Further Chemistry of Trimethylphosphine Complexes of Rhodium(I): *X*-Ray Crystal Structures of Dodeca(trimethylphosphine)tetrarhodium-hexamercury,† $Hg_6Rh_4(PMe_3)_{12}$, and *trans*-Chlorobis(trimethylphosphine)(triphenylphosphine)rhodium(I) ‡

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The interaction of sodium amalgam in tetrahydrofuran with $[Rh(PMe_3)_4]Cl$ or $RhCl(PMe_3)_3$ yields $Hg_6Rh_4(PMe_3)_{12}$ (1) in high yields. Similar reduction of $[RhH_2(PMe_3)_4]Cl$ yields $RhH(PMe_3)_4$ (2) and $RhCl(CO)(PMe_3)_2$ gives $[RhH(CO)(PMe_3)_3]_2$, (3). The syntheses of the following complexes are also reported: $RhCl(PMe_2Ph)(PMe_3)_2$, (4), $Rh(\eta\text{-}C_5H_5)(PMe_3)_2$, (5), $RhMe(PMe_3)_3$, (6), $Rh(C_6H_4Me\text{-}3)(PMe_3)_3$, (7), $RhClIMe(PMe_3)_3$, (8), $RhClI(C_6H_5)(PMe_3)_3$, (9), $[Rh(O_2)(PMe_3)_4]PF_6$, (10), and *trans*-$RhCl(PPh_3)(PMe_3)_2$, (11). The compounds have been studied by ^1H and ^{31}P n.m.r. and i.r. spectroscopy and the structures of (1) and (11) have been determined by *X*-ray crystallography. Complex (1) is orthorhombic, space group *Ccmm* or *Ccm*2 ,with a = 12.909(2), b = 25.274 (4), c = 25.176(4) Å, and Z = 4. Complex (11) is monoclinic, space group $P2_1/n$, with a = 17.006(3), b = 11.821(2), c = 12.884(2) Å, β = 96.46(2)°, and Z = 4. The structures were determined using 2 448 and 3 708 observed intensities measured on an automatic diffractometer and refined to R values of 0.083 and 0.038 respectively. For compound (1) only the Hg, Rh, and P atom positions could be determined with any certainty. The $Hg_6Rh_4P_{12}$ cluster has the form of an Hg_6 octahedron with four tetrahedrally related faces capped by $Rh(PMe_3)_3$ units; Hg–Hg and Hg–Rh distances lie in the ranges 3.131(3)—3.149(3) Å and 2.690(4)—2.724(4) Å respectively. Compound (11) has the PPh_3 groups *trans* to the chloride. Bond distances and angles are similar to those in the tris PPh_3 and PMe_3 analogues.

WE have reported the syntheses, chemistry, and crystal structures of tetrakis(trimethylphosphine)rhodium(I) chloride and chlorotris(trimethylphosphine)rhodium(I).[1] Here we describe reduction and oxidative-addition reactions of these complexes.

RESULTS AND DISCUSSION

The interaction with sodium amalgam in tetrahydrofuran (thf) gives the unique rhodium–mercury cluster $Hg_6Rh_4(PMe_3)_{12}$,(1), while similar reaction of $[RhH_2(PMe_3)_4]Cl$ yields $RhH(PMe_3)_4$, (2), and $RhCl(CO)(PMe_3)_2$ gives $[RhH(CO)(PMe_3)_3]_2$, (3). Using sodium alone, in benzene, $RhCl(PMe_2Ph)(PMe_3)_2$, (4), can be obtained in moderate yield.

We have also obtained $Rh(\eta\text{-}C_5H_5)(PMe_3)_2$, (5), $RhMe(PMe_3)_3$, (6), and $Rh(C_6H_4Me\text{-}3)(PMe_3)_3$, (7), by interaction with $Na(C_5H_5)$, LiMe, and LiMe respectively, in refluxing toluene.

The compounds $RhCl(PMe_3)_3$ and $[Rh(PMe_3)_4]Cl$ oxidatively add RI [R = Me, (8), R = Ph, (9)] giving $Rh^{III}ClIR(PMe_3)_3$; with molecular oxygen $[Rh(O_2)(PMe_3)_4]PF_6$, (10), can be isolated.

Interaction with PPh_3 in toluene or tetrahydrofuran leads to $RhCl(PPh_3)(PMe_3)_2$, (11), which has *trans* PMe_3 groups.

Analytical and n.m.r. (^1H and ^{31}P-{^1H}) spectroscopic data are given in Tables 1 and 2. The structures of $Hg_6Rh_4(PMe_3)_{12}$ and *trans*-$RhCl(PPh_3)(PMe_3)_2$ have been determined by *X*-ray diffraction.

TABLE 1

Analytical data

	Compound	Colour	Found (%)					Required (%)				
			C	H	P	Cl	M [a]	C	H	P	Cl	M [a]
(1)	$Hg_6Rh_4(PMe_3)_{12}$	Dark red	17.2	4.3	14.8		2 508	17.1	4.3	14.7		2 527
(2)	$RhH(PMe_3)_4$	Off-white	35.0	9.2	29.5	<0.2	400	35.3	9.1	30.4	0.0	406
(3)	$[RhH(CO)(PMe_3)_3]_2$	Yellow	33.3	7.7	26.5	<0.2	620	33.1	7.5	25.9	0.0	720
(4)	$RhCl(PMe_2Ph)(PMe_3)_2$	Orange	40.0	6.9	21.9	8.0	400 [b]	39.3	6.8	21.8	8.3	427
(5)	$Rh(\eta\text{-}C_5H_5)(PMe_3)_2$	Red-brown	40.6	7.4	19.6		315	41.3	7.2	19.4		320
(6)	$RhMe(PMe_3)_3$	Orange	34.3	8.7	27.7		360	34.5	8.7	26.9		346
(7)	$Rh(C_6H_4Me\text{-}3)(PMe_3)_3$	Orange	45.1	8.0	23.5	<0.2	390	45.5	8.1	22.0	0.0	422
(8)	$RhClIMe(PMe_3)_3$	Yellow										
		Orange	24.4	6.0	18.2	7.7 [c]	515	23.6	5.9	18.3	7.0	508
(9)	$RhClIPh(PMe_3)_3$	Orange	32.2	6.0	17.4	7.0 [d]	557	31.6	5.6	16.3	6.2	570
(10)	$[Rh(O_2)(PMe_3)_4]PF_6$	White	25.4	6.7	27.9	*e*		24.7	6.2	26.5		
(11)	*trans*-$RhCl(PPh_3)(PMe_3)_2$	Yellow	52.3	6.3	16.8	5.5	489	52.1	6.0	16.8	6.4	552

[a] Cryoscopically in benzene. [b] In CH_2Cl_2. [c] I 24.3 (25.0%). [d] I 20.0 (22.2%). [e] F 18.7 (19.5%).

Reduction with Sodium Amalgam and Sodium.—(i) $RhCl(PMe_3)_3$ *or* $[Rh(PMe_3)_4]Cl$. The interaction of either complex with sodium amalgam in thf gives the rhodium–mercury cluster $Hg_6Rh_4(PMe_3)_{12}$, (1), in high

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† 1,2,3;1,4,5;2,5,6;3,4,6-Tetrakis-μ_3-tris(trimethylphosphine)-rhodio-*octahedro*-hexamercury.

‡ No reprints available.

TABLE 2

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

	Compound	^{1}H/δ values [a]	Assignment	^{31}P-{^{1}H} [b]	^1J(Rh–P) (Hz)
(1)	$Hg_6Rh_4(PMe_3)_{12}$	1.68(s)	$\mathrm{P}Me_3$	51.62 (d,q) [c]	156.4 (d)
(2)	$RhH(PMe_3)_4$	1.17 (s, 36)	$\mathrm{P}Me_3$	−19.82 (d)	146.4
		−12.6(qn, 1) [^2J(P–H) = 15.8 Hz]	Rh–H		
(3)	$[RhH(CO)(PMe_3)_3]_2$	1.37 (s)	$\mathrm{P}Me_3$	−26.98 (d)	153.0
(4)	$RhCl(PMe_2Ph)(PMe_3)_2$	7.2—7.9 (br m, 5)	C_6H_5	−12.6 (m) [d]	
		1.30 (br m, 24)	$\mathrm{P}Me_3$		
(5)	Rh(η-C_5H_5)$(PMe_3)_2$	5.55 (s, 4) [e]	η-C_5H_5	−1.68 (d) [d]	218.0
		1.45 (m, 18)	$\mathrm{P}Me_3$		
(6)	$RhMe(PMe_3)_3$	0.1 (d, 3) (J = 2 Hz)	Rh–CH_3 [f]	6.80 (d)	190
		1.28 (s, 27)	$\mathrm{P}Me_3$	−20.2 (br m)	
(7)	Rh(C_6H_4Me-3)$(PMe_3)_3$	7.05—7.6 (m, 4)	–C_6H_4	−1.63(d) [d]	143.5
		2.2 (s, 3)	3-Me-C_6H_4		
		0.9 (d, 27)	$\mathrm{P}Me_3$		
(8)	$RhClIMe(PMe_3)_3$	2.0 (m, 27) [g]	$\mathrm{P}Me_3$	−16.3 (d,d) [g]	96.2
				[^2J(P–P) = 32 Hz]	
		1.5 (br q, 3) [^3J(P–H) = 4 Hz]	Me	2.70 (d,t)	133.5
(9)	$RhClI(C_6H_5)(PMe_3)_3$	6.95—7.60 (br m, 5) [g]	C_6H_5	−7.46 (d,d) [g]	96.9
		1.7 (m, 27)	$\mathrm{P}Me_3$	[^2J(P–P) = 32 Hz]	
				4.92 (d,t)	135.2
(10)	$[Rh(O_2)(PMe_3)_4]PF_6$	1.8 (m at 0 °C) [g]	$\mathrm{P}Me_3$	−5.68 (d,t) [g]	122
				[^2J(P–P) = 28 Hz]	
				2.04 (d,t)	88.9
			PF_6	40.3 (s)	
(11)	*trans*-$RhCl(PPh_3)(PMe_3)_2$	7.3—8.2 (br m, 15) [e]	$\mathrm{P}Ph_3$	−12.9 (d,d) [e]	87.1
		1.5 (s, 18)	$\mathrm{P}Me$	[^1J(Rh–P) = 41 Hz]	
				54.1 (d,t)	200

[a] In C_6D_6 solvent referenced to $SiMe_4$ (δ 0.0) at 90 MHz and 35 °C. [b] In C_6H_6–C_6D_6 (10%) and referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz and 28 °C. Peaks to high frequency (low field) of reference are positive. [c] Second-order pattern, see text, (q) J *ca.* 75 Hz. [d] See text. [e] In [$^2H_8$]C_6H_5Me. [f] ^{13}C-{^{1}H}; δ 23.8 (s) ($\mathrm{P}Me_3$), δ 8.3 (d)(J = 17.6 Hz), Rh–$C\mathrm{H}_3$ in C_6D_6 (δ 128.7) referenced to $SiMe_4$ (δ 0.0) at 25.2 MHz and 28 °C. [g] In CD_3NO_2.

yield (95%). This dark red, thermally stable, but air-sensitive complex can be readily recrystallised from light petroleum or thf. Cryoscopic molecular-weight studies (in benzene) show that the cluster remains intact in solution. The ^{1}H n.m.r. shows a slightly broadened singlet (δ 1.68, $\mathrm{P}Me_3$) while the ^{31}P-{^{1}H} has a very broad quartet (δ 51.62, J *ca.* 75 Hz) on which there is superimposed a sharp doublet (J = 156.4 Hz). The spectra are temperature and solvent independent.

Although X-ray study has not led to a complete structural characterisation of this compound, the nature and geometry of the [$Hg_6Rh_4P_{12}$] nucleus is well defined, and is shown in Figure 1. The six mercury atoms form a quite regular octahedron with Hg–Hg edge distances of 3.131(3)—3.149(3) Å (Table 3). The rhodium atoms cap four tetrahedrally related faces of this octahedron, giving the cluster essentially T_d symmetry, and the Hg–Rh distances are approximately equal at 2.690(4)—2.724(4) Å. The three phosphorus atoms attached to each rhodium are staggered with respect to the Rh–Hg_3 unit, giving the Rh atoms octahedral geometry. The Rh–P distances of 2.262—2.289(16) Å are slightly smaller than the Rh–PMe_3 distances in compound (11) (see below).

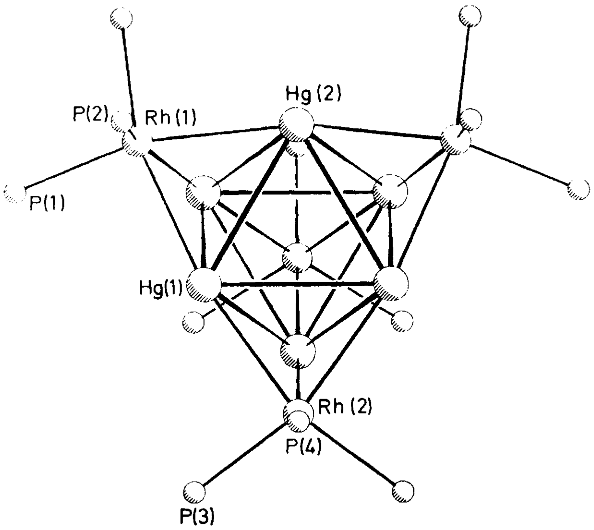


FIGURE 1 Geometry of the $Hg_6Rh_4P_{12}$ nucleus

TABLE 3

Interatomic distances (Å) in $Hg_6Rh_4(PMe_3)_{12}$, (1)

Hg(1)–Hg(2)	3.149(3)	Hg(1)–Hg(1)′	3.146(3)
Hg(1)–Hg(3)	3.144(3)	Hg(1)–Hg(1)″	3.131(3)

Symmetry operations Hg(1)′ = Hg(1) × ($x,y,\frac{1}{2} - z$)
Hg(1)″ = Hg(1) × ($x, -y, z$)

Rh(1)–Hg(1)′	2.712(4)	Rh(2)–Hg(1)	2.724(4)
Rh(1)–Hg(2)	2.697(4)	Rh(2)–Hg(3)	2.690(4)

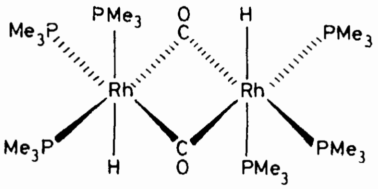
Symmetry operation Hg(1)′ = Hg(1) × ($x, -y, \frac{1}{2} - z$)

Rh(1)–P(1)	2.289(16)	Rh(2)–P(3)	2.262(14)
Rh(1)–P(2)	2.284(15)	Rh(2)–P(4)	2.278(23)

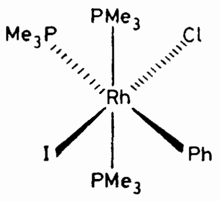
Although on the basis of preliminary X-ray data, we previously formulated the compound as $Hg_6Ph_4C(PMe_3)_{12}$ having an interstitial carbon atom, this has not been substantiated at the present stage of refinement. The ' peak ' which appeared to refine successfully ($U_{\mathrm{iso.}}$ = 0.12) in the earlier stages [1] (R = 0.13) subsequently became unstable and was probably a diffraction ripple. We have found no evidence for the carbon from ^{13}C n.m.r. studies.

(ii) $[RhH_2(PMe_3)_4]Cl$. Reduction with sodium amalgam in thf yields a dark red petroleum-soluble oil from which $RhH(PMe_3)_4$, (2), can be sublimed (90 °C, 10^{-2} mmHg) * in high yield. The triphenylphosphine and other analogues are known.[2] The compound $RhH(PMe_3)_4$ can be recrystallised from toluene as pale yellow needles and is quite air-sensitive. The n.m.r. spectra suggest a non-rigid five-co-ordinate molecule in solution and are unchanged at low temperature (−70 °C). Thus, the ^1H n.m.r. shows Rh–H at δ −12.6 [quintet $^2J(P-H) = 15.8$ Hz] and the $^{31}P-\{^1H\}$ is a doublet [$^1J(Rh-P) = 146.4$ Hz].

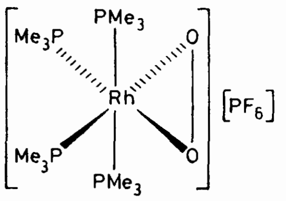
(iii) trans-$RhCl(CO)(PMe_3)_2$. Reduction with sodium amalgam in thf yields a dark red-brown homogeneous solution from which the yellow crystalline $[RhH(CO)(PMe_3)_3]_2$, (3), can be obtained in moderate yield. The complex is diamagnetic and although it gives $CHCl_3$ on treatment with CCl_4 (confirming the presence of Rh–H), no high-field signals in the ^1H n.m.r. have been detected. The i.r. shows a single sharp ν(Rh–H) at 1 958 cm^{-1} and several broad strong bands at *ca.* 1 650 to 1 700 cm^{-1} are assigned to bridging CO groups. Molecular-weight studies are consistent with the dimeric formulation (I) in which two CO groups bridge two 18-electron Rh^I atoms. There is no need to invoke a metal–metal bond. The $^{31}P-\{^1H\}$ n.m.r. spectrum shows a doublet [$^1J(Rh-P) = 153$ Hz] indicating that the PMe_3 groups are non-rigid.



(I)



(II)



(III)

(iv) *Interaction of* $RhCl(PMe_3)_3$ *or* $[Rh(PMe_3)_4]Cl$ *with sodium.* Stirring $RhCl(PMe_3)_3$ or $[Rh(PMe_3)_4]Cl$ in benzene in the presence of an excess of clean sodium yields an orange crystalline material in less than 50% yield. This complex retains chlorine and on the basis of analytical and spectroscopic data is formulated as $RhCl(PMe_2Ph)(PMe_3)_2$, (4). Thus, the ^1H n.m.r. spectrum shows a broad aryl resonance at δ 7.2—7.9. The i.r. shows weak bands at 3 050 and 1 570 cm^{-1} and two additional strong bands at 750 and 705 cm^{-1} indicative of a monosubstituted benzene ring. The $^{31}P-\{^1H\}$ spectra are temperature independent and show three rather broad multiplets close together, suggesting a mixture of isomers. There is no reaction on refluxing $RhCl(PMe_3)_3$ in benzene or with u.v. irradiation. The low yield of (4) suggests a complex mechanism for its formation, probably involving a PMe_2 phosphido-bridged species to which benzene is added oxidatively followed by phenyl transfer to phosphorus leading to co-ordinated PMe_2Ph.

(v) *Cyclopentadienyl, methyl, and aryl complexes.* (a) *Cyclopentadienyl.* Interaction of $[Rh(PMe_3)_4]Cl$ with sodium cyclopentadienide in thf yields red–brown crystalline $Rh(\eta-C_5H_5)(PMe_3)_2$, (5). While this work was in progress, synthesis of (5) from $[Rh(PMe_3)_4]Cl$ and $Tl(C_5H_5)$ was reported.[3]

(b) *Methyl.* Orange, crystalline, air-sensitive $RhMe(PMe_3)_3$, (6), can be isolated cleanly from the reaction of either LiMe or $MgMe_2$ with $[Rh(PMe_3)_4]Cl$ in toluene at 0 °C. Use of thf or diethyl ether at room temperature results in mixtures that are difficult to separate. In the ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra the Rh–CH_3 group gives a doublet (^1H: $J = 2$ Hz and $^{13}C-\{^1H\}$: $J = 17.6$ Hz).

A dark red petroleum-soluble material is formed on heating (6) in toluene although we have not yet isolated a pure compound.

(c) *Aryl.* If a solution of methyl-lithium is added to a refluxing toluene solution of $RhCl(PMe_3)_3$ (in a 1 : 1 molar ratio), the pale yellow volatile aryl $Rh(C_6H_4Me\text{-}3)(PMe_3)_3$, (7), is produced in good yield. Initial metallation of the toluene solvent probably occurs and the $Li(C_6H_4Me\text{-}3)$ formed then reacts with the rhodium complex to give (7), rather than a process which involves oxidative addition of toluene to the methyl complex, since the latter appears not to react with toluene in this way. Infrared data indicate that metallation occurs predominantly in the 1,3-position [δ(C–H) at 760s and 710s cm^{-1}]. The $^{31}P-\{^1H\}$ spectrum is a doublet [$^1J(Rh-P) = 143.5$ Hz] similar to that observed for $Rh(C_6H_5)(PMe_3)_3$.[4]

(vi) *Oxidations.* (a) *Alkyl and aryl halides.* Oxidative addition of RI (R = Me or Ph) to $RhCl(PMe_3)_3$ occurs readily at room temperature in toluene giving the rhodium(III) complexes $RhClI(R)(PMe_3)_3$, [(8), (9)], as yellow crystalline materials. Both complexes show triplet–doublet patterns in their $^{31}P-\{^1H\}$ n.m.r. spectra indicating *mer*-type structures (II) in which two phosphines are mutually *trans* and the other *cis* to both of them.

(b) *Oxygen.* The complex $[Rh(PMe_3)_4]Cl$ reacts with oxygen in aqueous solution and the white crystalline hexafluorophosphate salt $[Rh(O_2)(PMe_3)_4]PF_6$, (10), can be quantitatively precipitated on addition of $K[PF_6]$. Spectroscopic data are in accord with (III); other phosphine analogues are known.[5]

(vii) *Phosphine exchange with* PPh_3. The complex $[Rh(PMe_3)_4]Cl$ reacts slowly with triphenylphosphine in toluene or thf to give *trans*-$RhCl(PPh_3)(PMe_3)_2$, (11), in low yield. Spectroscopic and analytical data of this yellow crystalline complex are consistent with the results

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 atm = 101 325 Pa.

TABLE 4

Bond lengths and angles in *trans*-$RhCl(PPh_3)(PMe_3)_2$, (11)

(*a*) Bond lengths (Å)

Rh–Cl	2.418(2)	Rh–P(2)	2.231(1)
Rh–P(1)	2.314(1)	Rh–P(3)	2.309(1)

(*b*) Bond angles (°)

P(1)–Rh–Cl	82.4(1)	P(3)–Rh–P(2)	100.7(0)
P(1)–Rh–P(2)	93.3(0)	P(1)–Rh–P(3)	165.9(0)
P(3)–Rh–Cl	83.7(1)	P(2)–Rh–Cl	175.7(1)

of the crystal-structure determination by *X*-ray diffraction.

The structure is shown in Figure 2; important bond lengths and angles are given in Table 4. In this molecule the PPh_3 group is *trans* to the chlorine atom. Small distortions from an idealised square geometry are clearly due to steric factors. Thus, inspection of Figure 2 shows that the two PMe_3 groups are pushed towards the Cl atom by the PPh_3 phenyl groups and the 8° difference in P–Rh–P *cis* angles is due to difficulties in accommodating the three-fold stereochemistry of the PPh_3 group and the two-fold stereochemistry of the P–Rh–P unit. The Rh–P and Rh–Cl distances are very similar to those in the compounds $RhCl(PPh_3)_3$ [6] and $RhCl(PMe_3)_3$ [1] but there is further indication that Rh–P bonds to PMe_3 groups are very slightly shorter than bonds to PPh_3 groups.

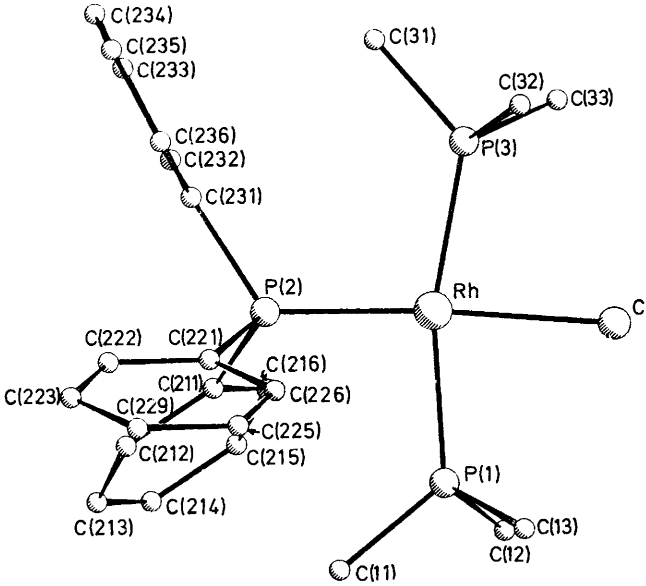

FIGURE 2 Structure of *trans*-$RhCl(PPh_3)(PMe_3)_2$

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Ltd., Pascher (Bonn), and Imperial College Laboratories.

Instruments.—Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R32 (^1H) and a Varian XL-100 (^{31}P, Fourier-transform). A Perkin-Elmer 597 was used for i.r. spectra. 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 argon or *in vacuo*. Tetrahydrofuran, toluene, and light 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 (uncorrected).

Dodeca(trimethylphosphine)tetrarhodiumhexamercury, (1).—A solution of $[Rh(PMe_3)_4]Cl$ [1] (0.3 g, 0.7 mmol) in thf ($100\ cm^3$) was added to sodium amalgam (30 g, 13 mmol Na) and the mixture stirred at room temperature (10 h). The resulting deep red solution was filtered and the solvent removed under vacuum. The residue was dissolved in light petroleum ($50\ cm^3$) and dark red crystals obtained on cooling (−20 °C). These were collected and dried under vacuum. Yield 1.7 g, 95%. The compound does not melt below 300 °C and darkens slightly at 300—360 °C. Infrared (Nujol, cm^{-1}) bands at: 1 290w, 1 285w, 1 270m, 1 260m, 935s, 925m, 840wm, 830w, 800w, 720w, 700w, 690w, and 660m.

Hydridotetrakis(trimethylphosphine)rhodium(I), (2).—The complex $[RhH_2(PMe_3)_4]Cl$ [1] (0.85 g, 2.0 mmol) suspended in thf ($100\ cm^3$) was added to sodium amalgam (70 g, 30 mmol Na) and the mixture stirred at room temperature (10 h). The red solution was filtered, evaporated to dryness, and redissolved in light petroleum ($50\ cm^3$). This solution was evaporated to dryness (4 h) and $RhH(PMe_3)_4$ sublimed at 90 °C (10^{-2} mmHg) as a yellow solid. This was recrystallised as pale yellow needles from toluene (m.p. 95—100 °C). Yield 0.54 g, 70%. Infrared (Nujol, cm^{-1}) bands at 1 715m br, 1 297m, 940s, 858m, 748m, and 725m.

Bis[carbonylhydridotris(trimethylphosphine)rhodium(I)], (3).—The complex *trans*-$RhCl(CO)(PMe_3)_2$[1] (0.5 g, 1.16 mmol) in thf ($100\ cm^3$) was added to sodium amalgam (50 g, 20 mmol Na) and the mixture stirred at room temperature (10 h). The solution was filtered and solvent removed under vacuum. The residue was extracted with light petroleum ($50\ cm^3$), filtered, and the solution evaporated to dryness *in vacuo* (2 h). The residue was dissolved in toluene ($10\ cm^3$), the volume of the solution reduced to *ca.* 3—4 cm^3, and cooled (−20 °C) to give yellow prisms which were collected and dried under vacuum. Yield 0.2 g, 25%, m.p. 162—165 °C. Infrared (Nujol, cm^{-1}) bands at: 1 958s (sh), 1 690s, 1 665s, 1 650s, 1 418m, 1 282m, 946s, 852m, 737m, and 671m.

Chloro(dimethylphenylphosphine)bis(trimethylphosphine)-rhodium(I), (4).—The complex $[Rh(PMe_3)_4]Cl$ (0.35 g, 0.8 mmol) in benzene ($100\ cm^3$) was stirred with freshly cut sodium (0.5 g, 22 mmol) at room temperature (15 h). The dark red solution was filtered and the solvent removed under vacuum. The residue was dissolved in light petroleum ($30\ cm^3$), filtered, and the solution evaporated under vacuum (to *ca.* 3—5 cm^3). Cooling (−20 °C) gave orange crystals which were collected and dried under vacuum. Yield 0.12 g, 35%, m.p. 110—120 °C (decomp.). Infrared (Nujol, cm^{-1}) bands at : 3 050w, 1 570w, 1 320w, 1 305w, 1 300w, 1 295w, 1 280m, 1 180w, 1 155w, 1 100m, 1 070w, 1 030w, 1 000w, 940s, 905s, 865s, 845m, 835m, 750s, 720s, 705s, 665s, 485m, and 455s.

η-Cyclopentadienylbis(trimethylphosphine)rhodium(I), (5).—The compound $[Rh(PMe_3)_4]Cl$ (0.4 g, 0.9 mmol) in thf ($100\ cm^3$) was added to a solution of sodium cyclopentadienide (0.1 g, 1.13 mmol in thf, $20\ cm^3$). The solution was stirred at room temperature (6 h). The red solution was filtered and the solvent removed under vacuum. The residue was extracted with light petroleum (30 cm^3), the solution filtered, and reduced in volume under vacuum (to *ca.* 10 cm^3). Cooling (−20 °C) yielded red-brown prisms which were washed with cold light petroleum (2 × 3 cm^3) and dried under vacuum. Yield 0.3 g, 97%, m.p. 85 °C. Infrared (Nujol, cm^{-1}) bands at: 3 090w, 1 330w, 1 295s, 1 275s, 1 175s, 1 140s, 1 100m, 1 005m, 955s, 945s, 935s, 870m, 860m, 840m, 805w, 745s, 705s, 710s, 395s, 380s, and 365s.

Methyltris(trimethylphosphine)rhodium(I), (6).—The compound [Rh(PMe$_3$)$_4$]Cl (0.5 g, 1.1 mmol) was suspended in toluene (100 cm^3) and methyl-lithium (10 cm^3, of a 0.2 mol dm^{-3} diethyl ether solution, 2.0 mmol) was added at −78 °C. The mixture was allowed to warm slowly to *ca.* 0 °C and was stirred at this temperature for 8 h. The solution was filtered (room temperature), solvent was removed under vacuum, and the residue redissolved in toluene (20 cm^3). The solution was again filtered and the volume reduced (to *ca.* 5—7 cm^3). Cooling (−20 °C) yielded orange prisms which were collected, washed with cold light petroleum (1 × 2 cm^3), and dried under vacuum. Yield 0.33 g, 87%, m.p. 70—84 °C (decomp.). Infrared (Nujol, cm^{-1}) bands at: 1 290s, 1 275s, 1 175s, 930s br, 840m, 700s, 655s, and 455w.

Using MgMe$_2$ instead of LiMe under similar conditions also gives high yields of (6).

3-*Methylphenyltris(trimethylphosphine)rhodium*(I), (7).—The compound [Rh(PMe$_3$)$_4$]Cl (0.3 g, 0.7 mmol) was dissolved in toluene (50 cm^3) and the solution gently refluxed while methyl-lithium (3.5 cm^3 of a 0.2 mol dm^{-3} diethyl ether solution, 0.7 mmol) was slowly added. The mixture was then heated under gentle reflux (10 h). On cooling (room temperature), the dark orange solution was filtered and the solvent removed under vacuum. The complex Rh(C$_6$H$_4$Me-3)(PMe$_3$)$_3$ was sublimed from the residue at 90 °C, 10^{-2} mmHg, as a yellow material. It was recrystallised from toluene at −20 °C. Yield 0.17 g, 60%, m.p. 100—105 °C (decomp.). Infrared (Nujol, cm^{-1}) bands at: 3 040w, 3 020w, 1 565w, 1 550w, 1 300m, 1 280s, 1 245w, 1 205w, 1 160w, 1 050w, 1 035w, 1 015w, 940s, 855m, 840m, 815w, 790w, 760s, 735w, 710s, 660s, 530w, and 550w.

Chloro(iodo)methyltris(trimethylphosphine)rhodium(III), (8).—To [Rh(PMe$_3$)$_4$]Cl (0.1 g, 0.23 mmol) in toluene (50 cm^3) was added MeI (0.1 cm^3, 1.6 mmol) at room temperature and the solution stirred (3 h). The yellow solution was filtered from a white precipitate (shown to be [PMe$_4$]I by ^{31}P n.m.r.) and the solvent removed under vacuum. The residue was extracted with thf (15 cm^3), the solution filtered, and cooled (−20 °C) to give yellow crystals. These were collected, washed with light petroleum (2 × 3 cm^3), and dried under vacuum. Yield 0.1 g, 90%, m.p. 176 °C (decomp.). Infrared (Nujol, cm^{-1}) bands at: 1 440m, 1 290m, 1 275m, 1 260s, 1 190s, 940s, 858m, 800m, 724s, 680w, 670w, 505w, 392s, 355s, and 300m.

Chloro(iodo)phenyltris(trimethylphosphine)rhodium(III), (9).—Iodobenzene (0.1 cm^3, 0.9 mmol) was added to a solution of [Rh(PMe$_3$)$_4$]Cl (0.1 g, 0.23 mmol) in toluene (50 cm^3) and the solution refluxed (24 h). After cooling to room temperature the solution was filtered and the solvent removed under vacuum. The residue was dissolved in a mixture of toluene and light petroleum (60 cm^3, 1 : 1); cooling (−20 °C) yielded orange crystals which were collected and recrystallised from toluene at −20 °C. Yield, 0.12g, 90%, m.p. 160 °C. Infrared (Nujol, cm^{-1}) bands at: 3 080w, 3 020w, 1 557w, 1 540w, 1 304w, 1 282w, 1 000w, 940s br, 855w, 740s, 720s, 710s, and 670m.

Dioxygentetrakis(trimethylphosphine)rhodium(III) *Hexafluorophosphate*, (10).—When dioxygen (1 atm) was passed through an orange aqueous solution of [Rh(PMe$_3$)$_4$]Cl (0.4 g, 0.93 mmol, 30 cm^3) it rapidly became colourless. Addition of potassium hexafluorophosphate (0.2 g, 1 mmol) in water (20 cm^3) gave a white microcrystalline precipitate which was collected, washed with water (2 × 5 cm^3) and thf (2 × 3 cm^3), and dried under vacuum. Yield 0.5 g, 95%, m.p. 108—110 °C (decomp.). Infrared (Nujol, cm^{-1}) bands at 1 315s, 1 295s, 1 280s, 1 170w, 950s, 835s br, 740s, 675s, 560s, 530s, 465m, 370m, and 350m.

trans-*Chlorobis(trimethylphosphine)(triphenylphosphine)rhodium*(I), (11).—A solution of triphenylphosphine (1.0 g) and [Rh(PMe$_3$)$_4$]Cl (0.5 g, 1.14 mmol) in toluene–thf (100 cm^3, 50 : 50) was heated under reflux (48 h). The solution was evaporated to dryness *in vacuo* and the residue dissolved in toluene (50 cm^3). The solution was filtered and the volume reduced to *ca.* 5 cm^3. Cooling (−20 °C) yielded a mixture of yellow needles of RhCl(PPh$_3$)(PMe$_3$)$_2$ and triphenylphosphine. The former were separated manually and recrystallised from toluene at −20 °C. Yield 0.13 g, 20%, m.p. 118—120 (decomp). Infrared (Nujol, cm^{-1}) bands at: 3 050w, 1 580w, 1 564w, 1 295m, 1 275m, 1 085m, 1 020w, 995w, 945s, 855s, 745s, 720s, 695s, 670s, 540s, 535s, 515s, 495s, 460m, 450m, 420w, and 350m.

Crystallographic Studies.—Crystals of both compounds, (1) and (11), were sealed under nitrogen in Lindemann capillaries. Approximate cell dimensions and crystal

TABLE 5

Crystal data and details of data collection and structural analysis

	Compound (1)	Compound (11)
(*a*) Crystal data		
Formula	Hg$_6$Rh$_4$(PMe$_3$)$_{12}$	RhCl(PMe$_3$)$_2$(PPh$_3$)
M	2 528.13	552.81
Crystal system	Orthorhombic	Monoclinic
a/Å	12.909(2)	17.006(3)
b/Å	25.274(4)	11.821(2)
c/Å	25.176(4)	12.884(2)
β/°		96.46(2)
U/Å^3	8 213.9	2 573.7
Space group	*Ccmm* or *Ccm*2	$P2_1/n$
Z	4	4
D_c/g cm^{-3}	2.05	1.43
F(000)	4 656	1 136
Linear absorption coefficient/cm^{-1}	117.2	8.67
Crystal size/mm	0.6 × 0.12 × 0.25	0.23 × 0.35 × 0.55
(*b*) Data collection		
X-Radiation	Mo-K_α	Mo-K_α
$\theta_{min.}$, $\theta_{max.}$	1.5, 30.0	1.5, 25.0
ω Scan width parameters A,B in width = $A + B\tan\theta$	0.75, 0.35	0.8, 0.15
Horizontal aperture parameters A,B in aperture = $A + B \tan\theta$	4.0, 0.0	4.0, 0.0
Total data collected	6 139	4 505
Observed data [$F_o > 3\sigma(F_o)$]	2 448	3 708
(*c*) Refinement		
No. of parameters	60	394
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + g\lvert F_o\rvert^2]$	Unit wts.	0.000 65
Final $R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.083	0.038
$R' = [\Sigma w(\Delta F)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.083	0.039

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 [1] and corrected for Lorentz and polarisation effects. The data for (1) were also corrected for absorption. Crystal data and details of the data collection are given in Table 5.

The structures of both compounds were solved by the heavy-atom method and refined by least squares. For compound (11) the process was quite routine, but for (1) both structure solution and refinement gave problems. Once the Patterson map had been interpreted and the cluster identified the refinement of the metal atoms was fairly straightforward in space group *Ccmm*. The phosphorus atoms on the rhodiums were easily located but refinement was not smooth and when anisotropic thermal parameters were incorporated, those for many of the phosphorus atoms showed large anisotropy, particularly P(4). Refinement in *Ccm*2 was also tried but this did not give any significant improvement. Location of the methyl carbon atoms also proved to be very difficult and although some peaks could be found in sensible positions (in some cases for all three carbons on the phosphorus) sensible refinement could not be achieved. It is possible therefore, that we have either some rotation of the PMe_3 groups about the P–Rh bonds *or* lower space-group symmetry. However, the Hg_6Rh_4 cluster clearly adopts an orientation consistent with or very close to that required for point symmetry *mm* in *Ccmm* and since this is such a dominating scatterer, we do not think that the present data in which so many reflections are weak (see Table 5) will allow us to make any further progress at the moment. We propose to recollect data at a much slower rate in the hope of recording significant intensities for more of the weak reflections.

TABLE 6

Heavy-atom fractional co-ordinates ($\times 10^4$) for $Hg_6Rh_4(PMe_3)_{12}$

Atom	*x*	*y*	*z*
Hg(1)	1 465(1)	619(1)	1 875(1)
Hg(2)	3 196(2)	0	$\frac{1}{4}$
Hg(3)	−260(2)	0	$\frac{1}{4}$
Rh(1)	2 952(3)	0	3 564(2)
Rh(2)	−29(3)	1 058(2)	$\frac{1}{4}$
P(1)	2 183(12)	0	4 384(6)
O(2)	4 050(13)	701(8)	3 666(6)
P(3)	−1 115(14)	1 155(7)	1 802(6)
P(4)	766(22)	1 863(8)	$\frac{1}{4}$

TABLE 7

Atomic co-ordinates ($\times 10^4$) for (11)

Atom	*x*	*y*	*z*
Rh	1 110	1 834	3 528
Cl	1 680(1)	180(2)	4 426(2)
P(1)	403(1)	484(1)	2 512(1)
P(2)	529(1)	3 271(1)	2 619(1)
P(3)	1 916(1)	2 802(1)	4 789(1)
C(11)	−380(4)	752(5)	1 453(5)
C(12)	1 054(4)	−411(5)	1 839(5)
C(13)	−104(4)	−510(5)	3 285(5)
C(211)	621(2)	3 131(3)	1 213(3)
C(212)	58(3)	3 460(4)	398(3)
C(213)	205(3)	3 281(4)	−635(3)
C(214)	881(3)	2 799(5)	−860(4)
C(215)	1 438(3)	2 474(5)	−70(4)
C(216)	1 309(3)	2 634(4)	953(3)
C(221)	−535(2)	3 434(3)	2 735(3)
C(222)	−992(3)	4 288(4)	2 278(3)
C(223)	−1 797(3)	4 375(4)	2 421(4)
C(224)	−2 119(3)	3 597(5)	3 034(4)
C(225)	1 683(3)	2 745(5)	3 509(4)
C(226)	883(3)	2 666(4)	3 365(3)
C(231)	859(2)	4 738(3)	2 842(3)
C(232)	1 498(2)	5 162(4)	2 378(3)
C(233)	1 793(3)	6 235(5)	2 630(4)
C(234)	1 470(3)	6 895(4)	3 316(4)
C(235)	821(3)	6 515(4)	3 774(4)
C(236)	512(3)	5 428(4)	3 545(3)
C(31)	2 135(4)	4 311(5)	4 853(5)
C(32)	1 571(3)	2 615(6)	6 067(4)
C(33)	2 926(3)	2 276(5)	5 000(4)

Details of the refinements are given in Table 5. Final atomic co-ordinates are given in Tables 6 and 7. Tables of thermal parameters and lists of F_o and F_c have been deposited as Supplementary Publication No. SUP 22919 (35 pp.).* The computer and programs used and the atomic scattering factor data sources are as in ref. 7.

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