Products of the Pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$; † the Molecular and Crystal Structure of $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$ ‡

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The pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ leads to the formation of four cluster carbonyl complexes containing five Os atoms which have been characterised as $[Os_5C(CO)_{14}H\{OP(OMe)_2\}]$ (3), $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$ (7a), $[Os_5C(CO)_{13}H\{OP(OMe)OP(OMe)_2\}]$ (5), and $[Os_5(CO)_{15}\{P(OMe)\}]$ (2) by spectroscopic and *X*-ray single-crystal analyses. The full crystal structure of (7a) is reported; the complex crystallises in the triclinic space group $P\bar{1}$, with $a = 11.623(2)$, $b = 15.937(2)$, $c = 18.515(4)$ Å, $\alpha = 104.01(2)$, $\beta = 98.85(2)$, $\gamma = 91.65(1)°$, and $Z = 4$. The structure has been solved by a combination of multisolution Σ_2 sign expansion and Fourier-difference techniques, and refined by blocked full-matrix least squares to $R = 0.054$ for 8 446 unique observed diffractometer data. The nature and mode of co-ordination of the ligands derived from the phosphite group varies from complex to complex, and there is a stepwise progression for the first three compounds in which replacement of a carbonyl group is followed by an eventual linking of two phosphite ligands on the cluster surface. The structures of the four complexes are discussed briefly in terms of the number of electrons present.

IT has been shown [1] that the pyrolysis of $[Os_3(CO)_{12}]$ in a sealed evacuated tube leads to the formation of polynuclear osmium carbonyl species containing between five and eight osmium atoms. These complexes have been formulated as $[Os_5(CO)_{16}]$, $[Os_5C(CO)_{15}]$, $[Os_6(CO)_{18}]$, $[Os_7(CO)_{21}]$, $[Os_8(CO)_{23}]$, and $[Os_8C(CO)_{21}]$, and for the first four compounds the formulations have been confirmed by single-crystal *X*-ray analyses.[2-5] In contrast, the pyrolysis of $[Ru_3(CO)_{12}]$ leads to only one hexanuclear carbido-cluster, $[Ru_6C(CO)_{17}]$.[6] Similarly, only one isolable product, $[Ru_2(CO)_3H\{P(OC_6H_4)(OPh)_2\}\{OP(OPh)_2\}]$, is obtained from the pyrolysis of the triphenyl phosphite derivative $[Ru_3(CO)_9\{P(OPh)_3\}_3]$.[7] An obvious extension to the work on the osmium system is the pyrolysis of phosphine- or phosphite-substituted trinuclear cluster derivatives to establish whether the chemistry of the substituted complexes parallels that of the binary carbonyls by yielding a number of products. Nyholm and Mason and co-workers [8] have studied the pyrolysis of $[Os_3(CO)_{12}]$ in the presence of triphenylphosphine, and six products all based on the Os_3 unit were characterised crystallographically. In an attempt to produce a series of high-nuclearity clusters containing phosphorus-donor ligands, the pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ was undertaken and we now report the results. A number of Os_5 clusters, containing phosphite-related ligands, were isolated, and the structures of the four major products established by *X*-ray analyses. Reports of three of the structures have appeared.[9-11]

RESULTS AND DISCUSSION

The pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ at 210 °C for 16 h yielded a red-brown solid, which upon separation with ethyl acetate and thin-layer chromatography (t.l.c.) with diethyl ether–n-hexane (1 : 5) as eluant gave four initial bands. In order of decreasing R_f values the first band was found to consist of a mixture of $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$, while the fourth yellow band was broad. Repeated extraction of the latter with diethyl ether–n-hexane (1 : 1) gave three further bands. The last two of these were very close to each other on the t.l.c. plate, and repeated treatment with diethyl ether–n-hexane (55 : 45) was required before successful separation was accomplished. However, the first of these two bands was found to be a mixture of Os_4 and Os_5 clusters, which it has not been possible to separate further. When the product from the second red band was treated with hot pentane and allowed to cool a yellow product with the same i.r. and mass spectrum as the red compound was obtained suggesting the presence of two isomeric products. Details of the separation together with mass spectroscopic data are given in Table 1. The four compounds (2), (3), (5), and (7a) were characterised by i.r., n.m.r., and mass spectroscopic techniques, and by single-crystal *X*-ray analyses; the data are presented in Table 2. Line diagrams of the molecular structures of the four compounds are shown in Figure 1. The geometry of the metal framework of the first three compounds [(3), (5), and (7a)] is based on the trigonal

TABLE 1

Details of t.l.c. separation in order of decreasing R_f value

Band	Colour	Mass [a]	Comment [b]
I	Yellow		Mixture of $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$
II	Red	1 434	Single compound, (2)
III	Yellow	1 466	Single compound, (3)
IV	Yellow		Mixture of compounds
	Further separation of band IV		
V	Yellow	1 516	Single compound, (5)
VI	Yellow		Mixture of Os_4 and Os_5 clusters
VII	Red	1 562	Single compound, (7)
VIIa	Yellow	1 562	Isomer of (7), (7a)

[a] *m/e* Values for molecular ions (based on ^{192}Os). [b] The compound designators for the complexes in the text correspond to the t.l.c. band from which they were isolated.

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† Undecacarbonyl(trimethyl phosphite)triosmium.

‡ μ_5-Carbido-1,1,1,2,2,2,3,3,4,4,5,5,5-tridecacarbonyl-3,4-μ-dimethyl phosphonato-*OP*-1,4-μ-hydrido-3-(trimethyl phosphite)-pentaosmium (6 *Os-Os*).

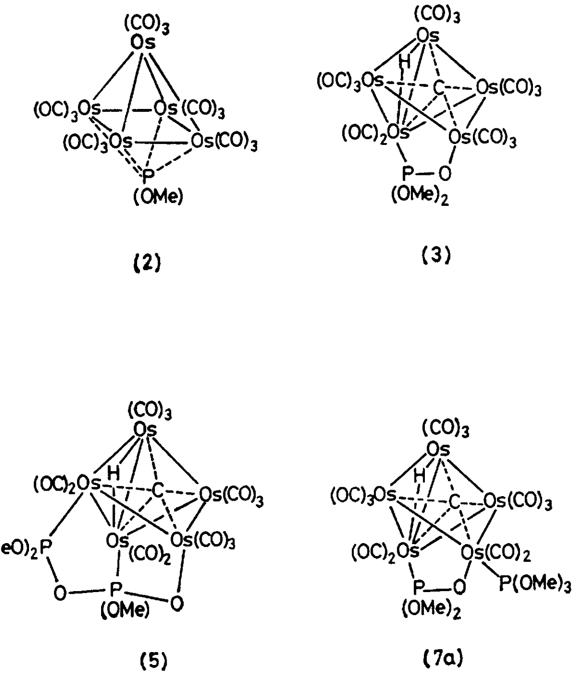
TABLE 2

Selected spectroscopic data

Complex	I.r. (cm^{-1})	N.m.r. (τ) *
(2) $[Os_5(CO)_{15}\{P(OMe)\}]$	2 085w, 2 064vs, 2 045w, 2 032vs, 2 021w, 1 998w(br)	6.57 (d), J= 17.6
(3) $[Os_5C(CO)_{14}H\{OP(OMe)_2\}]$	2 110w, 2 081vs, 2 063vs, 2 057 (sh), 2 027vs, 2 015m, 2 007m, 1 996w, 1 984w, 1 967w	6.68 (d), J = 11.9 33.76 (d), J = 35.1
(5) $[Os_5C(CO)_{13}H\{OP(OMe)OP(OMe)_2\}]$	2 104s, 2 077vs, 2 056vs, 2 035vs, 2 032 (sh), 2 026 (sh), 2 019s, 2 012s, 2 005s, 1 998s, 1 987w, 1 973m, 1 957m	6.17 (d), J = 13.9 6.19 (d), J = 12.7 6.52 (d), J = 13.1 34.08 (d), J = 30.3
(7) $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$	2 094vs, 2 053vs, 2 040 (sh), 2 034vs, 2 016 (sh), 2 011vs, 2 004 (sh), 1 995s, 1 980m, 1 970w, 1 964m, 1 958m	6.04 (d), J = 11.7 6.74 (d), J = 11.6 33.68 (d), J = 35.9

* Proton chemical shifts relative to $SiMe_4$, J in Hz.

bipyramid with various metal–metal bonds broken, and stabilised by the presence of the carbide. The metal geometry of the fourth compound (2) more closely resembles a square pyramid with the square face capped by the phosphorus-donor ligand. All the carbonyl groups in the four clusters are terminal. Although the hydride ligands in (3), (5), and (7a) were not located directly they are included in the diagrams in positions which are in agreement with the arrangement of the carbonyl groups and with the large splitting of the hydride signal in the n.m.r. spectrum by the ^{31}P nucleus.



(2) (3)

(5) (7a)

FIGURE 1 Line diagrams of the four structures isolated from the reaction showing the probable locations of the bridging hydrides

The full molecular structure of (7a) has not been reported previously, and details are given here. The crystal structure is built up from discrete molecules of $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$ held together by van der Waals forces. There are two crystallographically independent but structurally similar molecules, differing only in the orientation of the terminal phosphite ligand, in each asymmetric unit. Figures 2 and 3 are PLUTO[12] plots of the two independent molecules and include the atom-numbering scheme adopted; only one orientation of the disordered fragments has been included for clarity. The bond distances and interbond angles are presented in Tables 3 and 4 respectively.

The Os_5 cluster skeleton in (7a) may be considered as derived from the trigonal bipyramid of the parent carbonyl $[Os_5(CO)_{16}]^2$ by the breaking of one Os(equatorial)–Os(equatorial) and one Os(equatorial)–Os(axial) bond; Os(4) $\cdots$ Os(5) 3.987 Å and Os(1) $\cdots$ Os(3) 3.761 Å, and Os(9) $\cdots$ Os(10) 3.984 Å and Os(6) $\cdots$ Os(8) 3.752 Å. This ' open ' structure is stabilised by the presence of the carbide which donates four electrons to the cluster. It effectively replaces two carbonyl groups on the periphery of the molecule and thereby

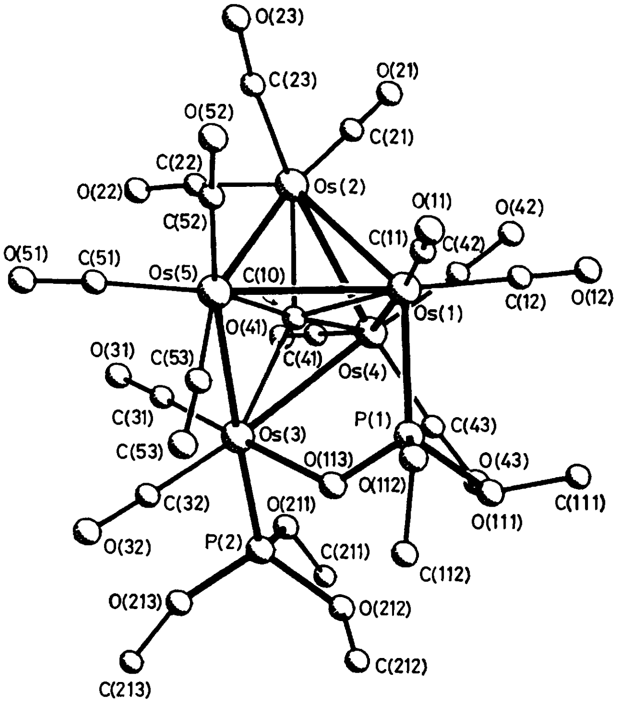


FIGURE 2 One independent molecule of $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$

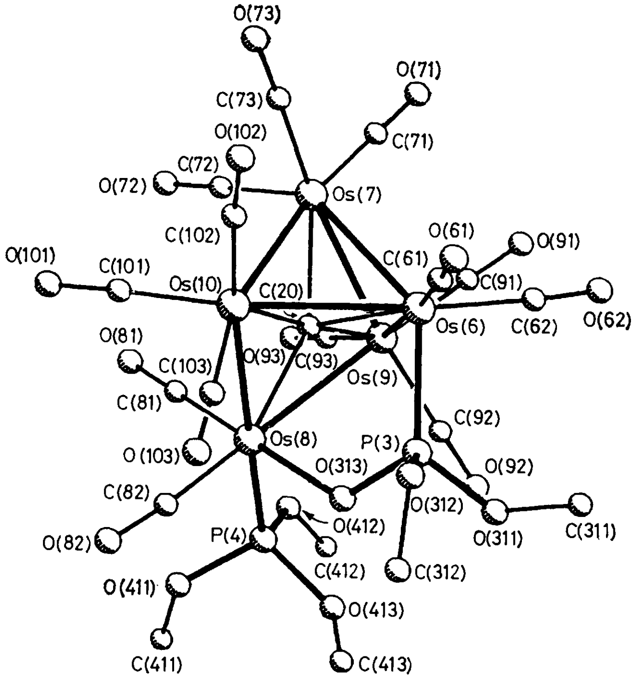


FIGURE 3 The second independent molecule of $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$

reduces the steric crowding between the bulky phosphite groups and the carbonyls around the cluster core. The carbide is approximately equidistant from all five Os atoms and it sits in the Os(1)Os(2)Os(3) plane [the Os(6)Os(7)Os(8) plane for the second molecule] (maximum deviation of 0.02 Å from the plane), lying close to the Os(4) · · · Os(5) [Os(9) · · · Os(10)] non-bonded edge. The carbide co-ordination sphere for the first molecule is illustrated in Figure 4. The individual Os–C distances are similar to those found in (3).[10]

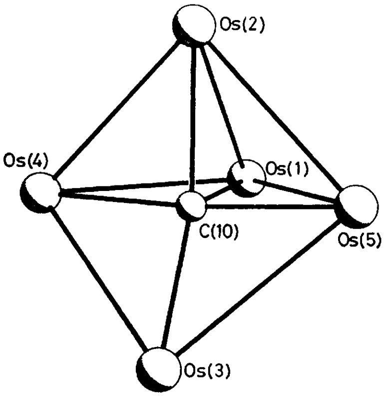


FIGURE 4 The co-ordination sphere of the carbide in $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$ showing the capped ' butterfly ' metal framework

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses *

Os(2)–Os(1)	2.893(2)	Os(7)–Os(6)	2.903(2)
Os(4)–Os(1)	2.872(2)	Os(9)–Os(6)	2.867(2)
Os(5)–Os(1)	2.873(2)	Os(10)–Os(6)	2.879(2)
C(10)–Os(1)	2.109(17)	C(20)–Os(6)	2.119(18)
P(1)–Os(1)	2.294(1)	P(3)–Os(6)	2.294(1)
C(11)–Os(1)	1.887(21)	C(61)–Os(6)	1.907(22)
C(12)–Os(1)	1.851(29)	C(62)–Os(6)	1.902(18)
Os(4)–Os(2)	2.881(2)	Os(9)–Os(7)	2.887(2)
Os(5)–Os(2)	2.868(2)	Os(10)–Os(7)	2.879(2)
C(10)–Os(2)	2.148(18)	C(20)–Os(7)	2.148(19)
C(21)–Os(2)	1.852(28)	C(71)–Os(7)	1.893(23)
C(22)–Os(2)	1.872(28)	C(72)–Os(7)	1.879(24)
C(23)–Os(2)	1.907(21)	C(73)–Os(7)	1.896(24)
Os(4)–Os(3)	2.969(2)	Os(9)–Os(8)	2.960(2)
Os(5)–Os(3)	2.939(2)	Os(10)–Os(8)	2.946(2)
C(10)–Os(3)	2.096(18)	C(20)–Os(8)	2.101(16)
O(113)–Os(3)	2.142(1)	O(313)–Os(8)	2.138(1)
P(2)–Os(3)	2.294(1)	P(4)–Os(8)	2.300(1)
C(31)–Os(3)	1.873(25)	C(81)–Os(8)	1.855(25)
C(32)–Os(3)	1.870(28)	C(82)–Os(8)	1.881(24)
C(10)–Os(4)	1.988(17)	C(20)–Os(9)	1.972(19)
C(41)–Os(4)	1.893(23)	C(91)–Os(9)	1.902(18)
C(42)–Os(4)	1.883(29)	C(92)–Os(9)	1.886(25)
C(43)–Os(4)	1.862(21)	C(93)–Os(9)	1.865(22)
C(10)–Os(5)	2.002(17)	C(20)–Os(10)	2.015(19)
C(51)–Os(5)	1.888(26)	C(101)–Os(10)	1.858(21)
C(52)–Os(5)	1.897(21)	C(102)–Os(10)	1.887(23)
C(53)–Os(5)	1.883(29)	C(103)–Os(10)	1.841(28)
O(111)–P(1)	1.608(15)	O(311)–P(3)	1.606(17)
O(112)–P(1)	1.615(15)	O(312)–P(3)	1.588(17)
O(113)–P(1)	1.506(14)	O(313)–P(3)	1.552(13)
C(111)–O(111)	1.413(33)	C(311)–O(311)	1.414(28)
C(112)–O(112)	1.469(35)	C(312)–O(312)	1.476(27)
O(211)–P(2)	1.549(19)	O(411)–P(4)	1.620(13)
O(212)–P(2)	1.620(22)	O(412)–P(4)	1.578(20)
O(12′)–P(2)	1.620(28)	O(11′)–P(4)	1.620(32)
O(213)–P(2)	1.571(21)	O(413)–P(4)	1.620(22)
C(211)–O(211)	1.491(25)	O(13′)–P(4)	1.620(31)
C(212)–O(212)	1.379(36)	C(411)–O(411)	1.434(35)
C(212)–O(12′)	1.267(48)	C(411)–O(11′)	1.531(64)
C(213)–O(213)	1.410(32)	C(412)–O(412)	1.450(36)
C(13′)–O(213)	1.410(49)	C(413)–O(413)	1.355(39)
		C(413)–O(13′)	1.409(65)
O(11)–C(11)	1.149(27)	O(61)–C(61)	1.135(30)
O(12)–C(12)	1.148(38)	O(62)–C(62)	1.114(22)
O(21)–C(21)	1.175(35)	O(71)–C(71)	1.191(30)
O(22)–C(22)	1.156(34)	O(72)–C(72)	1.141(31)
O(23)–C(23)	1.164(26)	O(73)–C(73)	1.142(31)
O(31)–C(31)	1.126(31)	O(81)–C(81)	1.170(32)
O(32)–C(32)	1.141(36)	O(82)–C(82)	1.160(32)
O(41)–C(41)	1.127(29)	O(91)–C(91)	1.152(24)
O(42)–C(42)	1.177(38)	O(92)–C(92)	1.127(32)
O(43)–C(43)	1.179(28)	O(93)–C(93)	1.172(28)
O(51)–C(51)	1.153(33)	O(101)–C(101)	1.205(27)
O(52)–C(52)	1.165(27)	O(102)–C(102)	1.158(30)
O(53)–C(53)	1.184(36)	O(103)–C(103)	1.190(35)

* Atoms with a prime are the second position of a disordered pair.

One of the phosphite ligands has undergone loss of a methyl group and the resultant $OP(OMe)_2$ species co-ordinates to Os(1) [Os(6)] *via* the P atom and to Os(3)-[Os(8)] *via* the O atom; the OsPOOs unit is planar. This ligand formally donates three electrons to the molecule while the terminal phosphite bound to Os(3)-[Os(8)] donates two electrons. The Os–P distances for the two phosphite ligands in each molecule are equivalent which suggests that the bonding for the bridged and terminal cases must be similar. These Os–P bond lengths and the bridging P–O(Os) distance are shorter than expected for a σ bond alone, while the bridging Os–O(P) distance is comparatively long. Similar trends have been observed in the Ru–P–O–Ru system of $[Ru_2(CO)_3H\{P(OC_6H_4)(OPh)_2\}\{OP(OPh)_2\}]$ [7] where the short bonds have been explained in terms of π interactions.

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

Os(4)–Os(1)–Os(2)	60.0(1)
Os(5)–Os(1)–Os(2)	59.6(1)
Os(5)–Os(1)–Os(4)	87.9(1)
C(10)–Os(1)–Os(2)	47.8(5)
C(10)–Os(1)–Os(4)	43.8(5)
C(10)–Os(1)–Os(5)	44.2(5)
P(1)–Os(1)–Os(2)	134.2(1)
P(1)–Os(1)–Os(4)	89.1(1)
P(1)–Os(1)–Os(5)	88.9(2)
P(1)–Os(1)–C(10)	86.5(5)
C(11)–Os(1)–Os(2)	116.3(7)
C(11)–Os(1)–Os(4)	176.2(7)
C(11)–Os(1)–Os(5)	89.8(8)
C(11)–Os(1)–C(10)	133.9(9)
C(11)–Os(1)–P(1)	93.9(8)
C(12)–Os(1)–Os(2)	112.4(8)
C(12)–Os(1)–Os(4)	87.1(7)
C(12)–Os(1)–Os(5)	172.0(8)
C(12)–Os(1)–C(10)	130.8(8)
C(12)–Os(1)–P(1)	97.3(8)
C(12)–Os(1)–C(11)	94.9(1)
Os(4)–Os(2)–Os(1)	59.7(1)
Os(5)–Os(2)–Os(1)	59.8(1)
Os(5)–Os(2)–Os(4)	87.8(1)
C(10)–Os(2)–Os(1)	46.6(5)
C(10)–Os(2)–Os(4)	43.6(5)
C(10)–Os(2)–Os(5)	44.2(5)
C(21)–Os(2)–Os(1)	112.4(8)
C(21)–Os(2)–Os(4)	86.0(7)
C(21)–Os(2)–Os(5)	171.9(8)
C(21)–Os(2)–C(10)	129.5(8)
C(22)–Os(2)–Os(1)	145.5(9)
C(22)–Os(2)–Os(4)	99.8(7)
C(22)–Os(2)–Os(5)	94.6(10)
C(22)–Os(2)–C(10)	99.0(12)
C(22)–Os(2)–C(21)	91.6(12)
C(23)–Os(2)–Os(1)	108.9(7)
C(23)–Os(2)–Os(4)	168.3(7)
C(23)–Os(2)–Os(5)	88.0(8)
C(23)–Os(2)–C(10)	131.5(9)
C(23)–Os(2)–C(21)	97.1(10)
C(23)–Os(2)–C(22)	91.5(10)
Os(5)–Os(3)–Os(4)	84.9(1)
C(10)–Os(3)–Os(4)	41.9(5)
C(10)–Os(3)–Os(5)	42.9(5)
O(113)–Os(3)–Os(4)	88.2(1)
O(113)–Os(3)–Os(5)	85.0(4)
O(113)–Os(3)–C(10)	85.1(5)
P(2)–Os(3)–Os(4)	97.1(2)
P(2)–Os(3)–Os(5)	173.7(1)
P(2)–Os(3)–C(10)	138.6(5)
P(2)–Os(3)–O(113)	89.1(3)
Os(9)–Os(6)–Os(7)	60.1(1)
Os(10)–Os(6)–Os(7)	59.7(1)
Os(10)–Os(6)–Os(9)	87.8(1)
C(20)–Os(6)–Os(7)	47.6(5)
C(20)–Os(6)–Os(9)	43.4(5)
C(20)–Os(6)–Os(10)	44.4(5)
P(3)–Os(6)–Os(7)	135.1(2)
P(3)–Os(6)–Os(9)	90.7(2)
P(3)–Os(6)–Os(10)	88.2(1)
P(3)–Os(6)–C(20)	87.6(5)
C(61)–Os(6)–Os(7)	115.9(7)
C(61)–Os(6)–Os(9)	175.9(6)
C(61)–Os(6)–Os(10)	89.4(5)
C(61)–Os(6)–C(20)	133.8(7)
C(61)–Os(6)–P(3)	92.2(6)
C(62)–Os(6)–Os(7)	111.0(7)
C(62)–Os(6)–Os(9)	85.3(6)
C(62)–Os(6)–Os(10)	170.5(7)
C(62)–Os(6)–C(20)	128.6(8)
C(62)–Os(6)–P(3)	98.3(6)
C(62)–Os(6)–C(61)	97.1(8)
Os(9)–Os(7)–Os(6)	59.4(1)
Os(10)–Os(7)–Os(6)	59.7(1)
Os(10)–Os(7)–Os(9)	87.4(1)
C(20)–Os(7)–Os(6)	46.7(5)
C(20)–Os(7)–Os(9)	43.1(5)
C(20)–Os(7)–Os(10)	44.4(5)
C(71)–Os(7)–Os(6)	110.9(8)
C(71)–Os(7)–Os(9)	88.2(7)
C(71)–Os(7)–Os(10)	170.6(8)
C(71)–Os(7)–C(20)	131.0(9)
C(72)–Os(7)–Os(6)	145.7(7)
C(72)–Os(7)–Os(9)	97.0(7)
C(72)–Os(7)–Os(10)	97.7(7)
C(72)–Os(7)–C(20)	99.0(8)
C(72)–Os(7)–C(71)	91.1(10)
C(73)–Os(7)–Os(6)	110.8(8)
C(73)–Os(7)–Os(9)	169.6(8)
C(73)–Os(7)–Os(10)	90.0(7)
C(73)–Os(7)–C(20)	133.7(9)
C(73)–Os(7)–C(71)	92.9(10)
C(73)–Os(7)–C(72)	93.4(10)
Os(10)–Os(8)–Os(9)	84.9(1)
C(20)–Os(8)–Os(9)	41.7(5)
C(20)–Os(8)–Os(10)	43.1(5)
O(313)–Os(8)–Os(9)	88.5(3)
O(313)–Os(8)–Os(10)	87.0(4)
O(313)–Os(8)–C(20)	87.1(6)
P(4)–Os(8)–Os(9)	95.9(1)
P(4)–Os(8)–Os(10)	177.8(2)
P(4)–Os(8)–C(20)	137.6(5)
P(4)–Os(8)–O(313)	90.9(4)
C(31)–Os(3)–Os(4)	90.5(9)
C(31)–Os(3)–Os(5)	96.3(6)
C(31)–Os(3)–C(10)	94.9(9)
C(31)–Os(3)–O(113)	178.1(7)
C(31)–Os(3)–P(2)	89.7(6)
C(32)–Os(3)–Os(4)	173.3(6)
C(32)–Os(3)–Os(5)	88.4(6)
C(32)–Os(3)–C(10)	131.4(8)
C(32)–Os(3)–O(113)	91.0(7)
C(32)–Os(3)–P(2)	89.6(6)
C(32)–Os(3)–C(31)	90.4(11)
Os(2)–Os(4)–Os(1)	60.4(1)
Os(3)–Os(4)–Os(1)	80.1(1)
Os(3)–Os(4)–Os(2)	88.3(1)
C(10)–Os(4)–Os(1)	47.2(5)
C(10)–Os(4)–Os(2)	48.2(5)
C(10)–Os(4)–Os(3)	44.8(5)
C(41)–Os(4)–Os(1)	157.6(7)
C(41)–Os(4)–Os(2)	98.8(7)
C(41)–Os(4)–Os(3)	91.7(9)
C(41)–Os(4)–C(10)	113.5(10)
C(42)–Os(4)–Os(1)	96.7(6)
C(42)–Os(4)–Os(2)	93.2(7)
C(42)–Os(4)–Os(3)	175.3(7)
C(42)–Os(4)–C(10)	134.6(8)
C(42)–Os(4)–C(41)	92.5(11)
C(43)–Os(4)–Os(1)	103.8(6)
C(43)–Os(4)–Os(2)	164.2(6)
C(43)–Os(4)–Os(3)	89.0(8)
C(43)–Os(4)–C(10)	122.3(9)
C(43)–Os(4)–C(41)	96.8(9)
C(43)–Os(4)–C(42)	88.3(11)
Os(2)–Os(5)–Os(1)	60.5(1)
Os(3)–Os(5)–Os(1)	80.6(1)
Os(3)–Os(5)–Os(2)	89.1(1)
C(10)–Os(5)–Os(1)	47.2(5)
C(10)–Os(5)–Os(2)	48.4(5)
C(10)–Os(5)–Os(3)	45.5(5)
C(51)–Os(5)–Os(1)	159.2(8)
C(51)–Os(5)–Os(2)	100.5(8)
C(51)–Os(5)–Os(3)	91.1(6)
C(51)–Os(5)–C(10)	114.5(8)
C(52)–Os(5)–Os(1)	94.3(9)
C(52)–Os(5)–Os(2)	92.8(9)
C(52)–Os(5)–Os(3)	172.8(8)
C(52)–Os(5)–C(10)	133.1(10)
C(52)–Os(5)–C(51)	95.4(10)
C(53)–Os(5)–Os(1)	101.8(8)
C(53)–Os(5)–Os(2)	162.1(8)
C(53)–Os(5)–Os(3)	84.7(7)

TABLE 4 (*continued*)

C(53)–Os(5)–C(10)	118.3(9)
C(53)–Os(5)–C(51)	96.4(12)
C(53)–Os(5)–C(52)	91.4(10)
C(81)–Os(8)–Os(9)	90.5(6)
C(81)–Os(8)–Os(10)	94.2(7)
C(81)–Os(8)–C(20)	93.0(8)
C(81)–Os(8)–O(313)	178.4(7)
C(81)–Os(8)–P(4)	87.9(7)
C(82)–Os(8)–Os(9)	174.5(8)
C(82)–Os(8)–Os(10)	90.8(7)
C(82)–Os(8)–C(20)	133.8(9)
C(82)–Os(8)–O(313)	87.9(9)
C(82)–Os(8)–P(4)	88.3(7)
C(82)–Os(8)–C(81)	93.2(11)
Os(7)–Os(9)–Os(6)	60.6(1)
Os(8)–Os(9)–Os(6)	80.2(1)
Os(8)–Os(9)–Os(7)	88.8(1)
C(20)–Os(9)–Os(6)	47.6(5)
C(20)–Os(9)–Os(7)	48.1(6)
C(20)–Os(9)–Os(8)	45.2(5)
C(91)–Os(9)–Os(6)	98.0(6)
C(91)–Os(9)–Os(7)	93.0(6)
C(91)–Os(9)–Os(8)	176.4(7)
C(91)–Os(9)–C(20)	135.2(8)
C(92)–Os(9)–Os(6)	102.1(8)
C(92)–Os(9)–Os(7)	162.7(8)
C(92)–Os(9)–Os(8)	88.7(7)
C(92)–Os(9)–C(20)	121.9(10)
C(92)–Os(9)–C(91)	88.7(9)
C(92)–Os(9)–Os(6)	159.0(6)
C(92)–Os(9)–Os(7)	101.1(7)
C(93)–Os(9)–Os(8)	89.9(6)
C(93)–Os(9)–C(20)	113.1(8)
C(93)–Os(9)–C(91)	92.9(9)
C(93)–Os(9)–C(92)	96.0(10)
Os(7)–Os(10)–Os(6)	60.5(1)
Os(8)–Os(10)–Os(6)	80.2(1)
Os(8)–Os(10)–Os(7)	89.3(1)
C(20)–Os(10)–Os(6)	47.4(5)
C(20)–Os(10)–Os(7)	48.2(5)
C(20)–Os(10)–Os(8)	45.5(5)
C(101)–Os(10)–Os(6)	156.7(7)
C(101)–Os(10)–Os(7)	98.7(7)
C(101)–Os(10)–Os(8)	89.7(6)
C(101)–Os(10)–C(20)	111.6(9)
C(102)–Os(10)–Os(6)	94.9(6)
C(102)–Os(10)–Os(7)	91.5(7)
C(102)–Os(10)–Os(8)	173.9(7)
C(102)–Os(10)–C(20)	132.6(8)
C(102)–Os(10)–C(101)	96.2(9)
C(103)–Os(10)–Os(6)	103.7(7)
C(103)–Os(10)–Os(7)	164.2(8)
C(103)–Os(10)–Os(8)	85.9(8)
C(103)–Os(10)–C(20)	120.8(10)
C(103)–Os(10)–C(101)	96.3(10)
C(103)–Os(10)–C(102)	91.8(11)
Os(2)–C(10)–Os(1)	85.6(6)
Os(3)–C(10)–Os(1)	126.9(6)
Os(3)–C(10)–Os(2)	147.5(9)
Os(4)–C(10)–Os(1)	89.0(7)
Os(4)–C(10)–Os(2)	88.2(8)
Os(4)–C(10)–Os(3)	93.2(6)
Os(5)–C(10)–Os(1)	88.6(6)
Os(5)–C(10)–Os(2)	87.3(6)
Os(5)–C(10)–Os(3)	91.6(8)
Os(5)–C(10)–Os(4)	175.1(10)
O(111)–P(1)–Os(1)	119.6(7)
O(112)–P(1)–Os(1)	111.6(6)
O(112)–P(1)–O(111)	101.8(8)
O(113)–P(1)–Os(1)	113.7(6)
O(113)–P(1)–O(111)	100.8(7)
O(113)–P(1)–O(112)	108.1(9)
C(111)–O(111)–P(1)	120.4(13)
C(112)–O(112)–P(1)	119.9(13)
P(1)–O(113)–Os(3)	127.5(9)
O(211)–P(2)–Os(3)	114.1(7)
O(212)–P(2)–Os(3)	118.4(8)
O(212)–P(2)–O(211)	94.5(10)
O(12′)–P(2)–Os(3)	117.1(13)
O(12′)–P(2)–O(211)	121.6(17)
O(213)–P(2)–Os(3)	110.6(7)
O(213)–P(2)–O(211)	106.1(10)
O(213)–P(2)–O(212)	111.6(13)
O(213)–P(2)–O(12′)	80.4(21)
C(211)–O(211)–P(2)	128.9(19)
C(212)–O(212)–P(2)	126.3(23)
C(212)–O(12′)–P(2)	135.8(21)
C(231) O(213)–P(2)	152.8(40)
O(11)–C(11)–Os(1)	174.9(24)
O(12)–C(12)–Os(1)	177.1(22)
O(21)–C(21)–Os(2)	176.1(19)
O(22)–C(22)–Os(2)	175.1(26)
O(23)–C(23)–Os(2)	173.4(23)
O(31)–C(31)–Os(3)	178.7(20)
O(32)–C(32)–Os(3)	174.9(20)
O(41)–C(41)–Os(4)	177.4(26)
O(42)–C(42)–Os(4)	176.0(19)
O(43)–C(43)–Os(4)	175.2(22)
O(51)–C(51)–Os(5)	177.0(19)
O(52)–C(52)–Os(5)	176.1(22)
O(53)–C(53)–Os(5)	173.0(20)
Os(7)–C(20)–Os(6)	85.7(6)
Os(8)–C(20)–Os(6)	125.5(10)
Os(8)–C(20)–Os(7)	148.7(10)
Os(9)–C(20)–Os(6)	88.9(6)
Os(9)–C(20)–Os(7)	88.9(7)
Os(9)–C(20)–Os(8)	93.1(7)
Os(10)–C(20)–Os(6)	88.2(7)
Os(10)–C(20)–Os(7)	87.4(7)
Os(10)–C(20)–Os(8)	91.4(7)
Os(10)–C(20)–Os(9)	175.5(9)
O(311)–P(3)–Os(6)	121.4(6)
O(312)–P(3)–Os(6)	110.4(6)
O(312)–P(3)–O(311)	103.3(9)
O(313)–P(3)–Os(6)	114.0(6)
O(313)–P(3)–O(311)	98.4(8)
O(313)–P(3)–O(312)	108.0(8)
C(311)–O(311)–P(3)	120.3(15)
C(312)–O(313)–P(3)	120.5(14)
P(3)–O(313)–Os(8)	125.7(8)
O(411)–P(4)–Os(8)	108.4(8)
O(11′)–P(4)–Os(8)	108.8(19)
O(412)–P(4)–Os(8)	114.1(7)
O(412)–P(4)–O(411)	108.7(11)
O(412)–P(4)–O(11′)	87.9(24)
O(413)–P(4)–Os(8)	119.6(8)
O(413)–P(4)–O(411)	107.1(9)
O(413)–P(4)–O(11′)	122.6(23)
O(413)–P(4)–O(412)	98.1(11)
O(13′)–P(4)–Os(8)	123.5(21)
O(13′)–P(4)–O(412)	119.0(22)
C(411)–O(411)–P(4)	124.8(19)
C(411)–O(11′)–P(4)	118.4(33)
C(412)–O(412)–P(4)	129.3(20)
C(413)–O(413)–P(4)	125.2(18)
C(413)–O(13′)–P(4)	121.5(30)
O(61)–C(61)–Os(6)	177.8(19)
O(62)–C(62)–Os(6)	176.3(17)
O(71)–C(71)–Os(7)	175.4(20)
O(72)–C(72)–Os(7)	176.0(21)
O(73)–C(73)–Os(7)	177.8(18)
O(81)–C(81)–Os(8)	178.5(20)
O(82)–C(82)–Os(8)	174.7(26)
O(91)–C(91)–Os(9)	174.2(19)
O(92)–C(92)–Os(9)	176.2(23)
O(93)–C(93)–Os(9)	178.6(17)
O(101)–C(101)–Os(10)	174.7(19)
O(102)–C(102)–Os(10)	175.2(19)
O(103)–C(103)–Os(10)	178.8(22)

The other bond parameters for the phosphite groups are similar to the values usually found.

The two longest Os–Os bonds in the structure are those involving Os(3)[Os(8)], which may help to redress any electron imbalance on this atom because of its co-ordination to the terminal phosphite, two carbonyls, the phosphonate O atom, as well as the carbide. An examination of the Os–Os distances combined with an analysis of the carbonyl arrangement, in particular the width of the *cis* Os–Os–C(carbonyl) angles, suggests that the hydride bridges the Os(1)–Os(2)[Os(6)–Os(7)] bond. The average *cis* Os–Os–C angle for the carbonyl groups around this bond is 113.9° compared to a value of 93.4° for the remainder. This indicates that the carbonyls bend away from this edge because of the steric influence of the hydride. Also, the Os(1)–Os(2) [Os(6)–Os(7)] bond is the third longest in the structure and the presence of a bridging hydride is often associated with a long metal–metal distance.

The carbonyl groups are all linear, and the mean Os–C and C–O lengths of 1.880 and 1.16 Å respectively are in good agreement with the values of 1.89 and 1.16 Å for $[Os_5(CO)_{16}]$.[2]

The structure of (7a) closely resembles that of (3).[10] One carbonyl group on the Os atom which is bonded to the bridging phosphonate O atom has been replaced by a terminal phosphite group. Otherwise the bond parameters of the Os_5C cluster core are effectively the same. In terms of a skeletal electron-counting scheme[1] these two complexes are 76-electron systems [eight electrons from each Os atom, four from the carbide, three from the bridging $OP(OMe)_2$, two from each carbonyl and the terminal phosphite, and one from the hydride]. The parent carbonyl, $[Os_5(CO)_{16}]$,[2] is considered as an 'electron-precise' 72-electron system, so the presence of four additional electrons in (3) and (7a) is consistent with there being two fewer Os–Os bonds in these complexes than in the binary carbonyl.

The relative positions of the bridging phosphonate and the terminal phosphite in (7a) are of interest when the structure is compared with that of (5).[9] This complex is also a 76-electron system and the cluster core resembles that in (3) and (7a) but the two phosphite groups have undergone a condensation to produce a $OP(OMe)OP(OMe)_2$ five-electron-donor ligand. Thus the series of complexes (3), (7a), and (5) (Figure 1) represents a stepwise substitution of a carbonyl group on a cluster by a phosphite ligand followed by ligand rearrangement to give the observed ligand linking three metal atoms *via* two P and an O atom. The crystal structure of (7a) confirms the isolation of an intermediate between the complexes (3) and (5), although because of the low yields and harsh reaction conditions it has not been possible to establish whether pyrolysis of (7a) yields (5). The position of substitution of the carbonyl group by the phosphite may be of importance if the rearrangement to give (5) is to occur. The incoming phosphite must be co-ordinated to an Os atom that is adjacent to the phosphorus-bonded Os participating in the bridging Os–P–O–Os linkage when the second P–O link forms.

The fourth complex (2)[11] isolated from the reaction is a 74-electron system with the P(OMe) ligand donating four electrons to the cluster. This structure bears less resemblance to the other three complexes but illustrates another degradation product of the phosphite ligand under the harsh reaction conditions. This complex has one more electron pair and consequently one metal–metal bond less than in $[Os_5(CO)_{16}]$,[2] and the metal framework has opened up to give the square-pyramidal geometry also observed in the structure of $[Os_5C(CO)_{15}]$.[3] In the latter complex the carbide donates four electrons to the cluster.

The description of (2) or indeed $[Os_5C(CO)_{15}]$ as a square pyramid permits a description of the four structures in terms of Wade theory.[13] A square-pyramidal geometry is predicted by this theory for a 74-electron system with seven skeletal electron pairs. Then the geometry of the Os_5C cluster core observed in the three 76-electron systems (3), (5), and (7a) is a consequence of breaking one metal–metal bond upon inclusion of two more electrons to give the distorted capped 'butterfly' metal framework (Figure 4).

EXPERIMENTAL

The cluster $[Os_3(CO)_{11}\{P(OMe)_3\}]$ was prepared by the literature method.[14] All reactions were carried out under dry oxygen-free nitrogen unless otherwise stated. Infrared spectra were recorded as solutions in 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer with polystyrene as calibrant. Mass spectra were obtained using an A.E.I. M.S. 12 instrument at 70 eV * ionising potential. Hydrogen-1 n.m.r. spectra were recorded on Perkin-Elmer R12b (60 MHz) and Varian Associates HA 100 or XL 100 spectrometers (100 MHz). Thin-layer chromatography plates were prepared in these laboratories using 20-cm square glass plates coated with a 0.3-mm layer of silica gel/CT (Reeve Angel Scientific, type code S13 FTLC). Carius-tube pyrolysis was achieved using either a tube furnace or a fan oven. All solvents were distilled and degassed before use.

Pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$.—The starting material (0.25 g) was placed in a Carius tube (85 cm^3) which was then evacuated, flamed, sealed, and heated to 210 °C for 16 h. After allowing the contents to cool, the tube was opened and the red-brown solid extracted into ethyl acetate. The solvent was removed *in vacuo* and the mixture separated by t.l.c. using diethyl ether–n-hexane (1 : 5) as eluant. Initially four bands were observed, the last of these, that with the lowest R_f value, was broad, and further separation with diethyl ether–n-hexane (1 : 1) produced three new bands. The last two of these were very close to each other on the t.l.c. plate and complete separation was achieved with diethyl ether–n-hexane (55 : 45) as eluant.

The various complexes were initially characterised using i.r. and mass spectral data. Their structures in solid and solution were regarded as being similar since their i.r. spectra in cyclohexane and Nujol mulls were identical.

Molecular-structure Determination.—Crystals of (7a)

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

$[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$ were obtained as yellow blocks from ethyl acetate–hexane. A single crystal (*ca.* 0.284 × 0.140 × 0.074 mm) was mounted on a glass fibre with epoxy-resin adhesive, and the unit-cell dimensions and space group determined *via* Weissenberg (Cu) *X*-ray photography.

This crystal was transferred to a Syntex $P2_1$ four-circle diffractometer, and accurate cell dimensions obtained by centring 15 strong reflections ($17.0 < 2\theta < 30.0°$). 12 553 Intensities were recorded in the range $3.0 < 2\theta < 60.0°$, using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha 1}$ 0.709 26, $\lambda_{\alpha 2}$ 0.713 54 Å) and a 96-step ω—2θ scan procedure; peaks were scanned from 1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$ at rates between 0.0250 and 0.4883° s^{-1}, dependent on an initial 2-s peak count; reflections with intensities of <8 counts s^{-1} were not remeasured. Two check reflections were monitored every 50 measurements throughout data collection and showed no significant variation.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 380 azimuthal scan data from 17 independent reflections was applied; transmission factors on the full data set ranged from 0.478 to 0.986. Lorentz polarisation corrections were also applied and equivalent reflections averaged to give 8 464 unique observed intensities $[F > 4\sigma(F)]$.

Crystal data. $C_{19}H_{16}O_{19}Os_5P_2$, M = 1 561.26, Triclinic, a = 11.623(2), b = 15.937(2), c = 18.515(4) Å, α = 104.01(2), β = 98.85(2), γ = 91.65(1)°, U = 3 280.19 Å^3, D_m not measured, Z = 4, D_c = 3.16 g cm^{-3}, $F(000)$ = 2 767.02, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 194.55 cm^{-1}, space group $P\bar{1}$ from successful refinement.

The 10 independent osmium-atom positions from the two molecules in the asymmetric unit were located by multisolution Σ_2 sign expansion. These atoms were assigned anisotropic thermal parameters, and subjected to three cycles of least-squares refinement. A difference electron-density map calculated using these refined parameters revealed the positions of most of the remaining non-hydrogen atoms. The terminal $P(OMe)_3$ groups in each molecule were partially disordered, but a subsequent difference map calculated on the heavy and light atom positions showed both locations of the disordered atoms. The structure was refined by blocked full-matrix least squares with the Os atoms and the ordered part of the phosphite ligands assigned anisotropic thermal parameters.

TABLE 5

Atom co-ordinates (× 10^4) with estimated standard deviations in parentheses *

Atom	*x/a*	*y/b*	*z/c*
Os(1)	1 468(1)	3 326(1)	6 337(1)
Os(2)	3 792(1)	2 782(1)	6 708(1)
Os(3)	2 218(1)	4 013(1)	8 454(1)
Os(4)	3 277(1)	4 558(1)	7 265(1)
Os(5)	1 930(1)	2 284(1)	7 403(1)
C(10)	2 583(15)	3 450(10)	7 375(10)
P(1)	149(5)	4 024(3)	7 033(3)
O(111)	−208(14)	4 969(8)	6 955(8)
C(111)	−775(25)	5 085(17)	6 257(16)
O(112)	−1 105(13)	3 484(9)	6 827(9)
C(112)	−2 020(24)	3 764(17)	7 282(18)
O(113)	542(12)	4 201(8)	7 873(7)
P(2)	2 226(5)	5 367(3)	9 243(3)
O(211)	3 293(17)	5 981(9)	9 261(9)
C(211)	3 441(28)	6 945(13)	9 523(18)
O(212)	1 274(17)	6 018(12)	9 007(15)
O(12′)	969(19)	5 735(27)	9 376(28)
C(212)	82(25)	5 911(25)	8 963(18)
O(213)	2 243(22)	5 307(11)	10 069(10)
C(213)	2 396(72)	5 668(59)	10 865(13)
C(13′)	2 200(52)	6 053(29)	10 664(31)
C(11)	349(21)	2 459(14)	5 728(14)
O(11)	−357(17)	1 924(11)	5 406(11)
C(12)	1 392(22)	4 001(15)	5 648(15)
O(12)	1 391(19)	4 434(13)	5 235(13)
C(21)	4 858(22)	3 220(14)	6 221(14)
O(21)	5 503(16)	3 463(11)	5 874(11)
C(22)	4 972(25)	2 686(16)	7 488(16)
O(22)	4 645(17)	2 646(11)	8 006(11)
C(23)	3 833(20)	1 591(14)	6 207(13)
O(23)	3 854(16)	889(11)	5 838(10)
C(31)	3 701(22)	3 883(14)	8 959(14)
O(31)	4 591(17)	3 819(11)	9 274(11)
C(32)	1 521(21)	3 540(14)	9 126(14)
O(32)	1 174(17)	3 264(11)	9 571(11)
C(41)	4 690(23)	4 959(15)	7 938(15)
O(41)	5 518(17)	5 181(11)	8 357(11)
C(42)	3 825(22)	4 916(15)	6 474(15)
O(42)	4 140(19)	5 093(13)	5 951(13)
C(43)	2 540(19)	5 590(13)	7 477(13)
O(43)	2 080(16)	6 248(11)	7 560(11)
C(51)	2 774(21)	1 802(14)	8 142(14)
O(51)	3 284(17)	1 541(11)	8 617(11)
C(52)	1 571(22)	1 216(15)	6 664(15)
O(52)	1 287(17)	577(12)	6 199(11)
C(53)	472(23)	2 209(15)	7 716(15)
O(53)	−387(17)	2 209(11)	7 987(11)
Os(6)	8 133(1)	9 857(1)	8 133(1)
Os(7)	7 731(1)	8 808(1)	9 163(1)
Os(8)	5 996(1)	8 034(1)	6 989(1)
Os(9)	5 797(1)	9 449(1)	8 324(1)
Os(10)	8 421(1)	8 023(1)	7 737(1)
C(20)	7 054(16)	8 716(11)	7 998(11)
P(3)	7 513(5)	9 763(3)	6 877(3)
O(311)	6 809(14)	10 514(9)	6 603(9)
C(311)	7 359(24)	11 351(14)	6 727(16)
O(312)	8 591(13)	9 689(9)	6 438(8)
C(312)	8 404(22)	9 521(24)	5 607(18)
O(313)	6 620(13)	8 985(8)	6 476(7)
P(4)	4 129(5)	8 063(3)	6 370(3)
O(411)	3 739(20)	7 116(7)	5 807(11)
O(11′)	3 522(50)	7 086(15)	6 111(36)
C(411)	2 581(25)	6 844(23)	5 405(19)
O(412)	3 198(15)	8 305(11)	6 910(10)
C(412)	2 083(25)	8 674(24)	6 775(19)
O(413)	3 844(18)	8 770(11)	5 880(11)
O(13′)	3 834(49)	8 176(37)	5 516(12)
C(413)	4 374(22)	8 857(17)	5 297(16)
C(61)	9 723(18)	10 070(12)	8 046(12)
O(61)	10 678(18)	10 201(11)	8 018(11)
C(62)	7 819(17)	11 030(11)	8 523(11)
O(62)	7 688(14)	11 721(9)	8 780(9)
C(71)	7 321(20)	9 498(14)	10 059(14)
O(71)	7 139(17)	9 962(12)	10 633(12)
C(72)	6 912(20)	7 828(14)	9 280(13)
O(72)	6 461(16)	7 205(11)	9 333(11)
C(73)	9 166(21)	8 548(14)	9 675(14)
O(73)	10 029(17)	8 368(11)	9 966(11)
C(81)	5 418(20)	7 227(13)	7 439(13)
O(81)	5 078(16)	6 714(11)	7 728(11)
C(82)	6 269(22)	7 180(15)	6 146(15)
O(82)	6 455(20)	6 611(14)	5 636(13)
C(91)	5 688(18)	10 410(12)	9 146(12)
O(91)	5 711(15)	11 019(10)	9 635(10)
C(92)	4 906(21)	10 024(14)	7 676(14)
O(92)	4 428(16)	10 384(11)	7 281(10)
C(93)	4 537(19)	8 824(12)	8 505(12)
O(93)	3 754(15)	8 415(10)	8 610(9)
C(101)	8 150(19)	6 865(13)	7 730(12)
O(101)	7 880(15)	6 126(10)	7 719(10)
C(102)	10 007(21)	8 125(14)	8 187(13)
O(102)	10 970(17)	8 249(11)	8 484(11)
C(103)	8 804(22)	7 820(15)	6 784(15)
O(103)	9 071(16)	7 683(11)	6 173(11)

* Where atoms are disordered the second position is indicated by a prime.

In molecule 1 one phosphite oxygen and one methyl carbon were each disordered between two positions in a *ca.* 2 : 1 ratio, while in molecule 2 two phosphite oxygen atoms were similarly disordered. For each of these atoms the occupancies of the two positions were assigned values of k and $1 - k$, and k refined, and both contributors given a common isotropic temperature factor. In the final stages of refinement 18 strong low-angle reflections, which were considered to be suffering severely from absorption, were zero weighted and a weighting scheme of the form $w = 1.0357/[\sigma^2(F) + 0.0007|F_o|^2]$ introduced; this reduced the dependence of $\omega\Delta^2$ on $|F_o|$ and $\sin\theta$. Refinement continued until the maximum shift-to-error ratio for any parameter was <0.01. The final residuals for the 8 446 reflections were $R = 0.054$ and $R' = (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|) = 0.050$, and a difference map calculated at this stage only showed ripple peaks of *ca.* 1.4 e Å^{-3} close to the Os atom positions. The hydride ligand and methyl-hydrogen atoms were not located.

Complex neutral-atom scattering factors were employed, and were modified for anomalous dispersion.[15] All computations were performed on the University of Cambridge IBM 370/165 computer, using programs written by Professor G. M. Sheldrick.[16] The atomic fractional co-ordinates are listed in Table 5, while details of thermal parameters, observed and calculated structure factors, and least-squares planes have been deposited as Supplementary Publication No. SUP 23119 (52 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.