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THE REACTION OF $Ru_3(CO)_{12}$ AND $Os_3(CO)_{12}$ WITH PH_2Ph; THE X-RAY CRYSTAL STRUCTURES OF $HRu_3(CO)_{10}(PHPh)$ AND $H_2Ru_3(CO)_9(PPh)$ *

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Summary

Twelve new trinuclear complexes containing terminal PH_2Ph, edge-bridging PHPh and/or capping PPh ligands have been isolated from the reaction of $M_3(CO)_{12}$ (M = Ru or Os) with PH_2Ph in refluxing solvents. $HRu_3(CO)_{10}(PHPh)$ (IIIa) crystallises in the monoclinic space group $P2_1/c$ with $a = 8.761(3)$, $b = 11.402(4)$, $c = 22.041(7)$ Å, $\beta = 98.89(2)°$, and $Z = 4$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least squares to $R = 0.027$ for 3676 unique observed intensities. The X-ray analysis shows that one edge of the Ru_3 triangle is bridged by a hydride and the PHPh ligand, and that the phosphorus-bound hydrogen atom lies over the metal triangle and the phenyl group away from it. This provides an explanation for the ready formation of the capped species $H_2Ru_3(CO)_9(PPh)$ (Va) on pyrolysis of the edge-bridged complex as opposed to the previously reported conversion of $HOs_3(CO)_{10}(NHPh)$ to an orthometallated derivative under similar conditions. An X-ray analysis of $H_2Ru_3(CO)_9$-(PPh) (Va) confirms the capped geometry. The complex crystallises in the monoclinic space group $P2_1/n$ with $a = 9.323(4)$, $b = 15.110(6)$, $c = 45.267(15)$ Å, $\beta = 91.84(3)°$, and $Z = 12$. The structure was solved and refined using the same techniques as described previously. The final residual R is 0.061 for 4839 reflections. Some reactions of Va show that the phosphorus cap is difficult to displace and stabilises the molecule with respect to decomposition to non-cluster species.

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* Dedicated to the memory of Professor Paolo Chini.

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Introduction

Although triruthenium and triosmium clusters capped by single carbon [1], nitrogen [2] and sulphur [3] atoms are well known, corresponding phosphorus-capped complexes have not been reported. Indeed the only triruthenium or triosmium cluster with a phosphorus cap which has been previously synthesised is $Ru_3(CO)_9(MeSi(PBu_2)_3)$, obtained from the reaction of $Ru_3(CO)_{12}$ with $MeSi(PBu_2)_3$ in refluxing benzene [4].

Our interest in the reactivity of clusters stabilised by bridging or capping phosphorus ligands [5] has led us to attempt the preparation of ruthenium and osmium complexes of this type, and in this paper we report the characterisation of several bridged and capped trinuclear complexes of these metals, which we have isolated from the reaction of PH_2Ph with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Two of the complexes obtained, $HRu_3(CO)_{10}(PHPh)$ and $H_2Ru_3(CO)_9(PPh)$, have been structurally characterised by single-crystal X-ray analyses. The reactivity of $H_2Ru_3(CO)_9(PPh)$ suggests that it is indeed stabilised with respect to break-up into mononuclear products by the presence of the capping ligand. Furthermore, whereas 2-electron donor ligands react with sulphur-capped analogues in such a way as to convert the cap into an edge-bridging ligand [6] we have observed that the phosphorus cap, once in place, is much more difficult to detach from any of the metal atoms to which it is bonded.

During the course of this work the synthesis of some analogous iron complexes has been reported [7].

Results and discussion

a) Synthesis and structural characterisation

The reaction of $M_3(CO)_{12}$ with PH_2Ph in refluxing solvents leads to the formation of complexes containing the edge-bridging ligand PHPh or the capping ligand PPh. Longer reaction times or higher boiling solvents give higher yields of capped species and this suggests that the edge-bridged species are intermediates in the formation of the capped complexes. The reaction conditions and the resulting products are shown in Table 1. Further evidence of the intermediacy of the edge-bridged species, $HM(CO)_{10}(PHPh)$, in the formation of the capped species, $H_2M(CO)_9(PPh)$, is provided by pyrolysis of the former to give the latter.

The infrared spectra of the new complexes prepared are shown in Table 2 and ^1H and ^{31}P NMR data are reported in Table 3. Analytical and mass spectroscopic data are given in Table 4 and proposed structures in Fig. 1.

(i) Complexes containing terminally bonded phosphines only. Ruthenium complexes of this type are, presumably, too readily converted into edge-bridged and capped species to permit their isolation, since none were obtained in any of the reactions of $Ru_3(CO)_{12}$ with PH_2Ph in the solvents studied (Table 1). Osmium complexes of this type are less labile, however, and both $Os_3(CO)_{11}(PH_2Ph)$ (I) and $Os_3(CO)_{10}(PH_2Ph)_2$ (II) were isolated from the reaction of $Os_3(CO)_{12}$ with PH_2Ph in toluene. Mass spectra and ^1H NMR data are consistent with the formulation given and infrared spectra are in good agreement with those reported by Bradford and Nyholm [8] for the corresponding tri-

TABLE 1

REACTION CONDITIONS

Reactants	Refluxing solvent (°C)	Time (minutes)	Products (% yield)
$Ru_3(CO)_{12}$ + PH_2Ph	Chloroform (62)	40	IIIa (31%)
	Hexane (69)	40	IIIa + Va (combined yield ca. 50%)
	Cyclohexane (81)	40	Va (46%) + IVa (6%)
IIIa	Cyclohexane (81)	30	Va (73%) + VIa (10%)
Va + PH_2Ph	Cyclohexane (81)	120	VIIa (17%)
$Os_3(CO)_{12}$ + PH_2Ph	Toluene (111)	180	I (9%), II (6%) + IIIb (25%)
II	Toluene (111)	120	IVb (10%)
IIIb	di(n-butyl)ether (142)	60	Vb (36%) + VIb (5%)
Vb + PH_2Ph	di(n-butyl)ether (142)	60	VIIb (9%)

phenylphosphine complexes with additional bands at ca. 2350 cm^{-1} being assigned to ν(P—H). It seems probable, therefore, that the complexes have the configurations shown in Fig. 1, as proposed for the triphenylphosphine analogues on the basis of ^{13}C NMR data [9].

(ii) Edge-bridged complexes. The complexes $HM(CO)_{10}(PHPh)$ (III) show molecular ion peaks in their mass spectra and fragmentation peaks corresponding to successive loss of 10 carbonyl groups. ν(P—H) is again seen in the infrared spectrum at ca. 2350 cm^{-1}. The P—H ^1H NMR resonance appears as a double doublet with $J(^1H—^{31}P) = 393$ Hz (M = Ru) and 422 Hz (M = Os). The other, smaller, coupling is to the bridging M—H—M with J(H—H) = 3 Hz (M = Ru and Os). That the larger coupling is to ^{31}P is confirmed by the ^{31}P-decoupled spectrum, in which the coupling of M—H—M to phosphorus [$J(^1H—^{31}P) = 28$ Hz for M = Ru, 18 Hz for M = Os] is also collapsed.

The conversion of the edge-bridged to the capped cluster can be thought of as an oxidative addition reaction. For the analogous complex $HOs_3(CO)_{10}$-(NHPh) such oxidative addition leads principally to the orthometallated complex $H_2Os_3(CO)_9(NHC_6H_4)$ resulting from C—H addition, whereas IIIa gives H_2-

TABLE 2

IR DATA (cm^{-1}).

Complex	$\nu(CO)$ [a]	ν(P-Ph) [b]	ν(P-H) [b]
I	2110m, 2055s, 2036s, 2021s, 2003m, 1991s, 1976m	1440m	2340m
II	2091w, 2034s, 2019m, 2007s, 1971m, 1955m	1440m	2340m
IIIa	2099m, 2060s, 2050s, 2025s, 2013s, 2001s, 1990m	1430m	2350w
IIIb	2105m, 2061s, 2053s, 2022s, 2007s, 1993s, 1981m	1430m	2350w
IVa	2096m, 2040s, 2035s, 2013s, 2005m, 1990m, 1976m	1420m	2340w
IVb	2088m, 2048s, 2039s, 2014s, 2002s, 1981m, 1961m	1420m	2340w
Va	2104m, 2073s, 2047s, 2045s, sh, 2028m, 2016s, 1997s, 1984m	1440m	—
Vb	2105m, 2076s, 2049s, 2045m, sh, 2032s, 2010s, 1991s, 1977m	1440m	—
VIa	2105m, 2076s, 2049s, 2032s, 2010s, 1990m, 1976m	1450w	2350w
VIb	2106m, 2081s, 2047s, 2037s, 2016s, 1992m, 1983m	1450w	2350w
VIIa	2077m, 2048s, 2041s, 2009s, 2001m, 1993m, 1978w	1440m	2340m
VIIb	2075m, 2043s, 2039s, 1999s, 1987m, 1981m, 1967w	1440m	2340m

w = weak, m = medium, s = strong, sh = shoulder

[a] Recorded in cyclohexane. [b] Recorded in chloroform.

TABLE 3

NMR DATA (ppm)

Complex	^{1}H ^{a}		
	δ(H—P)	δ(Ph—P)	δ(M—H—M)
I	6.37 d 2 H J(P—H) = 388 Hz	7.46m 5 H	—
II	6.39dd 4 H J(P(1)—H) = 388 Hz, J(P(2)—H) = 2 Hz	7.40m 10 H	—
IIIa	6.74dd 1 H J(P—H) = 393 Hz, J(H—H) = 3 Hz	7.38m 5 H	−16.73dd 1 H J(P—H) = 28 Hz, J(H—H) = 3 Hz
IIIb	7.09dd 1 H J(P—H) = 422 Hz, J(H—H) = 3 Hz	7.34m 5 H	−19.32dd 1 H J(P—H) = 18 Hz, J(H—H) = 3 Hz
Va	—	7.75m 5 H	−19.19d 2 H J(P—H) = 15 Hz
Vb	—	7.72m 5 H	−21.17d 2 H J(P—H) = 10 Hz
VIa	6.75br d 1 H J(P—H) = 358 Hz	7.37m 4 H	$\left.\begin{array}{l}-16.74\text{m}\\-16.99\text{m}\end{array}\right\}$ 2 H
VIIa	5.97br d 2 H J(P—H) = 354 Hz	7.70m 10 H	−19.02dd 2 H J(P(1)—H) = 14 Hz, J(P(2)—H) = 15 Hz

s = singlet, d = doublet, m = multiplet, br = broad, t = triplet

[a] Spectra recorded in CD_2Cl_2 at −70°C, δ rel. to TMS = 0. [b] Spectra recorded in 66% CD_2Cl_2/34%

$Os_3(CO)_9(PPh)$ (Va) as the major product, corresponding to the addition of P—H. The course of the reaction may well depend on the orientation of the phenyl group and the hydrogen in the ligand XHPh (X = N or P) with respect to the metal atom triangle and, in order to determine this orientation for X = P, an X-ray crystal structure determination was undertaken.

The molecular structure of $HRu_3(CO)_{10}(PHPh)$ is shown in Fig. 2 which includes the atom numbering scheme, while the corresponding bond lengths and angles are given in Tables 5 and 6, respectively. The crystal structure consists of discrete molecular units separated by normal Van der Waals distances.

The molecule has approximate $C_s(m)$ symmetry and consists of a distorted isosceles triangle of Ru atoms. The Ru(2)—Ru(3) edge is bridged by the hydride ligand and the PHPh group. The angle between the Ru_3 and the Ru_2P planes is 108.5°, while the Ru_2H plane makes an angle of 123.3° with the metal triangle. The plane of the phenyl ring is approximately perpendicular to the Ru(2)—Ru(3) edge and points away from the metal triangle. The phosphorus-bonded hydrogen atom of the PHPh group lies over the metal triangle in close proximity to the Ru atoms. This then allows oxidative addition of P—H with concommittant loss of a CO group. Presumably in $HOs_3(CO)_{10}(NHPh)$ the orientations of the hydrogen and phenyl groups are reversed. The possibility that thermodynamic factors are more favourable to formation of the orthometallated complex when X = N rather than P seems unlikely in view of the fact that the orthometallated complex $H_2Os_3(CO)_9(NHC_6H_4)$ isomerises slowly to the capped species $H_2Os_3(CO)_9(NPh)$ on extended heating [2].

^{31}P decoupled-^{1}H [a]			^{31}P [b]	^{1}H-decoupled ^{31}P [b]
δ(H—P)	δ(Ph—P) [c]	δ(M—H—M)	δ(P)	δ(P)
6.37s	7.46m	—	—	—
6.39s	7.40m	—	—	—
6.74d J(H—H) = 3 Hz	7.38m	—16.73d J(H—H) = 3 Hz	—	—
7.09d J(H—H) = 3 Hz	7.34m	—19.32d J(H—H) = 3 Hz	—	—
—	7.75m	—19.19s	165.9br t J(P—H_{aryl}) ca. 13 Hz	165.9s
—	7.72m	—21.17s	—	—
—	—	—	—	—
—	—	—	—	—

CH_2Cl_2 at 25°C; δ rel. to external P_4O_6. [c] Sharpening of Ph resonances was observed on decoupling the phosphorus.

The Ru(2)—Ru(3) distance is significantly longer than the two other Ru—Ru bonds in $HRu_3(CO)_{10}(PHPh)$. This is consistent with the fact that a μ_2-H bridge on a metal cluster normally causes the lengthening of the bridged metal—metal bond. The presence of another bridging group along the same edge, particularly

TABLE 4

MASS SPECTRAL AND MICROANALYTICAL DATA

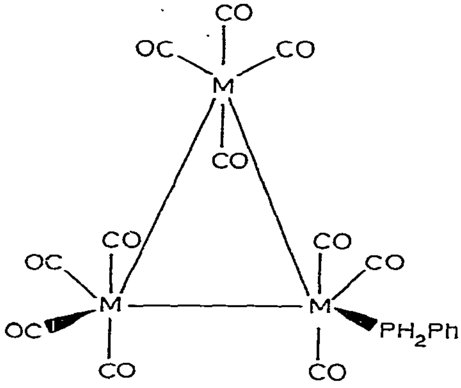
Complex	m/e (based on ^{192}Os or ^{101}Ru)		Analysis found (calcd.) (%)		
	$M^{+\cdot}$	Fragmentation pattern [a]	C	H	P
I	994	994 — x(28) x = 1—11	19.88(20.65)	1.07(0.71)	3.87(3.13)
II	1076	1076 — x(28) x = 1—10			
IIIa	693	693 — x(28) x = 1—10	27.71(27.71)	1.06(1.02)	4.39(4.47)
IIIb	966	966 — x(28) x = 1—10	19.72(20.00)	0.98(0.73)	3.61(3.22)
IVa	775	775 — x(28) x = 1— 9			
IVb	1048	1048 — x(28) x = 1— 9			
Va	665	665 — x(28) x = 1— 9	27.44 (27.08)	1.28(1.06)	4.65(4.65)
Vb	938	938 — x(28) x = 1— 9			
VIa	665	665 — x(28) x = 1— 9			
VIb	938	938 — x(28) x = 1— 9			
VIIa	747	747 — x(28) x = 1— 8			
VIIIb	1020	1020 — x(28) x = 1— 8			

[a] Additional fragmentation peaks involving loss of Ph(77) observed for all complexes except VIa and VIb.

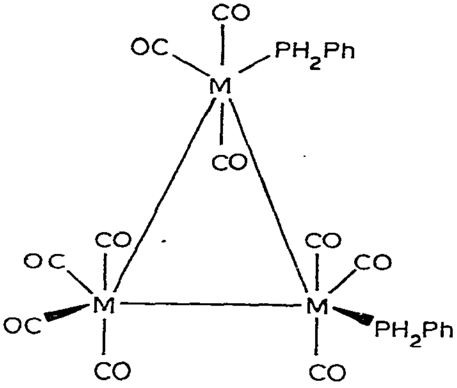
TABLE 5

BOND LENGTHS (Å) OF $HRu_3(CO)_{10}(PHPh)$

Ru(1)—Ru(2)	2.853(1)	Ru(1)—C(11)	1.913(4)
Ru(1)—Ru(3)	2.848(1)	Ru(1)—C(12)	1.936(5)
Ru(2)—Ru(3)	2.903(1)	Ru(1)—C(13)	1.943(5)
Ru(2)—P	2.338(1)	Ru(1)—C(14)	1.940(4)
Ru(3)—P	2.339(1)	Ru(2)—C(21)	1.916(5)
Ru(2)—H(1)	1.890(42)	Ru(2)—C(22)	1.890(4)
Ru(3)—H(1)	1.834(48)	Ru(2)—C(23)	1.954(5)
P—C(1)	1.818(4)	Ru(3)—C(31)	1.911(4)
P—H(7)	1.224(39)	Ru(3)—C(32)	1.883(4)
C(1)—C(2)	1.386(6)	Ru(3)—C(33)	1.945(4)
C(1)—C(6)	1.393(7)	O(11)—C(11)	1.131(5)
C(2)—C(3)	1.386(8)	O(12)—C(12)	1.125(6)
C(3)—C(4)	1.366(10)	O(13)—C(13)	1.139(6)
C(4)—C(5)	1.368(10)	O(14)—C(14)	1.135(5)
C(5)—C(6)	1.376(9)	O(21)—C(21)	1.132(6)
C(2)—H(2)	0.943(45)	O(22)—C(22)	1.137(5)
C(3)—H(3)	0.869(48)	O(23)—C(23)	1.126(6)
C(4)—H(4)	0.865(5)	O(31)—C(31)	1.137(5)
C(5)—H(5)	0.969(53)	O(32)—C(32)	1.138(6)
C(6)—H(6)	0.802(55)	O(33)—C(33)	1.135(5)



(I , M = Os)



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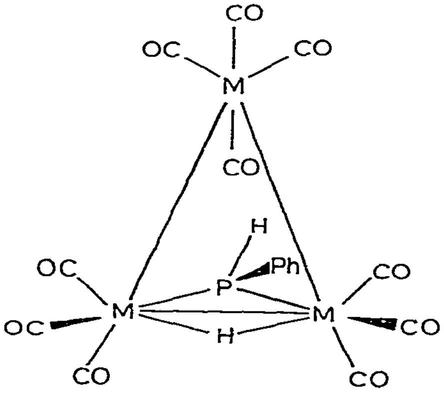
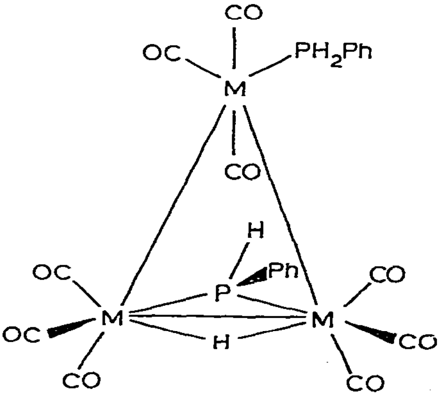


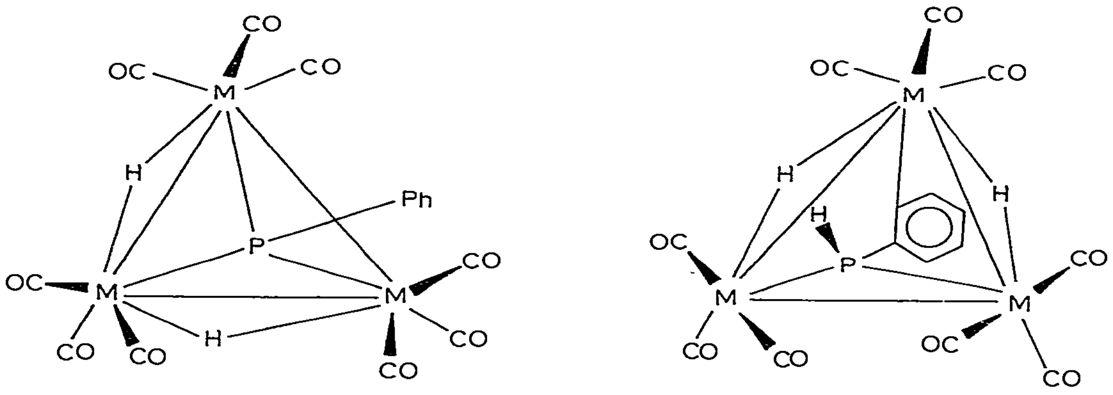
(IIIa , M = Ru ;

IIIb , M = Os)



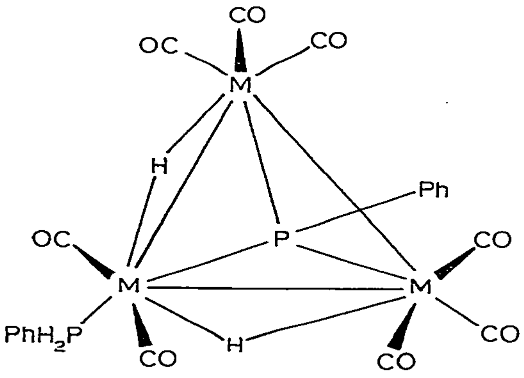
(IVa , M = Ru ,

IVb , M = Os)



(Va, M = Ru ;
Vb, M = Os)

(VIa, M = Ru ;
VIb, M = Os)



(VIIa, M = Ru ;
VIIb, M = Os)

Fig. 1. Proposed structures for new compounds.

if this group is a good π-acceptor, has a counterbalancing shortening effect on the bridged metal—metal bond. Here the bridged Ru(2)—Ru(3) bond is longer than the values found for the bridged edge in $HRu_3(CO)_{10}(CNMe_2)$ (2.802 Å) [10], $HRu_3(CO)_{10}(C_2Bu^t)$ (2.792 Å) [11] and $HRu_3(CO)_{10}(COCH_3)$ (2.803 Å) [12], and also longer than the mean bond length of 2.854 Å in the parent carbonyl $Ru_3(CO)_{12}$ [13]. Thus the PHPh ligand does not seem to be involved in delocalised back-bonding from the metal framework having little bond shortening effect.

The Ru—P distances (mean 2.339 Å) are close to the bridged Ru—P distances (mean 2.351 Å) in $Ru_3(CO)_6(C_2Bu^t)_2(PPh)_2(PhPC_2Bu^t)$ [14], and the P—C(1) distance is as expected for a single P—C(phenyl) bond. The Ru—H lengths and

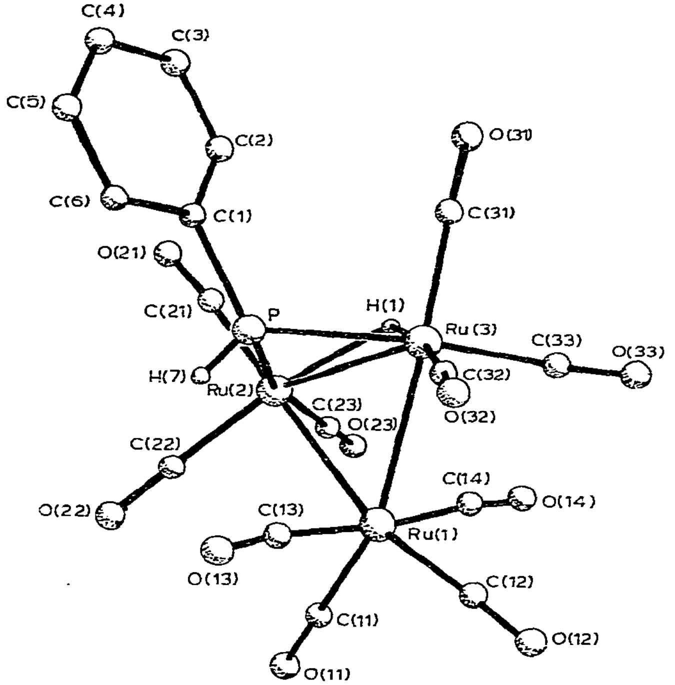


Fig. 2. Molecular structure of $HRu_3(CO)_{10}(PHPh)$. Phenyl H atoms have been omitted for clarity.

Ru—H—Ru angle for the hydride are similar to the corresponding values in $HRu_3(CO)_{10}(CNMe_2)$ [10].

The two equatorial Ru(2)—C(22) and Ru(3)—C(32) bonds (mean 1.887 Å) which are *trans* to the bridging hydride are shorter than those *trans* to the P atom (mean 1.950 Å). The wide Ru(3)—Ru(2)—C(21) and Ru(2)—Ru(3)—C(31) angles (mean 116.2°) show that these equatorial carbonyls bend away from the bridged Ru(2)—Ru(3) edge. Ru(1) has a distorted octahedral coordination geometry with the equatorial Ru—C(carbonyl) distances shorter (mean 1.925 Å) than the Ru—C(axial) distances (mean 1.942 Å). This is as expected because of the greater competition between *trans* carbonyls for back-donation from the same metal orbital resulting in a lengthening of both Ru—C bonds.

A minor product of the reaction of $Ru_3(CO)_{12}$ with PH_2Ph in cyclohexane is the disubstituted complex $HRu_3(CO)_9(PHPh)(PH_2Ph)$ (IVa) containing one edge-bridging and one terminal phosphorus ligand. The corresponding osmium complex (IVb) was not isolated directly from the reaction of $Os_3(CO)_{12}$ with PH_2Ph but was obtained in a separate experiment by pyrolysis of $Os_3(CO)_{10}$-$(PH_2Ph)_2$ in toluene. Both complexes show the expected loss of 9 CO groups in their mass spectra and have very similar infrared spectra. Neither was obtained in sufficient yield, however, for their NMR spectra to be recorded and the position of substitution of the terminal phosphine ligand is uncertain, although steric and electronic considerations suggest that it is most probably on the rear metal atom (Fig. 1). If this is the case it is at first sight surprising that the complexes IV do not give the capped species (VII) on pyrolysis, since the substitu-

TABLE 6

BOND ANGLES (deg.) OF $HRu_3(CO)_{10}$ (PHPh)

Ru(2)—Ru(1)—Ru(3)	61.2(1)	P—Ru(2)—C(21)	93.2(1)
Ru(1)—Ru(2)—Ru(3)	59.3(1)	P—Ru(2)—C(22)	96.1(2)
Ru(1)—Ru(3)—Ru(2)	59.5(1)	P—Ru(2)—C(23)	164.8(1)
Ru(1)—Ru(3)—P	83.4(1)	P—Ru(3)—C(31)	94.6(1)
Ru(3)—Ru(2)—P	51.6(1)	P—Ru(3)—C(32)	92.8(1)
Ru(1)—Ru(3)—P	83.5(1)	P—Ru(3)—C(33)	168.8(1)
Ru(2)—Ru(3)—P	51.6(1)	C(11)—Ru(1)—C(12)	101.1(2)
Ru(2)—P—Ru(3)	76.7(1)	C(11)—Ru(1)—C(13)	93.5(2)
Ru(2)—H(1)—Ru(3)	102.4(22)	C(12)—Ru(1)—C(13)	90.6(2)
Ru(1)—Ru(2)—H(1)	83.1(15)	C(11)—Ru(1)—C(14)	91.1(2)
Ru(3)—Ru(2)—H(1)	38.1(15)	C(12)—Ru(1)—C(14)	91.2(2)
Ru(1)—Ru(3)—H(1)	84.2(14)	C(13)—Ru(1)—C(14)	174.7(2)
Ru(2)—Ru(3)—H(1)	39.5(13)	C(21)—Ru(2)—C(22)	95.9(2)
P—Ru(2)—H(1)	80.0(14)	C(21)—Ru(2)—C(23)	92.9(2)
P—Ru(2)—H(1)	81.0(14)	C(22)—Ru(2)—C(23)	97.1(2)
C(21)—Ru(2)—H(1)	95.8(15)	C(31)—Ru(3)—C(32)	97.9(2)
C(22)—Ru(2)—H(1)	167.7(15)	C(31)—Ru(3)—C(33)	92.4(2)
C(23)—Ru(2)—H(1)	85.6(14)	C(32)—Ru(3)—C(33)	94.9(2)
C(31)—Ru(3)—H(1)	89.0(14)	Ru(1)—C(11)—O(11)	178.8(4)
C(32)—Ru(3)—H(1)	171.1(14)	Ru(1)—C(12)—O(12)	176.8(4)
C(33)—Ru(3)—H(1)	90.4(15)	Ru(1)—C(13)—O(13)	173.8(4)
Ru(2)—P—H(7)	118.0(17)	Ru(1)—C(14)—O(14)	174.3(4)
Ru(3)—P—H(7)	119.6(18)	Ru(2)—C(21)—O(21)	174.1(4)
C(1)—P—H(7)	101.4(18)	Ru(2)—C(22)—O(22)	178.2(4)
Ru(2)—P—C(1)	121.4(1)	Ru(2)—C(23)—O(23)	177.3(4)
Ru(3)—P—C(1)	120.1(1)	Ru(3)—C(31)—O(31)	177.1(4)
Ru(2)—Ru(1)—C(11)	94.8(1)	Ru(3)—C(32)—O(32)	177.8(4)
Ru(3)—Ru(1)—C(11)	155.7(1)	Ru(3)—C(33)O(33)	174.2(4)
Ru(2)—Ru(1)—C(12)	163.7(1)	P—C(1)—C(2)	120.7(3)
Ru(3)—Ru(1)—C(12)	102.6(1)	P—C(1)—C(6)	119.4(4)
Ru(2)—Ru(1)—C(13)	91.8(1)	C(2)—C(1)—C(6)	119.9(4)
Ru(3)—Ru(1)—C(13)	91.2(1)	C(1)—C(2)—C(3)	118.7(5)
Ru(2)—Ru(1)—C(14)	85.1(1)	C(2)—C(3)—C(4)	121.2(6)
Ru(3)—Ru(1)—C(14)	83.5(1)	C(3)—C(4)—C(5)	119.9(6)
Ru(1)—Ru(2)—C(21)	176.6(1)	C(4)—C(5)—C(6)	120.5(6)
Ru(3)—Ru(2)—C(21)	118.1(1)	C(1)—C(6)—C(5)	119.7(5)
Ru(1)—Ru(2)—C(22)	85.0(1)	C(1)—C(2)—H(2)	117.0(26)
Ru(3)—Ru(2)—C(22)	131.4(1)	C(3)—C(2)—H(2)	123.3(26)
Ru(1)—Ru(2)—C(23)	90.3(1)	C(2)—C(3)—H(3)	114.0(33)
Ru(3)—Ru(2)—C(23)	113.4(1)	C(4)—C(3)—H(3)	123.9(33)
Ru(1)—Ru(3)—C(31)	173.2(1)	C(3)—C(4)—H(4)	119.4(32)
Ru(2)—Ru(3)—C(31)	114.3(1)	C(5)—C(4)—H(4)	120.5(32)
Ru(1)—Ru(3)—C(32)	88.8(1)	C(4)—C(5)—H(5)	127.9(31)
Ru(2)—Ru(3)—C(32)	131.7(1)	C(6)—C(5)—H(5)	111.0(30)
Ru(1)—Ru(3)—C(33)	88.5(1)	C(1)—C(6)—H(6)	120.0(39)
Ru(2)—Ru(3)—C(33)	117.4(1)	C(5)—C(6)—H(6)	119.9(39)

tion of a phosphine ligand for a carbonyl group would be expected to increase the tendency of the metal atom concerned to undergo oxidative addition with the edge-bridging P—H. This requires loss of a further CO group, however, which is presumably inhibited by the phosphine substituent. That the failure to prepare VII from IV by pyrolysis is kinetic rather than thermodynamic in origin is suggested by its ready preparation via an alternative route (vide infra).

(iii) Capped complexes. The complex $H_2Ru_3(CO)_9(PPh)$ (Va) may be prepared directly from $Ru_3(CO)_{12}$ and PH_2Ph in cyclohexane whereas the osmium

analogue is best prepared from the pyrolysis of $HOs_3(CO)_{10}(PHPh)$ in di(n-butyl)ether. Both complexes show the expected loss of 9 CO groups in their mass spectra and ν(P—H) bands are absent from their infrared spectra. Both metal-bound H atoms are equivalent in the ^{1}H NMR at —70° C (J(P—H) = 15 Hz for M = Ru, 10 Hz for M = Os). The capped structures shown in Fig. 1 therefore seem the most reasonable and, for the ruthenium complex, this proposal has been confirmed by an X-ray crystal structure determination.

The crystal structure consists of discrete molecular units of $H_2Ru_3(CO)_9$-(PPh) which are separated by normal Van der Waals distances. There are three structurally equivalent but crystallographically independent molecules per asymmetric unit. Figure 3 shows one of these molecules and includes the atom numbering scheme in which the first digit designates the molecule to which the atom belongs. Bond lengths and angles for all three molecules are listed in Tables 7 and 8, respectively.

The three independent molecules each have approximate $C_s(m)$ symmetry and only differ slightly in the orientation of the phenyl group above the isosceles triangle of Ru atoms. The three metal atoms are capped by the phosphorus atom to give a distorted tetrahedral core. The Ru(11)—Ru(13) and Ru(12)—Ru(13) distances [similarly Ru(21)—Ru(22) and Ru(22)—Ru(23), and Ru(31)—Ru(33) and Ru(32)—Ru(33)] (mean 2.942 Å) are significantly longer than the Ru(11)—Ru(12)-type distances (mean 2.847 Å), and those in HRu_3-$(CO)_{10}(PHPh)$. The hydridic H atoms were not located directly, but in view of these two long Ru—Ru distances and the fact that equatorial carbonyls bend

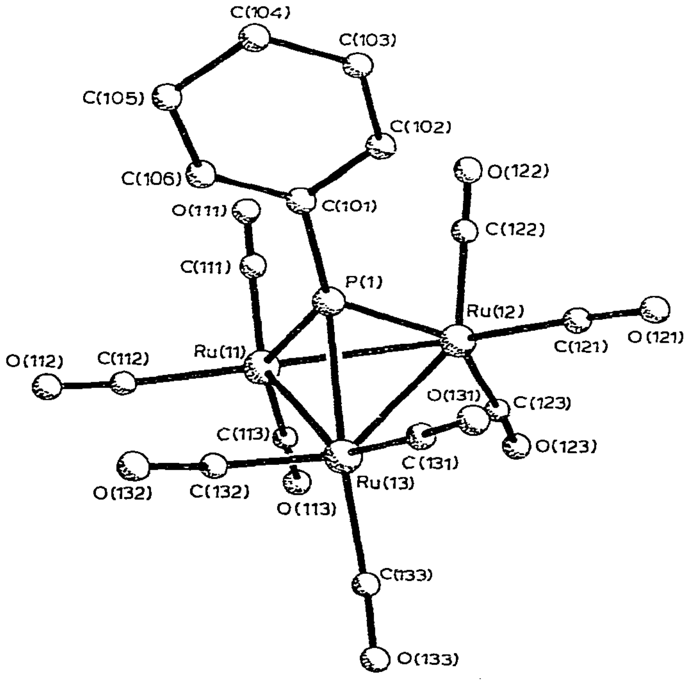


Fig. 3. Molecular structure of $H_2Ru_3(CO)_9(PPh)$. Phenyl H atoms have been omitted for clarity.

TABLE 7

BOND LENGTHS (Å) OR $H_2Ru_3(CO)_9$ (PPh)

Molecule 1		*Molecule 2*	
Ru(11)—Ru(12)	2.849(3)	Ru(21)—Ru(22)	2.842(3)
Ru(11)—Ru(13)	2.939(3)	Ru(21)—Ru(23)	2.947(3)
Ru(12)—Ru(13)	2.932(3)	Ru(22)—Ru(23)	2.938(3)
Ru(11)—P(1)	2.288(5)	Ru(21)—P(2)	2.296(5)
Ru(12)—P(1)	2.278(5)	Ru(22)—P(2)	2.279(5)
Ru(13)—P(1)	2.329(5)	Ru(23)—P(2)	2.333(5)
Ru(11)—C(111)	1.939(18)	Ru(21)—C(211)	1.887(22)
Ru(11)—C(112)	1.985(21)	Ru(21)—C(212)	1.867(23)
Ru(11)—C(113)	1.948(22)	Ru(21)—C(213)	1.944(21)
Ru(12)—C(121)	1.924(21)	Ru(22)—C(221)	1.915(20)
Ru(12)—C(122)	1.908(21)	Ru(22)—C(222)	1.920(20)
Ru(12)—C(123)	1.959(19)	Ru(22)—C(223)	1.924(21)
Ru(13)—C(131)	1.895(17)	Ru(23)—C(231)	1.898(19)
Ru(13)—C(132)	1.934(18)	Ru(23)—C(232)	1.937(20)
Ru(13)—C(133)	1.959(21)	Ru(23)—C(233)	1.969(18)
C(111)—O(111)	1.106(23)	C(211)—O(211)	1.133(27)
C(112)—O(112)	1.058(27)	C(212)—O(212)	1.177(29)
C(113)—O(113)	1.146(28)	C(213)—O(213)	1.146(26)
C(121)—O(121)	1.146(28)	C(221)—O(221)	1.116(25)
C(122)—O(122)	1.140(25)	C(222)—O(222)	1.114(24)
C(123)—O(123)	1.116(24)	C(223)—O(223)	1.138(26)
C(131)—O(131)	1.153(22)	C(231)—O(231)	1.137(23)
C(132)—O(132)	1.112(23)	C(232)—O(232)	1.099(25)
C(133)—O(133)	1.136(27)	C(233)—O(233)	1.135(23)
P(1)—C(101)	1.820(20)	P(2)—C(201)	1.787(19)
C(101)—C(102)	1.361(30)	C(201)—C(202)	1.354(26)
C(101)—C(106)	1.349(27)	C(201)—C(206)	1.423(31)
C(102)—C(103)	1.370(32)	C(202)—C(203)	1.425(37)
C(103)—C(104)	1.337(32)	C(203)—C(204)	1.379(40)
C(104)—C(105)	1.431(31)	C(204)—C(205)	1.310(35)
C(105)—C(105)	1.359(29)	C(205)—C(206)	1.397(37)
Molecule 3			
Ru(31)—Ru(32)	2.851(3)	C(312)—O(312)	1.094(26)
Ru(31)—Ru(33)	2.936(3)	C(313)—O(313)	1.142(26)
Ru(32)—Ru(33)	2.954(3)	C(321)—O(321)	1.168(31)
Ru(31)—P(3)	2.262(5)	C(322)—O(322)	1.149(28)
Ru(32)—P(3)	2.267(5)	C(323)—O(323)	1.132(27)
Ru(33)—P(3)	2.322(5)	C(331)—O(331)	1.069(28)
Ru(31)—C(311)	1.962(21)	C(332)—O(332)	1.159(25)
Ru(31)—C(312)	1.948(21)	C(333)—O(333)	1.129(27)
Ru(31)—C(313)	1.910(22)	P(3)—C(301)	1.817(19)
Ru(32)—C(321)	1.907(23)	C(301)—C(302)	1.399(31)
Ru(32)—C(322)	1.835(22)	C(301)—C(306)	1.329(33)
Ru(32)—C(323)	1.951(22)	C(302)—C(303)	1.422(38)
Ru(33)—C(331)	1.969(22)	C(303)—C(302)	1.422(38)
Ru(33)—C(332)	1.895(19)	C(303)—C(304)	1.324(41)
Ru(33)—C(333)	1.965(20)	C(304)—C(305)	1.322(40)
C(311)—O(311)	1.116(28)	C(305)—C(306)	1.463(40)

away from these edges [*cis* Ru—Ru—C(carbonyl) angles for these edges average 102.8° compared to 95.6° for the remainder] suggests that the two hydrides bridge these two edges. The three terminal carbonyl groups bonded to each metal are essentially linear, the bond parameters associated with the phenyl group do not deviate significantly from the idealised values.

A minor product obtained in each of the reactions giving rise to the capped

(Continued on p. 198)

TABLE 8

BOND ANGLES (deg.) OF $H_2Ru_3(CO)_9$ (PPh)

Molecule 1		*Molecule 2*	
Ru(12)—Ru(11)—Ru(13)	60.8(1)	Ru(22)—Ru(21)—Ru(23)	61.0(1)
Ru(11)—Ru(12)—Ru(13)	61.1(1)	Ru(21)—Ru(22)—Ru(23)	61.3(1)
Ru(11)—Ru(13)—Ru(12)	58.1(1)	Ru(21)—Ru(23)—Ru(22)	57.8(1)
Ru(12)—Ru(11)—P(1)	51.2(1)	Ru(22)—Ru(21)—P(2)	51.3(1)
Ru(13)—Ru(11)—P(1)	51.1(1)	Ru(23)—Ru(21)—P(2)	51.0(1)
Ru(11)—Ru(12)—P(1)	51.5(1)	Ru(21)—Ru(22)—P(2)	51.9(1)
Ru(13)—Ru(12)—P(1)	51.3(1)	Ru(23)—Ru(22)—P(2)	51.2(1)
Ru(11)—Ru(13)—P(1)	49.8(1)	Ru(21)—Ru(23)—P(2)	49.9(1)
Ru(12)—Ru(13)—P(1)	49.7(1)	Ru(22)—Ru(23)—P(2)	49.6(1)
Ru(11)—P(1)—Ru(12)	77.2(1)	Ru(21)—P(2)—Ru(22)	76.8(2)
Ru(11)—P(1)—Ru(13)	79.1(2)	Ru(21)—P(2)—Ru(23)	79.1(2)
Ru(12)—P(1)—Ru(13)	79.0(2)	Ru(22)—P(2)—Ru(23)	79.1(2)
Ru(12)—Ru(11)—C(111)	95.4(5)	Ru(22)—Ru(21)—C(211)	92.4(7)
Ru(13)—Ru(11)—C(111)	147.7(5)	Ru(23)—Ru(21)—C(211)	147.1(7)
Ru(12)—Ru(11)—C(112)	159.0(6)	Ru(22)—Ru(21)—C(212)	158.6(7)
Ru(13)—Ru(11)—C(112)	101.6(6)	Ru(23)—Ru(21)—C(212)	104.0(7)
Ru(12)—Ru(11)—C(113)	96.0(7)	Ru(22)—Ru(21)—C(213)	99.4(6)
Ru(13)—Ru(11)—C(113)	107.9(7)	Ru(23)—Ru(21)—C(213)	109.7(6)
Ru(11)—Ru(12)—C(121)	158.3(6)	Ru(21)—Ru(22)—C(221)	160.0(6)
Ru(13)—Ru(12)—C(121)	101.3(6)	Ru(23)—Ru(22)—C(221)	103.3(6)
Ru(11)—Ru(12)—C(122)	95.9(6)	Ru(21)—Ru(22)—C(222)	95.7(6)
Ru(13)—Ru(12)—C(122)	145.4(6)	Ru(23)—Ru(22)—C(222)	148.1(6)
Ru(11)—Ru(12)—C(123)	96.1(6)	Ru(21)—Ru(22)—C(223)	92.3(6)
Ru(13)—Ru(12)—C(123)	109.4(6)	Ru(23)—Ru(22)—C(223)	107.3(6)
Ru(11)—Ru(13)—C(131)	143.6(6)	Ru(21)—Ru(23)—C(231)	145.2(5)
Ru(12)—Ru(13)—C(131)	97.3(5)	Ru(22)—Ru(23)—C(231)	94.7(6)
Ru(11)—Ru(13)—C(132)	96.0(5)	Ru(21)—Ru(23)—C(232)	97.4(5)
Ru(12)—Ru(13)—C(132)	144.3(6)	Ru(22)—Ru(23)—C(232)	143.4(5)
Ru(11)—Ru(13)—C(133)	114.5(6)	Ru(21)—Ru(23)—C(233)	115.1(5)
Ru(12)—Ru(13)—C(133)	114.5(6)	Ru(22)—Ru(23)—C(233)	118.2(5)
C(111)—Ru(11)—C(112)	95.5(8)	C(211)—Ru(21)—C(212)	95.2(10)
C(111)—Ru(11)—C(113)	95.4(9)	C(211)—Ru(21)—C(213)	92.5(9)
C(112)—Ru(11)—C(113)	100.8(9)	C(212)—Ru(21)—C(213)	100.2(9)
C(121)—Ru(12)—C(122)	93.1(9)	C(221)—Ru(22)—C(222)	92.7(8)
C(121)—Ru(12)—C(123)	102.2(8)	C(221)—Ru(22)—C(223)	105.1(9)
C(122)—Ru(12)—C(123)	97.8(8)	C(222)—Ru(22)—C(223)	94.6(9)
C(131)—Ru(13)—C(132)	91.2(7)	C(231)—Ru(23)—C(232)	94.3(8)
C(131)—Ru(13)—C(133)	99.7(8)	C(231)—Ru(23)—C(233)	96.0(8)
C(132)—Ru(13)—C(133)	97.9(8)	C(232)—Ru(23)—C(233)	96.0(8)
P(1)—Ru(11)—C(111)	97.4(6)	P(2)—Ru(21)—C(211)	97.9(7)
P(1)—Ru(11)—C(112)	109.5(6)	P(2)—Ru(21)—C(212)	107.7(7)
P(1)—Ru(11)—C(113)	145.7(7)	P(2)—Ru(21)—C(213)	149.0(6)
P(1)—Ru(12)—C(121)	108.1(6)	P(2)—Ru(22)—C(221)	109.1(6)
P(1)—Ru(12)—C(122)	94.5(6)	P(2)—Ru(22)—C(222)	97.6(7)
P(1)—Ru(12)—C(123)	146.5(6)	P(2)—Ru(22)—C(223)	143.0(6)
P(1)—Ru(13)—C(131)	94.0(6)	P(2)—Ru(23)—C(231)	96.8(6)
P(1)—Ru(13)—C(132)	95.3(6)	P(2)—Ru(23)—C(232)	94.1(6)
P(1)—Ru(13)—C(133)	160.7(6)	P(2)—Ru(23)—C(233)	163.1(5)
Ru(11)—C(111)—O(111)	178.8(15)	Ru(21)—C(211)—O(211)	176.9(18)
Ru(11)—C(112)—O(112)	174.7(21)	Ru(21)—C(212)—O(212)	175.7(20)
Ru(11)—C(113)—O(113)	176.2(20)	Ru(21)—C(213)—O(213)	179.0(14)
Ru(12)—C(121)—O(121)	176.7(19)	Ru(22)—C(221)—O(221)	176.7(18)
Ru(12)—C(122)—O(122)	177.6(18)	Ru(22)—C(222)—O(222)	172.9(19)
Ru(12)—C(123)—O(123)	177.3(19)	Ru(22)—C(223)—O(223)	179.3(17)
Ru(13)—C(131)—O(131)	177.7(16)	Ru(23)—C(231)—O(231)	177.3(17)
Ru(13)—C(132)—O(132)	175.6(18)	Ru(23)—C(232)—O(232)	177.4(18)
Ru(13)—C(133)—O(133)	177.4(18)	Ru(23)—C(233)—O(233)	174.6(16)
Ru(11)—P(1)—C(101)	138.8(6)	Ru(21)—P(2)—C(201)	134.0(6)
Ru(12)—P(1)—C(101)	134.3(7)	Ru(22)—P(2)—C(201)	137.4(6)
Ru(13)—P(1)—C(101)	125.8(6)	Ru(23)—P(2)—C(201)	128.0(6)

TABLE 8 (continued)

Molecule 1		*Molecule 2*	
P(1)—C(101)—C(102)	120.3(15)	P(2)—C(201)—C(202)	122.9(15).
P(1)—C(101)—C(106)	120.0(15)	P(2)—C(201)—C(206)	117.3(15)
C(102)—C(101)—C(106)	119.6(19)	C(202)—C(201)—C(206)	119.9(19)
C(101)—C(102)—C(103)	118.3(21)	C(201)—C(202)—C(203)	121.2(21)
C(102)—C(103)—C(104)	123.1(23)	C(202)—C(203)—C(204)	117.1(24)
C(103)—C(104)—C(105)	118.8(21)	C(203)—C(204)—C(205)	121.7(27)
C(104)—C(105)—C(106)	116.3(19)	C(204)—C(205)—C(206)	123.3(26)
C(101)—C(106)—C(105)	123.7(19)	C(201)—C(206)—C(205)	116.6(22)
C(101)—C(102)—H(102)	120.6(12)	C(201)—C(202)—H(202)	119.3(12)
C(103)—C(102)—H(102)	121.0(14)	C(203)—C(202)—H(202)	119.4(14)
C(102)—C(103)—H(103)	118.6(14)	C(202)—C(203)—H(203)	121.4(14)
C(104)—C(103)—H(103)	118.3(14)	C(204)—C(203)—H(203)	121.5(16)
C(103)—C(104)—H(104)	120.7(14)	C(203)—C(204)—H(204)	118.8(16)
C(105)—C(104)—H(104)	120.6(12)	C(205)—C(204)—H(204)	119.5(17)
C(104)—C(105)—H(105)	121.7(12)	C(204)—C(205)—H(205)	118.3(17)
C(106)—C(105)—H(105)	122.0(12)	C(206)—C(205)—H(205)	118.5(15)
C(101)—C(106)—H(106)	118.0(12)	C(201)—C(206)—H(206)	121.5(13)
C(105)—C(106)—H(106)	118.3(12)	C(205)—C(206)—H(206)	121.9(15)
Molecule 3			
Ru(32)—Ru(31)—Ru(33)	61.4(1)	P(3)—Ru(31)—C(311)	93.3(6)
Ru(31)—Ru(32)—Ru(33)	60.7(1)	P(3)—Ru(31)—C(312)	110.6(6)
Ru(31)—Ru(33)—Ru(32)	57.9(1)	P(3)—Ru(31)—C(313)	147.0(7)
Ru(32)—Ru(31)—P(3)	51.1(1)	P(3)—Ru(32)—C(321)	108.3(7)
Ru(33)—Ru(31)—P(3)	51.1(1)	P(3)—Ru(32)—C(322)	98.0(7)
Ru(31)—Ru(32)—P(3)	50.9(1)	P(3)—Ru(32)—C(323)	146.2(7)
Ru(33)—Ru(32)—P(3)	50.8(1)	P(3)—Ru(33)—C(331)	91.3(7)
Ru(31)—Ru(33)—P(3)	49.3(1)	P(3)—Ru(33)—C(332)	95.2(6)
Ru(32)—Ru(33)—P(3)	49.1(1)	P(3)—Ru(33)—C(333)	162.4(6)
Ru(31)—P(3)—Ru(32)	78.0(2)	Ru(31)—C(311)—O(311)	177.1(17)
Ru(31)—P(3)—Ru(33)	79.6(2)	Ru(31)—C(312)—O(312)	173.9(19)
Ru(32)—P(3)—Ru(33)	80.1(2)	Ru(31)—C(313)—O(313)	175.8(22)
Ru(32)—Ru(31)—C(311)	95.7(6)	Ru(32)—C(321)—O(321)	174.2(20)
Ru(33)—Ru(31)—C(311)	144.2(6)	Ru(32)—C(322)—O(322)	177.3(19)
Ru(32)—Ru(31)—C(312)	160.1(6)	Ru(32)—C(323)—O(323)	175.8(21)
Ru(33)—Ru(31)—C(312)	103.0(6)	Ru(33)—C(331)—O(331)	177.9(20)
Ru(32)—Ru(31)—C(313)	96.8(7)	Ru(33)—C(332)—O(332)	174.5(18)
Ru(33)—Ru(31)—C(313)	111.2(7)	Ru(33)—C(333)—O(333)	176.8(18)
Ru(31)—Ru(32)—C(321)	158.0(7)	Ru(31)—P(3)—C(301)	132.3(7)
Ru(33)—Ru(32)—C(321)	101.7(7)	Ru(32)—P(3)—C(301)	137.1(7)
Ru(31)—Ru(32)—C(322)	96.1(7)	Ru(33)—P(3)—C(301)	128.1(7)
Ru(33)—Ru(32)—C(322)	148.1(7)	P(3)—C(301)—C(302)	114.9(16)
Ru(31)—Ru(32)—C(323)	96.2(7)	P(3)—C(301)—C(306)	123.9(17)
Ru(33)—Ru(32)—C(323)	110.4(7)	C(302)—C(301)—C(306)	121.2(20)
Ru(31)—Ru(33)—C(331)	140.3(7)	C(301)—C(302)—C(303)	118.0(23)
Ru(32)—Ru(33)—C(331)	95.5(6)	C(302)—C(303)—C(304)	114.4(26)
Ru(31)—Ru(33)—C(332)	94.5(6)	C(303)—C(304)—C(305)	134.0(27)
Ru(32)—Ru(33)—C(322)	143.4(6)	C(304)—C(305)—C(306)	109.2(26)
Ru(31)—Ru(33)—C(333)	117.2(6)	C(301)—C(306)—C(305)	123.1(24)
Ru(32)—Ru(33)—C(333)	115.9(6)	C(301)—C(302)—H(302)	120.5(13)
C(311)—Ru(31)—C(312)	91.3(9)	C(303)—C(302)—H(302)	121.5(16)
C(311)—Ru(31)—C(313)	97.8(9)	C(302)—C(303)—H(303)	122.3(16)
C(312)—Ru(31)—C(313)	100.8(9)	C(304)—C(303)—H(303)	123.3(17)
C(321)—Ru(32)—C(322)	94.0(10)	C(303)—C(304)—H(304)	112.7(17)
C(321)—Ru(32)—C(323)	102.8(10)	C(305)—C(304)—H(304)	113.2(17)
C(322)—Ru(32)—C(323)	92.6(9)	C(304)—C(305)—H(305)	125.7(17)
C(331)—Ru(33)—C(332)	92.7(8)	C(306)—C(305)—H(305)	125.2(16)
C(331)—Ru(33)—C(333)	100.3(9)	C(301)—C(306)—H(306)	118.4(14)
C(332)—Ru(33)—C(333)	97.5(8)	C(305)—C(306)—H(306)	118.6(16)

species $H_2M_3(CO)_9(PPh)$ is isomeric with the major species as judged by its mass spectrum. Its formulation as the orthometallated complex $H_2M_3(CO)_9(PHC_6H_4)$ (VI) is based on the observation of ν(P—H) at ca. 2350 cm^{-1} and the general similarity of the infrared spectra to that obtained by Deeming [2] for $H_2Os_3(CO)_9(NHC_6H_4)$. Furthermore the ^1H NMR spectrum of the ruthenium complex at —70° C shows a resonance at δ 6.75 ppm (J(P—H) = 358 Hz) attributable to a P—H resonance, in addition to two Ru—H—Ru multiplets centred at δ —16.74 and —16.99 ppm. It is not clear whether these multiplets represent two non-equivalent H atoms, as observed by Deeming for $H_2Os_3(CO)_9(NHC_6H_4)$ at low temperature [2], or whether the molecule is fluxional and the signals represent two equivalent H atoms with the splitting being due to coupling to phosphorus. Unfortunately, insufficient material was available for a ^{31}P-decoupled spectrum which would have resolved this point. The osmium orthometallated complex was obtained in such small amounts that only its mass and infrared spectra could be recorded.

B) Reactions of the capped species

Attempted reaction of $H_2Ru_3(CO)_9(PPh)$ with CO at pressures up to 70 atm and temperatures up to 75° C led only to recovery of the starting complex in ca. 100% yield. Reaction of $H_2M_3(CO)_9(PPh)$ with PH_2Ph in cyclohexane (M = Ru) or di(n-butyl)ether (M = Os) led to the isolation of $H_2M_3(CO)_8(PPh)(PH_2Ph)$ (VII) in low yields with much decomposition to non-cluster species. Much higher yields of $H_2Ru_3(CO)_8(PPh)(PH_2Ph)$ were obtained by treating $H_2Ru_3(CO)_9(PPh)$ in CH_2Cl_2 with a 1 : 1 molar ratio of $Me_3NO \cdot 2\,H_2O$ in methanol at room temperature prior to addition of the phosphine. This provides further evidence of the stabilisation introduced by the presence of the phosphorus cap since $Ru_3(CO)_{12}$ decomposes completely on treatment with Me_3NO [15]. These reactions may be contrasted with those of the sulphur-capped cluster, $HRu_3(CO)_9(SPr^i)$, for which reconversion of the capped to an edge-bridged species is the predominant reaction on treatment with 2-electron donors [6].

The complexes $H_2M_3(CO)_8(PPh)(PH_2Ph)$ were characterised by their mass spectra (loss of 8 CO groups), infra red (ν(P—H) ca. 2350 cm^{-1}) and, in the case of the Ru complex, ^1H NMR data. A double doublet at δ —19.02 ppm (—70° C in CH_2Cl_2 solution) presumably represents two equivalent metal-bound H atoms coupled to the non-equivalent P atoms (J(P—H) = 14 and 15 Hz). This implies that the two H atoms are disposed symmetrically with respect to the PH_2Ph substituent as in VII (Fig. 1). The possibility of non-equivalence of the H atoms with fluxional behaviour accounting for the observed data cannot, however, be eliminated. Unfortunately, the quantity of material available was again not sufficient for a ^{31}P-decoupled spectrum to be recorded.

Experimental

All reactions were carried out under nitrogen in degassed freshly redistilled solvents. The products are stable at room temperature in air, so separation procedures were carried out in the atmosphere using preparative TLC plates made up with silica gel (E. Merck; Kieselgel 50 F_{254}; 0.25 mm thickness). Eluant was hexane with just sufficient dichloromethane (ca. 5%) to give satisfactory movement of bands, which were finally extracted with dichloromethane.

IR spectra were recorded in 0.5 mm NaCl cells on a Perkin-Elmer 257 grating spectrometer using CO ($\nu = 2143$ cm^{-1}) as calibrant or a Perkin-Elmer 577 grating spectrometer using polystyrene ($\nu = 1603$ cm^{-1}) as calibrant. NMR spectra were recorded on a Varian XL-100 spectrometer in the Fourier Transform mode. Mass spectra were measured on an AEI MS12 spectrometer using tris(perfluoroheptyl)-*s*-triazine as reference. Microanalyses were carried by the microanalytical department at the University Chemical Laboratory at Cambridge University.

(i) Reaction of $Ru_3(CO)_{12}$ with PH_2Ph

To a refluxing solution of $Ru_3(CO)_{12}$ (50 mg) in chloroform was added 10 μl of PH_2Ph and the mixture heated under reflux for 40 minutes. The solvent was removed under reduced pressure and the residue chromatographed to give orange-red $HRu_3(CO)_{10}(PHPh)$ (17 mg, 31%).

The identical reaction using hexane as a solvent produced $HRu_3(CO)_{10}(PHPh)$ and $H_2Ru_3(CO)_9(PPh)$ as a mixture, which could not be separated on TLC plates (combined yield ca. 50%).

The identical reaction using cyclohexane as a solvent produced yellow $H_2Ru_3(CO)_9(PPh)$ (24 mg, 46%) and pale yellow $HRu_3(CO)_9(PHPh)(PH_2Ph)$ (4 mg, 6%).

(ii) Pyrolysis of $HRu_3(CO)_{10}(PHPh)$

$HRu_3(CO)_{10}(PHPh)$ (10 mg) was dissolved in cyclohexane and the solution heated under reflux and followed by IR. After 30 minutes, when no starting material remained, the reaction was ended and the products extracted as in (i) to give yellow $H_2Ru_3(CO)_9(PPh)$ (7 mg, 73%) and yellow $H_2Ru_3(CO)_9(PHC_6H_4)$ (1 mg, 10%).

(iii) Reaction of $H_2Ru_3(CO)_9(PPh)$ with PH_2Ph

To a refluxing solution of $H_2Ru_3(CO)_9(PPh)$ (20 mg) in cyclohexane was added 4 μl of PH_2Ph and the mixture heated under reflux for 120 minutes. The products were extracted as in (i) to give $H_2Ru_3(CO)_8(PPh)(PHPh)$ (4 mg, 17%).

(iv) Reaction of $Os_3(CO)_{12}$ with PH_2Ph

To a refluxing solution of $Os_3(CO)_{12}$ (100 mg) in toluene was added 14 μl of PH_2Ph and the mixture heated under reflux for 180 minutes. The products were extracted as in (i) to give yellow $HOs_3(CO)_{10}(PHPh)$ (26 mg, 25%), pale yellow $Os_3(CO)_{11}(PH_2Ph)$ (10 mg, 9%) and orange yellow $Os_3(CO)_{10}(PH_2Ph)_2$ (8 mg, 6%).

(v) Pyrolysis of $Os_3(CO)_{10}(PH_2Ph)_2$

$Os_3(CO)_{10}(PH_2Ph)$ (8 mg) was dissolved in toluene and the solution heated under reflux for 120 minutes. The products were extracted as in (i) to give $HOs_3(CO)_9(PHPh)(PH_2Ph)$ (1 mg, 10%).

(vi) Pyrolysis of $HOs_3(CO)_{10}(PHPh)$

$HOs_3(CO)_{10}(PHPh)$ (20 mg) was dissolved in di(n-butyl) ether and the solution heated under reflux for 60 minutes. The products were extracted as in (i) to give pale yellow $H_2Os_3(CO)_9(PPh)$ (7 mg, 36%) and pale yellow $H_2Os_3(CO)_9(PHC_6H_4)$ (1 mg, 5%).

(vii) Reaction of $H_2Os_3(CO)_9(PPh)$ with PH_2Ph

To a refluxing solution of $H_2Os_3(CO)_9(PPh)$ (10 mg) in di(n-butyl) ether was added 2 µl of PH_2Ph and the mixture heated under reflux for 60 minutes. The products were extracted as in (i) to give yellow $H_2Os_3(CO)_8(PPh)(PH_2Ph)$.

(viii) Reaction of $H_2Ru_3(CO)_9(PPh)$ with CO in an autoclave

A solution of $H_2Ru_3(CO)_9(PPh)$ in hexane was placed in an autoclave and the

TABLE 9

ATOM COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^3$) OF $HRu_3(CO)_{10}(PHPh)$

	x/a	*y/b*	*z/c*	*U*
Ru(1)	3147(1)	4441(1)	2782(1)	
Ru(2)	1324(1)	4140(1)	3737(1)	
Ru(3)	4621(1)	3673(1)	3957(1)	
P	2583(1)	2328(1)	3862(1)	
O(11)	499(4)	5416(4)	1863(2)	
O(12)	5800(4)	4658(3)	2035(2)	
O(13)	2586(5)	1922(3)	2297(2)	
O(14)	3845(4)	6927(3)	3287(2)	
O(21)	—621(4)	3678(4)	4743(2)	
O(22)	—1160(4)	3358(4)	2707(2)	
O(23)	484(5)	6764(3)	3700(2)	
O(31)	5949(4)	3007(3)	5272(1)	
O(32)	6582(4)	2036(3)	3324(2)	
O(33)	6908(4)	5731(3)	4008(2)	
C(11)	1486(5)	5046(4)	2200(2)	
C(12)	4854(5)	4564(4)	2323(2)	
C(13)	2782(5)	2831(4)	2509(2)	
C(14)	3578(5)	5991(4)	3130(2)	
C(21)	170(5)	3854(4)	4393(2)	
C(22)	—245(5)	3656(4)	3100(2)	
C(23)	821(5)	5810(4)	3706(2)	
C(31)	5415(5)	3250(4)	4785(2)	
C(32)	5864(5)	2671(4)	3562(2)	
C(33)	6002(5)	5013(4)	3978(2)	
C(1)	2357(5)	1359(4)	4498(2)	
C(2)	2345(6)	1806(5)	5082(2)	
C(3)	2190(8)	1034(7)	5555(3)	
C(4)	1996(8)	—141(7)	5449(3)	
C(5)	2004(8)	—579(5)	4871(3)	
C(6)	2176(6)	159(5)	4392(3)	
H(1)	3169(52)	4590(41)	4246(21)	80(13)
H(2)	2625(48)	2599(40)	5147(19)	68(12)
H(3)	2066(51)	1375(41)	5897(22)	76(12)
H(4)	1780(54)	—591(41)	5740(22)	79(13)
H(5)	1759(57)	—1369(47)	4726(22)	78(13)
H(6)	2287(60)	—110(49)	4066(24)	72(15)
H(7)	2400(42)	1643(35)	3429(18)	51(10)

vessel pressurised with CO to pressures up to 70 atmospheres. Reaction at a variety of temperatures was tried (up to 75°C) and the products examined after each run. In all cases, the starting capped cluster was recovered in ca. 100% yield.

(ix) *Reaction of $H_2Ru_3(CO)_9(PPh)$ with $Me_3NO \cdot 2\ H_2O$*

$H_2Ru_3(CO)_9(PPh)$ (20 mg) was dissolved in dichloromethane, a solution of $Me_3NO \cdot 2\ H_2O$ (3 mg) in methanol was added, and the mixture stirred at room temperature for 20 minutes. PH_2Ph (3 μl) was then added and stirring at room temperature was continued for 5 minutes. The products were extracted as in (i) to give yellow $H_2Ru_3(CO)_8(PPh)(PH_2Ph)$ (17 mg, 76%).

(x) *X-ray structural analysis of $HRu_3(CO)_{10}(PHPh)$*

Crystal data: $C_{16}H_7O_{10}PRu_3$, mol. wt. 693.41, Monoclinic, $a = 8.761(3)$, $b = 11.402(4)$, $c = 22.041(7)$ Å, $\beta = 98.89(2)°$, $U = 2175.29$ Å^3, $d_c = 2.12$ g cm^{-3}, $Z = 4$. Space group $P2_1/c$ from systematic absences. Graphite-monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 21.05 cm^{-1}. Intensity data was recorded from a crystal of dimensions 0.28 × 0.28 × 0.14 mm.

TABLE 10

ANISOTROPIC TEMPERATURE FACTORS (Å^2 × 10^3) OF $HRu_3(CO)_{10}$ (PHPh)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	41(1)	44(1)	34(1)	5(1)	7(1)	0(1)
Ru(2)	33(1)	46(1)	41(1)	4(1)	8(1)	2(1)
Ru(3)	33(1)	39(1)	34(1)	—2(1)	4(1)	0(1)
P	42(1)	41(1)	36(1)	0(1)	7(1)	—3(1)
O(11)	69(2)	106(3)	72(2)	21(2)	—14(2)	18(2)
O(12)	74(2)	83(3)	105(3)	4(2)	53(2)	0(2)
O(13)	118(3)	62(2)	58(2)	—13(2)	11(2)	—11(2)
O(14)	96(3)	50(2)	73(2)	2(2)	11(2)	—5(2)
O(21)	78(2)	104(3)	86(2)	19(2)	49(2)	12(2)
O(22)	67(2)	143(4)	79(2)	12(3)	—15(2)	—38(3)
O(23)	93(3)	59(2)	113(3)	11(2)	27(2)	25(2)
O(31)	77(2)	96(3)	43(2)	0(2)	—6(2)	21(2)
O(32)	71(2)	71(2)	81(2)	—10(2)	31(2)	17(2)
O(33)	64(2)	68(2)	100(3)	—9(2)	9(2)	—25(2)
C(11)	58(2)	60(3)	50(2)	5(2)	11(2)	2(2)
C(12)	54(2)	55(3)	61(3)	2(2)	12(2)	3(2)
C(13)	61(3)	59(3)	35(2)	5(2)	4(2)	—4(2)
C(14)	59(3)	52(2)	47(2)	8(2)	7(2)	1(2)
C(21)	53(3)	67(3)	60(3)	6(2)	22(2)	7(2)
C(22)	36(2)	77(3)	64(3)	10(2)	7(2)	—4(2)
C(23)	46(2)	63(3)	64(3)	5(2)	11(2)	8(2)
C(31)	48(2)	57(3)	46(2)	—8(2)	8(2)	8(2)
C(32)	51(2)	49(2)	47(2)	4(2)	10(2)	1(2)
C(33)	44(2)	50(2)	55(2)	—2(2)	6(2)	0(2)
C(1)	53(2)	46(2)	45(2)	9(2)	11(2)	2(2)
C(2)	78(3)	66(3)	50(3)	10(2)	17(2)	—1(3)
C(3)	116(5)	111(5)	62(3)	32(3)	35(3)	26(4)
C(4)	120(5)	105(5)	98(4)	67(4)	48(4)	37(4)
C(5)	112(5)	58(3)	115(5)	30(3)	41(4)	17(3)
C(6)	74(3)	51(3)	78(3)	14(3)	21(3)	13(2)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^\star + \ldots + 2U_{12}hka^\star b^\star)$

TABLE 11

ATOM COORDINATES (X 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^5) OF $H_2Ru_3(CO)_9(PPh)$

	x/a	*y/b*	*z/c*	*U*
Molecule 1				
Ru(11)	9548(2)	6000(1)	2611(1)	
Ru(12)	9535(2)	4374(1)	2292(1)	
Ru(13)	11256(2)	4506(1)	2844(1)	
P(1)	11426(5)	5284(3)	2402(1)	
O(111)	8673(15)	7153(9)	2084(3)	
O(112)	10712(19)	7548(11)	2974(4)	
O(113)	6505(18)	5784(14)	2854(5)	
O(121)	10647(21)	2642(12)	2029(4)	
O(122)	8856(16)	5201(11)	1690(3)	
O(123)	6434(15)	3881(13)	2435(4)	
O(131)	13551(15)	3174(9)	2679(4)	
O(132)	13481(15)	5648(10)	3170(3)	
O(133)	9937(17)	3585(11)	3382(4)	
C(111)	9001(19)	6729(12)	2274(4)	49(5)
C(112)	10290(22)	6991(14)	2860(5)	66(6)
C(113)	7612(23)	5883(15)	2756(5)	76(7)
C(121)	10273(22)	3299(14)	2127(5)	68(6)
C(122)	9140(21)	4886(13)	1913(5)	61(6)
C(123)	7567(20)	4038(13)	2382(4)	58(6)
C(131)	12683(18)	3671(11)	2747(4)	45(5)
C(132)	12653(19)	5217(12)	3062(4)	51(5)
C(133)	10428(21)	3904(13)	3182(5)	62(6)
C(101)	13081(20)	5555(13)	2220(4)	55(5)
C(102)	13599(23)	5008(15)	2010(5)	74(7)
C(103)	14841(24)	5242(15)	1877(6)	81(7)
C(104)	15547(24)	5994(15)	1938(5)	76(7)
C(105)	15035(22)	6557(14)	2166(5)	66(6)
C(106)	13780(20)	6314(13)	2287(5)	62(6)
H(102)	13040(23)	4404(15)	1950(5)	69(7)
H(103)	15272(24)	4801(15)	1714(6)	71(7)
H(104)	16486(24)	6173(15)	1817(5)	69(7)
H(105)	15618(22)	7141(14)	2237(5)	71(6)
H(106)	13311(20)	6754(13)	2446(5)	70(6)
Molecule 2				
Ru(21)	12669(2)	2742(1)	4183(1)	
Ru(22)	13007(2)	1137(1)	3865(1)	
Ru(23)	10144(2)	1604(1)	4069(1)	
P(2)	12273(5)	1318(3)	4337(1)	
O(211)	15842(17)	2812(13)	4336(6)	
O(212)	11803(21)	3954(11)	4683(4)	
O(213)	12934(19)	4078(11)	3670(4)	
O(221)	12668(19)	−779(10)	3679(4)	
O(222)	16153(14)	874(12)	4029(4)	
O(223)	13443(18)	2118(12)	3283(4)	
O(231)	9089(17)	−295(9)	4057(4)	
O(232)	8530(16)	2151(11)	4611(4)	
O(233)	7828(15)	2321(10)	3624(3)	
C(211)	14645(24)	2803(15)	4284(5)	79(7)
C(212)	12100(23)	3503(14)	4482(5)	73(7)
C(213)	12849(21)	3581(13)	3860(5)	61(6)
C(221)	12805(21)	−82(13)	3756(5)	62(6)
C(222)	15022(21)	1011(14)	3956(5)	64(6)
C(223)	13273(21)	1756(13)	3499(5)	62(6)
C(231)	9450(19)	424(12)	4063(4)	52(5)
C(232)	9096(19)	1936(12)	4415(4)	54(5)
C(233)	8726(18)	2069(12)	3777(4)	47(5)

TABLE 11 (continued)

C(201)	12493(18)	759(12)	4683(4)	45(5)
C(202)	13098(21)	—53(13)	4710(5)	62(6)
C(203)	13318(28)	—460(19)	4992(7)	108(9)
C(204)	12766(25)	—30(17)	5232(6)	89(8)
C(205)	12154(26)	749(17)	5206(6)	92(8)
C(206)	11973(26)	1194(17)	4937(6)	90(8)
H(202)	13418(21)	—399(13)	4514(5)	70(6)
H(203)	13891(28)	—1078(19)	5016(7)	70(9)
H(204)	12849(25)	—344(17)	5446(6)	71(8)
H(205)	11767(26)	1059(17)	5403(6)	72(8)
H(206)	11467(26)	1836(17)	4922(6)	71(8)
Molecule 3				
Ru(31)	9595(2)	905(1)	675(1)	
Ru(32)	9128(2)	2142(1)	1138(1)	
Ru(33)	7802(2)	370(1)	1166(1)	
P(3)	7508(5)	1500(3)	821(1)	
O(311)	9917(18)	2298(12)	186(4)	
O(312)	8882(22)	—534(11)	225(4)	
O(313)	12753(16)	592(11)	839(4)	
O(321)	7424(21)	3193(13)	1589(5)	
O(322)	9658(21)	3760(11)	780(4)	
O(323)	12243(17)	2085(12)	1386(4)	
O(331)	5164(18)	948(13)	1492(3)	
O(332)	6111(17)	—956(10)	784(4)	
O(333)	9090(17)	—910(12)	1637(4)	
C(311)	9838(21)	1796(14)	366(5)	64(6)
C(312)	9212(21)	—13(14)	381(5)	62(6)
C(313)	11580(23)	697(15)	767(5)	75(7)
C(321)	8108(23)	2770(14)	1430(5)	73(7)
C(322)	9489(22)	3136(14)	920(5)	72(7)
C(323)	11082(24)	2110(15)	1306(5)	79(7)
C(331)	6091(23)	759(14)	1374(5)	72(7)
C(332)	6750(19)	—482(12)	941(4)	53(5)
C(333)	8655(21)	—446(13)	1460(5)	64(6)
C(301)	5879(20)	1827(13)	619(5)	57(5)
C(302)	5099(25)	2504(16)	750(6)	83(7)
C(303)	3833(32)	2811(21)	600(7)	126(11)
C(304)	3520(27)	2394(16)	348(6)	91(8)
C(305)	4137(31)	1750(19)	201(7)	127(10)
C(306)	5422(28)	1454(18)	367(6)	99(9)
H(302)	5450(25)	2776(16)	961(6)	70(7)
H(303)	3192(32)	3343(21)	684(7)	73(11)
H(304)	2544(27)	2634(16)	241(6)	70(8)
H(305)	3761(31)	1485(19)	—9(7)	74(10)
H(306)	6018(28)	900(18)	283(6)	68(9)

Red blocks of $HRu_3(CO)_{10}(PHPh)$ were grown from hexane solution, and a single crystal mounted on a glass fibre. This was placed on a Stoe four-circle diffractometer and cell parameters determined from the accurate angular measurement of 20 strong reflections in the angular range $15 < 2\theta < 25°$. Intensities to a $2\theta_{max}$ of 55° were measured using graphite monochromated Mo-K_α radiation and an ω—θ scan technique. Two standard reflections, measured after every 50 reflections, showed no decrease in intensity during data collection. Lorentz polarisation corrections, and an empirical absorption correction were applied, and equivalent reflections averaged to give 3676 unique observed $[F > 3\sigma(F)]$ intensities.

The positions of the three Ru and the P atom were located by multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms from a subsequent electron-density difference map. The structure was refined by blocked-cascade least squares with all these atoms assigned anisotropic thermal parameters. A difference map computed at this stage revealed the positions of all the hydrogen atoms, and these were included in further cycles of least squares, each atom being assigned an isotropic temperature factors. The weighting scheme $w = [\sigma^2(F) + 0.0003|F|^2]^{-1}$ was introduced and refinement continued until conver-

TABLE 12

ANISOTROPIC TEMPERATURE FACTORS (Å^2 × 10^3) OF $H_2Ru_3(CO)_9$ (PPh)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule 1						
Ru(11)	41(1)	48(1)	44(1)	8(1)	5(1)	4(1)
Ru(12)	47(1)	51(1)	47(1)	2(1)	−6(1)	−9(1)
Ru(13)	45(1)	43(1)	36(1)	6(1)	1(1)	1(1)
P(1)	34(3)	43(3)	36(3)	2(2)	0(2)	0(2)
O(111)	85(11)	78(11)	63(11)	35(9)	−11(8)	−5(8)
O(112)	136(15)	76(11)	76(13)	−15(10)	−15(11)	−16(11)
O(113)	76(12)	181(19)	166(2)	76(17)	67(12)	14(12)
O(121)	159(18)	93(13)	112(16)	−36(12)	−29(13)	36(12)
O(122)	85(11)	114(13)	54(10	20(9)	−22(8)	−9(10)
O(123)	59(10)	157(17)	109(15)	27(13)	14(9)	−34(10)
O(131)	79(10)	55(9)	99(13)	6(9)	17(9)	27(8)
O(132)	84(11)	93(11)	68(11)	−17(9)	−15(8)	−22(9)
O(133)	100(13)	110(13)	87(13)	46(11)	27(10)	−33(10)
Molecule 2						
Ru(21)	46(1)	48(1)	43(1)	3(1)	−2(1)	−5(1)
Ru(22)	38(1)	55(1)	38(1)	3(1)	1(1)	5(1)
Ru(23)	35(1)	46(1)	42(1)	5(1)	0(1)	1(1)
P(2)	44(3)	53(3)	31(3)	3(2)	−4(2)	3(2)
O(211)	51(11)	143(17)	261(27)	−71(18)	−47(13)	1(1)
O(212)	169(18)	93(13)	70(12)	−12(11)	12(11)	−5(12)
O(213)	140(15)	88(12)	65(12)	24(10)	−14(10)	−16(11)
O(221)	140(16)	60(10)	119(16)	−27(10)	−28(12)	24(10)
O(222)	34(8)	133(14)	131(16)	18(12)	−6(9)	3(9)
O(223)	114(14)	129(15)	59(11)	35(11)	7(9)	−10(11)
O(231)	117(13)	55(10)	93(13)	−4(9)	1(10)	−16(9)
O(232)	93(12)	99(13)	84(13)	−1(10)	34(9)	33(10)
O(233)	70(10)	103(12)	82(12)	5(10)	−34(9)	0(9)
Molecule 3						
Ru(31)	52(1)	57(1)	55(1)	7(1)	11(1)	−5(1)
Ru(32)	60(1)	48(1)	54(1)	3(1)	−7(1)	−12(1)
Ru(33)	54(1)	48(1)	52(1)	10(1)	4(1)	−8(1)
P(3)	48(3)	51(3)	43(3)	9(3)	2(2)	−8(2)
O(311)	97(13)	131(15)	121(16)	94(13)	23(11)	6(11)
O(312)	188(19)	87(12)	74(13)	−52(10)	−7(12)	−27(12)
O(313)	69(11)	94(12)	147(17)	21(12)	−7(10)	5(9)
O(321)	127(17)	130(17)	152(20)	−52(15)	18(14)	15(13)
O(322)	158(17)	81(12)	118(16)	41(11)	−48(13)	−31(12)
O(323)	73(12)	139(16)	122(16)	30(13)	−19(10)	−10(11)
O(331)	114(14)	154(17)	61(11)	15(12)	32(10)	39(12)
O(332)	99(13)	70(11)	158(18)	−15(12)	−9(12)	−46(10)
O(333)	89(12)	116(14)	131(17)	72(13)	−7(11)	1(11)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2Uhka^*b^*)$

gence was reached. The final residuals were $R = 0.027$ and $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0|] = 0.028$. Final atomic coordinates and associated anisotropic thermal parameters are given in Tables 9 and 10, respectively.

(xi) X-ray structural analysis of $H_2Ru_3(CO)_9(PPh)$

Crystal data: $C_{15}H_7O_9PRu_3$, mol. wt. 665.40, monoclinic, $a = 9.323(4)$, $b = 15.110(7)$, $c = 45.267(11)$ Å, $\beta = 91.84(3)°$, $U = 6373.49$ Å^3, $d_c = 2.08$ g cm^{-3}, $Z = 12$. Space group $P2_1/n$ from systematic absences. Graphite monochromated Mo-K_α radiation $\lambda = 0.71069$ Å, μ(Mo-K_α) = 21.50 cm^{-1}. Intensity data were recorded from a crystal with dimensions 0.35 × 0.25 × 0.05 mm.

Pale yellow platelets of $H_2Ru_3(CO)_9(PPh)$ were deposited from hexane solution. Cell dimensions were determined and intensity data recorded as described for $HRu_3(CO)_{10}(PHPh)$. Lorentz polarisation and numerical absorption corrections were applied, and equivalent reflections averaged to give 4839 unique observed $[F > 3\sigma(F)]$ intensities.

The positions of all nine independent Ru atoms were located by multisolution Σ_2 sign expansion, and all the non-hydrogen atoms from subsequent electron-density difference syntheses. The structure was refined by blocked-cascade least squares with anisotropic temperature factors for Ru, P and O, and isotropic for C. The hydrogen atoms were not located directly, but those on the phenyl ring were placed in geometrically idealised positions (C—H, 1.08 Å; C—C—H, 120.0°) and constrained to ride on the relevant C atom. Each H atom was assigned an individual isotropic temperature factor. The weighting scheme $w = [\sigma^2(F) + 0.002|F|^2]^{-1}$ was introduced, and refinement continued until convergence was reached with $R = 0.061$ and $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0|] = 0.061$. Final atomic parameters are listed in Tables 11 and 12, respectively.

Complex neutral-atom scattering factors were employed throughout [16]. Calculations were performed on the University of Cambridge IBM 370/165 computer using programs written by Professor G.M. Sheldrick. The molecular diagrams were drawn using PLUTO written by Dr. W.D.S. Motherwell. Copies of observed and calculated structure factor tables may be obtained from the authors.

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