Trimethylphosphine Hydrido- and Hydroxo-complexes of Ruthenium. Multinuclear Magnetic Resonance Studies on μ-Hydrido-μ-hydroxo-hexakis(trimethylphosphine)diruthenium(I). Crystal Structures of Di-μ-hydrido-dihydridohexakis(trimethylphosphine)diruthenium(II) and Tri-μ-hydrido-hexakis(trimethylphosphine)diruthenium(II) Tetrafluoroborate †

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The synthesis and characterisation of the following trimethylphosphine stabilised hydride and hydroxo-compounds of ruthenium are reported; $(Me_3P)_3HRu(\mu\text{-}H)_2RuH(PMe_3)_3$, (1), $[Ru_2(\mu\text{-}H)_3(PMe_3)_6][BF_4]$, (2), $Ru_2(\mu\text{-}H)(\mu\text{-}OH)(PMe_3)_6$, *cis*-$RuH_2(PMe_3)_4$, and $Ru_2(OH)_4(PMe_3)_6$. The compounds have been studied by i.r. and n.m.r. (^1H and ^{31}P) spectroscopy; for $Ru_2(\mu\text{-}H)(\mu\text{-}OH)(PMe_3)_6$ a multinuclear n.m.r. study (^1H, ^{13}C, and ^{31}P) has been made.

The structures of $Ru_2H_4(PMe_3)_6$, (1), and $[Ru_2(\mu\text{-}H)_3(PMe_3)_6][BF_4]$, (2), have been determined by single-crystal *X*-ray diffraction methods. Compound (1) is triclinic, space group $P\bar{1}$, with $a = 9.277$, $b = 15.861$, $c = 17.958$ Å, $\alpha = 110.13$, $\beta = 94.59$, $\gamma = 90.61°$, and $Z = 3$. The structure was refined to an R of 0.049 for 7 744 observed reflections measured on a diffractometer. The unit cell contains three molecules, one having crystallographic $\bar{1}$ symmetry, the others lying in symmetry related general positions. The molecular structures of the crystallographically independent molecules are very similar and are probably chemically equivalent, although the hydride atoms were not all located. The Ru–Ru distances are identical, at 2.811(1) Å, and the Ru–P bond lengths show a consistent trend, with those *trans* to the terminal hydrides longer (*ca.* 2.35 Å) than the others (*ca.* 2.23—2.24 Å). Compound (2) is monoclinic, space group $P2/n$, with $a = 15.087$, $b = 9.796$, $c = 12.330$ Å, $\beta = 108°$, and $Z = 2$. The structure was refined to an R of 0.046 for 3 774 observed data. The cation in (2) has C_2 symmetry with one bridging hydride lying on the symmetry axis. The Ru–Ru distance is 2.540(1) Å and the three independent Ru–P lengths are equal at *ca.* 2.265(1) Å. The hydride atoms were all located and refined, giving Ru–H distances of *ca.* 1.9 Å.

ALTHOUGH many triphenylphosphine hydride and hydroxo-complexes of ruthenium are known[1] few stabilised by trimethylphosphine are known. Monomeric $[RuH(PMe_3)_5]^+$ has been reported.[2]

We now describe binuclear neutral and cationic hydrido-complexes obtained by interaction of hydrogen with the neutral triple methylene ($-CH_2-$) bridged complex $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ [3] and its derivatives $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ and $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$. Interaction of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ with water yielded a hydrido-hydroxo-bridged complex $Ru_2(\mu\text{-}H)(\mu\text{-}OH)(PMe_3)_6$ and reduction of either of the acetates $Ru_2(O_2CMe)_4Cl$ or $[Ru_3O(O_2CMe)_6(OH_2)_3][CO_2Me]$ with sodium amalgam in tetrahydrofuran (thf) under hydrogen (3 atm) ‡ in the presence of an excess of PMe_3 yielded *cis*-$RuH_2(PMe_3)_4$. This reacts with water in tetrahydrofuran to give $Ru_2(OH)_4(PMe_3)_6$ in high yield. Nuclear magnetic resonance spectra of the new compounds are collected in Table 1.

RESULTS AND DISCUSSION

(a) *Di-μ-hydrido-dihydridohexakis(trimethylphosphine)diruthenium*(II), (1).—The complex $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ is quantitatively converted to red, crystalline diamagnetic $Ru_2H_4(PMe_3)_6$, (1), by reaction with hydrogen (3 atm) in light petroleum. The binuclear formulation is confirmed by cryoscopic molecular-weight measurements, and i.r. spectra (solution or solid state) show the presence of terminal Ru–H bonds [ν(Ru–H) = 1 872 cm^{-1}, strong, broad]. However, the ^1H n.m.r. spectrum shows three broad Ru–H resonances at δ −3.8, −5.0, and −13.1 (areas *ca.* 1 : 1 : 2). The first two resonances are assigned to terminal Ru–H and the last to bridging Ru–H–Ru units by comparison with $[Ru_2(\mu\text{-}H)_3(PMe_3)_6][BF_4]$ (see later).

The resonances become quite broad on heating (80 °C, PhMe) and sharpen considerably on cooling (−80 °C). The $^{31}P\{^1H\}$ spectrum shows two broad resonances (area *ca.* 1 : 2) and no further information was obtained from selective partial decoupling experiments.

The molecular structure of this complex was confirmed by crystal-structure analysis. The crystallographic unit cell contains a total of three dimer molecules, two in the symmetry related general positions and one sited on a crystallographic centre of symmetry. Apart from the difficulty in locating all the hydride atoms and the disorder in some of the PMe_3 groups (see Experimental

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† No reprints available.

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

section), the structures are very similar indeed, and suggest that the crystallographic differences between the two independent molecules are not paralleled by chemical differences.

TABLE 1

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

Compound	^1H δ values [a]	Assignment	$^{31}P\{^1H\}$ δ values [b]
(1) $(Me_3P)_3HRu(\mu\text{-}H)_2RuH(PMe_3)_3$	−3.8 (br, s, 1)	Ru–*H*	15.23 (br, s, 2)
	−5.0 (br, s, 1)	Ru–*H*	−6.29 (br, s, 1)
	−13.1 (br, s, 2)	$\overset{H}{\mathrm{Ru}{\diagup\!\diagdown}\mathrm{Ru}}$	
	1.3 (br, s, 54)	P*Me*$_3$	
(2) $[Ru_2(\mu\text{-}H)_3(PMe_3)_6][BF_4]$	−11.2 (br, s, 3) [c]	$\overset{H}{\mathrm{Ru}{\diagup\!\diagdown}\mathrm{Ru}}$	13.9 (s) [c]
	1.46 (br, s, 54)	P*Me*$_3$	
(3) $(Me_3P)_3Ru(\mu\text{-}H)(\mu\text{-}OH)Ru(PMe_3)_3$	−9.9 (t of t of t, 1) [d]	$\overset{H}{\mathrm{Ru}{\diagup\!\diagdown}\mathrm{Ru}}$	21.6 (m) (P_A) [d]
	−4.0 (s, 1)	μ-O*H*	6.9 (m) (P_B)
	1.5 (m)	P*Me*$_3$	−19.5 (m) (P_C)
cis-$RuH_2(PMe_3)_4$	−10.1 (m,[d,e] 2)	Ru–*H*	−6.40 (t)
	1.37 (t, 18)	P*Me*$_3$	[^2J(P–P) = 26.1 Hz]
	[^2J(P–H) = 3 Hz]		
	1.27 (d, 18)	P*Me*$_3$	−8.42 (t)
	[^2J(P–H) = 6 Hz]		[^2J(P–P) = 25.8 Hz]
$(Me_3P)_3(OH)Ru(\mu\text{-}OH)_2Ru(OH)(PMe_3)_3$	0.00 −0.06 (s, 4) [f]	O*H*	23.2 (s) (28 °C) [f]
	1.43 (t, 54)	P*Me*$_3$	24.9 (s, 1) 24.4 (s, 2) (−80 °C)

[a] In [$^2H_6$]benzene with $SiMe_4$ internal standard (δ 0.0) at 90 MHz, 35 °C. [b] In benzene–10% [$^2H_6$]benzene and referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz, 28 °C. [c] In [$^2H_3$]nitromethane. [d] See text and Table 4 for coupling constants. [e] See text. [f] In [$^2H_6$]acetone with benzene as internal standard (δ 7.27).

A diagram of one of the molecules is given in Figure 1. Their structure is basically that of two *fac*-RuP_3H_3 octahedra, sharing a common H_2 edge. The two Ru–Ru distances are equal at 2.811(1) Å and the bond lengths and angles involving the RuP_3 units are also very similar between the two molecules, as can be seen in Table 2. In particular, we note that all P–Ru–P angles are in the range 97—100°, implying that the three Ru–H bonds at each metal have almost full stereochemical influence in the metal octahedral geometry. We also note that in each case the bond to the phosphine *trans* to a terminal hydride is lengthened relative to the other two (Δ ≈ 0.11 Å). Although the values found for the Ru–H_t distances in molecule 1 [*i.e.* from Ru(1) and Ru(2)] are subject to considerable experimental errors, they are quite short and imply strong bonding, and so the Ru–P lengthening may be *via* a σ *trans* influence. The distances to the experimentally determined bridging H atoms in molecule 2 [from Ru(3), Ru(3)′] suggest an asymmetric bridge, although the difference is only 3σ. The equality of the two ' equatorial ' Ru–P bonds *trans* to these bridge bonds implies that the difference is indeed not real. This result contrasts with that found for the analogous molybdenum(II) compound,[4] $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$, where an apparently asymmetric Mo–H–Mo bridge system produced significantly different equatorial Mo–P bond lengths.

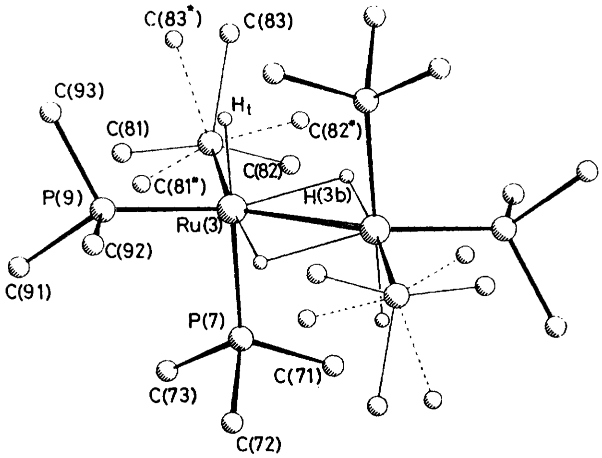


FIGURE 1 The structure of $Ru_2H_4(PMe_3)_6$, (1), as found for the centrosymmetric molecule. Atom H_t has been inserted in an idealised position

(b) *Tri-μ-hydrido-hexakis(trimethylphosphine)diruthenium*(II) *Tetrafluoroborate*, (2).—The complex $Ru_2H_4(PMe_3)_6$ is quantitatively converted to (2), with one equivalent (or an excess) of aqueous tetrafluoroboric acid in thf. This can also be obtained from the interaction of hydrogen (3 atm) with either of the cationic derivatives,[3] $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$ or $Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$ in methanol. Spectroscopic data for this orange, crystalline diamagnetic air-stable salt are consistent with a triple hydride-bridged structure. Thus, there is now no strong terminal Ru–H stretch (i.r.), and in the ^1H n.m.r. there is a singlet (δ −11.2) assigned to μ-H; although rather broad, it is considerably sharper than that at δ −13.1 in $Ru_2H_4(PMe_3)_6$. The $^{31}P\{^1H\}$ spectrum is a sharp, temperature-independent singlet indicating equivalent phosphine groups.

The complex was previously found to be a good hydrogenation catalyst for hex-1-ene.[5]

TABLE 2

Important bond lengths and angles for (1) with estimated standard deviations in parentheses †

(*a*) Bond lengths (Å)

Ru(2)–Ru(1)	2.811(4)	C(33 *)–P(3)	1.869(26)
P(1)–Ru(1)	2.347(4)	C(41)–P(4)	1.868(13)
P(2)–Ru(1)	2.238(4)	C(42)–P(4)	1.834(10)
P(3)–Ru(1)	2.237(4)	C(43)–P(4)	1.882(10)
H(1t)–Ru(1)	1.648(71)	C(51)–P(5)	1.827(21)
P(4)–Ru(2)	2.348(4)	C(51 *)–P(5)	1.839(30)
P(5)–Ru(2)	2.231(4)	C(52)–P(5)	1.801(23)
P(6)–Ru(2)	2.241(4)	C(52 *)–P(5)	1.893(21)
H(2t)–Ru(2)	1.720(51)	C(53)–P(5)	1.893(25)
P(7)–Ru(3)	2.352(3)	C(53 *)–P(5)	1.883(25)
P(8)–Ru(3)	2.232(4)	C(61)–P(6)	1.881(13)
P(9)–Ru(3)	2.237(4)	C(62)–P(6)	1.851(14)
H(3b)–Ru(3)′	1.954(67)	C(63)–P(6)	1.885(14)
Ru(3)–Ru(3)	2.811(4)	C(63 *)–P(6)	1.866(21)
C(11)–P(1)	1.863(10)	C(71)–P(7)	1.838(11)
C(12)–P(1)	1.853(13)	C(72)–P(7)	1.833(10)
C(13)–P(1)	1.880(12)	C(73)–P(7)	1.847(9)
C(21)–P(2)	1.795(17)	C(81)–P(8)	1.821(13)
C(22)–P(2)	1.944(21)	C(81 *)–P(8)	1.950(25)
C(22 *)–P(2)	1.833(23)	C(82)–P(8)	1.901(19)
C(31)–P(3)	1.905(18)	C(82 *)–P(8)	1.809(29)
C(23)–P(2)	1.828(27)	C(83)–P(8)	1.869(19)
C(23 *)–P(2)	1.876(25)	C(83 *)–P(8)	1.843(24)
C(31 *)–P(3)	1.680(37)	C(91)–P(9)	1.853(9)
C(32)–P(3)	1.844(16)	C(92)–P(9)	1.824(11)
C(33)–P(3)	1.787(18)	C(93)–P(9)	1.850(11)

(*b*) Bond angles (°)

P(1)–Ru(1)–Ru(2)	93.0(1)	C(23)–P(2)–Ru(1)	130.6(9)
P(2)–Ru(1)–Ru(2)	130.4(1)	C(23 *)–P(2)–Ru(1)	121.7(9)
P(2)–Ru(1)–P(1)	98.1(2)	C(31)–P(3)–Ru(1)	111.1(5)
P(3)–Ru(1)–Ru(2)	128.6(2)	C(31 *)–P(3)–Ru(1)	115.5(12)
P(3)–Ru(1)–P(1)	99.5(2)	C(32)–P(3)–Ru(1)	116.9(4)
P(3)–Ru(1)–P(2)	97.0(2)	C(33)–P(3)–Ru(1)	124.6(7)
H(1t)–Ru(1)–Ru(2)	80.7(26)	C(33 *)–P(3)–Ru(1)	121.3(8)
H(1t)–Ru(1)–P(1)	167.2(21)	C(41)–P(4)–Ru(2)	115.7(4)
H(1t)–Ru(1)–P(2)	78.0(27)	C(42)–P(4)–Ru(2)	118.4(4)
H(1t)–Ru(1)–P(3)	93.1(22)	C(43)–P(4)–Ru(2)	120.1(5)
P(4)–Ru(2)–Ru(1)	92.9(1)	C(51 *)–P(5)–Ru(2)	116.0(7)
P(5)–Ru(2)–Ru(1)	129.7(1)	C(51 *)–P(5)–Ru(2)	121.1(9)
P(5)–Ru(2)–P(4)	98.2(2)	C(52)–P(5)–Ru(2)	118.0(9)
P(6)–Ru(2)–Ru(1)	128.8(2)	C(52 *)–P(5)–Ru(2)	111.8(9)
P(6)–Ru(2)–P(4)	99.5(2)	C(53)–P(5)–Ru(2)	122.1(9)
P(6)–Ru(2)–P(5)	97.4(2)	C(53 *)–P(5)–Ru(2)	127.2(9)
H(2t)–Ru(2)–Ru(1)	82.6(18)	C(61)–P(6)–Ru(2)	111.1(4)
H(2t)–Ru(2)–P(4)	173.8(14)	C(62)–P(6)–Ru(2)	119.1(4)
H(2t)–Ru(2)–P(5)	81.6(19)	C(63)–P(6)–Ru(2)	124.8(5)
H(2t)–Ru(2)–P(6)	86.7(15)	C(63 *)–P(6)–Ru(2)	123.9(7)
P(8)–Ru(3)–P(7)	97.3(2)	C(71)–P(7)–Ru(3)	118.4(3)
P(9)–Ru(3)–P(7)	100.1(2)	C(72)–P(7)–Ru(3)	116.6(3)
P(9)–Ru(3)–P(8)	97.1(2)	C(73)–P(7)–Ru(3)	119.9(3)
H(3b)–Ru(3)–P(7)	101.9(20)	C(81)–P(8)–Ru(3)	126.2(5)
H(3b)–Ru(3)–P(8)	92.7(19)	C(81 *)–P(8)–Ru(3)	123.3(10)
H(3b)–Ru(3)–P(9)	154.5(19)	C(82)–P(8)–Ru(3)	113.2(5)
C(11)–P(1)–Ru(1)	118.3(4)	C(82 *)–P(8)–Ru(3)	116.1(8)
C(12)–P(1)–Ru(1)	117.6(4)	C(83)–P(8)–Ru(3)	115.2(6)
C(13)–P(1)–Ru(1)	119.3(5)	C(83 *)–P(8)–Ru(3)	115.7(8)
C(21)–P(2)–Ru(1)	119.2(5)	C(91)–P(9)–Ru(3)	124.9(4)
C(22)–P(2)–Ru(1)	110.5(8)	C(93)–P(9)–Ru(3)	117.5(4)
C(22 *)–P(2)–Ru(1)	118.3(9)		

† Primed atoms are related to the corresponding unprimed atoms by the centre of symmetry at ½, ½, ½. Asterisks indicate alternative positions of C atoms due to disorder in the PMe_3 groups.

The structure of this compound was also confirmed by single-crystal *X*-ray structure analysis. A view of the cation structure is shown in Figure 2. It is analogous to those of the cations in the species $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)Ru(PMe_3)_3][BF_4]$[3] and $[(Me_3P)_3Ru(\mu\text{-}OH)_3Ru(PMe_3)_3][BF_4]$,[5] with which (2) is isostructural. The former complex, which is formally a Ru^{III} derivative with a Ru–Ru single bond, has a metal–metal distance of 2.732(1) Å; the hydroxo-compound is a ruthenium(II) compound with no metal–metal interaction and has a Ru–Ru distance of 3.004(1) Å. In (2), which is also formally a ruthenium(II) complex, the Ru–Ru distance is 2.540(1) Å (see Table 3), which is shorter than either of the other two. Clearly the overlap requirements of the three bridges will pull the two metal atoms together, but there is the possibility that the metal atoms might be linked by a double Ru=Ru bond, which would give a formal 18-electron configuration at each metal atom.

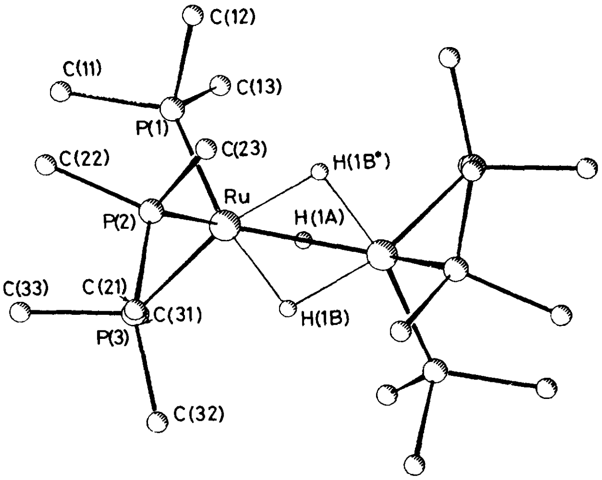


FIGURE 2 The structure of the cation $[Ru_2H_3(PMe_3)_6]^+$ of (2) viewed down the C_2 axis

TABLE 3

Important bond lengths and angles for (2) with estimated standard deviations in parentheses †

(*a*) Bond lengths (Å)

Ru′–Ru	2.540(1)	H(1a)–Ru	1.860(35)
P(1)–Ru	2.269(3)	H(1b)–Ru	1.934(33)
P(2)–Ru	2.262(3)	H(1b′)–Ru	1.933(34)
P(3)–Ru	2.265(3)		

(*b*) Bond angles (°)

H(1b)–Ru–Ru′	48.9(10)	H(1a)–Ru–Ru′	46.9(10)
H(1b)–Ru–P(1)	170.1(9)	H(1a)–Ru–P(1)	92.8(7)
H(1b)–Ru–P(2)	90.5(11)	H(1a)–Ru–P(2)	168.8(10)
H(1b)–Ru–P(3)	92.1(10)	H(1a)–Ru–P(3)	91.6(7)
H(1b)–Ru–H(1a)	81.0(13)	H(1b′)–Ru–Ru′	49.0(9)
P(1)–Ru–Ru′	121.4(1)	H(1b′)–Ru–P(1)	91.9(10)
P(2)–Ru–Ru′	121.9(1)	H(1b′)–Ru–P(2)	90.4(11)
P(2)–Ru–P(1)	94.7(1)	H(1b′)–Ru–P(3)	169.5(9)
P(3)–Ru–Ru′	120.6(1)	H(1b′)–Ru–H(1a)	81.0(13)
P(3)–Ru–P(1)	95.8(1)	H(1b′)–Ru–H(1b)	79.5(17)
P(3)–Ru–P(2)	95.9(2)		

† The primed atoms are related to the unprimed ones by the two-fold axis through ¼, *y*, ¼.

(c) *μ-Hydrido-μ-hydroxo-hexakis(trimethylphosphine)-diruthenium*(I), (3).—When $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ is heated

(60 °C) in light petroleum or thf with an excess of water the red-orange solution becomes paler and a complex of formula $Ru_2(H)(OH)(PMe_3)_6$, (**3**), can be isolated in good yield. The complex forms pale yellow crystals, is diamagnetic and light-petroleum soluble, and decomposes rapidly in air.

The proposed structure, which is based on n.m.r. spectra (see Table 1), has H and OH groups bridging two formally Ru^I atoms linked by a single metal–metal bond (to account for the diamagnetism). Each Ru atom has three stereochemically inequivalent PMe_3 groups. The presence of Ru–H is confirmed by reaction with CCl_4 to give chloroform. The hydroxo-proton is observed as a slightly broadened singlet in the ^1H n.m.r. (δ −4.0). Other ruthenium hydroxo-compounds have high-field shifts for the OH protons,[1] although they were not observed for $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6][BF_4]$.[5]

TABLE 4

Couplings involving the ^{31}P nuclei and the hydride proton in $(Me_3P)_3Ru(\mu\text{-}H)(\mu\text{-}OH)Ru(PMe_3)_3$. All values are in Hz ± 0.3 Hz

$J(P_AP_B)$	37.6	$J(P_AP_B')$	2.1	$J(P_AP_A')$	0
$J(P_BP_B')$	45.8	$J(P_AP_C)$	13.0	$J(P_AP_C')$	0
$J(P_BP_C)$	5.5	$J(P_BP_C')$	0	$J(P_CP_C')$	9.0
$J(P_AH)$	9.5	$J(P_BH)$	45.0	$J(P_CH)$	11.2

The acidic nature of the μ-OH group is shown by rapid exchange with D_2O on shaking in benzene solution.

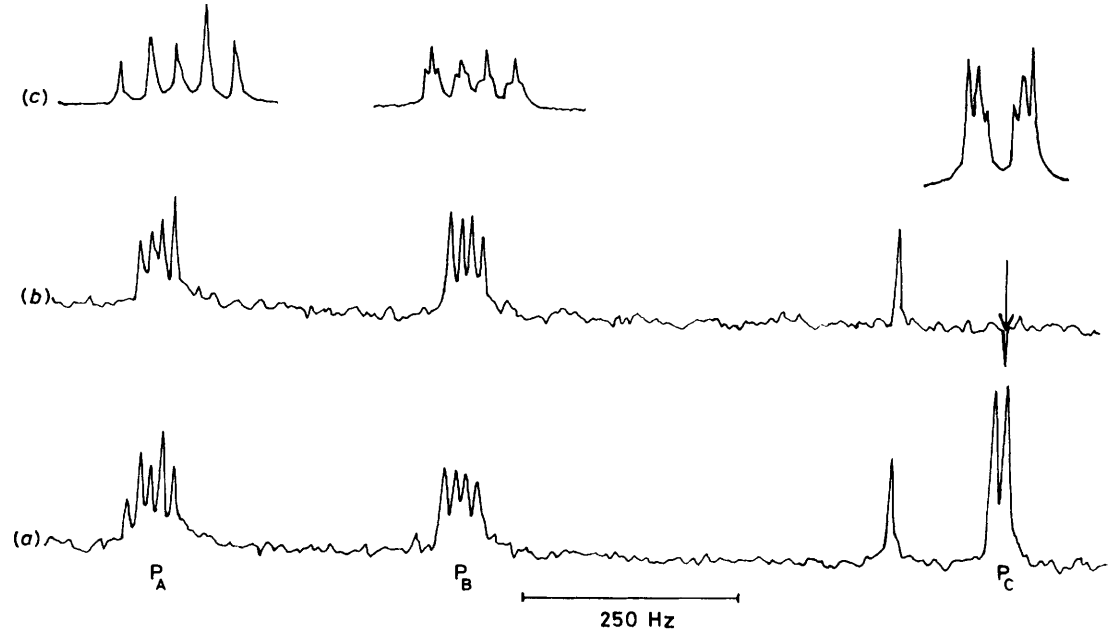
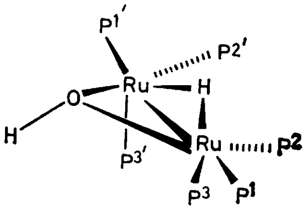


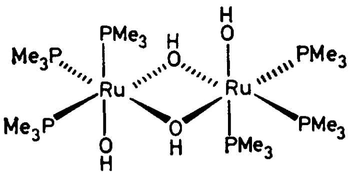
FIGURE 3 Phosphorus-31 n.m.r. spectrum of (**3**). (*a*) Under conditions of complete proton decoupling, (*b*) decoupling of P_c in a homonuclear $^{31}P\{^{31}P, {}^1H_{noise}\}$ experiment, (*c*) high resolution and/or sensitivity fine structure

Nuclear magnetic resonance spectra were temperature independent and analysis was substantially aided by the application of multiple resonance techniques. The data are consistent with a rigid structure (I) in which there is chemical equivalence but magnetic inequivalence between corresponding phosphine nuclei at opposite ends of the molecule. The overall spin system including the hydride proton (but ignoring the OH and $-CH_3$ groups) is AA'KK'MM'X, in which the hydride proton X is related symmetrically to the primed and unprimed sets of nuclei.

(i) *Proton spectra*. The proton spectrum of (**3**) contains three groups of resonances: at δ = 1.5 arising from $P(CH_3)_3$, at δ = −4.0 from the O*H* proton, and at δ = −9.9 from the hydridic proton. This last resonance appeared to consist of a triplet of triplets, but was shown by selective $^1H\{^{31}P\}$ experiments to be a triplet of triplets of triplets as a result of coupling to all three pairs of phosphorus nuclei designated P_A, P_B, P_C, P_A', P_B', P_C'. These selective decoupling experiments also made possible the assignments of the three values of $J(^{31}P\text{–}H)$ in Table 4, and it is especially important to notice that the hydridic proton must be related symmetrically to the two members of each pair of phosphorus nuclei, since in no case is $J(^{31}P\text{–}^{31}P)$ large enough to introduce sufficient deceptive simplicity to give an apparently normal triplet with a 1 : 2 : 1 intensity pattern.



(I)



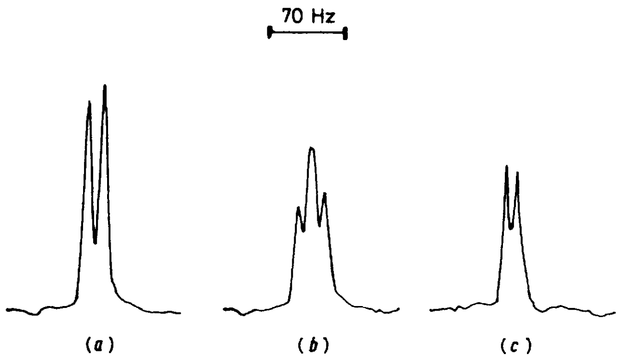
(II)

The CH_3 resonances formed an overlapping set of two doublets arising from the P_A and P_C groups with $^2J(^{31}P\text{–}$

H) = 10 Hz, and a deceptively simple triplet with a broad central component arising from the P_B group for which $J(P_BP_B') = 45.8$ Hz. These assignments were confirmed by $^1H\{^{31}P\}$ selective decoupling experiments.

(ii) *Phosphorus*-31 *spectra.* Under conditions of *complete* proton decoupling the phosphorus spectrum of (3) is shown in Figure 3(*a*), and because the splittings within the individual multiplets are small compared with the chemical-shift differences a first-order treatment suffices, although the final parameters were refined by a computer-based analysis. Decoupling of P_C in a homonuclear $^{31}P\{^{31}P, ^1H_{noise}\}$ experiment [Figure 3(*b*)] gave a sharpening of the P_B resonance [*i.e.*, $J(P_BP_C)$ is small but non-zero], and reduced the multiplicity of the P_A resonance, thus showing $J(P_AP_C)$ to be 13.4 Hz. In fact, with P_C decoupled, the P_A and P_B resonances gave a characteristic AA'KK' pattern which shows that these two resonances arise from *two* ^{31}P nuclei each. From the overall intensity pattern it was then clear that P_C also arises from *two* ^{31}P nuclei, although these are spin coupled asymmetrically with the nuclei of the P_A/P_B system so that the complex spin system with protons fully decoupled is AA'KK'MM'. Under conditions of high resolution and/or sensitivity additional fine structure was revealed in the ^{31}P spectrum [see insets (*c*) in Figure 3] and a complete analysis by standard methods [6] gave the parameters listed in Table 4.

In the 59.8 MHz proton spectrum the separation of the methyl and the hydrido-resonances is 680 Hz and it was therefore possible to decouple selectively only the methyl protons from phosphorus and thus demonstrate that only a *single* hydridic proton is present, since each component of the phosphorus multiplets was split into a doublet by interaction with this proton. This result was confirmed by various selective $^{31}P\{^{31}P, ^1H\}$ triple resonance experiments such as those illustrated inFigure 4.



(*a*) (*b*) (*c*)

FIGURE 4 Selective $^{31}P\{^{31}P, ^1H\}$ triple resonance spectra of (3)

(iii) *Carbon*-13 *spectra.* The proton-decoupled ^{13}C spectrum of (3) is shown in Figure 5, together with its assignment. In addition, a spectrum was recorded without proton decoupling, and this showed that all the ^{13}C resonances were split into quartets by coupling to the directly bound protons, *i.e.* all belong to methyl groups and there are no methylene bridges. The assignments were confirmed by selective $^{13}C\{^{31}P, ^1H_{noise}\}$ decoupling experiments involving irradiation at various ^{31}P resonance frequencies with the following results.

(*i*) P_A: The high-frequency double doublet was collapsed to a single doublet with a *narrow* splitting, the central doublet was unaffected, and the low-frequency multiplet lost a *ca.* 0.5 Hz splitting. (*ii*) P_B: The low-frequency multiplet was collapsed to a line of width *ca.* 8 Hz, and the central doublet lost *ca.* 0.7 Hz of broadening. (*iii*) P_C: The high-frequency double doublet was collapsed to a singlet, and the low frequency multiplet lost a 3 Hz splitting.

An important feature of the above results is that only the carbon multiplet at lowest frequency has the appearance expected from the X part of an AA'X spin system in which $J(AA')$ is not small. Taken together with experiment (*ii*) this shows unequivocally that in the phosphorus AA'KK'MM spin system it is $J(P_BP_B')$ which is large and confirms the results of Table 4. Table 5 summarises the ^{13}C parameters for (3).

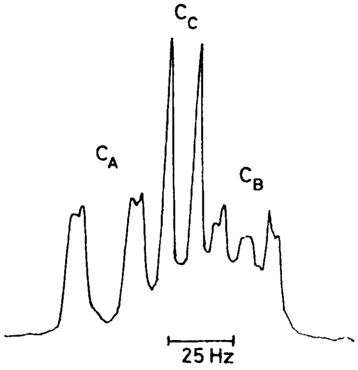


FIGURE 5 Proton decoupled ^{13}C n.m.r. spectrum of (3) with assignment of peaks

It is to be expected that in a structure such as (I) the various ^{31}P–^{31}P and ^{31}P–H spin coupling constants would be highly stereospecific and the following three potentially diagnostic features of the parameters are noteworthy. (*i*) $J(P_BP_B')$ is the only large three-bond ^{31}P–^{31}P coupling constant. (*ii*) $^1J(^{31}P_C–^{13}C)$ is much smaller than the other two one-bond ^{31}P–^{13}C coupling constants, and since this type of coupling is known [7] to be very sensitive to the phosphorus hybridisation this implies a special environment for P_C and P_C'. Furthermore, these are the only phosphorus nuclei in (I) whose

TABLE 5

Carbon-13 n.m.r. parameters for $(Me_3P)_3Ru(\mu-H)(\mu-OH)-Ru(PMe_3)_3$

	C_A	C_B	C_C
$\delta(^{13}C)$/p.p.m.[a]	24.9 ± 0.1	21.2 ± 0.1	22.9 ± 0.1
$J(^{31}P_A–^{13}C)$/Hz [b]	23.3 ± 0.5	0.0 ± 0.5	0.5 ± 0.3
$J(^{31}P_B–^{13}C)$/Hz [b]	0.0 ± 0.5	21.4 ± 0.5	0.7 ± 0.5
$J(^{31}P_C–^{13}C)_4$Hz [b]	3.6 ± 0.5	3.0 ± 0.5	12.6 ± 0.5

[a] To high frequency of $SiMe_4$. [b] Strictly refers to $J(PC) + J(P'C)$, but in all cases the latter coupling constant is very small and may be ignored.

methyl carbons are not additionally coupled to other phosphorus nuclei on the same ruthenium atom. (*iii*) The coupling of the hydride proton to P_B and P_B' is very much larger than to the other phosphorus nuclei, and this would normally imply [8] a *trans* relationship on the basis of which it is tempting to equate P_B with P^3.

It must be stressed, however, that the present state of knowledge of the n.m.r. parameters of this type of structure is such that we are unwilling to draw firm conclusions regarding the relation between the alphabetic subscripts and the numeric phosphorus superscripts.

(d) cis-*Dihydridotetrakis(trimethylphosphine)ruthenium*(II).—Both acetates of ruthenium $Ru_2(O_2CMe)_4Cl$ and $[Ru_3O(O_2CMe)_6(OH_2)_3][CO_2Me]$ react with sodium amalgam in thf in the presence of an excess of PMe_3 under hydrogen (3 atm) giving deep red-brown solutions from which *cis*-$RuH_2(PMe_3)_4$ can be isolated in high yield. Many other phosphine analogues [9] and also the iron compound $FeH_2(PMe_3)_4$ [10] have been described.

The white, diamagnetic complex is extremely soluble in light petroleum and can be crystallised with difficulty at −70 °C. However, it is volatile and is best isolated by sublimation (80 °C, 10^{-2} mmHg). The ^1H n.m.r. hydride resonance (δ −10.0) is a complex multiplet identical with those of the PMe_2Ph [9] and $PMePh_2$ [8b] analogues while the $^{31}P\{^1H\}$ is two triplets confirming the *cis* stereochemistry. The spectra are temperature independent.

(e) *Di-μ-hydroxo-dihydroxohexakis(trimethylphosphine)-diruthenium*(II).—When *cis*-$RuH_2(PMe_3)_4$ in tetrahydrofuran is heated to 60 °C, with excess of water, the dinuclear hydroxo-complex $Ru_2(OH)_4(PMe_3)_6$ is formed in high yield. The compound is sparingly soluble in aromatic hydrocarbons but very soluble in acetone. The i.r. spectrum has both sharp (3 652 cm^{-1}) and broad (3 400 cm^{-1}) peaks due to OH and the ^1H n.m.r. spectrum has two sharp singlets at δ 0.0 and δ − 0.06 (areas 1 : 2). These peaks coalesce at 70 °C in toluene and appear as a very broad resonance at −80 °C. The $^{31}P\{^1H\}$ n.m.r. spectrum is a sharp singlet at room temperature but has a shoulder at −80 °C.

The formula and spectra are consistent with a dinuclear structure (II), similar to that found for the analogous hydride, (1), containing both terminal and bridge hydroxo-groups. In solution, the n.m.r. spectra show that there is non-rigidity.

EXPERIMENTAL

Microanalyses were by Pascher, Bonn. The spectrometers used were Perkin-Elmer P.E. 597 (i.r.), Perkin-Elmer R32 (^1H), Varian XL-100 (^1H, ^{13}C, ^{31}P, Fourier transform).

Double and triple magnetic resonance experiments on (3) were performed on a modified JEOL FX-60 spectrometer operated in the pulsed Fourier-transform observing mode for ^1H (59.8 MHz), ^{13}C (15.0 MHz), and ^{31}P (24.2 MHz). The deuterium resonance from the C_6D_6 solvent was used for field-frequency locking of the spectrometer and the solution was examined in a 10 mm tube at 23 ± 1 °C. A Schlumberger FS-30 frequency synthesiser phase-locked to the spectrometer master oscillator provided r.f. power at *ca.* 24.2 MHz for the $^1H\{^{31}P\}$, $^{13}C\{^{31}P, ^1H_{noise}\}$, and $^{31}P\{^{31}P, ^1H_{noise}\}$ multiple resonance experiments, and was connected to the normal proton decoupling coils *via* a tuned r.f. amplifier and matching r.f. network. For the partially homonuclear $^{31}P\{^{31}P, ^1H_{noise}\}$ experiments, the irradiating ^{31}P r.f. field and the receiver were gated at 5 kHz to avoid electronic interference. Spectral widths, acquisition times, and the weighting of the free induction decay were optimised for the particular experiment being performed.

All operations were performed under oxygen-free nitrogen or argon or *in vacuo*. Diethyl ether, thf, 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 were obtained on a Mullard conductivity bridge type E7566/3 with a matching conductivity cell. Melting points were determined in sealed capillaries under nitrogen (uncorrected). Molecular weights were determined cryoscopically in benzene.

(1) *Di-μ-hydrido-dihydridohexakis(trimethylphosphine)-diruthenium*(II).—A solution of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ (1.0 g, 1.43 mmol) in light petroleum (50 cm^3) was heated (60 °C) under hydrogen (3 atm, 48 h). The solution became very slightly darker. Volatile materials were removed under vacuum and the residue dissolved in light petroleum (30 cm^3). Evaporation (to *ca.* 10 cm^3) of the filtered solution and cooling (−20 °C) yielded red *prisms*. Yield 0.93 g, 98% (Found: C, 33.1; H, 8.9; P, 28.4%. *M* 625. $C_{18}H_{58}P_6Ru_2$ requires C, 32.6; H, 8.8; P, 28.1%. *M* 662).

I.r. (cm^{-1}), Nujol mull, bands at 1 872s,br, 1 455s, 1 415m, 1 365m, 1 290m, 1 285m, 1 270m, 1 260m, 935s,br, 846s,br, 705m, 696m, 670m, 660m, and 567w. Light petroleum solution (matched KBr cells) ν(Ru–H) 1 880s,br.

The compound did not react with styrene at room temperature.

(2) *Tri-μ-hydrido-hexakis(trimethylphosphine)diruthenium*(II) *Tetrafluoroborate*.—(a) *From* $Ru_2H_4(PMe_3)_6$. Aqueous tetrafluoroboric acid [0.17 cm^3, 40% aqueous, 0.70 mmol; or 5.0 cm^3 (excess)] was added dropwise to a solution of $Ru_2H_4(PMe_3)_6$ (0.5 g, 0.76 mmol) in tetrahydrofuran (20 cm^3). The solution was stirred (0.5 h), the orange precipitate collected, washed with thf (2 × 25 cm^3), and dried under vacuum. Methanol (20 cm^3) was added and the solution filtered, and evaporated (to *ca.* 5 cm^3). Cooling (−20 °C) yielded orange *prisms*. Yield 0.4 g, 90%; m.p. 300—320 °C (decomp.) (Found: C, 28.9; H, 7.7; F, 10.2; P, 25.5. $C_{18}H_{57}BF_4P_6Ru_2$ requires C, 28.9; H, 7.6; F, 10.2; P, 24.9%). Conductivity $\Lambda_M = 98$ S cm^2 mol^{-1} in $MeNO_2$, 10^{-3} mol dm^{-3}, 25 °C.

I.r. (cm^{-1}), Nujol mull, bands at 1 472m, 1 365w, 1 307m, 1 302m, 1 285m, 1 266m, 1 098m, 1 060s, 1 040s, 1 025m, 940s,br, 850s, 725m, 715m, 677m, 668m, and 522w.

(b) *From* $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6][BF_4]$, *or* $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$. A solution of either starting material in methanol was stirred under hydrogen (3 atm) for 5 h at 50 °C. The solvent was removed under vacuum and the residue recrystallised as above. Yield *ca.* 80%.

(3) *μ-Hydrido-μ-hydroxo-hexakis(trimethylphosphine)-diruthenium*(I).—Distilled water (2 cm^3) was added to a solution of $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ (0.4 g, 0.57 mmol) in light petroleum (30 cm^3) and the mixture stirred rapidly under reflux (5 h). Volatile materials were removed under vacuum, the residue extracted into light petroleum (40

cm³), and the solution filtered. Evaporation (to *ca.* 3 cm³) and cooling (−20 °C) yielded pale yellow *plates* which were recrystallised from light petroleum. These were collected and dried under vacuum. Yield 0.2 g, 50%; m.p. 190—210 °C (decomp.) (Found: C, 32.4; H, 8.4; O, 2.3; P, 27.1%. *M* 675. $C_{18}H_{56}OP_6Ru_2$ requires C, 32.0; H, 8.3; O, 2.4; P, 27.5%. *M* 676).

I.r. (cm⁻¹), Nujol mull, bands at 1 413m, 1 365m, 1 286m, 1 265s, 1 090m,br, 1 020m,br, 932s,br, 842w, 834w, 806m, 710m, 697m, 658m, and 637w. Light petroleum solution (matched KBr cells); 1 735m, 1 600w, and 1 578w.

(4) cis-*Dihydridotetrakis*(*trimethylphosphine*)*ruthenium*-(II).—The complex $Ru_2(O_2CMe)_4Cl$ (1.0 g, 2.2 mmol) and sodium amalgam (50 g, 1% Na) in thf (50 cm³) and trimethylphosphine (2 cm³) were stirred under hydrogen (3 atm) (room temperature, 24 h).

The dark red-brown solution was evaporated to dryness under vacuum and the residue extracted into light petroleum (100 cm³). The solution was filtered and solvent removed under vacuum. The compound was sublimed directly onto a −78 °C cold probe (100 °C, 10^{-3} mmHg). Cooling of concentrated light petroleum solutions (−78 °C) also yields the compound as analytically pure *needles*. Yield 0.69 g, 80%; m.p. 160—164 °C (Found: C, 35.2; H, 9.3; P, 29.5%. *M* 404. $C_{12}H_{38}P_4Ru$ requires C, 35.4; H, 9.3; P, 30.5%. *M* 407).

TABLE 6

Crystal data and details of structure analyses

(*a*) Crystal data	Compound (1)	Compound (2)
Formula	$[RuH_2(PMe_3)_3]_2$	$[Ru_2(\mu\text{-}H)_3(PMe_3)_6][BF_4]$
M	662.6	784.4
Crystal system	Triclinic	Monoclinic
a/Å	9.277(1)	15.087(1)
b/Å	15.861(2)	9.796(2)
c/Å	17.958(3)	12.330(2)
α/°	110.13(1)	90
β/°	94.59(1)	108.00(1)
γ/°	90.61(1)	90
U/Å³	2 471.0	1 733.2
Space group	$P\bar{1}$	*P*2/*n* (no. 13)
Z	3	2
D_c/g cm⁻³	1.34	1.44
F(000)	1 032	768
μ(Mo-K_α)/cm⁻¹	11.0	10.6
(*b*) Data collection		
Crystal size/mm	0.25 × 0.5 × 0.5	0.42 × 0.3 × 0.12
θ_{min}, $\theta_{max.}$ (°)	1.5, 30	1.5, 30
Scan width parameters *A*, *B* in width = *A* + *B* tan θ	0.8, 0.35	0.8, 0.35
Horizontal aperture parameters *A*, *B* in aperture = *A* + *B* tan θ	4.0, 0.0	4.0, 0.0
Total data	9 844	5 701
Total unique data	9 601	5 057
Observed data	7 744	3 774
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
(*c*) Refinement		
No. of parameters	354	271
Weighting scheme coefficient *g* in *w* = $\Sigma 1/[\sigma^2(F_o) + g(F_o)^2]$	0.000 5	0.000 6
Final *R* = $\Sigma\Delta F/\Sigma\|F_o\|$	0.049	0.045
$R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$	0.066	0.050

TABLE 7

Fractional co-ordinates (Ru × 10^5; others × 10^4) of the non-hydrogen atoms for (1)

Atom	*x*	*y*	*z*
Ru(1)	87 660(4)	16 069(3)	75 446(2)
Ru(2)	85 408(4)	20 327(3)	91 844(2)
Ru(3)	50 837(4)	43 930(3)	42 228(2)
P(1)	253(2)	398(1)	7 469(1)
P(2)	89(2)	2 271(1)	6 898(1)
P(3)	7 116(2)	922(1)	6 529(1)
P(4)	7 083(2)	3 255(1)	9 260(1)
P(5)	7 189(2)	1 370(1)	9 815(1)
P(6)	195(2)	2 705(1)	205(1)
P(7)	2 609(2)	3 973(1)	4 073(1)
P(8)	5 921(2)	3 009(1)	3 790(1)
P(9)	5 259(2)	4 694(1)	3 104(1)
C(11)	2 017(8)	631(6)	8 090(5)
C(12)	9 496(12)	−543(5)	7 726(7)
C(13)	968(13)	−253(7)	6 493(5)
C(21)	9 390(12)	3 217(8)	6 675(9)
C(32) *	5 858(13)	1 648(8)	6 206(8)
C(41)	7 932(12)	4 178(5)	8 998(7)
C(42)	5 356(8)	3 044(6)	8 641(5)
C(43)	6 411(11)	3 948(7)	238(5)
C(61)	1 741(10)	3 223(7)	9 873(6)
C(62)	1 249(11)	2 009(7)	677(6)
C(71)	1 910(7)	3 509(5)	4 787(4)
C(72)	1 331(7)	4 854(5)	4 097(5)
C(73)	1 840(8)	3 070(6)	3 163(5)
C(91)	4 139(10)	4 138(7)	2 153(4)
C(92)	4 960(11)	5 871(5)	3 239(5)
C(93)	7 061(9)	4 615(7)	2 716(5)

* The site occupation factor for C(32) was refined to 0.845 3.

I.r. (cm⁻¹), Nujol mull, bands at 1 820vs, 1 435w, 1 418m, 1 355w, 1 292s, 1 275s, 938s,br, 855s, 712s, 700s, and 663w.

The compound was also obtained in high yield from a similar reaction using $[Ru_3O(O_2CMe)_6(OH_2)_3][CO_2Me]$ instead of $Ru_2(O_2CMe)_4Cl$.

(5) *Di-μ-hydroxo-dihydroxohexakis*(*trimethylphosphine*)-*diruthenium*(II).—To a solution of *cis*-$RuH_2(PMe_3)_4$ (1.0 g) in thf (50 cm³) was added distilled water (2 cm³) and the

TABLE 8

Fractional co-ordinates (× 10^4), isotropic temperature factors (Å² × 10^3), and site occupation factors (S.O.F.) of the disordered atoms in (1) †

Atom	*x*	*y*	*z*	*U*	S.O.F.
C(22)	1 534(23)	3 109(15)	7 634(12)	115(6)	0.5259
C(22 *)	2 027(23)	2 489(14)	7 209(13)	100(6)	0.4741
C(23)	1 503(27)	1 834(16)	6 230(14)	131(7)	0.5299
C(23 *)	403(26)	1 700(16)	5 823(14)	111(7)	0.4701
C(31)	5 552(16)	403(10)	6 872(8)	97(4)	0.6817
C(31 *)	6 300(35)	−13(21)	6 562(18)	118(9)	0.3733
C(33)	7 408(19)	−76(12)	5 715(11)	113(5)	0.6197
C(33 *)	7 595(26)	537(16)	5 475(14)	118(7)	0.4800
C(51)	7 839(18)	315(11)	−114(10)	92(4)	0.5599
C(51 *)	8 019(26)	739(15)	414(13)	103(6)	0.4401
C(52)	5 303(23)	1 129(14)	9 469(12)	98(6)	0.4583
C(52 *)	5 984(24)	423(15)	9 092(13)	122(7)	0.5417
C(53)	6 926(26)	1 908(16)	911(14)	125(7)	0.5069
C(53 *)	5 656(25)	1 867(15)	432(14)	115(7)	0.4931
C(63)	9 918(15)	3 771(9)	1 055(8)	75(3)	0.6256
C(63 *)	9 739(22)	3 458(14)	1 204(12)	64(5)	0.3744
C(81)	5 595(14)	2 192(8)	2 786(7)	92(3)	0.7822
C(81 *)	4 966(31)	2 027(18)	2 898(16)	47(6)	0.2178
C(82)	5 251(16)	2 263(9)	4 333(8)	80(4)	0.6074
C(82 *)	6 105(26)	2 444(16)	4 510(14)	86(7)	0.3926
C(83)	7 885(18)	2 929(11)	4 069(10)	95(4)	0.5756
C(83 *)	7 824(23)	2 935(14)	3 555(13)	88(6)	0.4244

† See footnote to Table 2.

mixture heated at 60 °C for 12 h. After removal of volatile materials the residue was extracted with toluene (50 cm^3) at 65 °C, the solution filtered and evaporated at 60 °C to *ca.* 10 cm^3. After cooling, the colourless crystals were collected, washed with light petroleum (2 × 10 cm^3), and dried *in vacuo*. Yield *ca.* 90%; m.p. 169—171 °C (Found: C, 30.8; H, 8.3; O, 10.0; P, 23.5%. *M* 740. $C_{18}H_{58}O_4Ru_2$ requires C, 29.8; H, 8.3; O, 8.8; P, 25.6%. *M* 726).

I.r. (cm^{-1}), Nujol mull, bands at 3 652m, 3 400m,br, 1 655m,br, 1 613m, 1 433m, 1 300m, 1 282m, 1 242w, 1 235w, 986s,br, 975s, 940s,br, 851m, 840w, 792m, 764m, 717s, 665s, 460w, 410w, and 380m.

X-Ray Crystallography.—Crystals of both compounds (1) and (2) 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 values by least-squares refinement of setting angles for 25 automatically centred, high angle reflections. The indication of the triclinic system for (1) was accepted after careful inspection of the Niggli matrix and the space group *P*2/*n* for (2) was selected by comparison with previously determined isostructural species.[3] The intensity data were recorded in a manner described in detail previously;[3] control reflections showed no significant changes in diffracting power of the crystals during data collection. Structure (1) was solved by the Patterson method, developed by successive electron-density syntheses and refined by least squares.

TABLE 9

Fractional co-ordinates (Ru × 10^5; others × 10^4) for (2)

Atom	*x*	*y*	*z*	*U* [a]
Ru	26 863(3)	32 062(3)	15 637(3)	
P(1)	4 009(1)	2 234(1)	1 415(1)	
P(2)	2 861(1)	5 167(1)	683(1)	
P(3)	1 713(1)	2 193(2)	−6(1)	
C(11)	4 243(5)	1 831(9)	77(6)	
C(12)	5 058(4)	3 205(9)	2 133(6)	
C(13)	4 277(6)	598(8)	2 133(8)	
C(21)	1 779(6)	6 081(9)	21(8)	
C(22)	3 419(5)	5 279(8)	−450(6)	
C(23)	3 532(8)	6 448(8)	1 645(9)	
C(31)	1 700(7)	323(8)	45(7)	
C(32)	486(4)	2 578(12)	−206(6)	
C(33)	1 742(5)	2 457(10)	−1 462(4)	
B	7 500 [b]	1 211(11)	2 500 [b]	
F(1) [c]	6 753(5)	425(8)	2 123(8)	
F(2a)	7 325(8)	1 766(12)	3 317(10)	176(5)
F(2b)	7 500 [b]	2 657(18)	2 500 [b]	77(4)
F(2c)	7 969(15)	1 289(24)	3 856(18)	32(4)
F(2d)	6 726(19)	1 006(29)	2 795(23)	43(5)
F(2e)	7 266(17)	2 452(25)	2 833(21)	0(4)
H(1a)	2 500	1 819(46)	2 500	37(13)
H(1b)	1 659(22)	3 994(35)	1 971(27)	28(8)

[a] Isotropic temperature factor (Å^2 × 10^3). [b] Parameters held invariant due to symmetry requirements. [c] Site occupation factors of the fluorine atoms in the disordered BF_4 anion were as follows: F(1) 0.90, F(2a) 0.60, F(2b) 0.15, F(2c) 0.08, F(2d) 0.08, F(2e) 0.04.

For (2), the relevant co-ordinates for Ru, P, and C atoms were used as a starting set. Positions for the atoms in the BF_4 group (disordered) and for the hydrogen atoms (both Ru–H and some P–methyl) were located from difference syntheses computed during the refinement. Details of crystal data, intensity data collection, and refinement for both compounds are given in Table 6. Refinement for (2) was straightforward, except for the disorder of the BF_4 anion. In (1), some of the PMe_3 groups appeared to be disordered and after several unsuccessful attempts to find a refinable model based on orientationally disordered rigid PC_3 groups, we found that the best solution was simply to include isotropically refined partial C atoms (with occupancy factors normalised to 3) at the sites of all the significant peaks around the phosphorus atoms concerned. [A similar procedure was used for the BF_4 group in (2).] Accordingly, some of the PMe_3 geometry parameters deviate somewhat from expected values, but the geometry of the inner core of the molecule seems well defined.

Final atomic co-ordinates (excluding H) are given in Tables 7 and 8 for (1) and 9 for (2). Hydrogen-atom parameters, all thermal parameters, and lists of F_o and F_c have been deposited as Supplementary Publication No. SUP 22880 (55 pp.).* All computations were carried out on the ICL 2980 at Queen Mary College, using programs listed in ref. 3, which also gives the sources of scattering factor data used here.

We thank the S.R.C. for support of this work, and Johnson Matthey Ltd. for the loan of ruthenium chloride.

[0/445 *Received, 20th March,* 1980]

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

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