Alkyl, Hydrido-, and Related Compounds of Ruthenium(II) with Trimethylphosphine. *X*-Ray Crystal Structures of Hydrido(tetrahydroborato-*HH'*)tris(trimethylphosphine)ruthenium(II), Tri-μ-chloro-bis[tris(trimethylphosphine)ruthenium(II)] Tetrafluoroborate, and Bis[*cis*-methyltetrakis(trimethylphosphine)ruthenio]mercury(II)–Tetrahydrofuran(1/1) †

John A. Statler and Geoffrey Wilkinson *
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY
Mark Thornton-Pett and Michael B. Hursthouse *
Chemistry Department, Queen Mary College, London E1 4NS

A number of trimethylphosphine complexes of ruthenium(II) with alkyl, hydrido-, halogeno-, acetato-, and tetrahydroborato-ligands and in addition the halide-bridged complex $[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]BF_4$ and the mercury-bridged species $[cis\text{-}RuMe(PMe_3)_4]_2Hg$ have been synthesized. The *X*-ray crystal structures of $RuH(BH_4)(PMe_3)_3$ and of the tri-μ-chloro- and mercury-bridged complexes have been determined. In the borohydride the metal atom has an octahedral co-ordination, with a bidentate BH_4^- ligand. The two Ru–H(borohydride) bonds [1.81(4) and 1.85(4) Å] are *trans* to the hydride [Ru–H 1.49(4) Å] and one phosphine [Ru–P 2.259(3) Å]; the latter is shorter than those to the other phosphines [2.304(3) and 2.305(3) Å] which are *trans* to each other. The chloro-bridged complex has the usual confacial bioctahedral $X_3MY_3MX_3$ structure with Ru–P and Ru–Cl bond lengths in the ranges 2.248(4)—2.256(4) and 2.463(4)—2.488(4) Å respectively. In the mercury-bridged species as the tetrahydrofuran solvate, the Ru–Hg distances are 2.798(4) and 2.800(4) Å and the Ru–Hg–Ru angle is 170.7(2)°; Ru–C distances are 2.21(1) and 2.23(1) Å whilst Ru–P distances range from 2.308(4) to 2.344(4) Å with those *trans* to the Ru–Me bonds shorter than the rest. The mercury atom makes close contacts with a number of hydrogens from methyl groups.

There have been relatively few studies of ruthenium(II) phosphine complexes with mixed hydrido-, alkyl, or halide ligands. Halogeno- and hydrido-alkyls having bidentate phosphines are known [1,2] as well as five-co-ordinate, mono-alkyl triphenylphosphine complexes,[3,4] *e.g.* $RuClMe(PPh_3)_3$.[4] No compounds of the type $RuXR(PR'_3)_4$ (R,R' = alkyl; X = halide, hydride, or alkyl other than R) are known. The syntheses and reactions of ruthenium compounds with trimethylphosphine as the ligand are now described. The various reactions are summarized in the Scheme.

Results and Discussion

Protic Cleavages.—(*a*) *cis*-$RuMe_2(PMe_3)_4$. Tertiary phosphine complexes of ruthenium with *cis*-halogeno- and alkyl groups have been synthesized from the corresponding halide using an excess of trialkylaluminium.[1,4] We have synthesized *cis*-$RuClMe(PMe_3)_4$ from the corresponding dimethyl compound, *cis*-$RuMe_2(PMe_3)_4$,[5] by the slow addition of 1 equivalent of hydrogen chloride in diethyl ether at −78 °C, when the reaction is immediate and virtually quantitative. The product precipitates from the cold solution as a yellow powder. The addition of a second equivalent of HCl in Et_2O to the product mixture in Et_2O cleaves the remaining methyl and produces $[Ru(\mu\text{-}Cl)(PMe_3)_4]_2Cl_2$.[6]

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of *cis*-$RuClMe(PMe_3)_4$ shows an A_2BC pattern. The metal-bound methyl is coupled to all phosphorus atoms and appears as an eleven-line multiplet in the ^1H spectrum.

Using acetic acid instead of HCl, *cis*-$Ru(O_2CMe)Me(PMe_3)_4$ is obtained. The i.r. spectrum has both a C–O band (1 573 cm^{-1}) and a C=O band (1 702 cm^{-1}), indicating a unidentate acetate ligand. The $^{31}P\text{-}\{^1H\}$ spectrum is similar to that of *cis*-$RuClMe(PMe_3)_4$, having an A_2BC pattern.

(*b*) *Metallocycles.* When HCl was added slowly to 1 equivalent of $Ru[(CH_2)_2CMe_2](PMe_3)_4$[5] in Et_2O at −78 °C the product was $[Ru(\mu\text{-}Cl)(PMe_3)_4]_2Cl_2$. The analogous reaction with $(Me_3P)_4\overline{RuCH_2C}_6H_4$ (see below) gave a similar result.

(*c*) *cis*-$RuH_2(PMe_3)_4$. The dropwise addition of 1 equivalent of HCl to a solution in ether of *cis*-$RuH_2(PMe_3)_4$[7] at −78 °C gave a high yield of *cis*-$RuClH(PMe_3)_4$. The earlier procedure gave low yields and oily side products that interfered with the purification.

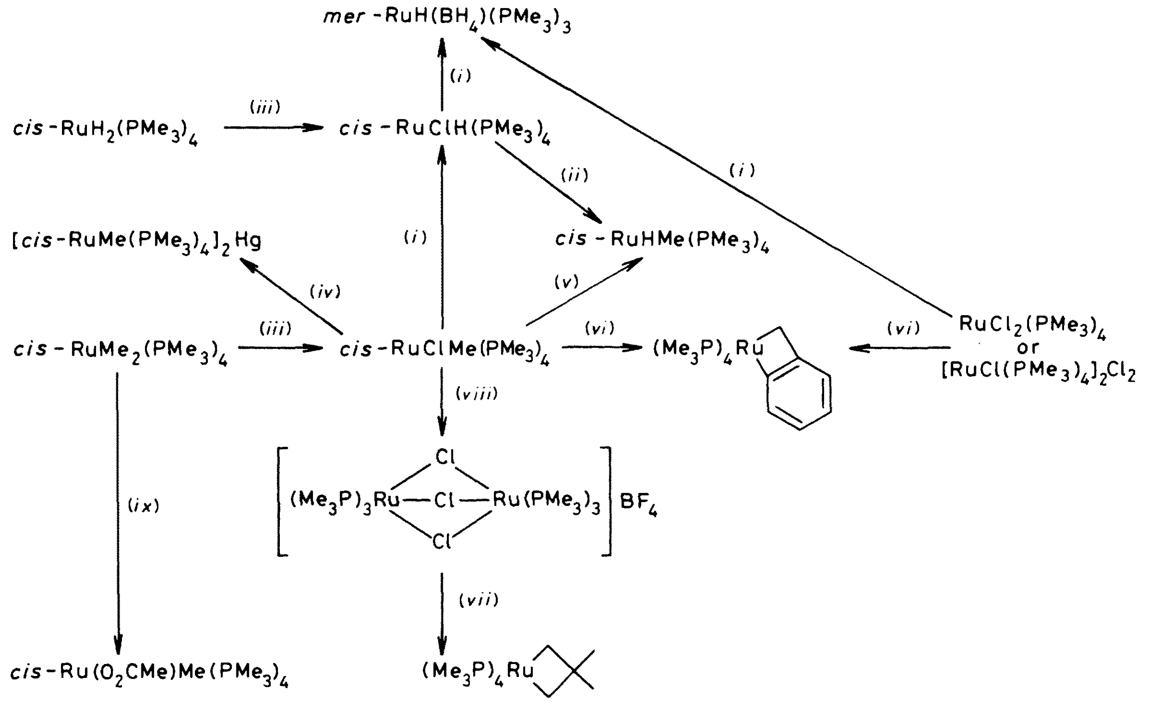
Alkylation Studies.—The interaction of *cis*-$RuClMe(PMe_3)_4$ with 1 equivalent of MgMeCl or half an equivalent of $MgMe_2$ in diethyl ether gave *cis*-$RuMe_2(PMe_3)_4$ as expected. A similar reaction with $Mg(CH_2Bu^t)Cl$ gave the known metallacycle $Ru[(CH_2)_2CMe_2](PMe_3)_4$[5] in low yield. The interaction with $Mg(CH_2Ph)Cl$ produces the cyclometallated compound, $(Me_3P)_4\overline{RuCH_2C}_6H_4$. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this compound is a A_2BC pattern with B and C overlapping. The $^{13}C\text{-}\{^1H\}$ and ^1H spectra are consistent only with that of an orthometallated benzyl.

Whereas $Mg(CH_2Bu^t)Cl$ appears not to react with either *trans*-$RuCl_2(PMe_3)_4$ or $[Ru(\mu\text{-}Cl)(PMe_3)_4]_2Cl_2$ in Et_2O or tetrahydrofuran (thf), $Mg(CH_2Ph)Cl$ reacts readily in Et_2O with either compound to produce the benzyl metallacycle. The interaction of $RuClMe(PMe_3)_4$ with $MgEt_2$ will be described separately.

Hydride Substitutions of cis-$RuClMe(PMe_3)_4$.—(*a*) *Lithium tetrahydroborate.* One equivalent of $LiBH_4$ reacts with *cis*-

---

† *Supplementary data available* (No. SUP 23951, 69 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, F-atom occupancies, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme. Reactions of ruthenium phosphine complexes: (*i*) $LiBH_4$; (*ii*) MgMeCl; (*iii*) HCl; (*iv*) Na/Hg; (*v*) NaOMe; (*vi*) $Mg(CH_2Ph)Cl$; (*vii*) $Mg(CH_2Bu^t)Cl$; (*viii*) $AgBF_4$; (*ix*) $MeCO_2H$

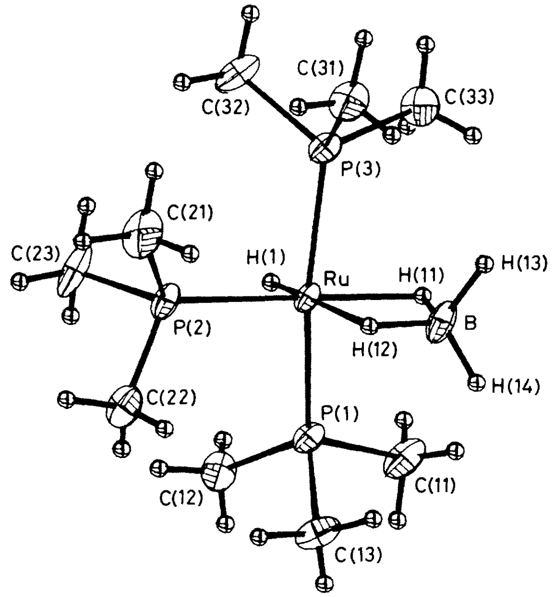


Figure 1. The structure of $RuH(BH_4)(PMe_3)_3$

$RuClMe(PMe_3)_4$ in Et_2O to produce the known complex *cis*-$RuClH(PMe_3)_4$.[6] When $\gtrsim$ 2 equivalents of $LiBH_4$ were used, the reaction under identical conditions resulted in the formation of *mer*-$RuH[(\mu\text{-}H)_2BH_2](PMe_3)_3$. This borohydride was also made from *trans*-$RuCl_2(PMe_3)_4$ and from $[Ru(\mu\text{-}Cl)(PMe_3)_4]_2Cl_2$ using an excess of $LiBH_4$.

Other compounds of stoicheiometry $MH(H_2BH_2)(PR_3)_n$, $n = 3$ or 4, are known [8–11] but the only crystal structure available is that of $MoH(H_2BH_2)(PMe_3)_4$.[11] The variable-temperature ^1H n.m.r. spectra in C_6D_6 for the ruthenium compounds are similar to those observed by Meek and co-workers.[10] The bridging hydride *trans* to the lone Ru–H exchanges positions with the two non-bridging hydrides on the boron at 80 °C. These hydrogens further exchange with the bridging hydride *trans* to PMe_3 at 110 °C.

Table 1. Selected bond lengths (Å) and angles (°) for $RuH(H_2BH_2)(PMe_3)_3$

Ru–H(1)	1.49(4)	Ru–P(1)	2.305(3)
Ru–H(11)	1.81(4)	Ru–P(2)	2.259(3)
Ru–H(12)	1.85(4)	Ru–P(3)	2.304(3)
P–C(Me)	1.820—1.835(6)		
P(1)–Ru–H(1)	72.4(14)	P(2)–Ru–H(1)	89.0(14)
P(2)–Ru–P(1)	95.6(5)	P(3)–Ru–H(1)	95.7(14)
P(3)–Ru–P(1)	163.5(5)	P(3)–Ru–P(2)	95.6(5)
B ··· Ru–H(1)	133.7(13)	B ··· Ru–P(1)	89.6(2)
B ··· Ru–P(2)	136.0(1)	B ··· Ru–P(3)	90.7(2)
H(11)–Ru–H(1)	100.6(16)	H(11)–Ru–P(1)	86.9(8)
H(11)–Ru–P(2)	170.4(8)	H(11)–Ru–P(3)	84.1(8)
H(11)–Ru ··· B	34.5(8)	H(12)–Ru–H(1)	167.6(17)
H(12)–Ru–P(1)	97.6(11)	H(12)–Ru–P(2)	9.5(12)
H(12)–Ru–P(3)	92.4(11)	H(12)–Ru ··· B	36.6(11)
H(12)–Ru–H(11)	70.9(14)		

The structure of the compound $RuH(H_2BH_2)(PMe_3)_3$ in the solid state has been determined by *X*-ray crystallography. A diagram of the structure is shown in Figure 1 whilst selected bond lengths and angles are given in Table 1. The proposed *mer*-octahedral geometry is confirmed. The two Ru–H bonds to the chelating BH_4^- ligand are essentially equal, within experimental error, and are *trans* to the terminal Ru–H bond and one PMe_3 ligand. The Ru–P distance to this ligand is 0.045 Å shorter than those to the other two phosphines, which are *trans* to each other.

(*b*) *Lithium aluminium hydrides*. By contrast with a similar reaction,[1] the interaction of *cis*-$RuClMe(PMe_3)_4$ and excess of $LiAlH_4$ in refluxing thf did not produce the hydridomethyl complex, but only *cis*-$RuH_2(PMe_3)_4$. Similarly, the reaction

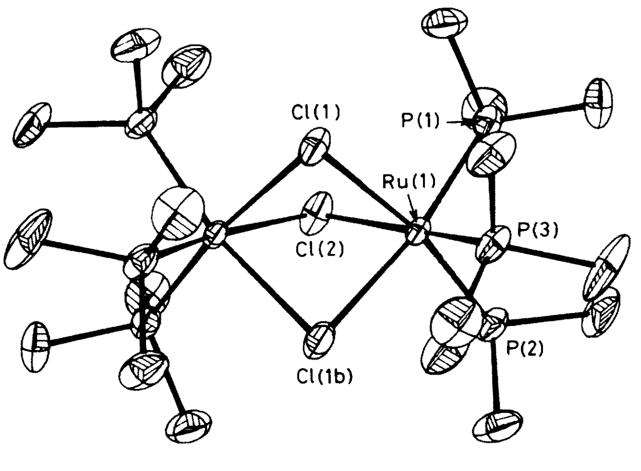


Figure 2. The structure of the cation $[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]^+$

Table 2. Selected bond lengths (Å) and angles (°) for $[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]BF_4$

Ru(1)–P(1)	2.256(4)	Ru(1)–Cl(1)	2.488(4)
Ru(1)–P(2)	2.255(4)	Ru(1)–Cl(2)	2.463(4)
Ru(1)–P(3)	2.248(4)	Ru(1)–Cl(1a)	2.481(4)
P–C(Me)	1.81—1.85(2)		
P(2)–Ru(1)–P(1)	95.7(2)	P(3)–Ru(1)–P(1)	95.3(2)
P(3)–Ru(1)–P(2)	95.1(2)	Cl(1)–Ru(1)–P(1)	93.1(2)
Cl(1)–Ru(1)–P(2)	169.2(1)	Cl(1)–Ru(1)–P(3)	90.2(2)
Cl(1)–Ru(1)–Cl(1a)	80.5(2)	Cl(2)–Ru(1)–P(1)	89.3(2)
Cl(2)–Ru(1)–P(2)	92.7(2)	Cl(2)–Ru(1)–P(3)	170.5(1)
Cl(2)–Ru(1)–Cl(1)	81.2(2)		
Ru(1)–Cl(1)–Ru(1a)	82.4(2)	Ru(1)–Cl(2)–Ru(1a)	83.3(2)

of *cis*-$RuClMe(PMe_3)_4$ in toluene at ambient temperature using only 0.25 equivalent of $LiAlH_4$ resulted only in *cis*-$RuH_2(PMe_3)_4$ and unreacted starting compound. A 1 : 1 mixture of *cis*-$RuClMe(PMe_3)_4$ and $LiAlH(OMe)_3$, when refluxed in thf for *ca.* 1 h or when stirred for 1 week at ambient temperature in toluene, yielded *cis*-$RuClH(PMe_3)_4$.

(*c*) *Sodium methoxide.* The hydridoalkyl complex, *cis*-$RuHMe(PMe_3)_4$, was also formed readily from *cis*-$RuClMe(PMe_3)_4$ by the reaction of an excess of NaOMe in thf. The mechanism of such a reaction for a triphenylphosphine complex has been discussed,[12] although by contrast in the present instance no carbonyl complex was formed. The hydridoalkyl was also synthesized by methylation of *cis*-$RuClH(PMe_3)_4$ using MgMeCl. The ^1H n.m.r. spectrum of the complex has a 12-line pattern at δ 9.80 p.p.m., indicating a *cis* geometry, which is further substantiated by the A_2BC pattern of $^{31}P\text{-}\{^1H\}$ resonances. The $^{31}P\text{-}\{^1H\}$ spectrum reveals strong hydride coupling to the phosphorus atom at δ −11.2 p.p.m., indicating a *trans* H–Ru–P group. The hydride is not coupled to the methyl hydrogens.

The interaction of *cis*-$RuClMe(PMe_3)_4$ with NaOMe in MeOH again gave *cis*-$RuHMe(PMe_3)_4$.

Reaction of cis-$RuClMe(PMe_3)_4$ *with* $AgBF_4$.—When $AgBF_4$ was added to *cis*-$RuClMe(PMe_3)_4$ in thf a precipitate containing Ag, Cl, and PMe_3 was produced. A solid recovered from the yellow solution, when recrystallised from MeOH, was shown to be the previously unreported halide-bridged $[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]BF_4$. Many analogous bridged compounds are known,[13–19] although few crystal structures have been reported.[16,17,19] Evidently, $AgBF_4$ more efficiently abstracts phosphine than chlorine in this instance.

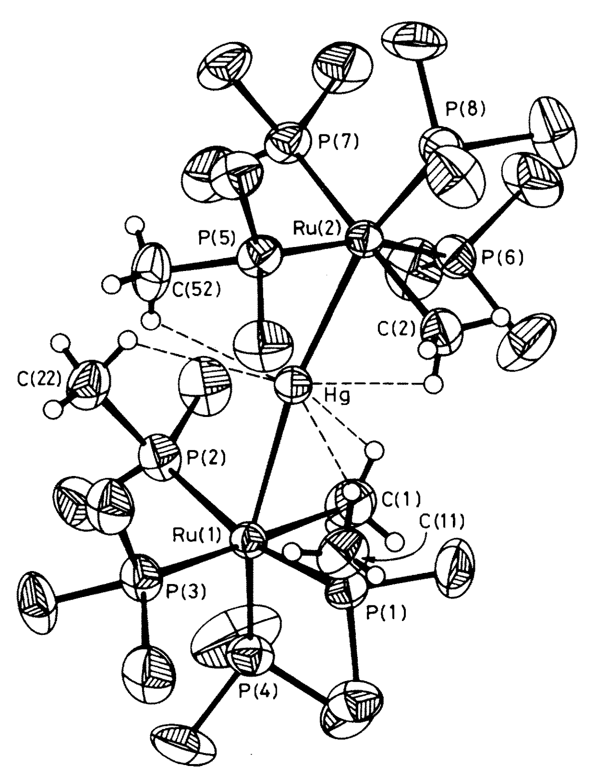


Figure 3. The structure of $[cis\text{-}RuMe(PMe_3)_4]_2Hg$

The ^1H n.m.r. spectrum of the salt is extremely complex, although the ^{31}P spectrum is merely a singlet at δ 22.6 p.p.m. Although the ^{19}F n.m.r. spectrum clearly establishes that all fluorine present is as BF_4^- because of the characteristic pattern of a broad singlet and a 1 : 1 : 1 : 1 quartet due to the two isotopes of boron, both F and Cl analyses were unsatisfactory as is sometimes observed with such ruthenium complexes.

The identity of this compound has been confirmed by *X*-ray crystallography. The structure of the cation is shown in Figure 2 and selected bond lengths and angles are given in Table 2. The cation, which has a confacial bioctahedral structure, is sited on a two-fold axis and the compound is isostructural with the cation $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)Ru(PMe_3)_3]^+$ in its tetrafluoroborate salt.[20] In the present cation the Ru–P and Ru–Cl distances are internally almost equal, the small variations present being due, possibly, to crystal-packing effects.

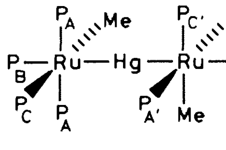
Reaction of cis-$RuClMe(PMe_3)_4$ *with Sodium Amalgam.*—Whereas the reaction of *trans*-$RuCl_2(PMe_3)_4$ with Na/Hg in thf produces *cis*-$RuClH(PMe_3)_4$,[6] interaction of *cis*-$RuClMe(PMe_3)_4$ with 1% sodium amalgam over a period of 3 d at ambient temperature yields $[cis\text{-}RuMe(PMe_3)_4]_2Hg$. This appears to be the first ruthenium–mercury complex containing phosphines, although some carbonyl analogues have been reported.[21–23] When the reaction was run in thf, recrystallization from light petroleum produced a thf solvate. However, when the reaction was run in toluene no solvate was produced, although this product was contaminated with an oily substance even after several recrystallizations. The crystal structure of the tetrahydrofuran solvate shows the complex to have two eclipsed octahedra with one vertex in common at the mercury, see Figure 3 and Table 3. The Ru–Hg–Ru angle is 171° and, when viewed along this direction, the methyl

Table 3. Selected bond lengths (Å) and angles (°) for [*cis*-RuMe$(PMe_3)_4]_2Hg$

Ru(1)–Hg	2.800(4)	Ru(2)–Hg	2.798(4)
Ru(1)–P(1)	2.327(4)	Ru(2)–P(5)	2.312(4)
Ru(1)–P(2)	2.318(4)	Ru(2)–P(6)	2.344(4)
Ru(1)–P(3)	2.312(4)	Ru(2)–P(7)	2.308(4)
Ru(1)–P(4)	2.313(4)	Ru(2)–P(8)	2.325(4)
Ru(1)–C(1)	2.23(1)	Ru(2)–C(2)	2.21(1)
Ru(2)–Hg–Ru(1)	170.7(2)		
P(1)–Ru(1)–Hg	83.4(5)	P(2)–Ru(1)–Hg	81.2(5)
P(2)–Ru(1)–P(1)	164.5(1)	P(3)–Ru(1)–Hg	101.5(5)
P(3)–Ru(1)–P(1)	90.8(2)	P(3)–Ru(1)–P(2)	91.8(2)
P(4)–Ru(1)–Hg	158.2(1)	P(4)–Ru(1)–P(1)	96.5(2)
P(4)–Ru(1)–P(2)	98.0(2)	P(4)–Ru(1)–P(3)	100.2(2)
C(1)–Ru(1)–Hg	78.1(3)	C(1)–Ru(1)–P(1)	89.0(3)
C(1)–Ru(1)–P(2)	88.4(3)	C(1)–Ru(1)–P(3)	179.6(1)
C(1)–Ru(1)–P(4)	80.2(3)		
P(5)–Ru(2)–Hg	80.2(5)	P(6)–Ru(2)–Hg	83.5(2)
P(6)–Ru(2)–P(5)	163.7(1)	P(7)–Ru(2)–Hg	100.1(2)
P(7)–Ru(2)–P(5)	91.5(2)	P(7)–Ru(2)–P(6)	91.4(2)
P(8)–Ru(2)–Hg	161.2(1)	P(8)–Ru(2)–P(5)	95.6(2)
P(8)–Ru(2)–P(6)	99.9(2)	P(8)–Ru(2)–P(7)	98.3(2)
C(2)–Ru(2)–Hg	79.9(3)	C(2)–Ru(2)–P(5)	91.2(3)
C(2)–Ru(2)–P(6)	85.8(3)	C(2)–Ru(2)–P(7)	177.3(2)
C(2)–Ru(2)–P(8)	81.9(3)		

groups are orientated approximately 90° from one another [dihedral angle C(1)Ru(1)Hg(1)/C(2)Ru(2)Hg(1) = 92.63°]. A particular feature of this structure is the proximity to the mercury atom of several methyl hydrogens, from both metal and phosphine methyl groups [Hg–H(13) 2.83, –H(23) 2.83, –H(113) 2.88, –H(223) 2.94, and –H(522) 2.73 Å]. This may well account for the low-energy C–H stretch in the solid-state i.r. spectrum at 2 810 cm^{-1}.

The n.m.r. data are in accord with the solid-state structure. Thus, the ^1H spectrum for the PMe_3 groups shows a triplet, a doublet, and a singlet in a 2 : 1 : 1 ratio. The methyl appears as a broad nine-line resonance. The $^{31}P-\{^1H\}$ spectrum at high field (101 MHz) is a triplet, a doublet, and a singlet having mercury-coupled sidebands. The singlet is assigned as the phosphine *trans* to mercury because of its larger coupling to Hg. The $^{31}P-\{^1H\}$ spectrum at low field (36 MHz) is an $A_2A'_2BB'CC'$ pattern. Table 4 summarizes the P–P couplings for the structure 1.



(1)

Experimental

Microanalyses were by Pascher (Bonn). Infrared spectra were obtained on a Perkin-Elmer 683 spectrometer using Nujol mulls unless otherwise specified. Nuclear magnetic resonance spectra were recorded on Bruker WM250 (^1H and ^{31}P) and JEOL FX90Q (^{13}C and ^{19}F) instruments. The conductivities were measured using a Data Scientific PTI-18 conductivity meter.

All operations were carried out under argon or *in vacuo*. Tetrahydrofuran, diethyl ether, and light petroleum (b.p. 40—60 °C) were distilled under dinitrogen from sodium-benzophenone, toluene from sodium, acetonitrile from CaH_2, and methanol from $Mg(OMe)_2$ prior to use. Melting points were determined in sealed, evacuated capillaries and are uncorrected.

Table 4. Phosphorus–phosphorus coupling constants for [*cis*-$RuMe(PMe_3)_4]_2Hg$

$J(AA') = J(BB') = J(CC') = J(AC') = J(A'C) = 0$ Hz
$J(AB) = J(AB') = J(BC) = J(BC') = J(A'B) = J(A'B') = J(B'C) = J(B'C') = 9$ Hz
$J(AC) = J(A'C') = 31$ Hz

The compounds *trans*-$RuCl_2(PMe_3)_4$,[6,24] $[Ru(\mu-Cl)(PMe_3)_4]_2Cl_2$,[6] and $LiAlH(OMe)_3$[25] were prepared by published procedures; *cis*-$RuMe_2(PMe_3)_4$ was prepared from either $Ru_2(O_2CMe)_4Cl$[5] or by the reaction of MgMeCl with *trans*-$RuCl_2(PMe_3)_4$ or $[Ru(\mu-Cl)(PMe_3)_4]_2Cl_2$. HCl in ether was prepared by bubbling anhydrous HCl through dry Et_2O under argon, and was diluted and standardized before each use.

Analytical and other data for new compounds are collected in Table 5. N.m.r. data for ^1H, $^{31}P-\{^1H\}$, and $^{13}C-\{^1H\}$ are in Tables 6—8.

cis-*Chloro(methyl)tetrakis(trimethylphosphine)ruthenium*(II).—A 0.25 mol dm^{-3} solution of HCl in Et_2O (5.2 cm^3, 1.3 mmol) was added dropwise to a stirred solution of *cis*-$RuMe_2(PMe_3)_4$ (0.55 g, 1.3 mmol) in Et_2O (40 cm^3) at −78 °C. The pale yellow suspension was stirred for about 1 h at −78 °C, then warmed to ambient temperature. Solvent was removed under vacuum and the residue extracted with toluene (2 × 25 cm^3), which was filtered and concentrated to about 20 cm^3. Cooling the solution to −20 °C yielded yellow *prisms*, which were washed with light petroleum (2 × 2 cm^3) and dried *in vacuo*. Yield (two crops): 0.47 g, 79%.

Alternatively, a slight deficiency of HCl was used and the dried residue washed with light petroleum (*ca.* 5 cm^3) to remove unreacted *cis*-$RuMe_2(PMe_3)_4$. This latter method produced a sample sufficiently pure for synthetic purposes (typically above 97% by $^{31}P-\{^1H\}$ n.m.r.) in greater than 90% yield. I.r.: 1 295 m, 1 277m, 1 165w, 1 149w, 939s, 854m, 717m, 704m, 657m, and 460w cm^{-1}. The solid compound can be handled in air for brief periods.

cis-*Acetato(methyl)tetrakis(trimethylphosphine)ruthenium*(II).—To a solution of *cis*-$RuMe_2(PMe_3)_4$ (0.81 g, 1.9 mmol) in Et_2O (50 cm^3) at −78 °C was added dropwise a 1.83 mol dm^{-3} solution of $MeCO_2H$ (1.0 cm^3, 1.8 mmol) in Et_2O. The solution was allowed to warm to ambient temperature and, after stirring for 3 h, the solvent was removed under vacuum. The residue was extracted with toluene (20 cm^3), which was filtered, concentrated to *ca.* 10 cm^3, and cooled to −20 °C to give off-white *microcrystals* which were washed with light petroleum (2 × 1 cm^3) and dried *in vacuo*. Yield (two crops): 0.57 g, 64%. I.r.: 1 702, 1 573s, 1 402s, 1 333m, 1 299s, 1 277s, 971m, 941s, 854m, 722m, 699m, 659m, and 616w cm^{-1}. The solid darkens quickly upon exposure to air; it also appears to be somewhat hygroscopic.

(2,2-*Dimethylpropane*-1,3-*diyl)tetrakis(trimethylphosphine)ruthenium*(II).—To a stirred suspension of *cis*-$RuClMe(PMe_3)_4$ (0.41 g, 0.90 mmol) in Et_2O (80 cm^3) was added an ether solution of $Mg(CH_2Bu^t)Cl$ (1.7 cm^3, 0.54 mol dm^{-3}, 0.93 mmol). A white precipitate formed instantly and gas was evolved. After stirring for 2 h, the Et_2O was removed under

Table 5. Analytical and physical data for new ruthenium compounds

			Analysis (%)							
			Found				Required			
Compound	Colour	M.p.[a] (θ/°C)	C	H	P	Other	C	H	P	Other
cis-$RuClMe(PMe_3)_4$	Pale yellow	*b*	34.4	8.6	27.0	8.2 (Cl)	34.3	8.6	27.2	7.8
cis-$Ru(O_2CMe)Me(PMe_3)_4$	Off-white	166—169	37.0	8.4	25.2		37.6	8.8	25.8	
$(Me_3P)_4\overline{RuCH_2C}_6H_4$	White	156—170	46.0	8.5	25.0		46.0	8.5	25.0	
mer-$RuH(BH_4)(PMe_3)_3$	Yellow	116—119	31.4	9.2	27.1	3.2 (B)	31.3	9.3	26.9	3.2
cis-$RuHMe(PMe_3)_4$	White	156—163	36.6	9.1	28.5		37.0	9.6	29.4	
[*cis*-$RuMe(PMe_3)_4]_2Hg\cdot$thf	Red-orange	200—202	32.2	7.8	22.4		32.4	7.8	22.3	
[*cis*-$RuMe(PMe_3)_4]_2Hg$	Dark red	194—195	31.0	8.0	23.4		30.0	7.6	23.8	
$[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]BF_4$	Yellow	>300	25.7	6.4	22.3	10.0 (F) 1.3 (B) 10.2 (Cl)	25.4	6.4	21.9	8.9 1.3 12.5

[a] All compounds decomposed upon melting. [b] Decomposed without melting below 300 °C.

Table 6. ^1H N.m.r. data

Compound	δ/p.p.m. [a]	*J*/Hz	Assignment
cis-$RuClMe(PMe_3)_4$	1.27 t(18)	*J*(PH) = 3	*trans* PMe_3
	1.19, d(9)	*J*(PH) = 5	*cis* PMe_3
	0.90, d(9)	*J*(PH) = 8	*cis* PMe_3
	0.29, d of d(3)	*J*(PH) = 8, 5, 4	Me
cis-$Ru(O_2CMe)Me$-$(PMe_3)_4$	2.18, s(3)		O_2CMe
	1.31, d(9)	*J*(PH) = 6	*cis* PMe_3
	1.23, t(18)	*J*(PH) = 3	*trans* PMe_3
	0.90, d(9)	*J*(PH) = 7	*cis* PMe_3
	0.04, t of d(3)	*J*(PH) = 3, 1	Me
$(Me_3P)_4\overline{RuCH_2C}_6H_4$	7.52, d(1)	*J*(HH) = 7	phenyl H
	7.20, t(1)	*J*(HH) = 7	
	7.11, t(1)	*J*(HH) = 7	
	6.61, d(1)	*J*(HH) = 7	
	1.35, m(2)		CH_2
	1.17, d(9)	*J*(PH) = 5	*cis* PMe_3
	1.03, t(18)	*J*(PH) = 3	*trans* PMe_3
	0.93, d(9)	*J*(PH) = 5	*cis* PMe_3
mer-$RuH(BH_4)$-$(PMe_3)_3$	6.1—4.5, m(2)		BH_4
	1.31, t(18)	*J*(PH) = 3	*trans* PMe_3
	1.08, d(9)	*J*(PH) = 8	*cis* PMe_3
	−6.1 to −9.6, m(1)		μ-H, *trans* to H
	−8.7 to −9.6, m(1)		μ-H, *trans* to PMe_3
	−15.46, d of t(1)	*J*(PH) = 33, 24	Ru–H
cis-$RuHMe(PMe_3)_4$	1.29, t(18)	*J*(PH) = 3	*trans* PMe_3
	1.22, d(9)	*J*(PH) = 5	*cis* PMe_3
	−0.24, d of d(3)	*J*(PH) = 9, 8, 5	Me
	−9.80, d of d(1)	*J*(PH) = 91, 31, 9	H
[*cis*-$RuMe(PMe_3)_4]_2$-$Hg\cdot$thf	1.50, t(36)	*J*(PH) = 2	*trans* PMe_3
	1.34, d(18)	*J*(PH) = 5	*cis* PMe_3, *trans* to Me
	1.19, s(18)		*cis* PMe_3, *trans* to Hg
	−0.27, m(6)		Me
[*cis*-RuMe-$(PMe_3)_4]_2Hg$	1.50, t(36)	*J*(PH) = 2	*trans* PMe_3
	1.33, d(18)	*J*(PH) = 5	*cis* PMe_3, *trans* to Me
	1.19, t(18)	*J*(PH) = 2	*cis* PMe_3, *trans* to Hg
	−0.27, m(6)		Me
$[(Me_3P)_3Ru(\mu\text{-}Cl)_3$-$Ru(PMe_3)_3]BF_4$ [b]	1.33—1.47, m		PMe_3

[a] In C_6D_6 solvent referenced to $SiMe_4$ (δ 0.0), 250 MHz. [b] In CD_3CN.

vacuum. The residue was extracted with toluene (2 × 30 cm^3) and filtered. Concentration of the filtrate to 20 cm^3 and cooling to −20 °C yielded 0.17 g (38%) of the known compound.[5]

(o-Methylenephenyl-C′C^{α}*)tetrakis(trimethylphosphine)-ruthenium*(II).—(*a*) A 0.93 mol dm^{-3} solution of $Mg(CH_2Ph)Cl$ in Et_2O (0.7 cm^3, 0.7 mmol) was added to a stirred solution of *cis*-$RuClMe(PMe_3)_4$ (0.28 g, 0.6 mmol) in Et_2O (40 cm^3). A white precipitate formed immediately. After 1 h the Et_2O was removed under vacuum and the residue extracted with light petroleum (2 × 40 cm^3). The filtered solution was concentrated to about 10 cm^3, then cooled to −20 °C to give white *prisms* which were washed with cold (0 °C) light petroleum (1 cm^3) and dried *in vacuo*. Yield: 0.18 g, 59%.

(*b*) To a suspension of *trans*-$RuCl_2(PMe_3)_4$ (2.27 g, 4.76 mmol) in Et_2O (80 cm^3) was added a 0.93 mol dm^{-3} solution of $Mg(CH_2Ph)Cl$ (11.0 cm^3, 10.2 mmol) in Et_2O. The mixture was stirred until all orange material had reacted (*ca.* 4 h), then filtered, and the Et_2O removed under vacuum. The residue was extracted with toluene (2 × 50 cm^3) and filtered. Concentration of the filtrate to 20 cm^3 and recrystallization at −20 °C yielded white prisms which were washed with cold (0 °C) light petroleum (2 cm^3), then dried *in vacuo*. Yield (two crops): 1.24 g, 53%. I.r.: 1 295 m, 1 278m, 1 261w, 940s, 854m, 805w, 725m, 702w, and 660m cm^{-1}. The solid darkens in air in a few seconds. The product also may be synthesized from $[Ru(\mu\text{-}Cl)(PMe_3)_4]_2Cl_2$ by the same procedure, with similar results.

mer-*Hydrido(tetrahydroborato-HH′)tris(trimethylphosphine)-ruthenium*(II).—(*a*) A solution of *cis*-$RuClMe(PMe_3)_4$ (1.01 g, 2.22 mmol) in Et_2O (100 cm^3) was stirred with $LiBH_4$ (0.1 g, 5 mmol) for *ca.* 15 h. The Et_2O was removed under vacuum and the residue extracted with toluene (2 × 20 cm^3). The extracts were filtered, concentrated to 5 cm^3, and cooled to −20 °C to give yellow *prisms* which were washed with light petroleum (2 × 1 cm^3) and dried *in vacuo*. Yield (two crops): 0.17 g, 92%.

(*b*) The compound *trans*-$RuCl_2(PMe_3)_4$ (0.63 g, 1.32 mmol) and $LiBH_4$ (0.7 g, 30 mmol) in Et_2O (40 cm^3) were stirred for *ca.* 15 h. The Et_2O was removed under vacuum and the residue extracted with toluene (2 × 30 cm^3), which was filtered, concentrated to about 10 cm^3, and cooled to −20 °C. The resulting yellow prisms were washed with light petroleum (2 × 1 cm^3) and dried *in vacuo*. Yield (two crops): 0.36 g, 79%. I.r.: 2 383s, 2 369s, 2 318s, 1 932s, 1 422m, 1 352s, 1 295m, 1 278s, 1 274s, 1 183s, 938s, 879m, 853m, 844m, 716s, 691w, 666s, 572w, 411w, and 350w cm^{-1}. In air the solid darkens after several seconds and solutions are extremely air sensitive.

Table 7. $^{31}P-\{^1H\}$ N.m.r. data

Compound	δ/p.p.m.[a]	*J*/Hz	Assignment
cis-$RuClMe(PMe_3)_4$	14.9, t of d	*J*(PP) = 34, 18	*cis* PMe_3, *trans* to Cl
	−5.8, d of d	*J*(PP) = 34, 24	*trans* PMe_3
	−16.3, t of d	*J*(PP) = 24, 18	*cis* PMe_3, *trans* to Me
cis-$Ru(O_2CMe)Me(PMe_3)_4$	18.2, t of d	*J*(PP) = 36, 21	*cis* PMe_3, *trans* to O_2CMe
	−13.7, t of d	*J*(PP) = 21, 21	*cis* PMe_3, *trans* to Me
$(Me_3P)_4\overline{RuCH_2C}_6H_4$	−5.6, d of d	*J*(PP) = 27, 27	*trans* PMe_3
	−10.4, t of d	*J*(PP) = 27, 13	*cis* PMe_3
	−10.7, t of d	*J*(PP) = 27, 13	*cis* PMe_3
mer-$RuH(BH_4)(PMe_3)_3$	18.0, t	*J*(PP) = 34	*cis* PMe_3
	1.2, d	*J*(PP) = 34	*trans* PMe_3
cis-$RuHMe(PMe_3)_4$	0.1, d of d	*J*(PP) = 26, 25	*trans* PMe_3
	−6.9, t of d	*J*(PP) = 26, 21	*cis* PMe_3, *trans* to Me [b]
	−11.2, t of d [c]	*J*(PP) = 25, 21	*cis* PMe_3, *trans* to H [b]
[*cis*-$RuMe(PMe_3)_4]_2Hg\cdot$thf	12.1, t (1 : 10 : 1)	*J*(HgP) = 780	*cis* PMe_3, *trans* to Hg
	−6.2, t (1 : 10 : 1) of d	*J*(HgP) = 341, *J*(PP) = 31	*trans* PMe_3
	−12.8, t	*J*(PP) = 31	*cis* PMe_3, *trans* to Me
$[(Me_3P)_3Ru(\mu-Cl)_3Ru(PMe_3)_3]BF_4$ [e]	22.6, s		PMe_3

[a] In C_6D_6, referenced to external 85% H_3PO_4 (δ 0.0), 101 MHz. [b] These assignments may be reversed. [c] When ^1H-decoupled from −5 to +5 p.p.m. only, the resonance appears as a doublet of doublets, *J*(PH) = 90 Hz. [d] See Table 4 for *J*(PP) values. [e] In CD_3CN.

Table 8. Selected $^{13}C-\{^1H\}$ n.m.r. data

Compound	δ/p.p.m. [a]	*J*(PC)/Hz	Assignment
$(Me_3P)_4\overline{RuCH_2C}_6H_4$	138.0, s		CH_2-C' (phenyl)
	124.1, s		phenyl C
	122.9, s		
	120.2, s		
	26.1, d of m	12	*cis* PMe_3 (*trans* to C)
	24.5, d of m	14	
	19.7, t of t	13, 4	*trans* PMe_3 (*cis* to C)
	−3.5, d of q	51, 8	CH_2
$(Me_3P)_4\overline{RuCH_2C}_6H_4$ [b]	138.6, s		CH_2-C' (phenyl)
	128.3, d of q	20, 5	Ru–C(Ph)
	124.0, s		phenyl C
	122.8, s		
	122.6, s		
	120.0, s		
	20.0, t	13	*trans* PMe_3 (*cis* to C)
	−3.5, d of m	56	CH_2
[*cis*-$RuMe(PMe_3)_4]_2$-Hg	29.5, d	15	*cis* PMe_3 [$P_{B,\ C}$ in structure (1)]
	26.2, t	5.5	*trans* PMe_3 [P_A in (1)]
	−12.7, d of d	46, 10, 6	Me

[a] In C_6D_6, referenced to $SiMe_4$ (δ 0.0), 22.5 MHz. [b] In $[^2H_8]$thf.

cis-*Hydridomethyltetrakis*(*trimethylphosphine*)*ruthenium*(II).—(*a*) To a stirred solution of *cis*-$RuClH(PMe_3)_4$ (0.10 g, 0.23 mmol) in Et_2O (30 cm^3) was added a 0.64 mol dm^{-3} ether solution of MgMeCl (0.4 cm^3, 0.25 mol). A white precipitate slowly formed. The mixture was stirred for 2 h, then the Et_2O was removed under vacuum. The residue was extracted with light petroleum (2 × 15 cm^3), which was filtered, concentrated to 1 cm^3, and cooled to −20 °C to give white *crystals*. These were isolated and dried *in vacuo*. Yield: 0.06 g, 58%.

(*b*) A solution of *cis*-$RuClMe(PMe_3)_4$ (0.88 g, 1.91 mmol) in thf (50 cm^3) was added to a suspension of NaOMe (0.17 g, 3.2 mmol) in thf (50 cm^3). The mixture was stirred at ambient temperature for 1 week. The thf was removed under vacuum and the residue was extracted with light petroleum (2 × 20 cm^3). The extracts were filtered, concentrated to 5 cm^3, and cooled to −20 °C, producing pale yellow prisms which were dried *in vacuo*. Yield (two crops): 0.59 g, 73%. I.r.: 1 810s, 1 421m, 1 292s, 1 275s, 1 021w, 938s, 852m, 699m, and 660s cm^{-1}.

Tri-μ-chloro-bis[*tris*(*trimethylphosphine*)*ruthenium*(II)] *Tetrafluoroborate*.—Protected from direct light, a solution of $AgBF_4$ (0.52 g, 2.67 mmol) in thf (50 cm^3) was added to a solution of *cis*-$RuClMe(PMe_3)_4$ (1.19 g, 2.67 mmol) in thf (50 cm^3). A white precipitate formed immediately. The reaction mixture was stirred for 2 h then filtered and the solution dried to a pale yellow solid under vacuum. The residue was extracted with MeOH (50 cm^3), the extract concentrated to about 30 cm^3 and cooled to −20 °C, giving pale yellow *prisms* which were washed with Et_2O (5 cm^3), then with light petroleum (5 cm^3), and dried *in vacuo*. Yield (two crops): 0.45 g, 40%. I.r.: 1 304s, 1 287s, 1 098m, 1 061s, 1 040m, 968s, 948s, 857m, 844w, 723s, 670m, 523w, and 377w cm^{-1}. Λ_M = 87.2 Ω^{-1} m^{-1}. ^{19}F N.m.r. (CD_3CN): δ −150.02 (s, br, 1 F) and −150.07 (q, 1 : 1 : 1 : 1, 4 F). The product is stable in air for several days. It is insoluble in light petroleum, toluene, and Et_2O, only slightly soluble in thf, but soluble in MeOH and MeCN.

Bis[cis-*methyltetrakis*(*trimethylphosphine*)*ruthenio*]*mercury*(II)-*Tetrahydrofuran*(1/1).—A solution of *cis*-$RuClMe(PMe_3)_4$ (0.72 g, 1.6 mmol) in thf (50 cm^3) was added to 1% sodium amalgam (40 g) and stirred for 2 d, when it was decanted from the Hg and the thf removed under vacuum. The residue was extracted with light petroleum (2 × 30 cm^3) which was filtered and concentrated to *ca.* 10 cm^3. The orange-brown solution was cooled to −20 °C, producing dark orange *prisms*, which were washed with cold (0 °C) light petroleum (1 cm^3) and dried *in vacuo*. Yield (three crops): 0.73 g, 83%. I.r.: 2 810w, 1 422m, 1 291s, 1 271s, 1 264m, 1 173w, 933s, 848s, 838s, 707m, 690s, 664s, 651s, 442w, and 367w; in $(Cl_2CCClF)_n$, 2 972m, 2 914s, 2 810w, 1 418m, and 705m cm^{-1}. The solid is extremely air sensitive, releasing free phosphine as it decomposes. It is very soluble in light petroleum, toluene, and ethers.

Table 9. Crystal data, intensity data collection, and refinement

(*a*) Crystal data			
Formula	$RuH(BH_4)(PMe_3)_3$	$[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]BF_4$	$[cis\text{-}RuMe(PMe_3)_4]_2Hg\cdot thf$
M	344.8	850.3	1 113.54
Crystal system	Triclinic	Monoclinic	Triclinic
a/Å	9.603(2)	15.224(2)	14.232(1)
b/Å	12.566(2)	9.706(3)	9.326(1)
c/Å	8.572(2)	13.135(2)	18.728(4)
α/°	91.11(2)	—	90.34(1)
β/°	117.43(2)	111.90(1)	89.08(1)
γ/°	75.30(1)	—	104.21(1)
U/Å^3	882.3	1 800.9	2 409.1
Space group	$P\bar{1}$	$P2/n$	$P\bar{1}$
Z	2	2 *	2
D_c/g cm^{-3}	1.30	1.57	1.53
F(000)	374	740	1 188
μ/cm^{-1}	10.27	8.85	38.80
(*b*) Data collection			
Total data	3 412	3 624	5 566
Total unique	3 102	3 174	5 154
Total observed ($F_o > 3\sigma F_o$)	2 910	2 585	4 564
(*c*) Refinement			
No. of parameters	255	156	661
Weight applied	Unit weights	$1/[\sigma^2(F) + 0.000\,25F^2]$	$1/[\sigma^2(F) + 0.0002F^2]$
R	0.0235	0.0481	0.0289
R'	0.0235	0.0526	0.0316

* Cation thus has C_2 symmetry.

Table 10. Atom co-ordinates (× 10^4) for $RuH(BH_4)(PMe_3)_4$

Atom	x	y	z
Ru	4 841(0.5)	2 519(0.5)	4 609(0.5)
P(1)	2 124(1)	3 466(1)	3 501(1)
C(11)	1 325(6)	3 293(4)	5 019(7)
C(12)	626(5)	3 061(5)	1 511(7)
C(13)	1 479(6)	4 980(3)	3 047(7)
P(2)	4 893(1)	2 658(1)	2 014(1)
C(21)	6 843(6)	2 714(6)	2 203(7)
C(22)	3 605(6)	3 928(4)	513(6)
C(23)	4 366(8)	1 623(5)	480(7)
P(3)	7 341(1)	1 224(1)	6 072(1)
C(31)	9 220(5)	1 650(5)	6 998(8)
C(32)	7 834(6)	27(4)	4 991(7)
C(33)	7 561(6)	503(4)	8 040(7)
B	5 441(6)	3 461(4)	6 969(6)

Bis[cis-*methyltetrakis*(*trimethylphosphine*)*ruthenio*]*mercury*(II).—Using *cis*-$RuClMe(PMe_3)_4$ (0.53 g, 1.16 mmol) in toluene (50 cm^3), the above procedure was repeated. Yield: 0.044 g, 72%. I.r.: 2 801w, 1 421m, 1 292s, 1 271s, 1 117w, 935s, 848s, 837m, 705w, 689s, 662s, 651s, 445w, and 364w cm^{-1}; in $(Cl_2CCClF)_n$, 2 971m, 2 910s, 2 805w, 1 418m, and 708m cm^{-1}.

Table 11. Atom co-ordinates (× 10^4) for $[(Me_3P)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_3]BF_4$

Atom	x	y	z
Ru(1)	2 329(0.5)	8 247(1)	−1 341(0.5)
P(1)	3 345(1)	7 153(2)	148(2)
C(11)	3 255(7)	5 252(9)	63(8)
C(12)	4 584(6)	7 412(11)	383(8)
C(13)	3 384(8)	7 479(11)	1 551(7)
P(2)	1 005(1)	7 332(2)	−1 234(2)
C(21)	−35(6)	8 462(10)	−1 798(9)
C(22)	889(7)	6 847(11)	53(8)
C(23)	624(7)	5 762(10)	−2 040(9)
P(3)	2 269(1)	10 200(2)	−449(2)
C(31)	3 424(7)	11 020(10)	235(9)
C(32)	1 610(9)	11 596(9)	−1 311(10)
C(33)	1 795(9)	10 226(11)	677(9)
Cl(1)	3 625(1)	9 232(2)	−1 838(2)
Cl(2)	2 500	6 352(3)	−2 500
B	0	6 138(13)	0
F(11)	−2 183(10)	6 678(12)	−3 179(11)
F(12)	−1 765(9)	5 313(12)	−2 022(10)
F(21)	−1 837(14)	6 242(17)	−1 335(15)
F(22)	−2 708(13)	7 461(16)	−2 323(15)
F(31)	−3 360(18)	5 928(20)	−2 562(19)
F(32)	−2 258(18)	4 733(19)	−2 497(20)

Crystallography.—The structures of the three compounds were determined using routine methods with intensity data collected in the ω—2θ scan mode at 295 K on a CAD 4 diffractometer using Mo-K_α radiation.[20] Details of the crystal data, intensity recording, and refinements are given in Table 9. All intensity data were corrected for absorption.[26] Final atomic co-ordinates are given in Tables 10—12. For the borohydride and mercury compounds all hydrogen-atom positions were experimentally determined and refined freely with isotropic thermal parameters. No hydrogen atoms were included for the BF_4^- salt, where anion disorder has resulted in a less accurate structure analysis. The disorder of the anion, which sits on a two-fold axis, is quite complex, and could not easily be modelled in terms of interlocking tetrahedra. The most stable refinement was obtained by including partial F atoms at the sites of the major electron-density peaks, and adjusting the partial occupancies such that (*a*) all isotropic thermal parameters refined to broadly similar values and (*b*) the occupancies summed to *ca.* 2. Details of the values obtained are given in SUP 23951.

Table 12. Atom co-ordinates (× 10^4) for [*cis*-RuMe(PMe_3)$_4$]$_2$Hg

Atom	*x*	*y*	*z*
Hg	8 143(0.5)	3 866(0.5)	2 758(0.5)
Ru(1)	7 012(1)	1 932(0.5)	3 146(0.5)
P(1)	8 685(2)	1 638(1)	2 296(1)
C(11)	10 605(8)	2 359(6)	2 328(5)
C(12)	9 083(9)	421(6)	2 216(5)
C(13)	8 358(10)	1 794(6)	1 357(4)
P(2)	5 620(2)	2 655(1)	3 910(1)
C(21)	4 340(9)	1 933(6)	4 592(5)
C(22)	6 562(8)	3 644(6)	4 517(4)
C(23)	4 273(8)	3 243(6)	3 526(5)
P(3)	8 597(2)	1 780(2)	4 057(1)
C(31)	9 709(9)	866(6)	3 998(5)
C(32)	10 077(8)	2 828(6)	4 329(5)
C(33)	7 840(9)	1 381(6)	4 957(4)
P(4)	5 469(2)	388(2)	3 126(1)
C(41)	5 692(11)	−584(6)	3 703(6)
C(42)	5 275(10)	−328(7)	2 291(5)
C(43)	3 490(8)	278(7)	3 248(7)
C(1)	5 494(8)	2 089(6)	2 263(5)
Ru(2)	9 218(1)	5 683	2 143
P(5)	10 930(2)	5 782(1)	3 046(1)
C(51)	12 174(8)	4 968(6)	3 016(5)
C(52)	10 294(8)	5 511(6)	3 974(4)
C(53)	12 306(8)	6 932(6)	3 250(5)
P(6)	7 214(2)	5 147(1)	1 365(1)
C(61)	5 378(8)	4 703(7)	1 714(5)
C(62)	7 203(9)	4 160(6)	751(5)
C(63)	6 665(10)	5 935(7)	705(5)
P(7)	7 930(2)	6 589(1)	2 804(1)
C(71)	8 899(9)	7 618(6)	3 362(5)
C(72)	6 558(9)	6 020(6)	3 466(5)
C(73)	6 764(9)	7 247(6)	2 334(5)
P(8)	10 656(2)	6 929(2)	1 471(1)
C(81)	12 621(9)	6 937(7)	1 354(5)
C(82)	10 983(11)	8 209(6)	1 717(6)
C(83)	10 308(10)	7 056(8)	532(5)
C(2)	10 362(8)	4 802(5)	1 472(4)
O(1a)	6 850(12)	8 174(9)	−621(7)
C(1a)	5 729(15)	8 296(12)	−79(10)
C(2a)	6 347(15)	8 921(12)	443(10)
C(3a)	7 678(15)	9 586(12)	−41(10)
C(4a)	7 646(15)	9 200(12)	−703(10)

Acknowledgements

We thank the National Science Foundation for a NATO Postdoctoral Fellowship and the Ramsay Memorial Trust for an honorary fellowship (to J. A. S.). We also thank Johnson Matthey PLC for a loan of ruthenium trichloride and the S.E.R.C. for the *X*-ray facility.

References

1 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1963, 6017.
2 J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.
3 D. J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 797.
4 R. A. Porter and D. F. Shriver, *J. Organomet. Chem.*, 1975, **90**, 41.
5 R. A. Andersen, R. A. Jones, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 446.
6 R. A. Jones, F. Mayor Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 551.
7 R. A. Jones, G. Wilkinson, I. J. Colquohoun, W. McFarlane, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1980, 2480.
8 R. H. Crabtree and A. J. Pearman, *J. Organomet. Chem.*, 1978, **157**, 335.
9 D. J. Holah, A. N. Hughes, B. C. Hui, and C. T. Kan, *J. Catal.*, 1977, **48**, 340.
10 J. B. Letts, T. J. Mazanec, and D. W. Meek, *Organometallics*, 1983, **2**, 695; J. B. Letts, T. J. Mazanec, and D. W. Meek, *J. Am. Chem. Soc.*, 1982, **104**, 3898; T. J. Mazanec, J. B. Letts, and D. H. Meek, *J. Chem. Soc., Chem. Commun.*, 1982, 356.
11 J. L. Atwood, W. E. Hunter, E. Carmona Guzman, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 467.
12 B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 1546.
13 K. G. Srinivasamurthy, N. M. Nanji Gowda, and G. K. N. Reddy, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1977.
14 P. W. Armir and T. A. Stephenson, *J. Organomet. Chem.*, 1973, **57**, C80.
15 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.
16 N. W. Alcock and K. A. Raspin, *J. Chem. Soc., Dalton Trans.*, 1982, 2108.
17 R. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 1968, 1981.
18 L. W. Gosser, W. H. Knoth, and G. W. Parshall, *J. Am. Chem. Soc.*, 1973, **95**, 3436.
19 T. W. Ashworth, M. J. Nolte, and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1977, 936.
20 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
21 S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 1971, 2874.
22 T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 2931.
23 R. D. Fischer, A. Volger, and K. Noack, *J. Organomet. Chem.*, 1967, **7**, 135.
24 D. Sellmann and E. Bohlen, *Z. Naturforsch., Teil B*, 1982, **37**, 1026.
25 H. V. Brown and C. J. Shoaf, *J. Am. Chem. Soc.*, 1968, **86**, 1079.
26 A. C. T. North, D. C. Phillips, and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

Received 26*th October* 1983; *Paper* 3/1907