Further Chemistry of Tris(μ-methylene)-hexakis(trimethylphosphine)-diruthenium(III). Synthesis and *X*-Ray Crystal Structures of Bis[bis(μ-methylene)-tetrakis(trimethylphosphine)ruthenium(III)]ruthenium(IV)-(*Ru–Ru–Ru*) Bis(tetrafluoroborate), Tris(μ-hydroxo)-hexakis(trimethylphosphine)diruthenium(II) Tetrafluoroborate, and Tricarbonylbis(trimethylphosphine)ruthenium(0) †

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Further chemistry of the triple methylene ($-CH_2-$) bridged compound $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ and its derivatives is described. The compounds $[(Me_3P)_4Ru(\mu\text{-}CH_2)_2Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_4][BF_4]_2$, (1), and $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6][BF_4]$, (2), have been isolated from the interaction of aqueous fluoroboric acid with a red oil obtained during the synthesis of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$. Interaction of carbon monoxide (5 atm) with $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ gives *trans*-$Ru(PMe_3)_2(CO)_3$, (3). The compounds have been studied by i.r. and n.m.r. (^1H and ^{31}P) spectroscopy and their *X*-ray structures have been determined.

Compound (1) is monoclinic, space group *C2/c*, with $a = 32.793$, $b = 9.578$, $c = 19.821$ Å, $\beta = 123.36°$, and $Z = 4$. The structure was solved *via* the heavy-atom method and refined to an *R* of 0.055 using 4 036 diffractometer data with $F_o > 3\sigma(F_o)$. The cation is a linear trinuclear species with the Ru atoms linked by bridging methylenes and Ru–Ru bonds [Ru–Ru = 2.637(1) Å]. The central Ru^{IV} atom is tetrahedral with Ru–C bond lengths of 1.98(1) Å whilst the terminal Ru^{III} atoms are octahedral with two Ru–C distances of 2.09(1) Å, two Ru–P distances at 2.391, 2.402(3) Å and two at 2.424, 2.427(3) Å. Compound (2) is monoclinic, space group *P2/n*, with $a = 15.075$, $b = 9.771$, $c = 12.709$ Å, $\beta = 109.9°$, and $Z = 2$. The structure was refined to an *R* of 0.052 using 2 583 data with $F_o > 4\sigma(F_o)$. The cation is dinuclear with three Ru(μ-OH)Ru bridges [Ru–O 2.134—2.144(3) Å] and no metal–metal bond [Ru ··· Ru = 3.004(1) Å]. The Ru–P distances are short, at 2.231—2.234(2) Å, and imply strong Ru $\longrightarrow$ P π back bonding. Compound (3) is a monomeric Ru^0 species with *trans* axial phosphines [Ru–P = 2.334, 2.345(1) Å] and equatorial carbonyls [Ru–C = 1.877, 1.905(4) Å]. Crystals are orthorhombic, space group *Pnma*, with $a = 10.253$, $b = 10.650$, $c = 14.045$ Å, and $Z = 4$. The structure was solved by heavy-atom methods and refined to an *R* of 0.043 using 1 757 data with $F_o > 3\sigma(F_o)$.

THE synthesis, characterisation, and *X*-ray structure determinations of the triple methylene-bridged complex $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ and its mono- and di-cationic derivatives, $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ and $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$, have been reported.[1]

The neutral compound $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ readily loses the $-CH_2-$ bridge groups in a number of reactions. Here we describe reactions with Ph_3CBF_4 and CO; in a future paper we will describe reactions with H_2 and H_2O.

In the synthesis of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ by the interaction of $[Ru_3O(O_2CMe)_6(OH_2)_3][CO_2Me]$ with dimethylmagnesium and trimethylphosphine, a red oil was also obtained. Although we have been unable to crystallise or properly characterise this material it has been found to react with aqueous fluoroboric acid in tetrahydrofuran to yield two products that can be readily crystallised, namely, $[(Me_3P)_4Ru(\mu\text{-}CH_2)_2Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_4][BF_4]_2$, (1) and $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6][BF_4]$, (2).

The interaction of the di- and mono-cationic derivatives of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ with LiMe gives stepwise addition of CH_3 bridging groups and α-hydrogen elimination respectively. The catalytic activity of some of the complexes is also noted. Spectroscopic (^1H and ^{31}P n.m.r.) data are collected in Table 1.

TABLE 1

Hydrogen-1 and $^{31}P\{^1H\}$ nuclear magnetic resonance data

Compound	^1H δ Values [a]	Assignment	$^{31}P\{^1H\}$ δ Values [b]
$[(Me_3P)_4Ru(\mu\text{-}CH_2)_2Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_4][BF_4]_2$	6.67 (t,[c] 8 H)	$\mu\text{-}CH_2$	-11.6 [t, $^2J(^{31}P-^{31}P) = 32.7$ Hz]
	2.65 (m, 72 H)	PMe_3	-23.4 [t, $^2J(^{31}P-^{31}P) = 32.9$ Hz]
$[Ru_2(\mu\text{-}OH)_3(PMe_3)_6][BF_4]$	2.45 (m)	PMe_3	36.56 (s) [d]
			32.08 (s)
trans-$Ru(PMe_3)_2(CO)_3$	1.65 (t) [e]	PMe_3	1.31 (s) [f]

[a] In $[^2H_3]$nitromethane as solvent with $SiMe_4$ as internal reference (δ 0.0), at 90 MHz, 35 °C. Relative intensity in parentheses. [b] In nitromethane + 10% $[^2H_6]$benzene and referenced to external 85% H_3PO_4 (δ 0.0), at 90 MHz, 35 °C. [c] $^3J(^{31}P-^1H) = 12.6$ Hz. [d] See text. [e] In $[^2H_6]$acetone, a 1 : 1 : 1 triplet, $J(^{31}P-^1H) = 2.3$ Hz. [f] In $[^2H_6]$benzene.

RESULTS AND DISCUSSION

1. *Interaction of Red Oil with Fluoroboric Acid.*—The interaction of $[Ru_3O(O_2CMe)_6(OH_2)_3][CO_2Me]$ with PMe_3 and $MgMe_2$ gives *ca.* 30% of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$[1] and 25% of *cis*-$RuMe_2(PMe_3)_4$.[2] The remaining deep red oily material contains much ruthenium and on interaction with an excess of aqueous fluoroboric acid in

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† No reprints available.

tetrahydrofuran (thf) there is rapid evolution of methane; after *ca.* 10 min a precipitate is formed which consists of a mixture of $[\mathrm{Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6}][\mathrm{BF_4}]$ and $[\mathrm{Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6}][\mathrm{BF_4}]_2$ [1] (in *ca.* 10% yield), both of which were previously obtained by protonation of $\mathrm{Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6}$. On stirring the residual dark orange tetrahydrofuran solution, containing an excess of fluoroboric acid for several hours, an orange precipitate is obtained. Crystallisation of the latter from methanol yields a mixture of dark red (1) and white (2) crystalline compounds.

(a) *Bis[bis(μ-methylene)-tetrakis(trimethylphosphine)-ruthenium*(III)*]ruthenium*(IV) *bis(tetrafluoroborate).* $[(\mathrm{Me_3P})_4\mathrm{Ru(\mu\text{-}CH_2)_2Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_4}][\mathrm{BF_4}]_2$,(1). The red crystalline substance (1) has bridging methylene units [broad triplet δ 6.67, ^3J(P–H) = 12.6 Hz] according to the ^{1}H n.m.r. spectrum and the ^{31}P n.m.r. spectrum, analysis, and conductivity are in accord with the structure determined by *X*-ray crystallography.

The dication, which has C_2 symmetry, comprises three metal atoms arranged in an almost linear fashion, with Ru ··· Ru ··· Ru = 179.3(1)°. The cation geometry is illustrated in Figure 1, and some important bond lengths and angles are listed in Table 2. Each pair of metal atoms is bridged by two $\mathrm{CH_2}$ groups. The central Ru atom is formally co-ordinated only by the four bridging $\mathrm{CH_2}$ groups and has a tetrahedral geometry; the outer Ru atoms are octahedral with bonds to two $\mathrm{CH_2}$ groups and four phosphines. However, the Ru ··· Ru distances of 2.637(1) Å, the C–Ru–C angle of 103.0(5)°, and the Ru–C–Ru angles of 80.7(4)° are indicative of metal–metal interactions. This raises questions concerning the nature of the metal–metal bonding and which formal oxidation states can be assigned to the metals.

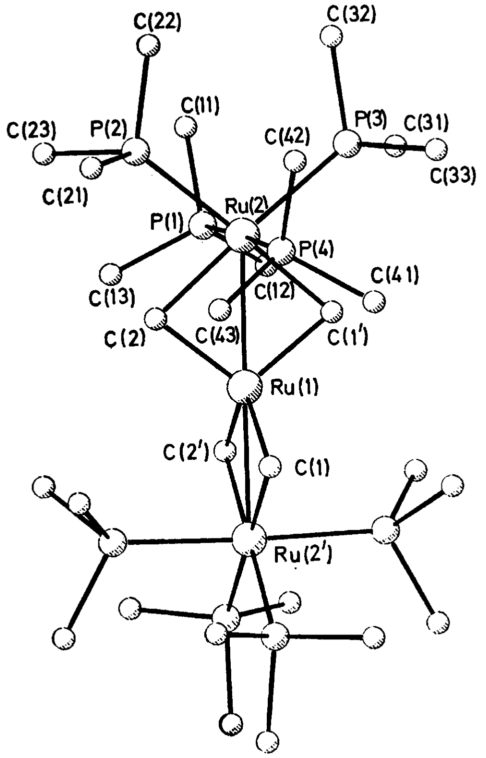


FIGURE 1 The molecular structure of $[\mathrm{Ru_3(CH_2)_4(PMe_3)_8}]^{2+}$ showing the atom-numbering scheme. The hydrogen atoms have been omitted. Primed atoms are related to unprimed atoms by a two-fold axis

TABLE 2

Interatomic distances and interbond angles for (1) * with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Ru(1)–Ru(2)	2.637(1)	P(1)–C(11)	1.852(13)
Ru(1)–C(1)	1.979(12)	P(1)–C(12)	1.831(13)
Ru(1)–C(2)	1.983(8)	P(1)–C(13)	1.848(12)
Ru(2)–C(1)	2.094(12)	P(2)–C(21)	1.846(16)
Ru(2)–C(2)	2.087(12)	P(2)–C(22)	1.840(11)
Ru(2)–P(1)	2.391(3)	P(2)–C(23)	1.841(12)
Ru(2)–P(2)	2.427(2)	P(3)–C(31)	1.836(16)
Ru(2)–P(3)	2.424(3)	P(3)–C(32)	1.834(11)
Ru(2)–P(4)	2.402(3)	P(3)–C(33)	1.849(13)
		P(4)–C(41)	1.835(10)
		P(4)–C(42)	1.872(10)
		P(4)–C(43)	1.839(16)

(*b*) Bond angles (°)

C(1)–Ru(1)–Ru(2)	127.9(2)	P(1)–Ru(2)–P(2)	90.9(1)
C(2)–Ru(1)–Ru(2)	51.4(3)	P(1)–Ru(2)–P(3)	90.1(1)
C(1)–Ru(1)–C(2)	111.6(5)	P(1)–Ru(2)–P(4)	177.6(1)
C(1)–Ru(1)–C(2′)	103.0(5)	P(2)–Ru(2)–P(3)	102.2(1)
Ru(1)–C(1)–Ru(2′)	80.7(4)	P(2)–Ru(2)–P(4)	90.3(1)
Ru(1)–C(2)–Ru(2′)	80.7(4)	P(3)–Ru(2)–P(4)	91.7(1)
Ru(1)–Ru(2)–P(1)	88.5(1)		
Ru(1)–Ru(2)–P(2)	129.4(1)	C(2)–Ru(2)–P(1)	89.1(3)
Ru(1)–Ru(2)–P(3)	128.4(1)	C(2)–Ru(2)–P(2)	81.5(2)
Ru(1)–Ru(2)–P(4)	89.1(1)	C(2)–Ru(2)–P(3)	176.2(2)
		C(2)–Ru(2)–P(4)	89.0(3)
Ru(2)–P(1)–C(11)	116.7(4)	C(11)–P(1)–C(12)	100.2(7)
Ru(2)–P(1)–C(12)	119.8(4)	C(11)–P(1)–C(13)	101.7(6)
Ru(2)–P(1)–C(13)	118.9(6)	C(12)–P(1)–C(13)	95.7(6)
Ru(2)–P(2)–C(21)	117.9(4)	C(21)–P(2)–C(22)	99.1(6)
Ru(2)–P(2)–C(22)	120.9(5)	C(21)–P(2)–C(23)	98.0(7)
Ru(2)–P(2)–C(23)	117.9(4)	C(22)–P(2)–C(23)	98.7(7)
Ru(2)–P(3)–C(31)	117.9(4)	C(31)–P(3)–C(32)	96.6(7)
Ru(2)–P(3)–C(32)	122.5(6)	C(31)–P(3)–C(33)	96.6(8)
Ru(2)–P(3)–C(33)	118.6(7)	C(32)–P(3)–C(33)	99.5(7)
Ru(2)–P(4)–C(41)	118.6(4)	C(41)–P(4)–C(42)	101.0(5)
Ru(2)–P(4)–C(42)	116.7(5)	C(41)–P(4)–C(43)	96.5(6)
Ru(2)–P(4)–C(43)	118.7(5)	C(42)–P(4)–C(43)	101.7(6)

* Individual geometry parameters are not quoted for the $\mathrm{BF_4}$ anions which are highly disordered. The range of B–F distances is 1.02(9)—1.43(7) Å.

Naturally, a proper molecular orbital (m.o.) treatment of the bonding would be desirable, but we can consider simple valence-bond models.

Considering the four $\mathrm{CH_2}$ groups and the overall 2+ charge, the formal oxidation states of the three metal atoms must add to ten. The differences between the Ru–C bond lengths suggest that the central Ru atom $\mathrm{Ru_c}$–C = 1.98, 1.98(1) Å has a higher oxidation state than the outer atoms [$\mathrm{Ru_o}$–C = 2.09, 2.09 (1) Å]. If we assume that the two outer $\mathrm{Ru_o}$ atoms, which are crystallographically and stereochemically equivalent, are also electronically equivalent, then we can devise two possible arrangements, namely $\mathrm{Ru^{III}}$–$\mathrm{Ru^{IV}}$–$\mathrm{Ru^{III}}$ and $\mathrm{Ru^{II}}$–$\mathrm{Ru^{VI}}$–$\mathrm{Ru^{II}}$. Intuitively, the latter can be rejected since the oxidation-state differences are too large. Both models, however, have paramagnetic ($\mathrm{Ru^{III}}$ or $\mathrm{Ru^{VI}}$) and diamagnetic ($\mathrm{Ru^{II}}$ or $\mathrm{Ru^{IV}}$) moieties neighbouring each other, a situation not at first sight conducive to metal–metal bonding, although in $[Ru_2(O_2CMe)_4]Cl$ which formally contains Ru^{II} and Ru^{III}, and is paramagnetic[3] with three unpaired electrons,[3a] there are equivalent metal atoms with a Ru–Ru bond of order 2.5.[3b]

If we take the former arrangement Ru^{III}–Ru^{IV}–Ru^{III} without metal–metal interactions and count electrons we have a 17e–12e–17e arrangement. If we assume that the half-filled t_{2g} orbital on each octahedral Ru_o atom lies in the equatorial plane (*i.e.* containing the two bridging methylenes) these can σ interact with, say, an empty d_{z^2} orbital on Ru_c to produce a three-centre two-electron system. The two Ru–Ru interactions have bond order $\frac{1}{2}$ and the electron count is now 18e–14e–18e. A π-type interaction between a filled t_{2g} orbital on each Ru_o atom with the mutually orthogonal, empty d_{xz}, d_{yz} orbitals on Ru_c gives a final Ru–Ru bond order of 1.5, for each interaction, an 18e–18e–18e system, and, with the remaining four non-bonding *d* electrons on Ru_c spin paired in d_{xy}, $d_{x^2-y^2}$, a diamagnetic system. Whilst this interpretation is based on formalisms it produces an explanation of the diamagnetism and an indication as to how the orbitals may be ordered and combined in an m.o. approach. That the model is a reasonable indication of the bonding situation is supported by the structural data. The differences between the Ru–C bond lengths for Ru_o and Ru_c indicate an oxidation-state difference of about one. The Ru–Ru distances indicate a bond order of at least one (*cf.* ref. 1). Furthermore, the Ru–P distances, which show differences for the axial [2.391, 2.402(3) Å] and equatorial [2.424, 2.427(3) Å], are relatively long compared with those of $(Me_3P)_3Ru(CH_2)_3Ru(PMe_3)_3$ and related species,[1] and indicate reduced Ru $\rightarrow$ P back bonding. This would support the proposal that some of the *d* electrons on Ru_o are also involved in Ru–Ru π bonding.

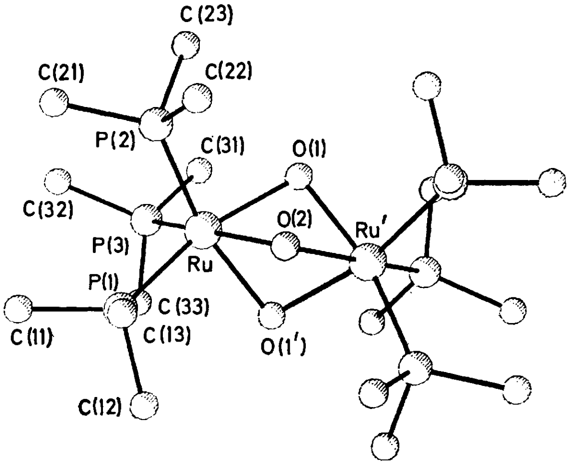


FIGURE 2 The structure of the $[Ru_2(OH)_3(PMe_3)_6]^+$ cation showing the atom-numbering scheme in the asymmetric unit. Primed atoms are related to unprimed atoms by a two-fold axis

(b) *Tris*(μ-*hydroxo*)-*hexakis*(*trimethylphosphine*)*diruthenium*(II) *tetrafluoroborate*, (2), $[(Me_3P)_3Ru(\mu\text{-}OH)_3Ru(PMe_3)_3][BF_4]$. Analytical and spectroscopic data for the white crystalline material show that it is the compound designated above. It has also been obtained[1] from the interaction of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ with an excess of Ph_3CBF_4 in thf (see later). On the initial crystallisation from methanol the compound appears orange but this colour disappears after several recrystallisations.

The i.r. spectrum of the diamagnetic complex showed only a very weak peak (3 610 cm^{-1}) assigned to μ-OH. Although the (μ-OH) ^1H n.m.r. resonance in other hydroxo-bridged complexes of ruthenium(II) was observed at *ca.* δ —2.5 to —3.5,[4] hydroxo-resonances have not been clearly identified in our complex and they could be obscured by PMe_3 resonances.

The $^{31}P\{^1H\}$ n.m.r. spectrum shows two sharp, intense lines (separation *ca.* 181 Hz); the region between them contains many weaker lines in a complex pattern. We have not attempted a detailed analysis.

A diagram of the cation $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6]^+$ is given in Figure 2, and the bond lengths and angles in Table 3.

TABLE 3

Interatomic distances and angles for the ion $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6]^+$ in (2) [a]

(*a*) Bond lengths (Å)

Ru–O(1)	2.142(2)	P(1)–C(11)	1.835(8)
Ru–O(1′)	2.144(2) [b]	P(1)–C(12)	1.821(8)
Ru–O(2)	2.134(3)	P(1)–C(13)	1.800(10)
Ru–P(1)	2.232(2)	P(2)–C(21)	1.823(8)
Ru–P(2)	2.234(2)	P(2)–C(22)	1.819(9)
Ru–P(3)	2.231(2)	P(2)–C(23)	1.823(8)
		P(3)–C(31)	1.829(10)
Ru · · · Ru′	3.004(1)	P(3)–C(32)	1.836(8)
		P(3)–C(33)	1.825(8)

(*b*) Bond angles (°)

Ru–O(1)–Ru′	89.0(2)	O(1)–Ru–O(2)	76.3(1)
Ru–O(2)–Ru′	89.5(2)	O(1)–Ru–O(1′)	75.9(2)
P(1)–Ru–O(1)	165.6(1)	P(3)–Ru–O(1)	93.4(1)
P(1)–Ru–O(1′)	93.2(1)	P(3)–Ru–O(1′)	93.0(1)
P(1)–Ru–O(2)	92.0(1)	P(3)–Ru–O(2)	166.6(1)
P(2)–Ru–O(1)	92.6(1)	P(1)–Ru–P(2)	96.6(1)
P(2)–Ru–O(1′)	166.0(1)	P(1)–Ru–P(3)	96.6(1)
P(2)–Ru–O(2)	93.5(1)	P(2)–Ru–P(3)	95.7(1)
Ru–P(1)–C(11)	124.4(3)	C(11)–P(1)–C(12)	100.3(5)
Ru–P(1)–C(12)	111.7(3)	C(11)–P(1)–C(13)	103.3(5)
Ru–P(1)–C(13)	113.4(3)	C(12)–P(1)–C(13)	100.6(6)
Ru–P(2)–C(21)	126.5(3)	C(21)–P(2)–C(22)	100.8(5)
Ru–P(2)–C(22)	112.0(3)	C(21)–P(2)–C(23)	101.8(4)
Ru–P(2)–C(23)	111.2(3)	C(22)–P(2)–C(23)	101.2(5)
Ru–P(3)–C(31)	110.8(3)	C(31)–P(3)–C(32)	101.9(6)
Ru–P(3)–C(32)	124.5(4)	C(31)–P(3)–C(33)	101.6(6)
Ru–P(3)–C(33)	113.0(4)	C(32)–P(3)–C(33)	102.2(5)

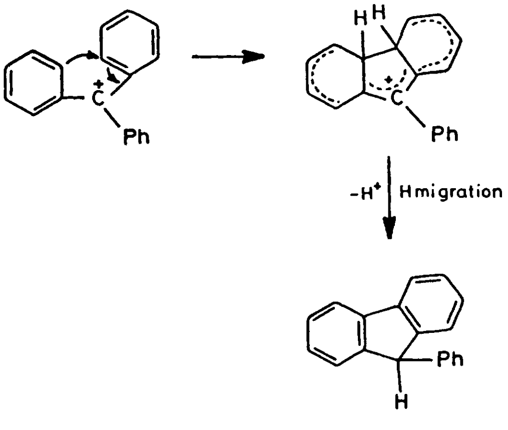
[a] Individual geometry parameters are not quoted for the BF_4 anion, which is highly disordered. The range of B–F distances is 1.26(4)—1.47(3) Å. [b] The primed atom is related to the unprimed one by the two-fold axis at $\frac{1}{4}$, y, $\frac{1}{4}$.

It has a crystallographic two-fold axis passing through one bridging hydroxo-oxygen atom and bisecting the Ru–Ru vector. Although the Ru–O distances to the unique oxygen atom, 2.134(3) Å, are slightly shorter than those to the other oxygen atoms, 2.142, 2.144(2) Å, the differences are barely significant, and we consider all bridging groups to be chemically equivalent. Their assignment as hydroxo-groups could not be confirmed by the *X*-ray study, since no hydrogen atoms could be found on the oxygens, but is based on i.r. evidence and other considerations. The original starting material, $[Ru_2$-

$(CH_2)_3(PMe_3)_6]$, is a Ru^{III} species, with a Ru–Ru bond in addition to the bridges. In the early stages of our analysis of (2), we considered it to be $[Ru^{III}_2(OH)(O)_2(PMe_3)_6]^+BF_4^-$ which would also be a Ru^{III} species and directly analogous to the compound $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$.[1] In fact (2) is essentially isostructural with this compound in which the cation also has a metal–metal bond. However, in (2) the cation shows a Ru $\cdots$ Ru distance of 3.004(1) Å and Ru–O–Ru bridge angles of *ca.* 89°, compared with corresponding parameters of 2.732(2) Å and *ca.* 81° in the methyl/methylene bridged species. Furthermore, all geometric parameters for the cation in (2) correspond very closely to those in the analogous Ru^{II} species $[Ru_2(OH)_3(PMe_2Ph)_6]^+$, studied as the BPh_4^- salt.[4] In particular the Ru–P distances in (2), *ca.* 2.232(2) Å, compared with 2.28 Å in the dimethylphenylphosphine complex. Both sets of values are lower than those for the ruthenium(III) parent compounds [1] and this in fact contradicts normal relationships between oxidation states and bond lengths. However, we could explain this in terms of increased Ru $\longrightarrow$ P π bonding for the Ru^{II} 18-e systems.

2. *Reactions of* $Ru_2(CH_2)_3(PMe_3)_6$.—(a) *With trityl tetrafluoroborate.* The interaction of one equivalent of Ph_3CBF_4 with $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ in thf yields the cationic species $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ and with two or more equivalents $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$ is obtained.[1]

We first assumed that the initial protonation was due to the breakdown of tetrahydrofuran.[1] However, we have since repeated the reaction in $[^2H_8]$thf and instead of forming a CH_2D bridged cation we obtained protonated $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$.[1] The only other likely source of the proton in the reaction mixture could be the Ph_3C^+ groups. This now seems most probable since it has been shown recently that pure Ph_3CClO_4 decomposes *in vacuo* at room temperature giving 9-phenylfluorene [see (1) below].[5]



(1)

In our system the H^+ could be rapidly transferred onto a CH_2 bridge. The remaining thf solution contains a mixture of compounds which we have not attempted to separate. However, if a large excess of Ph_3CBF_4 in only a small volume of thf is used, a thick yellow slurry is obtained, from which the triple-hydroxo-bridged compound (2) described above can be isolated in moderate yield.

The hydroxo-bridges formed in this case doubtless come from breakdown of the thf solvent and care must be taken in the work-up to prevent polymerisation of the solvent.

(b) *With carbon monoxide.* The compound $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ does not react with CO at 1 atm * (room temperature, 30 min), but at 5 atm (60 °C) after several hours in benzene or toluene, light orange solutions are obtained from which we have been able to isolate only *trans*-$Ru(PMe_3)_2(CO)_3$, (3), as large, colourless air-stable prisms. An intractable orange tar remains. The fate of the $-CH_2-$ bridges is unknown and no methane could be detected (mass spectroscopy) in the residual gases.

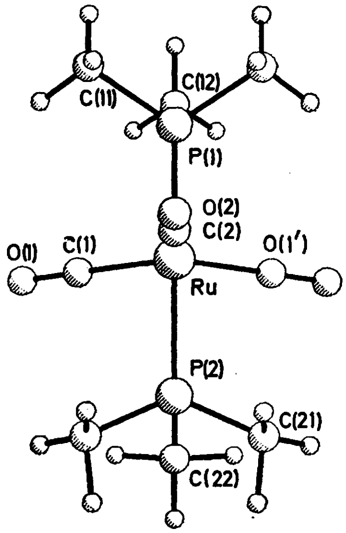


FIGURE 3 The molecular structure of $Ru(PMe_3)_2(CO)_3$ showing the atom-numbering scheme. The smallest circles represent the hydrogen atoms and are not numbered

In the i.r. spectrum *trans*-$Ru(PMe_3)_2(CO)_3$ has a single intense band at 1 885 cm^{-1} [for the PPh_3 analogue, $\nu(CO) = 1\,895\ cm^{-1}$].[6] The data are consistent with the structure as determined by *X*-ray diffraction.

The compound (3) (Figure 3) has a trigonal-bipyramidal structure with equatorial CO groups and *trans* axial PMe_3 groups, and is analogous to the corresponding ruthenium [6] and osmium [7] triphenylphosphine compounds $M(CO)_3(PPh_3)_2$. The molecule has crystallographic mirror symmetry but the geometry is close to D_3. Thus, the independent Ru–P bond lengths (Table 4), are 2.334, 2.345(1) Å, the Ru–C distances 1.877, 1.905(6) Å, the equatorial C–Ru–C angles are 119.2(3) and 120.4(1)°, and the six C–P–C angles in the phosphines lie within the small range 100.5(4)—104.7(7)°. These deviations from three-fold symmetry are probably due to intermolecular packing effects since there are no short ($\leqslant$3.56 Å) intramolecular contacts. In fact the PMe_3 and $Ru(CO)_3$ fragments adopt a mutually staggered

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* Throughout this paper: 1 atm = 101 325 Pa.

arrangement as shown in Figure 4, which minimises interligand repulsions.

3. *Interaction of* $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ *and* $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$ *with Methyl-lithium*.—We have previously noted that the interaction of $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ with LiMe in thf smoothly reforms the neutral triple methylene-bridged complex.[1] Other bases (LiR; R = Bu^t or Bu^n) react similarly. Virtually no reaction takes place in diethyl ether as solvent even after several days.

TABLE 4

Interatomic distances and angles for $Ru(PMe_3)_2(CO)_3$, (3)

(*a*) Bond lengths (Å)

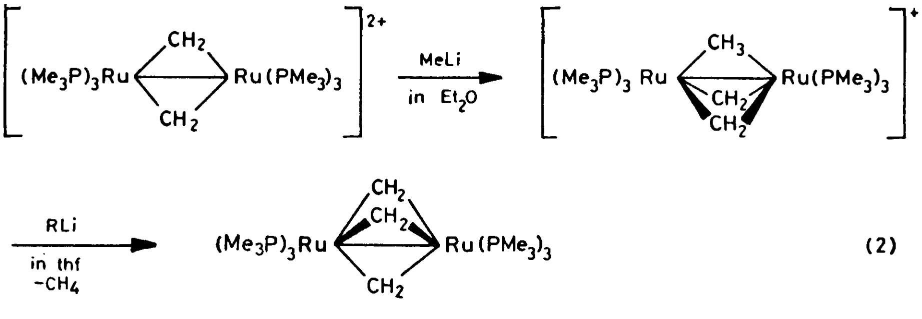
Ru–P(1)	2.345(1)	P(1)–C(11)	1.822(5)
Ru–P(2)	2.334(1)	P(1)–C(12)	1.845(9)
Ru–C(5)	1.905(4)	P(2)–C(21)	1.794(6)
Ru–C(6)	1.877(6)	P(2)–C(22)	1.829(8)
C(1)–O(1)	1.144(5)		
C(2)–O(2)	1.142(8)		

(*b*) Bond angles (°)

P(1)–Ru–P(2)	178.1(1)	Ru–C(1)–O(1)	179.4(4)
P(1)–Ru–C(1)	91.0(1)	Ru–C(2)–O(2)	178.6(7)
P(1)–Ru–C(2)	88.1(2)	Ru–P(1)–C(11)	115.6(2)
P(2)–Ru–C(1)	89.9(1)	Ru–P(1)–C(12)	117.0(3)
P(2)–Ru–C(2)	90.0(2)	C(11)–P(1)–C(12)	101.1(3)
C(1)–Ru–C(2)	120.4(1)	C(11)–P(1)–C(11′)	104.1(4)
C(1)–Ru–C(1′)	119.2(3)	Ru–P(2)–C(21)	116.5(3)
		Ru–P(2)–C(22)	115.6(3)
		C(21)–P(2)–C(22)	100.5(4)
		C(21)–P(2)–C(21′)	104.7(7)

A μ-methyl unit can be added to the 2+ salt $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$ by reaction with an excess of LiMe in diethyl ether thus giving the mono-cation $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$. Using thf as solvent for this step, a rapid reaction takes place and an oily red petroleum-soluble material is obtained.

This stepwise methylation and α-hydrogen abstraction could represent the process by which the original neutral methylene-bridged compound is formed. The second stage [equation (2)] is analogous to the α-hydrogen abstraction from $[TaMe_2(C_5H_5)_2]^+$ giving a terminal methylene unit [equation (3)].[8]



(2)

$$[TaMe_2(C_5H_5)_2]^+ \xrightarrow{MeO^-} TaMe(CH_2)(C_5H_5)_2 \qquad (3)$$

4. *Catalytic Studies*.—The compound $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ showed inappreciable activity for hydrogenation of hex-1-ene (3 atm, 60 °C, 24 h) although small amounts of hexane (6%) and *cis* + *trans* hex-2-ene (20%) were detected. Under these conditions a ruthenium hydride complex, which will be described in a subsequent paper, is formed. With hex-1-ene and H_2 + CO (1 : 1) (5 atm, 60 °C, 24 h) in benzene, $Ru(PMe_3)_2(CO)_3$ is formed in good yield and no heptaldehydes were detected. There was no reaction with hex-1-ene alone either under reflux (4 days) or with u.v. irradiation.

Both the mono- and di-cations $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$ and $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$ catalyse the hydrogenation of hex-1-ene in methanol, giving good yields of hexane (90%) at room temperature after several hours. Under these conditions both salts give the same monocationic hydride species which will be described separately.

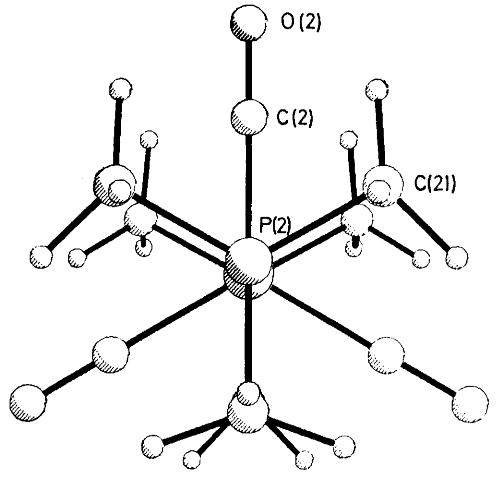


FIGURE 4 View of the $Ru(PMe_3)_2(CO)_3$ molecule showing the staggering of the $Ru(CO)_3$ and PMe_3 groups

EXPERIMENTAL

Microanalyses were by Pascher (Bonn) and Imperial College laboratories. The spectrometers used were as follows: Perkin-Elmer R12B and R32 (^1H n.m.r.), Varian XL-100 (^1H, ^{13}C, and ^{31}P n.m.r., Fourier transform), and Perkin-Elmer P.E. 597 (i.r.). All operations were performed under oxygen-free nitrogen or argon, or *in vacuo*. Diethyl ether, tetrahydrofuran, and light petroleum (b.p. 40—60 °C) were dried over sodium–benzophenone and distilled under nitrogen before use. Nitromethane was dried over

4A-molecular sieves before use. Methanol was dried over magnesium methoxide and distilled under nitrogen. Conductivity data was obtained on a Mullard Conductivity Bridge type E7566/3 with a matching conductivity cell. Melting points (uncorrected) were determined in sealed capillaries under nitrogen.

1. *Bis[bis(μ-methylene)-tetrakis(trimethylphosphine)ruthenium*(III)*]ruthenium*(IV)(Ru–Ru–Ru)*Bis(tetrafluoroborate)*, (1), *and Tris(μ-hydroxo)-hexakis(trimethylphosphine)diruthenium*(II) *Tetrafluoroborate*, (2).—The red solution remaining after the crystallisation of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$[1] was evaporated *in vacuo* yielding a red oily material. This material (2 g) was dissolved in thf (30 cm) and HBF_4 (5 cm^3, 40% aqueous) in thf (20 cm^3) was added at room temperature. Rapid gas evolution occurred and an orange-red precipitate was formed. Hydrogen-1 n.m.r. spectroscopy showed this to be a mixture of $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ and $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$.[1] The solution was filtered and stirred for a further 3 h (ambient temperature), yielding an orange precipitate which was collected and washed with thf (3 × 25 cm^3) and dried *in vacuo*. Methanol (30 cm^3) was added and the solution warmed briefly (50 °C), to dissolve most of the solid, filtered, evaporated (to *ca.* 5 cm^3), and cooled (−20 °C). The mixture of pale orange and dark red crystals was recrystallised twice more from methanol, dried *in vacuo*, and separated by handpicking.

TABLE 5

Crystal data and details of structure analyses

Formula	$[Ru(CH_2)_4\{Ru(PMe_3)_4\}_2][BF_4]_2$	$[Ru_2(OH)_3(PMe_3)_6][BF_4]$	$Ru(PMe_3)_2(CO)_3$
(*a*) Crystal data	(1)	(2)	(3)
M	1 141.6	794 4	337.3
Crystal system	Monoclinic	Monoclinic	Orthorhombic
a/Å	32.793(5)	15.075(3)	10.253(2)
b/Å	9.578(1)	9.771(1)	10.650(1)
c/Å	19.821(4)	12.709(2)	14.045(1)
α/°	90	90	90
β/°	123.36(1)	109.89(1)	90
γ/°	90	90	90
U/Å^3	5 199.3	1 760.3	1 533.6
Space group	$C2/c$ (no. 15)	$P2/n$ (no. 13)	$Pnma$ (no. 62)
Z	4	2	4
D_c/g cm^{-3}	1.46	1.50	1.46
$F(000)$	2 328	816	680
μ(Mo-K_α)/cm^{-1}	10.4	11.1	11.6
(*b*) Data collection			
Crystal size/mm	0.63 × 0.3 × 0.13	0.30 × 0.30 × 0.22	0.28 × 0.15 × 0.12
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 27	1.5, 27	1.5, 30
Scan width parameters A, B in width = $A + B \tan \theta$	0.8, 0.15	0.75, 0.25	0.80, 0.35
Horizontal aperture parameters, A, B in aperture = $A + B \tan \theta$	4.0, 0.0	4.0, 0.0	4.0, 0.0
Total data	6 309	4 333	4 985
Total unique data	5 656	4 032	2 344
Observed data	4 036	2 583	1 757
Significant test	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$
(*c*) Refinement			
No. of parameters	307	224	108
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + gF_o^2]$	(unit weights)	0.000 8	0.000 65
Final $R = \Sigma\Delta F/\Sigma\lvert F_o\rvert$	0.055	0.052	0.043
$R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.066	0.055	0.052

Dark red crystals of (1). Yield 50 mg, m.p. 260—280 °C (decomp.), darkens at *ca.* 180 °C (Found: C, 29.2; H, 7.2; P, 21.1. $C_{28}H_{80}B_2F_8P_8Ru_3$ requires C, 29.4; H, 7.0; P, 21.7%). I.r. (cm^{-1}, KBr disc); 2 960m, 2 900m, 2 810w, 1 424m, 1 345w, 1 302m, 1 282m, 1 095s(br), 1 050s(br), 1 030s(br), 940s(br), 845m, 716m, 665m, 530w, 519w, 504w, 455w, 432w, 385w, 364m, and 300m.

White crystals of (2). Yield 0.5 g. This compound was also prepared from Ph_3CBF_4 and $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ in thf as follows. A mixture of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ (0.30 g, 0.43 mmol) and Ph_3CBF_4 (0.75 g, 2.5 mmol) was stirred with thf (2 cm^3) so that a thick paste was formed. After *ca.* 15 min, more thf (15 cm^3) was added and the mixture stirred for a further 30 min. The yellow-orange precipitate was collected and washed with thf (3 × 50 cm^3) and dried *in vacuo*. It was recrystallised twice from methanol at −20 °C giving off-white prisms which were collected and dried *in vacuo*. Yield, 0.2 g, 58% (Found: C, 27.2; H, 6.9; P, 24.1. $C_{18}H_{57}BF_4O_3P_6Ru_2$ requires C, 27.1; H, 7.2; P, 23.4%). Conductivity Λ = 86 ohm^{-1} cm^2 mol^{-1} in $MeNO_2$, 10^{-3} mol dm^{-3}, 25 °C. M.p. 290—310 °C (decomp.). I.r. (cm^{-1}, Nujol mull); 3 610w, 1 430m, 1 424m, 1 415m, 1 305s, 1 300s, 1 283s, 1 277s, 1 098s(br), 1 055s(br), 940s(br), 852s, 839m, 745w, 725s, 715s, 655s, 520m, 433m, 389m, 375m, and 368m.

2. trans-*Tricarbonylbis(trimethylphosphine)ruthenium*(0), (3).—The compound $Ru_2(CH_2)_3(PMe_3)_6$ (1.0 g, 1.43 mmol) in toluene (40 cm^3) was heated (60 °C) under CO (5 atm) for 24 h. The solution was cooled to room temperature and the pressure reduced to 1 atm. Volatile material was then removed *in vacuo*, the residue dissolved in toluene (25 cm^3), and the resulting solution filtered. Evaporation (to *ca.* 5 cm^3) and cooling (−20 °C or −78 °C) gave only an orange oily material. However, by warming this to *ca.* 50 °C and further removing solvent *in vacuo*, large white prisms are rapidly formed. These were separated by handpicking and dried *in vacuo*. Yield 0.6 g, 62% (Found: C, 31.6; H, 5.2; P, 19.0. $C_9H_{18}O_3P_2Ru$ requires C, 32.0; H, 5.3; P, 18.4%). I.r. (cm^{-1}, Nujol mull); 1 885vs, 1 417s, 1 306w, 1 290s, 1 110m(br), 945s, 861m, 735m, 678m, 615w, 586s, 491m, and 460s.

3. *Interaction of* LiMe *with* $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ *and* $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$.—(a) *Formation of* $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$ *from* $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$ Methyl-lithium (5.0 cm^3 of a 1.5 mol dm^{-3} Et_2O solution, 7.5 mmol) was added dropwise to a suspension of $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$ (0.5 g, 0.58 mmol) in diethyl ether (40 cm^3) at room temperature and the mixture stirred (1 h). The pink powder was collected, washed with diethyl ether (2 × 50 cm^3), and dried *in vacuo*. The material was recrystallised from methanol as previously described.[1] Yield 0.40 g, 90%. A similar reaction with thf as solvent resulted in the rapid formation of an homogeneous red solution which gave an oily petroleum-soluble material. No compounds have been isolated.

TABLE 6

Fractional co-ordinates (Ru × 10^5, others × 10^4) of the non-hydrogen atoms for compound (1) with estimated standard deviations in parentheses

Atom	x	y	z
Ru(1)	0	872(11)	2 500 *
Ru(2)	9 561(2)	703(7)	35 283(4)
P(1)	1 009(1)	1 881(3)	2 750(1)
P(2)	1 458(1)	1 408(3)	4 760(1)
P(3)	1 560(1)	−1 278(3)	3 465(2)
P(4)	865(1)	−1 736(3)	4 277(1)
C(1)	−491(3)	−1 061(10)	2 531(6)
C(2)	402(3)	1 189(10)	3 505(5)
C(11)	1 629(4)	2 529(13)	3 109(7)
C(12)	771(5)	1 582(13)	1 682(6)
C(13)	675(5)	3 530(11)	2 590(7)
C(21)	1 342(4)	1 211(13)	5 567(6)
C(22)	2 127(4)	1 216(16)	5 371(7)
C(23)	1 424(6)	3 325(12)	4 685(7)
C(31)	1 557(4)	−1 172(13)	2 538(7)
C(32)	2 218(4)	−1 010(16)	4 173(8)
C(33)	1 537(6)	−3 204(13)	3 501(10)
C(41)	568(4)	−3 375(10)	3 759(7)
C(42)	1 439(4)	−2 409(13)	5 195(7)
C(43)	483(4)	−1 393(12)	4 673(6)
B(1)	2 287(10)	5 415(20)	2 360(13)
B(2)	4 338(10)	882(39)	4 112(23)
F(11)	2 394	4 084	2 411
F(12)	2 646	6 087	3 005
F(13)	2 332	6 023	1 818
F(14)	1 806	5 721	2 007
F(21)	4 576	1 280	4 943
F(22)	4 644	−157	4 271
F(23)	4 385	1 776	3 878
F(24)	3 959	361	3 891

* Parameters held invariant due to symmetry requirements.

(b) *Formation of* $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ *from* $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$. Methyl-lithium (5.0 cm^3 of a 1.5 mol dm^{-3} Et_2O solution, 7.5 mmol) was added dropwise to a suspension of $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ (0.5 g, 0.65 mmol) in thf (30 cm^3) at room temperature and the mixture stirred (1 h). Volatile material was removed *in vacuo* and the residue extracted into light petroleum (40 cm^3). The solution was filtered and evaporation (to *ca.* 5 cm^3) and cooling (−20 °C) yielded $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$, 0.36 g, 80%.

Other Reactions.—Reaction of $[Ru_3O(O_2CMe)_6(OH_2)_3][CO_2Me]$ with $MgMe_2$ in the presence of an excess of pyridine or C_6Me_6 under similar conditions to those used for the preparation of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ yielded dark red thf-soluble materials (insoluble in light petroleum) and no pure compounds could be isolated. With $MgEt_2$ instead of $MgMe_2$ a dark red petroleum-soluble oily material was obtained although no pure compounds could be obtained. Interactions of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ with an excess of $OEt_2{\cdot}BF_3$ in diethyl ether gave the dication $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]$ [1] quantitatively.

Although we were unable to isolate any pure compounds both $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ and $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ form carbonyl-containing species (i.r. evidence) with loss of $-CH_2-$ (and $-CH_3$) bridges (n.m.r. evidence) when warmed in methanol (60 °C) for *ca.* 10 h.

Crystallographic Studies.—Crystals of compounds (1), (2), and (3) were sealed under nitrogen in Lindemann capillaries. Unit-cell and crystal orientation data were obtained using the SEARCH and INDEX routines on a Nonius CAD4 diffractometer and accurate cell parameters by least-squares refinement of setting angles for 25 automatically centred, high-angle reflections. The Laue groups were confirmed by comparison of symmetry related intensities and space groups assigned on the basis of systematic absences indicated by the lists of processed intensity data [only absences due to lattice centering in (1) were omitted during data collection]. The crystal data and details of data collection are given in Table 5.

The intensity data were recorded in a manner described, in detail, previously;[1] control reflections showed only statistical fluctuations in diffracting power of the crystals. All data were corrected for Lorentz and polarisation effects but not for absorption.

The structures of compounds (1) and (3) were determined from Patterson and difference electron-density syntheses.

TABLE 7

Fractional atomic co-ordinates (Ru × 10^5, others × 10^4) for compound (2)

Atom	x	y	z
Ru	27 009(3)	17 826(4)	14 206(3)
P(1)	1 704(1)	2 803(2)	−92(1)
P(2)	4 016(1)	2 741(2)	1 322(1)
P(3)	2 844(1)	−168(2)	580(2)
O(1)	3 413(2)	991(4)	3 064(3)
O(2)	2 500 [a]	3 333(5)	2 500 [a]
C(11)	1 697(7)	2 533(13)	−1 524(6)
C(12)	481(5)	2 402(14)	−275(8)
C(13)	1 690(9)	2 638(10)	26(9)
C(21)	4 266(6)	3 141(11)	50(8)
C(22)	4 263(7)	4 381(10)	2 041(10)
C(23)	5 057(5)	1 760(11)	2 116(8)
C(31)	3 539(8)	−1 416(9)	1 602(10)
C(32)	3 362(8)	−306(12)	−531(9)
C(33)	1 727(7)	−1 072(12)	−29(10)
B [b]	2 500 [a]	6 159(16)	7 500 [a]
F(1)	1 869(31)	5 088(48)	7 340(35)
F(2)	3 348(28)	5 655(32)	7 791(54)
F(3)	2 210(23)	6 592(32)	8 348(27)
F(4)	2 688(20)	7 302(31)	7 073(21)
F(5)	2 086(48)	6 329(37)	6 282(24)
F(6)	3 155(32)	5 524(95)	8 224(49)
F(7)	2 500 [a]	7 568(28)	7 500 [a]

[a] Parameters held invariant duc to space-group symmetry requirements. [b] Site occupation factors for the atoms in the BF_4^- anion are: B = 0.50, F(1) = 0.34, F(2) = 0.34, F(3) = 0.27, F(4) = 0.27, F(5) = 0.24, F(6) = 0.24, F(7) = 0.15.

For (2), the parameters from the isostructural compound $[Ru_2(CH_2)_2(CH_3)(PMe_3)_6][BF_4]$ [1] were used as a starting set. Refinement by full-matrix, least squares incorporated anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were successfully located and refined isotropically for (3), but only some of the hydrogens could be located for (1) and none at all for (2). We have often found this to be the case with structures containing disordered BF_4 anions, and in fact in structure (1) this disordering is extremely severe.

A summary of the refinement details is given in Table 5. Final lists of atomic co-ordinates are given in Tables 6—8.

TABLE 8

Fractional atomic co-ordinates (Ru × 10^5, others × 10^4) for compound (3)

Atom	*x*	*y*	*z*
Ru	30 642(4)	25 000 [a]	−2 935(2)
P(1)	1 261(2)	25 000 [a]	733(1)
P(2)	4 905(1)	2 500 [a]	−1 272(1)
O(1)	2 188(4)	33(4)	−1 189(3)
O(2)	4 818(8)	2 500	1 432(5)
C(1)	2 512(4)	958(4)	−849(3)
C(2)	4 140(8)	2 500 [a]	787(4)
C(11)	1 132(6)	1 151(5)	1 525(4)
C(12)	−370(8)	2 500 [a]	177(6)
C(21)	5 965(8)	3 834(9)	−1 178(7)
C(22)	2 579(9)	2 500 [a]	−2 552(5)
H(11a) [b]	1 178(104)	381(59)	1 026(52)
H(11b)	142(37)	1 145(94)	1 793(60)
H(11c)	1 933(67)	1 262(92)	2 018(59)
H(12a)	−588(98)	1 809(64)	−363(46)
H(12b)	−1 172(98)	2 500 [a]	675(81)
H(21a)	6 406(88)	3 793(62)	−460(32)
H(21b)	5 546(66)	4 562(42)	−1 625(58)
H(21c)	6 708(66)	3 728(57)	−1 747(53)
H(22a)	4 279(91)	1 550(27)	−2 709(15)
H(22b)	5 531(12)	2 500 [a]	−2 883(9)

[a] See footnote *a* in Table 7. [b] H atoms are numbered according to the parent C atom and distinguished by suffices a—c.

Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22804 (41 pp.).* Computers and programs and sources of scattering-factor data are as given in ref. 1. In all three structures, non-bonded intermolecular contacts conform to normal van der Waals distances.

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

REFERENCES

[1] M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1979, **101**, 4128.

[2] R. A. Andersen, R. A. Jones, and G. Wilkinson, *J.C.S. Dalton*, 1978, 446.

[3] (*a*) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2285; (*b*) J. G. Norman, jun., and H. J. Kolari, *J. Amer. Chem. Soc.*, 1978, **100**, 791; R. J. Clark and M. L. Franks, *J.C.S. Dalton*, 1976, 1825; F. A. Cotton and E. Pederson, *Inorg. Chem.*, 1975, **14**, 388.

[4] T. V. Ashworth, M. J. Nolte, and E. Singleton, *J.C.S. Chem. Comm.*, 1977, 936, and refs. therein.

[5] D. Lloyd, D. J. Walton, J. P. Declercq, G. Germain, and M. Van Meerssche, *J. Chem. Res.* (*S*), 1979, **7**, 249.

[6] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.

[7] J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 419.

[8] R. R. Schrock and R. P. Sharp, *J. Amer. Chem. Soc.*, 1978, **100**, 2389.