{-1}. The compound is soluble in H$_2$O and MeNO$_2$ and insoluble in hydrocarbons and ethers.

(6) *Carbonylchlorobis(trimethylphosphine)rhodium*(I) (F).—A stream of CO was passed through a solution of RhCl(PMe$_3$)$_3$ {or [Rh(PMe$_3$)$_4$Cl} (0.3 g, 0.8 mmol) in toluene (50 cm^3) with stirring (0.5 h). The solution, which became pale yellow, was filtered, its volume reduced (*ca.* 3 cm^3), and it was cooled (−20 °C) to yield lemon yellow *prisms* which were collected, washed with cold petroleum (2 × 3 cm^3) at 5 °C, and dried *in vacuo*, yield 1.69 g (65%), m.p. 181 °C. I.r. (Voltalef) 2 970w, 2 910w, 1 960s,br; (Nujol) 1 960s,br, 1 420m, 1 425m, 1 305m, 1 275s, 950s, 855s, 735s, 670s, 575s, 555s, 500w, 470w, 340s, 300w, 275m, and 245m cm^{-1}. The solid compound is stable in air for several days. It is soluble in toluene and nitromethane, insoluble in water and petroleum.

(7) *Chlorotris(trimethylphosphine)rhodium*(I) *Dichloromethane* (G).—Dichloromethane (20 cm^3) was added to solid [Rh(PMe$_3$)$_3$]Cl (0.2 g, 0.45 mmol) and the solution stirred (0.5 h). The pale yellow microcrystalline precipitate was collected, washed with petroleum (5 cm^3), and dried *in vacuo*, yield 0.3 g (70%), m.p. 145—170 °C (decomp.); i.r. (Nujol) 1 305m, 1 287m, 1 277m, 1 018m, 840s,br, 850m, 730s, 675m, 530w, 389w, and 377w cm^{-1}. The compound is soluble in nitromethane and water.

Reaction of [Rh(PMe$_3$)$_4$]Cl *with Chlorocarbons.*—Dichloromethane, chloroform, or carbon tetrachloride (20 cm^3) was added to a fresh solution of [Rh(PMe$_3$)$_4$]Cl (0.2 g) in thf (10 cm^3). The solution was stirred (0.5 h) and filtered from a white precipitate. The pale yellow solution was evaporated (to *ca.* 5 cm^3) and cooled (−20 °C) yielding pale yellow crystals (75%) which were identified as RhCl$_3$(PMe$_3$)$_3$[17] from analytical and ^{1}H and ^{31}P{^{1}H} n.m.r. data.

(8) *Bis[μ-chloro-bis(trimethylphosphine)ruthenium*(I)](Ru–Ru) (H).—The products from the reaction of Ru$_2$(O$_2$CMe)$_4$Cl with (2-MeOC$_6$H$_4$)$_2$Mg in thf and PMe$_3$[18] were chromatographed on Fluorosil, and the toluene fraction evaporated to low volume and cooled (−20 °C) to yield orange *prisms*. These were collected, washed with petroleum, and dried *in vacuo*, yield *ca.* 20%. Crystals of the compound (sealed under N$_2$) became a pale yellow powder when heated to 220 °C, but do not melt below 300 °C; i.r. (Nujol) 1 440m, 1 420m, 1 365w, 1 297s, 1 281s, 1 270m, 935s,br, 855m, 721m, 702s, 660s, 365w, 317m, and 290w cm^{-1}. The compound is insoluble in acetone, H$_2$O, MeOH, and MeNO$_2$, but is soluble in CH$_2$Cl$_2$ toluene and thf and is air-stable for several days.

(9) *Chlorotetrakis(trimethylphosphine)ruthenium*(II) *Tetrafluoroborate* (I).—The products from Ru$_2$(O$_2$CMe)$_4$Cl, (2-MeOC$_6$H$_4$)$_2$Mg, and PMe$_3$ (in thf) were treated with an excess of Ph$_3$C$^+$BF$_4$$^-$, in thf, and the mixture stirred over-

TABLE 6

Crystal data and details of data collection and structure analyses

	Compound (A) $[Rh(PMe_3)_4]Cl$	Compound (B) $RhCl(PMe_3)_3$
Formula weight	442.67	366.59
Crystal system	Orthorhombic	Triclinic
a/Å	12.366(2)	8.842(1)
b/Å	13.584(2)	8.982(1)
c/Å	12.554(2)	11.825(1)
α/°	90	98.74(1)
β/°	90	92.38(1)
γ/°	90	116.09(1)
U/Å^3	2 108.8	827.4
Space group	*Ccmm* (No. 63)	$P\bar{1}$ (No. 2)
Z	4	2
D_c/g cm^{-3}	1.39	1.47
F(000)	920	376
Linear absorption coefficient/ cm^{-1}	11.2	13.3
Crystal size/mm	0.40 × 0.30 × 0.20	0.20 × 0.18 × 0.16
Data collection		
X-radiation	Mo-K_α (λ = 0.71069 Å)	
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 28	1.5, 25
ω-scan width parameters A, B (°) in width = A + B tanθ	0.75, 0.25	
Horizontal aperture parameters A, B (mm) in APT = A + B tanθ	4.0, 0.0	
Total data	1 767	2 947
Total unique data	1 657	2 891
Observed data [$F_o > 3\sigma(F_o)$]	1 476	2 695
Merging R	0.007	0.005
Refinement		
No. of parameters	80	235
Weighting scheme coefficient g in $\omega = 1/[\sigma^2(F_o) + g F_o^2]$	0.0004	0.003
Final $R = \Sigma\Delta F/\Sigma F_o$	0.0304	0.0234
$R' = [\Sigma\omega\Delta F^2/\Sigma\omega F_o^2]^{\frac{1}{2}}$	0.0380	0.0290

night at room temperature. The pale yellow solid was collected, washed with thf, and dried *in vacuo*. It was recrystallised from methanol at −20 °C (the salt $[Ph_3CPMe_3]BF_4$ [23] is also obtained as white needles, but the two compounds can be separated by fractional crystallisation), yield *ca*. 20%, m.p. 280—320 °C (decomp.); i.r. (Nujol) 1 438m, 1 428m, 1 419m, 1 305s, 1 285s, 1 095s, 1 055s, 1 055s,br, 960s,sh, 950s,br, 856m, 845m, 722s, 670s, 522w, 375m cm^{-1}.

TABLE 7

Fractional co-ordinates (Rh × 10^5; other × 10^4) for (A)

Atom	x	y	z
Rh	20 888(2)	0 [a]	0.25 [a]
Cl	741(2)	0.5 [a]	0.25 [a]
P(1)	1 631(1)	1 637(1)	0.25 [a]
P(2)	2 597(1)	0 [a]	738(1)
C(11)	740(3)	1 968(2)	3 603(3)
C(12)	2 588(4)	2 674(3)	0.25 [a]
C(21)	3 494(3)	1 017(3)	420(3)
C(22)	1 698(5)	0 [a]	−419(4)
H(11a) [b]	1 120(30)	2 002(30)	4 278(32)
H(11b)	64(33)	1 461(31)	3 681(31)
H(11c)	436(26)	2 629(26)	3 548(29)
H(12a)	2 220(43)	3 169(52)	0.25 [a]
H(12b)	2 982(26)	2 776(34)	3 329(28)
H(21a)	3 127(29)	1 710(32)	477(35)
H(21b)	4 066(33)	1 028(28)	962(35)
H(21c)	3 796(30)	903(26)	−228(40)
H(22a)	2 083(44)	0 [a]	−1 039(51)
H(22b)	1 211(28)	−471(27)	341(35)

[a] Parameters held invariant due to space group requirements.
[b] The hydrogen atoms are numbered according to their parent carbon atoms, and distinguished by the suffixes a, b, or c

(10) trans-*Dichlorotetrakis*(*trimethylphosphine*)*ruthenium*(II) (J).—This compound was previously prepared in these laboratories by the interaction of $RuCl_2(PPh_3)_3$ with an excess of PMe_3 in petroleum.[21] To a suspension of $Ru_2(O_2CMe)_4Cl$ (0.30 g, 0.63 mmol), anhydrous LiCl (0.15 g, 3.5 mmol), and 1% sodium amalgam (7.3 g, 3.2 mmol Na) in thf (50 cm^3), trimethylphosphine (0.75 cm^3) was added and the mixture stirred at room temperature (12 h). The orange solution was filtered, evaporated to dryness *in vacuo*, and the residue washed with petroleum (40 cm^3), dried, and extracted into toluene (30 cm^3). The solution was filtered, evaporated (*ca*. 10 cm^3), and cooled (−20 °C), yielding orange *prisms*. They were washed with petroleum (5 cm^3) and dried *in vacuo*, yield 0.4 g (66%). The crystals turn pale yellow at 175—180 °C; i.r. (Nujol) as for (H).

TABLE 8

Fractional co-ordinates (Rh × 10^5; others × 10^4) for (B)

Atom	x	y	z
Rh	3 843(2)	432(2)	24 683(1)
Cl	−1 979(1)	663(1)	2 192(1)
P(1)	−1 235(1)	−2 562(1)	1 333(1)
P(2)	2 825(1)	−43(1)	2 347(1)
P(3)	1 442(1)	2 353(1)	3 941(1)
C(11)	−922(6)	−4 350(4)	1 635(4)
C(12)	−1 302(5)	−2 843(5)	−229(3)
C(13)	−3 501(4)	−3 379(5)	1 482(4)
C(21)	3 102(5)	−1 195(7)	1 024(4)
C(22)	3 694(4)	−817(5)	3 408(3)
C(23)	4 611(4)	2 004(5)	2 312(5)
C(31)	3 141(6)	2 746(5)	5 063(4)
C(32)	2 179(5)	4 402(4)	3 509(3)
C(33)	−130(7)	2 382(6)	4 880(4)
H(11a) *	−963(86)	−4 386(87)	2 459(59)
H(11b)	309(55)	−4 123(49)	1 471(32)
H(11c)	−1 688(61)	−5 357(61)	1 153(41)
H(12a)	−2 227(56)	−3 847(55)	−626(37)
H(12b)	−1 783(50)	−2 049(50)	−396(33)
H(12c)	−162(54)	−2 604(51)	−459(34)
H(13a)	−4 003(57)	−4 586(57)	1 105(38)
H(13b)	−3 565(51)	−3 364(51)	2 292(38)
H(13c)	−4 114(70)	−2 851(72)	889(49)
H(21a)	2 691(53)	−891(49)	391(37)
H(21b)	2 604(66)	−2 361(67)	1 029(43)
H(21c)	4 268(46)	−1 018(42)	1 021(29)
H(22a)	3 716(51)	−203(51)	4 160(39)
H(22b)	4 802(46)	−703(41)	3 300(27)
H(22c)	2 919(48)	−1 892(48)	3 487(31)
H(23a)	4 696(52)	2 828(53)	2 855(35)
H(23b)	4 379(64)	2 470(67)	1 671(44)
H(23c)	5 692(47)	1 908(41)	2 309(28)
H(31a)	3 379(43)	3 773(46)	5 631(31)
H(31b)	4 249(49)	2 972(46)	4 710(32)
H(31c)	2 826(63)	1 848(64)	5 366(42)
H(32a)	2 424(47)	5 302(49)	4 153(33)
H(32b)	3 166(47)	4 702(45)	3 110(31)
H(32c)	1 231(44)	4 374(40)	2 968(28)
H(33a)	234(80)	3 488(77)	5 286(54)
H(33b)	−445(67)	1 485(69)	5 177(44)
H(33c)	−1 053(60)	2 314(57)	4 444(39)

* See footnote *b* in Table 7.

(11) *Bis*[μ-*chloro-tetrakis*(*trimethylphosphine*)*ruthenium*(II)] *Dichloride* (K).—A solution of *trans*-$RuCl_2(PMe_3)_4$ (0.2 g, 0.42 mmol) in benzene (25 cm^3) yielded pale yellow crystals after two weeks at room temperature. A pale yellow powder is produced after several hours refluxing. The compound was collected, washed with petroleum (2 × 25 cm^3), and dried *in vacuo*, yield 0.16 g (80%). It decomposes slowly over the range 300—360 °C, giving a grey powder; i.r.

(Nujol) 1 440s, 1 410m, 1 405s, 1 303s, 1 280s, 975sh, 945s,br, 857s, 720s, 710s, 680m, 660m, 380m, 365m, and 220—240w,br cm^{-1}.

(12) cis-*Chlorohydridotetrakis*(*trimethylphosphine*)-*ruthenium*(II) (L).—(*a*) A solution of *trans*-RuCl$_2$(PMe$_3$)$_4$ (0.45 g, 0.95 mmol) in thf (50 cm^3) was stirred with an excess of 1% sodium amalgam (8.0 g, 3.5 mmol Na) at room temperature (1 week). The solution was filtered, evaporated to dryness, and extracted into petroleum (40 cm^3). This solution was filtered, evaporated to *ca.* 5 cm^3, and cooled (−20 °C). The crystals were collected, recrystallised twice more from petroleum, and dried *in vacuo*, yield 0.1 g (24%).

(*b*) A solution of diethylmagnesium (5.5 cm^3 of a 0.55 mol dm^{-3} diethyl ether solution, 3 mmol) was added to a suspension of Ru$_2$(O$_2$CMe)$_4$Cl (0.57 g, 1.2 mmol) in thf (35 cm^3) and PMe$_3$ (1 cm^3). The mixture was stirred at room temperature (24 h) and evaporated to dryness *in vacuo*. The orange residue was extracted into petroleum (60 cm^3) and the solution filtered, evaporated to *ca.* 20 cm^3, and re-filtered. Evaporation to *ca.* 10 cm^3 and cooling (−20 °C) yielded white *prisms*, which were collected and recrystallised from petroleum at −20 °C, yield 0.2 g (19%), m.p. 165—170 °C; i.r. (Nujol) 1 808s, 1 450s, 1 430s, 1 410s, 1 360s, 1 294s, 1 274s, 935s,br, 852, 775w, 720s, 705s, and 660 cm^{-1}.

Crystallographic Studies.—Crystals of both compounds were sealed *in vacuo* in Lindemann capillaries. Approximate cell dimensions and crystal systems were determined from oscillation and Weissenberg photographs. Accurate cell parameters, and orientation matrices used for data collection, were determined by least-squares refinement of the setting angles for 25 reflections automatically centred on a Nonius CAD4 diffractometer. Intensity data were recorded in a manner described previously [24] and corrected for Lorentz and polarisation effects but not for absorption, in view of the low values of, and variation in, μR. Both the crystals remained stable during data collection as indicated by no significant variations in the standard intensities. For (A), the systematic absences (hkl absent for $h + k$ = odd and $0kl$ absent for l odd) indicated the space group $Ccmm$ (No. 63) or $Ccm2_1$ (No. 36); the former, with $Z = 4$, was found to be the correct space group by successful refinement. (B) was successfully refined in the centrosymmetric space group $P\bar{1}$ ($Z = 2$).

Both the structures were solved by the Patterson and Fourier methods and refined by full-matrix least-squares,[25] using those data with $F_o > 3\sigma(F_o)$. All the hydrogen atoms were determined from difference maps and refined with individual values of U_{iso} for (B); a common U_{iso} for all the hydrogens in (A) refined to 0.089(4) Å^2. With anisotropic thermal parameters for all non-hydrogen atoms, the refinements finally converged at $R = 0.030\,4$ (A) and 0.023 4 (B). Details of the refinement, data collection, and crystal data are presented in Table 6. Final atomic fractional coordinates are given in Tables 7 and 8. Tables of thermal parameters and lists of observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22676 (26 pp.).* Atomic scattering factors for neutral Rh, Cl, P, and C atoms were taken from reference 26, and for H, from reference 27. All computations were done on the Queen Mary College, ICL 1904S and University of London CDC 7600 computers.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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