Preparation and Some Reactions of $[Os_5(CO)_{19}]$; the Molecular Structures of $[Os_5(CO)_{19}]$ and $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$ †

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The reaction of $[Os_6(CO)_{18}]$ with carbon monoxide at 160 °C and 90 atm leads to the formation of $[Os_5(CO)_{19}]$ (1) in high yields. This complex crystallises in the triclinic space group $P\bar{1}$ with $a = 8.880(4)$, $b = 10.244(5)$, $c = 16.529(7)$ Å, $\alpha = 99.98(2)$, $\beta = 93.44(2)$, $\gamma = 110.37(3)°$, and $Z = 2$. The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by blocked-cascade least squares to $R = 0.040$ for 2 616 observed diffractometer data. The metal-atom skeleton consists of two triangles sharing a vertex. The Os atom common to both triangles is co-ordinated to three terminal carbonyl groups, and the other four metal atoms are each co-ordinated to four carbonyl groups, two in axial and two in equatorial sites. Complex (1) reacts with ligands L = $P(OMe)_3$ (a) or PEt_3(b) to produce complexes with the general formula $[Os_5(CO)_{16-n}L_n]$ [n = 1 (2a,b) or 2 (3a,b)]. On heating, $[Os_5(CO)_{19}]$ decarbonylates to give $[Os_5(CO)_{16}]$ (4) which subsequently reacts with ligands L = CO, $P(OMe)_3$ (a), or PEt_3 (b) to produce $[Os_5(CO)_{16}L_3]$ (1), (5a), and (5b) respectively. The molecular structure of $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$ (5a) has been solved using the same techniques as for (1), and refined by blocked full-matrix least squares to $R = 0.071$ for 2 144 observed diffractometer data. This complex crystallises in the triclinic space group $P\bar{1}$ with $a = 11.150(5)$, $b = 11.792(6)$, $c = 18.581(10)$ Å, $\alpha = 106.91(3)$, $\beta = 92.67(3)$, $\gamma = 109.45(3)°$, and $Z = 2$. The molecular geometry resembles that of (1) except that three equatorial carbonyls on three different Os atoms have been replaced by phosphite groups. The relationship between the structures of (1) and (4) is discussed briefly in terms of transformations of the metal cluster skeleton. These two compounds represent the first case where two binary carbonyls with the same number of metal atoms have different numbers of carbonyls bonded to them.

Osmium cluster carbonyls or their derivatives containing between three and eight metal atoms are known,[1] and there are now examples of osmium clusters containing ten metal atoms.[2] Hitherto the binary carbonyls of osmium that have been fully characterised are $[Os_3(CO)_{12}]$,[3] $[Os_5(CO)_{16}]$,[4] $[Os_6(CO)_{18}]$,[5] and $[Os_7(CO)_{21}]$,[6] and $[Os_8(CO)_{23}]$ has been identified by spectroscopic techniques.[7] There is one parent, neutral binary carbonyl for each of the series of Os_3, Os_5, Os_6, Os_7, and Os_8 carbonyl clusters. The parent Os_4 cluster, $Os_4(CO)_{14}$, has not been obtained, as yet. It has been suggested that the reason for this is that there are too many carbonyls to pack around the Os_4 tetrahedron required by electron-counting rules.

All the higher binary carbonyls may be prepared by the pyrolysis of $[Os_3(CO)_{12}]$, but all are obtained under the same conditions and in fairly low yield together with some higher carbido-clusters.[7] From the pyrolysis of one of these products, $[Os_6(CO)_{18}]$, under carefully controlled conditions it has been possible to obtain another cluster, $[Os_5(CO)_{19}]$, in high yield. A preliminary report of this work has appeared.[8] This complex reacts readily with phosphines and phosphites under mild conditions to give $[Os_5(CO)_{16-n}(PR_3)_n]$ (n = 1 or 2; R = OMe or Et). Upon heating $[Os_5(CO)_{19}]$ gives $[Os_5(CO)_{16}]$ by decarbonylation, and this reacts with PR_3 (R = OMe or Et) species to yield $[Os_5(CO)_{16}(PR_3)_3]$, and with CO it reverts to $[Os_5(CO)_{19}]$.

Results and Discussion

The reaction of $[Os_6(CO)_{18}]$ in heptane at 160 °C with carbon monoxide under 90 atm pressure for *ca.* 1 h gives an orange crystalline product in yields approaching 80%. The major product is purified by recrystallisation from dichloromethane to give orange block-shaped crystals. The mass spectroscopic and i.r. data for this compound are given in Table 1, and are consistent with the formulation $[Os_5(CO)_{19}]$ (1). The other product of the reaction [equation (i)] has been identified, on

$$[Os_6(CO)_{18}](soln.) + 6CO \longrightarrow [Os_5(CO)_{19}]\ (1) + [Os(CO)_5] \quad (i)$$

the basis of i.r. spectroscopy and physical properties, as $[Os(CO)_5]$. The reaction has been followed by monitoring the change in i.r. spectrum with time. At no stage was it possible to detect other intermediate compounds. However, the conditions for the reaction are critical. Over longer periods of time (*ca.* 2.5 h) or at higher temperatures (*ca.* 170 °C) or pressures (*ca.* 100 atm) a range of products is observed.[8]

In order to establish the molecular structure of the new binary carbonyl cluster, $[Os_5(CO)_{19}]$ (1), a single-crystal *X*-ray analysis was undertaken. The molecular structure of (1) is illustrated in Figure 1 and the bond lengths and interbond angles are listed in Table 2. In the solid state the molecules exist as discrete, neutral $[Os_5(CO)_{19}]$ units separated by normal van der Waals distances.

The five Os atoms define two triangles sharing a vertex. The two triangles are not coplanar but skewed with respect to each other so that the dihedral angle between the Os(1)-Os(2)Os(3) and the Os(3)Os(4)Os(5) planes is 21.2°; Os(4) lies 0.74(1) Å above the Os(1)Os(2)Os(3) triangle and Os(5) 0.26(1) Å below it. This arrangement of the Os atoms resembles the shape of a ' bow-tie; ' the central metal atom, Os(3), is co-ordinated to three terminal carbonyl ligands giving this atom

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† μ-Tricarbonylosmio-bis[bis(tetracarbonylosmium)(*Os-Os*)]-(4 *Os-Os*) and μ-tricarbonylosmio-{bis[tricarbonyl(trimethyl phosphite)osmium](*Os-Os*)}[heptacarbonyl(trimethyl phosphite)-diosmium(*Os-Os*)](4 *Os-Os*).

Supplementary data available (No. SUP 23376, 34 pp.): thermal parameters, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Spectroscopic properties of $[Os_5(CO)_{19}]$ and some of its derivatives

Compound	$\tilde{\nu}$(CO)/cm^{-1}	*m/e*	Yield(%)
(1a) $[Os_5(CO)_{19}]$	2 099m, 2 073s, 2 068w (sh), 2 040s (br), 2 035m (sh), 2 027w (sh), 2 000w (br), 1 980w (br) [a]	1 484 [b]	80
(2a) $[Os_5(CO)_{15}\{P(OMe)_3\}]$	2 084w, 2 064m (br), 2 031s, 2 000w (sh) [c]	1 496 [d]	35
(3a) $[Os_5(CO)_{14}\{P(OMe)_3\}_2]$	2 096w, 2 073m, 2 045m, 2 019s, 1 979m (sh) [c]	1 592 [e]	45
(3b) $[Os_5(CO)_{14}(PEt_3)_2]$ isomer 1	2 117w, 2 081m, 2 064m, 2 038m (sh), 2 018s, 2 013m (sh), 1 970w (br), 1 944w (sh) [c]	1 580 [e]	35
isomer 2	2 098w, 2 068m, 2 034m (sh), 2 013s, 1 966m, 1 949w (sh) [c]	1 580 [e]	45
(5a) $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$	2 094w, 2 057m, 2 035m, 2 010s, 1 988m (sh) [c]	1 688 [f]	80
(5b) $[Os_5(CO)_{16}(PEt_3)_3]$	2 085w, 2 042m, 2 024m, 2 002s, 1 975m (sh), 1 942w(sh) [c]	1 670 [f]	60

[a] In heptane solution. [b] The parent ion and ions corresponding to the loss of three CO groups are weak; ions corresponding to $Os_5(CO)_{16-n}$ (n = 0—16) are strong. [c] In CH_2Cl_2. [d] Loss of 15 CO groups. [e] Loss of 14 CO groups. [f] Parent peak not observed; first peak $Os_5(CO)_{13}(PR_3)_3$, then loss of 13 CO, then complex.

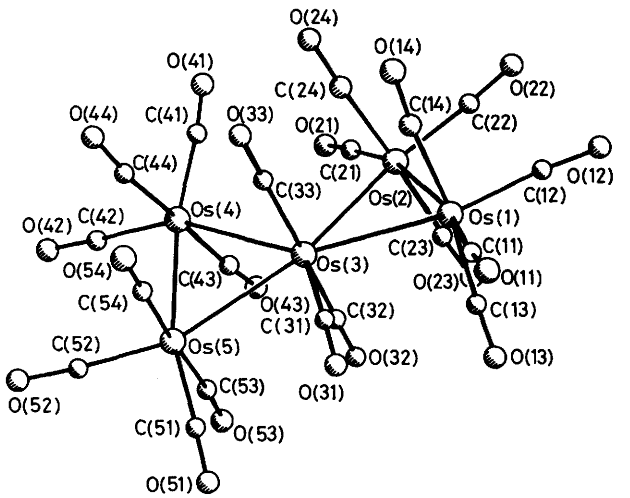


Figure 1. The molecular structure of $[Os_5(CO)_{19}]$ (1) showing the atom-numbering scheme

a formal co-ordination number of seven. The other four Os atoms are six-co-ordinate, each co-ordinating to two equatorial and two axial terminal carbonyls.

The Os(1)–Os(2) and Os(4)–Os(5) bonds, between six-co-ordinate metal atoms, are *ca.* 0.03 Å shorter than the average Os–Os distance of 2.877(3) Å in $[Os_3(CO)_{12}]$.[3] The four metal–metal bonds involving Os(3) are significantly longer, and show asymmetry [average of Os(1)–Os(3) and Os(3)–Os(5) 2.916(3) Å, of Os(2)–Os(3) and Os(3)–Os(4) 2.945(3) Å]. In other complexes such as $[Fe_4Pt(CO)_{16}]^{2-}$ [9] and $[Os_6Au(CO)_{20}H_2]^-$,[10] where the metal skeleton also contains two triangles sharing a vertex, there is no asymmetry between the bonds from the central metal atom to the other metals. However, the bonding in these two complexes is somewhat different from that in $[Os_5(CO)_{19}]$. In the $[Fe_4Pt(CO)_{16}]^{2-}$ anion [9] the Pt atom exhibits the normal square-planar geometry, while in the $[Os_6Au(CO)_{20}H_2]^-$ anion [10] the Au^I atom is *sp* hybridised and the lobe of this orbital points at the centre of an Os–Os link to form a multicentre bonding unit. In $[Os_5(CO)_{19}]$ the longest metal–metal bonds, Os(2)–Os(3) and Os(3)–Os(4), are associated with the narrowest Os–Os(3)–Os angle, Os(2)–Os(3)–Os(4). This asymmetry of the metal bonds to Os(3) may result from steric interactions between the carbonyls; there is a contact between two equatorial carbonyls on Os(2) and Os(4) [O(21) ··· C(41) 3.206(19) Å] which would become abnormally short with shorter Os–Os bonds assuming that the remainder of the geometry stays the same. An alternative explanation based on electronic arguments would suggest that a seven-co-ordinate metal atom would not be expected to exhibit a regular co-ordination geometry because of the uneven hybridisation of the metal orbitals.

The average Os–Os bond length of 2.80(2) Å in the Os_5 binary carbonyl cluster, $[Os_5(CO)_{16}]$,[4] is shorter than the average value of 2.90(2) Å in $[Os_5(CO)_{19}]$. The longest bonds [2.867(3) and 2.889(3) Å] in the former are associated with the eight-co-ordinate metal atom.

Although the high estimated standard deviations on the carbonyl bond parameters make difficult an assessment of the nature of the bonding, the trends indicate that the axial Os–C(carbonyl) distances [mean 1.95(3) Å] on the four six-co-ordinate Os atoms are longer than the Os–C(carbonyl) equatorial distances [mean 1.91(2) Å]. This reflects the greater competition between two *trans* carbonyls for back donation from the same filled metal orbital as compared to that between a carbonyl and a *trans* Os atom which is the case for the equatorial carbonyl groups. The Os(3)–C(carbonyl) distances [mean 1.90(3) Å] are similar to those of the equatorial Os–C bond lengths for the Os atoms. Although all the carbonyls are essentially linear the average values for the axial and equatorial Os–C–O angles are 174(2) and 177(2)°, respectively. The greater deviation of the axial bond angles probably reduces the steric crowding between the axial groups on adjacent Os atoms.

The complexes $[Os_5(CO)_{16}]$ and $[Os_5(CO)_{19}]$ represent the first example of two binary carbonyls containing the same number of metal atoms having different numbers of carbonyl groups. The probability of this situation occurring increases as the size of the cluster increases. It is possible in larger clusters to break some metal–metal bonds, and occupy the vacant metal co-ordination sites with carbonyls, without reducing the nuclearity of the metal framework.

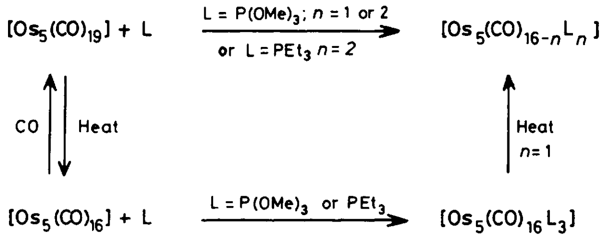
The cluster $[Os_5(CO)_{19}]$ (1) is fairly stable in non-co-ordinating solvents, but reacts slowly with co-ordinating solvents, such as acetonitrile or tetrahydrofuran, to produce substituted triosmium clusters $[Os_3(CO)_{12-n}(solv)_n]$ (n = 0, 1, or 2; solv = solvent). The carbonylation of (1) results in the formation of $[Os_3(CO)_{12}]$ presumably eliminating $[Os_2(CO)_9]$. While $[Os_2(CO)_9]$ cannot be identified unambiguously, it can be shown that $[Os(CO)_5]$ is not produced in this reaction. Thus the reaction of $[Os_5(CO)_{19}]$ with carbon monoxide at 160 °C and 90 atm for *ca.* 1 h, followed by evaporation, results in an 80% conversion into $[Os_3(CO)_{12}]$.

Reaction of $[Os_5(CO)_{19}]$ (1) with the ligands L [L = $P(OMe)_3$ (a) or PEt_3 (b)] at 40 °C for 20 h gives $[Os_5(CO)_{16-n}L_n]$ [n = 1 (2a, b) or 2 (3a, b)]. Complex (3b) exists in two isomeric forms which have been characterised by i.r. and mass spectroscopic techniques (Table 1). Presumably these clusters have a

Table 2. Bond lengths (Å) and angles (°) for $[Os_5(CO)_{19}]$ (1)

Os(1)-Os(2)	2.853(2)	Os(3)-Os(4)	2.940(2)	C(31)-O(31)	1.150(29)	Os(3)-C(31)	1.889(24)
Os(1)-Os(3)	2.918(2)	Os(3)-Os(5)	2.913(2)	C(32)-O(32)	1.180(29)	Os(3)-C(32)	1.895(23)
Os(2)-Os(3)	2.950(2)	Os(4)-Os(5)	2.848(2)	C(33)-O(33)	1.162(27)	Os(3)-C(33)	1.911(21)
C(11)-O(11)	1.122(25)	Os(1)-C(11)	1.936(21)	C(41)-O(41)	1.116(31)	Os(4)-C(41)	1.934(24)
C(12)-O(12)	1.143(29)	Os(1)-C(12)	1.899(23)	C(42)-O(42)	1.159(25)	Os(4)-C(42)	1.902(20)
C(13)-O(13)	1.152(30)	Os(1)-C(13)	1.924(24)	C(43)-O(43)	1.111(34)	Os(4)-C(43)	1.979(27)
C(14)-O(14)	1.142(29)	Os(1)-C(14)	1.957(24)	C(44)-O(44)	1.128(32)	Os(4)-C(44)	1.965(27)
C(21)-O(21)	1.115(25)	Os(2)-C(21)	1.940(21)	C(51)-O(51)	1.118(31)	Os(5)-C(51)	1.903(26)
C(22)-O(22)	1.172(29)	Os(2)-C(22)	1.889(23)	C(52)-O(52)	1.135(29)	Os(5)-C(52)	1.911(24)
C(23)-O(23)	1.135(34)	Os(2)-C(23)	1.940(27)	C(53)-O(53)	1.130(30)	Os(5)-C(53)	1.955(24)
C(24)-O(24)	1.160(30)	Os(2)-C(24)	1.920(24)	C(54)-O(54)	1.149(31)	Os(5)-C(54)	1.936(25)

Os(2)-Os(1)-Os(3)	61.5(1)	Os(2)-Os(1)-C(11)	169.1(7)	C(41)-Os(4)-C(42)	98.9(9)	Os(2)-Os(3)-C(33)	95.6(6)
Os(1)-Os(2)-Os(3)	60.4(1)	Os(3)-Os(1)-C(11)	109.1(6)	C(41)-Os(4)-C(43)	92.2(11)	Os(4)-Os(3)-C(33)	80.3(5)
Os(1)-Os(3)-Os(2)	58.2(1)	Os(2)-Os(1)-C(12)	91.8(6)	C(42)-Os(4)-C(43)	90.0(10)	Os(5)-Os(3)-C(33)	92.7(6)
Os(1)-Os(3)-Os(4)	150.1(1)	Os(3)-Os(1)-C(12)	153.1(6)	C(41)-Os(4)-C(44)	89.2(11)	Os(3)-Os(4)-C(41)	105.6(6)
Os(2)-Os(3)-Os(4)	95.2(1)	Os(2)-Os(1)-C(13)	92.7(6)	C(42)-Os(4)-C(44)	91.9(10)	Os(5)-Os(4)-C(41)	163.9(6)
Os(1)-Os(3)-Os(5)	150.8(1)	Os(3)-Os(1)-C(13)	84.7(6)	C(43)-Os(4)-C(44)	177.4(8)	Os(3)-Os(4)-C(42)	154.9(7)
Os(2)-Os(3)-Os(5)	150.3(1)	Os(2)-Os(1)-C(14)	88.2(6)	C(51)-Os(5)-C(52)	96.5(10)	Os(5)-Os(4)-C(42)	96.0(7)
Os(4)-Os(3)-Os(5)	58.2(1)	Os(3)-Os(1)-C(14)	90.3(5)	C(51)-Os(5)-C(53)	87.5(11)	Os(3)-Os(4)-C(43)	83.6(6)
Os(3)-Os(4)-Os(5)	60.4(1)	Os(1)-Os(2)-C(21)	165.8(7)	C(52)-Os(5)-C(53)	91.8(10)	Os(5)-Os(4)-C(43)	93.9(7)
Os(3)-Os(5)-Os(4)	61.4(1)	Os(3)-Os(2)-C(21)	107.4(7)	C(51)-Os(5)-C(54)	90.3(11)	Os(3)-Os(4)-C(44)	93.9(6)
C(11)-Os(1)-C(12)	97.8(9)	Os(1)-Os(2)-C(22)	97.7(6)	C(52)-Os(5)-C(54)	91.9(10)	Os(5)-Os(4)-C(44)	84.2(7)
C(11)-Os(1)-C(13)	91.8(9)	Os(3)-Os(2)-C(22)	157.3(6)	C(53)-Os(5)-C(54)	175.9(8)	Os(3)-Os(5)-C(51)	105.4(8)
C(12)-Os(1)-C(13)	94.1(10)	Os(1)-Os(2)-C(23)	84.9(7)	Os(1)-C(11)-O(11)	173.1(18)	Os(4)-Os(5)-C(51)	165.2(9)
C(11)-Os(1)-C(14)	86.4(9)	Os(3)-Os(2)-C(23)	92.5(8)	Os(1)-C(12)-O(12)	175.5(19)	Os(3)-Os(5)-C(52)	158.0(7)
C(12)-Os(1)-C(14)	92.1(10)	Os(1)-Os(2)-C(24)	93.7(6)	Os(1)-C(13)-O(13)	174.6(19)	Os(4)-Os(5)-C(52)	97.0(7)
C(13)-Os(1)-C(14)	173.7(10)	Os(3)-Os(2)-C(24)	83.1(7)	Os(1)-C(14)-O(14)	172.6(17)	Os(3)-Os(5)-C(53)	90.5(6)
C(21)-Os(2)-C(22)	95.1(9)	Os(1)-Os(3)-C(31)	74.1(7)	Os(2)-C(22)-O(22)	178.5(21)	Os(4)-Os(5)-C(53)	86.0(6)
C(21)-Os(2)-C(23)	88.8(10)	Os(2)-Os(3)-C(31)	130.8(7)	Os(2)-C(24)-O(24)	176.1(19)	Os(3)-Os(5)-C(54)	86.8(7)
C(22)-Os(2)-C(23)	91.3(11)	Os(4)-Os(3)-C(31)	134.0(7)	Os(3)-C(32)-O(32)	176.8(17)	Os(4)-Os(5)-C(54)	95.3(7)
C(21)-Os(2)-C(24)	91.6(10)	Os(5)-Os(3)-C(31)	76.7(7)	Os(4)-C(41)-O(41)	174.5(23)	Os(2)-C(21)-O(21)	179.8(27)
C(22)-Os(2)-C(24)	93.2(10)	Os(1)-Os(3)-C(32)	96.3(6)	Os(4)-C(43)-O(43)	173.3(20)	Os(2)-C(23)-O(23)	174.9(24)
C(23)-Os(2)-C(24)	175.4(10)	Os(2)-Os(3)-C(32)	81.9(7)	Os(5)-C(51)-O(51)	176.9(28)	Os(3)-C(31)-O(31)	177.3(14)
C(31)-Os(3)-C(32)	92.6(10)	Os(4)-Os(3)-C(32)	92.6(5)	Os(5)-C(53)-O(53)	172.3(20)	Os(3)-C(33)-O(33)	174.1(16)
C(31)-Os(3)-C(33)	94.5(10)	Os(5)-Os(3)-C(32)	86.0(6)	Os(4)-C(42)-O(42)	179.2(22)	Os(5)-C(52)-O(52)	177.7(26)
C(32)-Os(3)-C(33)	172.3(8)	Os(1)-Os(3)-C(33)	88.5(5)	Os(4)-C(44)-O(44)	172.7(20)	Os(5)-C(54)-O(54)	178.9(14)



Scheme 1. Some reactions of $[Os_5(CO)_{19}]$

trigonal-bipyramidal metal skeleton analogous to $[Os_5(CO)_{16}]$ (4).[4] The decarbonylation of (1), at 120 °C for 0.25 h, results in the formation of $[Os_5(CO)_{16}]$ (4).

The carbonylation of $[Os_5(CO)_{16}]$ (4), at 155 °C and 50 atm for *ca.* 1 h, gives $[Os_5(CO)_{19}]$ (1). Similarly, it has been established that (4) undergoes addition of other ligands, L = $P(OMe)_3$ or PEt_3, to produce the clusters $[Os_5(CO)_{16}L_3]$ [L = $P(OMe)_3$ (5a) or PEt_3 (5b)]. These clusters were initially characterised by i.r. and mass spectroscopic techniques (Table 1), and a single-crystal *X*-ray analysis of (5a) revealed it to be analogous to $[Os_5(CO)_{19}]$ (1). These reactions are summarised in Scheme 1.

The molecular structure of $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$ (5a) is shown in Figure 2, the bond lengths and angles being given in Table 3. Neutral molecules of (5a) are separated by normal van der Waals distances.

The structure of (5a) closely resembles that of $[Os_5(CO)_{19}]$ (1), the most significant difference is that three equatorial carbonyls on atoms Os(1), Os(2), and Os(5) have been replaced by phosphite ligands. In this complex the dihedral angle between the triangles defined by Os(1)Os(2)Os(3) and Os(3)Os(4)Os(5) is 24.8° while Os(4) lies 0.95(1) Å above the Os(1)Os(2)Os(3) plane and Os(5) 0.18(1) Å below it. This indicates a slight increase in the twisting of the two triangles over that in the $[Os_5(CO)_{19}]$ cluster. The Os–Os bonds in (5a) are generally similar to those in (1) and the angles within the ' bow-tie ' show little deviation from the values in (1). However, the Os(1)–Os(3) and the Os(4)–Os(5) bonds in (5a) are *ca.* 0.025 Å longer than the equivalent bonds in (1), and these bonds are *cis* to two of the equatorial Os–P bonds. The increase in length may partially reduce the steric crowding between the phosphite and the adjacent equatorial carbonyl group [O(3) • • • O(31) 3.14(3), O(7) • • • O(42) 3.07(3) Å]. The third Os–Os bond with a *cis* phosphite group is not significantly longer than the equivalent bond in (1), but the orientation of the phosphite group is such that the shortest contact between the phosphite and the adjacent carbonyl [O(6) • • • O(11) 3.23(3) Å] is longer and does not require a lengthening of the Os(1)–Os(2) bond.

The Os(1)–P(1) bond *trans* to the Os(1)–Os(2) bond, where both the metal atoms are six-co-ordinate, is *ca.* 0.03 Å longer than the average value of 2.25(2) Å for the two Os–P bonds *trans* to Os–Os bonds involving the seven-co-ordinate Os(3) atom. The longer Os–P bond is similar in length to the value of 2.285(5) Å for the bond in the trinuclear $[Os_3(CO)_{11}\{P(OMe)_3\}]$ complex,[11] and similar to that in the pentanuclear

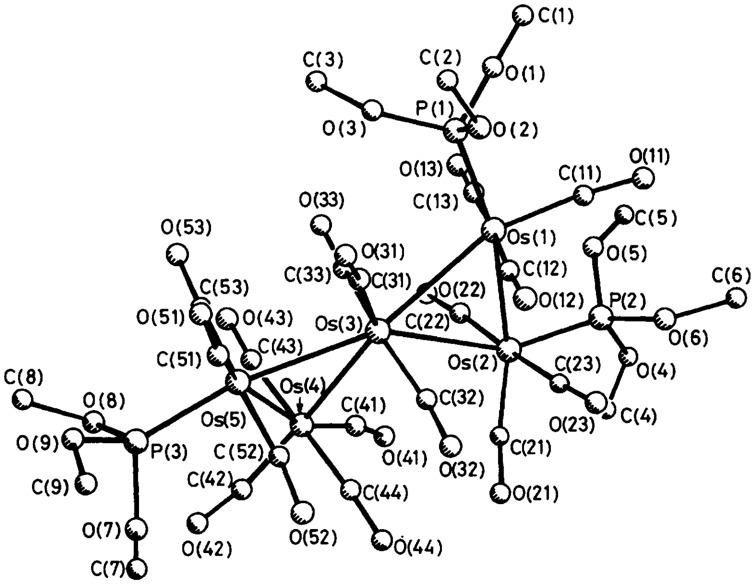


Figure 2. The molecular structure of [Os$_5$(CO)$_{16}${P(OMe)$_3$}$_3$] (5a) showing the atom-numbering scheme

cluster [Os$_5$(CO)$_{15}$H$_2${P(OMe)$_3$}].[12] The high estimated standard deviations on the bond parameters of the phosphite and carbonyl ligands precludes a detailed discussion, and the high thermal parameters of the atoms in the phosphite groups indicates some positional disorder.

When [Os$_5$(CO)$_{16}${P(OMe)$_3$}$_3$] (5a) is heated the monosubstituted complex [Os$_5$(CO)$_{15}${P(OMe)$_3$}] is formed. This indicates the structural relationship between the trigonal-bipyramidal structure of [Os$_5$(CO)$_{16}$][4] and the ' bow-tie ' structure of [Os$_5$(CO)$_{19}$]. A possible pathway for the conversion of [Os$_5$(CO)$_{16}$] into [Os$_5$(CO)$_{19}$] is presented in Scheme 2, although the postulated intermediates, obtained by the addition or loss of carbonyl groups, have not been detected.

The transformations between pentanuclear metal frameworks may be extended further. In osmium cluster chemistry it has been suggested that the addition of a pair of electrons to a cluster is concomitant with the breaking of a metal–metal bond.[13] Then considering sequential bond ruptures, each formally caused by the donation of an additional electron pair, all the unique interrelated arrangements of pentanuclear metal clusters are shown in Figure 3. These do not include cases where bond ruptures would lead to terminal metal atoms or those where further bond rupture would not lead to a change in geometry. The parent polyhedron in this series is the trigonal bipyramid, the best known example of which in osmium chemistry is [Os$_5$(CO)$_{16}$],[4] an electron-precise 72-electron system. There are two different types of bond in the trigonal bipyramid, marked α and β in structure (a) of Figure 3. The rupture of bond α produces the square-based pyramidal geometry (b) which has been observed in the structure of [Os$_5$(CO)$_{15}$C].[14] The rupture of bond β gives an edge-bridged tetrahedron (c) which is exemplified by the structure of [Os$_5$(CO)$_{16}$H$_2$].[15] Both these complexes are 74-electron systems. For the square-based pyramid (b) there are two unique types of bonds, α and β in structure (b), which on breaking lead to different geometries. The breaking of bond α results in a structure where three triangles share two common edges (d). This geometry has been described as an edge-bridged ' butterfly ' in the structure of [Os$_5$(CO)$_{13}$(PhCCPh)$_2$],[16] and as a ' swallow-shaped ' cluster in [Ru$_5$(CO)$_{14}$(CNBu^t)$_2$].[17] Bruce *et al.*[17] have also suggested that the latter structure respresents a step in the breakdown of the trigonal bipyramid, to more open cluster geometries. When bond β in the square-based pyramid is broken a bridged ' butterfly ' geometry (e) is observed. This geometry has been observed in a number of Os clusters including [Os$_5$(CO)$_{15}$H$_2${CC(H)Ph}].[16] Both the geometries (d) and (e) may also be obtained by rupturing the bonds α and β, respectively, in the alternative 74-electron species, the edge-bridged tetrahedron (c). It is also possible to obtain a third arrangement from (c) by rupturing the γ bond. In this structure three triangles share a common edge (f). No osmium cluster with this geometry has been reported as yet, but the [Rh$_5$(CO)$_{15}$]$^-$ anion [18] does have a distorted trigonal-bipyramidal structure in which two equatorial–axial distances [3.032(1) Å] may be non-bonding. The three structures (d)—(f) represent 76-electron systems. There is only one bond, denoted α in (d), which, when broken, gives a structure without terminal Os atoms, and this is the ' bow-tie ' structure (g) found in [Os$_5$(CO)$_{19}$]. Similarly, there is only one bond in (e), denoted α, that leads to a different geometry when it is ruptured. This structure is shown as (h) and comprises an Os$_4$ square with one edge bridged by a fifth metal atom. At present there are no cluster structures with this geometry.

Although Figure 3 shows all the possible transformations of Os$_5$ clusters obtained by rupturing bonds it is not possible to predict which bond will break under what circumstances. This depends on the reaction conditions and the nature of the species present.

Experimental

All operations were performed with the exclusion of air, except for chromatography. Reaction solvents were purified, dried, and deoxygenated by distillation under N$_2$ over appropriate drying agents. These solvents were stored under N$_2$.

Product separation was achieved using thin-layer chromatography (t.l.c.) with plates precoated to 0.25 mm thickness with Merck Kieselgel 60F$_{254}$.

Reactions under pressure were performed in a Roth laboratory autoclave of 100-cm^3 capacity; a glass liner was not used. The autoclave was purged of air by pressurising to *ca.* 50 atm with the reaction gas and venting, repeating this

Table 3. Bond lengths (Å) and angles (°) for $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$ (5a)

Os(2)–Os(1)	2.843(4)	Os(3)–Os(1)	2.949(4)	O(11)–C(11)	1.208(74)	O(12)–C(12)	1.169(63)
P(1)–Os(1)	2.286(21)	C(11)–Os(1)	1.847(55)	O(13)–C(13)	1.218(64)	O(4)–P(2)	1.527(82)
C(12)–Os(1)	1.850(40)	C(13)–Os(1)	1.849(40)	O(5)–P(2)	1.599(75)	O(6)–P(2)	1.527(74)
Os(3)–Os(2)	2.929(5)	P(2)–Os(2)	2.257(24)	C(4)–O(4)	1.481(97)	C(5)–O(5)	1.477(99)
C(21)–Os(2)	1.849(20)	C(22)–Os(2)	1.848(38)	C(6)–O(6)	1.481(99)	O(21)–C(21)	1.207(51)
C(23)–Os(2)	1.849(36)	Os(4)–Os(3)	2.951(4)	O(22)–C(22)	1.141(58)	O(23)–C(23)	1.187(54)
Os(5)–Os(3)	2.923(5)	C(31)–Os(3)	1.844(42)	O(31)–C(31)	1.106(62)	O(32)–C(32)	1.204(71)
C(32)–Os(3)	1.848(54)	Os(5)–Os(4)	2.872(5)	O(33)–C(33)	1.182(73)	O(41)–C(41)	1.191(89)
C(41)–Os(4)	1.828(73)	C(42)–Os(4)	1.854(26)	O(42)–C(42)	1.176(37)	O(43)–C(43)	1.174(72)
C(43)–Os(4)	1.849(53)	C(44)–Os(4)	1.856(46)	O(44)–C(44)	1.177(64)	O(7)–P(3)	1.723(63)
P(3)–Os(5)	2.250(23)	C(51)–Os(5)	1.849(30)	O(8)–P(3)	1.700(54)	O(9)–P(3)	1.559(72)
C(52)–Os(5)	1.848(55)	C(53)–Os(5)	1.850(56)	C(7)–O(7)	1.480(85)	C(8)–O(8)	1.480(99)
O(1)–P(1)	1.450(73)	O(2)–P(1)	1.611(63)	C(9)–O(9)	1.480(91)	O(51)–C(51)	1.133(67)
O(3)–P(1)	1.636(94)	C(1)–O(1)	1.477(99)	O(52)–C(52)	1.251(75)	O(53)–C(53)	1.218(76)
C(2)–O(2)	1.479(99)	C(3)–O(3)	1.477(99)				

Os(3)–Os(1)–Os(2)	60.7(1)	P(1)–Os(1)–Os(2)	167.2(5)	C(44)–Os(4)–Os(5)	88.8(15)	C(44)–Os(4)–C(41)	94.2(26)
P(1)–Os(1)–Os(3)	108.7(5)	C(11)–Os(1)–Os(2)	99.2(19)	C(44)–Os(4)–C(42)	90.2(17)	C(44)–Os(4)–C(43)	177.4(22)
C(11)–Os(1)–Os(3)	158.9(19)	C(11)–Os(1)–P(1)	92.1(20)	Os(4)–Os(5)–Os(3)	61.2(1)	P(3)–Os(5)–Os(3)	157.4(6)
C(12)–Os(1)–Os(2)	96.9(21)	C(12)–Os(1)–Os(3)	81.9(18)	P(3)–Os(5)–Os(4)	96.2(6)	C(51)–Os(5)–Os(3)	107.2(16)
C(12)–Os(1)–P(1)	88.0(22)	C(12)–Os(1)–C(11)	95.1(26)	C(51)–Os(5)–Os(4)	165.7(20)	C(51)–Os(5)–P(3)	95.3(17)
C(13)–Os(1)–Os(2)	82.2(21)	C(13)–Os(1)–Os(3)	94.8(17)	C(52)–Os(5)–Os(3)	90.0(17)	C(52)–Os(5)–Os(4)	92.0(17)
C(13)–Os(1)–P(1)	92.2(22)	C(13)–Os(1)–C(11)	88.3(26)	C(52)–Os(5)–P(3)	92.2(17)	C(52)–Os(5)–C(51)	79.1(25)
C(13)–Os(1)–C(12)	176.5(26)	Os(3)–Os(2)–Os(1)	61.4(1)	C(53)–Os(5)–Os(3)	88.5(17)	C(53)–Os(5)–Os(4)	88.8(17)
P(2)–Os(2)–Os(1)	97.7(5)	P(2)–Os(2)–Os(3)	156.5(6)	C(53)–Os(5)–P(3)	89.8(17)	C(53)–Os(5)–C(51)	99.7(25)
C(21)–Os(2)–Os(1)	160.8(20)	C(21)–Os(2)–Os(3)	101.9(22)	C(53)–Os(5)–C(52)	177.7(19)	O(1)–P(1)–Os(1)	118.5(37)
C(21)–Os(2)–P(2)	100.3(22)	C(22)–Os(2)–Os(1)	93.7(17)	O(2)–P(1)–Os(1)	112.1(30)	O(2)–P(1)–O(1)	90.3(34)
C(22)–Os(2)–Os(3)	83.7(15)	C(22)–Os(2)–P(2)	87.3(15)	O(3)–P(1)–Os(1)	117.7(22)	O(3)–P(1)–O(1)	104.5(42)
C(22)–Os(2)–C(21)	93.8(23)	C(23)–Os(2)–Os(1)	84.1(17)	O(3)–P(1)–O(2)	110.3(41)	C(1)–O(1)–P(1)	153.3(58)
C(23)–Os(2)–Os(3)	96.0(14)	C(23)–Os(2)–P(2)	92.1(14)	C(2)–O(2)–P(1)	127.0(71)	C(3)–O(3)–P(1)	148.0(72)
C(23)–Os(2)–C(21)	88.6(23)	C(23)–Os(2)–C(22)	177.6(24)	O(11)–C(11)–Os(1)	172.6(51)	O(12)–C(12)–Os(1)	173.4(59)
Os(2)–Os(3)–Os(1)	57.8(1)	Os(4)–Os(3)–Os(1)	148.1(1)	O(13)–C(13)–Os(1)	173.4(59)	O(4)–P(2)–Os(2)	123.6(27)
Os(4)–Os(3)–Os(2)	95.5(1)	Os(5)–Os(3)–Os(1)	151.1(1)	O(5)–P(2)–Os(2)	112.5(33)	O(5)–P(2)–O(4)	99.5(40)
Os(5)–Os(3)–Os(2)	150.7(1)	Os(5)–Os(3)–Os(4)	58.5(1)	O(6)–P(2)–Os(2)	111.8(32)	O(6)–P(2)–O(4)	98.3(44)
C(31)–Os(3)–Os(1)	75.0(16)	C(31)–Os(3)–Os(2)	129.0(19)	O(6)–P(2)–O(5)	109.5(35)	C(4)–O(4)–P(2)	136.7(77)
C(31)–Os(3)–Os(4)	135.1(18)	C(31)–Os(3)–Os(5)	76.8(17)	C(5)–O(5)–P(2)	134.9(84)	C(6)–O(6)–P(2)	136.2(69)
C(32)–Os(3)–Os(1)	94.2(15)	C(32)–Os(3)–Os(2)	73.7(18)	O(21)–C(21)–Os(2)	170.1(46)	O(22)–C(22)–Os(2)	174.1(46)
C(32)–Os(3)–Os(4)	94.3(14)	C(32)–Os(3)–Os(5)	93.4(17)	O(23)–C(23)–Os(2)	176.4(44)	O(31)–C(31)–Os(3)	172.2(44)
C(32)–Os(3)–C(31)	93.0(24)	C(33)–Os(3)–Os(1)	83.4(15)	O(32)–C(32)–Os(3)	171.4(53)	O(33)–C(33)–Os(3)	172.0(45)
C(33)–Os(3)–Os(2)	95.2(17)	C(33)–Os(3)–Os(4)	81.9(14)	O(41)–C(41)–Os(4)	169.0(47)	O(42)–C(42)–Os(4)	168.9(33)
C(33)–Os(3)–Os(5)	94.3(16)	C(33)–Os(3)–C(31)	97.7(24)	O(43)–C(43)–Os(4)	171.7(54)	O(44)–C(44)–Os(4)	167.3(35)
C(33)–Os(3)–C(32)	168.0(25)	Os(5)–Os(4)–Os(3)	60.2(1)	O(7)–P(3)–Os(5)	121.2(26)	O(8)–P(3)–Os(5)	116.4(23)
C(41)–Os(4)–Os(3)	101.2(16)	C(41)–Os(4)–Os(5)	160.7(16)	O(8)–P(3)–O(7)	93.0(25)	O(9)–P(3)–Os(5)	120.7(19)
C(42)–Os(4)–Os(3)	161.0(19)	C(42)–Os(4)–Os(5)	102.4(19)	O(9)–P(3)–O(7)	98.7(32)	O(9)–P(3)–O(8)	101.8(33)
C(42)–Os(4)–C(41)	96.7(25)	C(43)–Os(4)–Os(4)	96.0(14)	C(7)–O(7)–P(3)	107.2(44)	C(8)–O(8)–P(3)	129.8(54)
C(43)–Os(4)–Os(5)	88.7(17)	C(43)–Os(4)–C(41)	88.0(28)	C(9)–O(9)–P(3)	113.5(57)	O(51)–C(51)–Os(5)	154.1(46)
C(43)–Os(4)–C(42)	90.9(18)	C(44)–Os(4)–Os(3)	82.2(12)	O(52)–C(52)–Os(5)	172.5(36)	O(53)–C(53)–Os(5)	172.1(41)

operation several times. Pressures quoted were measured at room temperature.

Infrared spectra between 2 150 and 1 600 cm^{-1} were recorded on a Perkin-Elmer 257 spectrometer with the absorption of CO(g) at 2 143 cm^{-1} as calibrant. Mass spectra were recorded on an A.E.I. MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17} J) ionising potential at 100 ± 30 °C. Tris(perfluoroheptyl)-*s*-triazine was used as a reference.

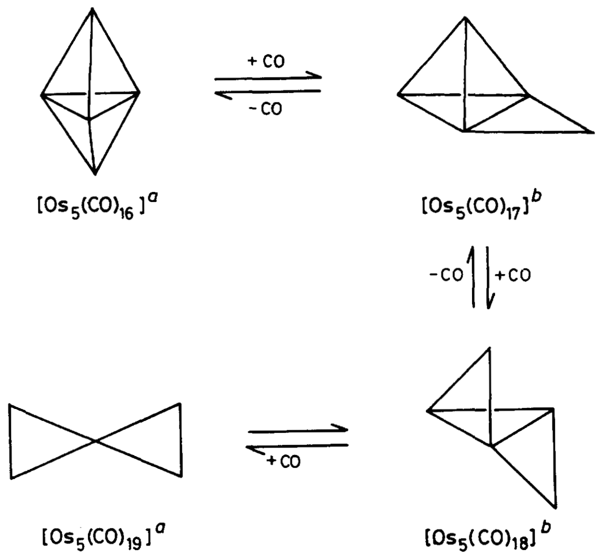
Preparations.—$[Os_5(CO)_{19}]$. In a typical reaction $[Os_6(CO)_{18}]$ (100 mg) was dissolved in heptane (50 cm^3) and treated with carbon monoxide at 160 °C and 90 atm for 1 h. The orange product $[Os_5(CO)_{19}]$ was purified by t.l.c. and subsequent recrystallisation from dichloromethane.

$[Os_5(CO)_{15}(PR_3)]$, $[Os_5(CO)_{14}(PR_3)_2]$, *and* $[Os_5(CO)_{16}(PR_3)_3]$. In a typical reaction $[Os_5(CO)_n]$ ($n = 16$ or 19) (10 mg) in CH_2Cl_2 (15 cm^3) was refluxed with PR_3 (R = OMe or Et) for 20 h. The solvent was removed by evaporation, and the products separated by t.l.c. eluting with $Et_2O–C_6H_{14}$ (1 : 1).

X-*Ray Crystal Structure Determinations of* $[Os_5(CO)_{19}]$ (1), *and* $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$ (5a).—Single crystals of each compound were mounted on the ends of glass fibres with epoxy-resin, and the space groups and approximate cell dimensions determined *via* Weissenberg (Cu) *X*-ray photography.

The crystals were transferred to a Stoe four-circle diffractometer, and accurate cell dimensions determined from the angular measurement of 20 strong reflections in the range $15 < 2\theta < 25°$. Intensity data for the two compounds were recorded using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha1}$ 0.709 26, $\lambda_{\alpha2}$ 0.713 54 Å) and an ω—θ scan procedure. Two check reflections were monitored every 50 measurements throughout the data collection and showed no significant variation. The crystal data and other parameters for the two complexes are listed in Table 4.

The two data sets were corrected for Lorentz polarisation factors and for absorption. For complex (1) a semi-empirical absorption based on a pseudo-ellipsoid model and 464 azimuthal scan data from 49 independent reflections was applied. For complex (5a) a numerical absorption correction



Scheme 2. A pathway for the conversion of [$Os_5(CO)_{16}$] into [$Os_5(CO)_{19}$]. ^{a} Observed cluster. ^{b} Postulated intermediate

Table 4. Crystal data and data-collection parameters for the structures of [$Os_5(CO)_{19}$] (1) and [$Os_5(CO)_{16}\{P(OMe)_3\}_3$] (5a) *

	(1)	(5a)
Molecular formula	$C_{19}O_{19}Os_5$	$C_{25}H_{27}O_{25}Os_5P_3$
Crystal habit	Elongated rectangular blocks	Irregular plates
Colour	Orange	Red
Crystal size (mm)	0.115 × 0.135 × 0.154	0.073 × 0.162 × 0.231
Molecular weight	1 483.19	1 771.38
a/Å	8.880(4)	11.150(5)
b/Å	10.244(5)	11.792(6)
c/Å	16.529(7)	18.581(10)
α/°	99.98(2)	106.91(3)
β/°	93.44(2)	92.67(3)
γ/°	110.37(3)	109.45(3)
U/Å^3	1 376.4	2 176.0
D_c/g cm^{-3}	3.58	2.70
F(000)	1 291.5	1 603.5
μ(Mo-$K_α$)/cm^{-1}	230.73	147.15
Transmission factors	0.409—0.987	0.375—0.988
Reflections measured	3 260	3 882
$2θ_{max.}$/°	45.0	50.0
σ limit [$F > nσ(F)$]	$n = 3$	$n = 5$
Unique observed reflections	2 616	2 144
Number of steps	140	150
Background counting time/s	17.5	18.75
Weighting scheme, w	$[σ^2(F) + 0.0005\|F_o\|^2]^{-1}$	$0.6894/[σ^2(F) + 0.002\|F_o\|^2]$
Converged residuals,		
R	0.040	0.071
R' (= $Σw^{½}Δ/Σw^{½}\|F_o\|$)	0.039	0.071

* Parameters common to both structures: crystal system, triclinic; space group, $P\bar{1}$; $Z = 2$; D_m, not measured; $2θ_{min} = 3.0°$; ω—θ step width, 0.01°; step time, 0.5 s; counts per second below which reflections were not removed on a 1-s prescan, 7.

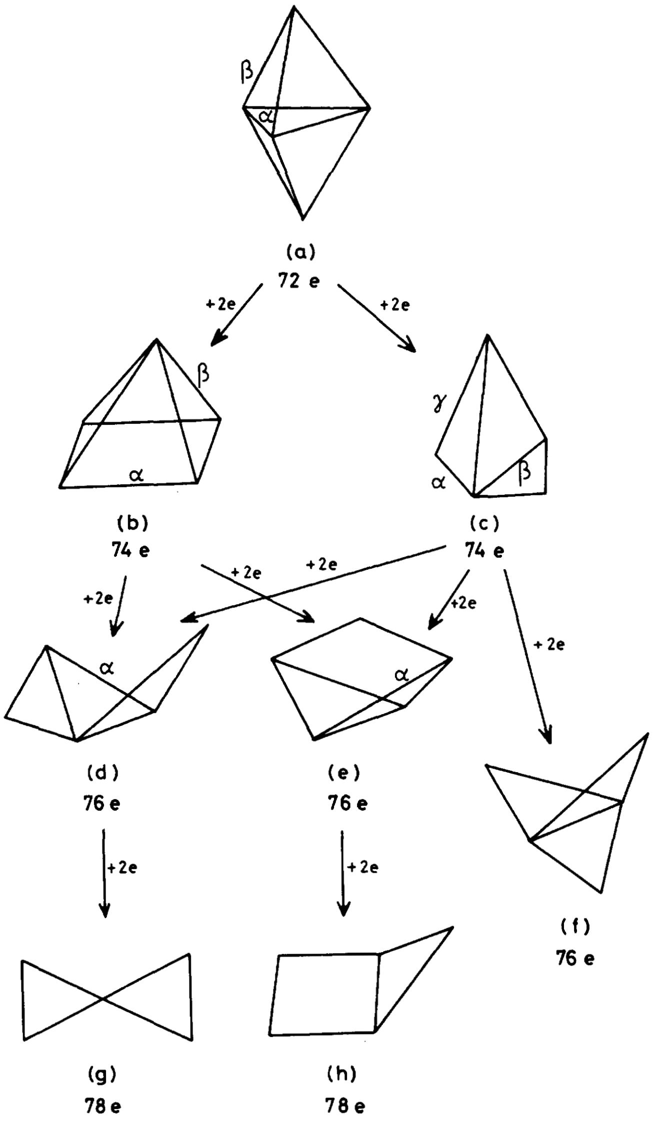


Figure 3. Transformations between pentanuclear metal clusters

was applied with the crystal bounded by the planes ($\bar{1}$00), (100), (0$\bar{1}$0), (010), (001), and (00$\bar{1}$).

In both structures the five Os atom positions were determined by multisolution $Σ_2$ sign expansion, and all the remaining atoms located from subsequent electron-density difference syntheses. Structure (1) was refined by blocked-cascade least squares with the Os and O atoms assigned anisotropic thermal parameters and the C atoms individual isotropic thermal parameters. Structure (5a) was refined by blocked full-matrix least squares with the Os and P atoms assigned anisotropic thermal parameters. Because of the high uncertainty in the positional parameters of the light atoms in structure (5a) due to the high absorption and disorder problems, additional constraints were placed on the bond parameters. The Os–C(carbonyl) and C–O(carbonyl) distances were constrained to 1.85(1) and 1.17(1) Å, respectively, and the O–C(phosphite) distances to 1.48(1) Å. The C(carbonyl), O(carbonyl), C(phosphite), and O(phosphite) atoms were assigned common isotropic thermal parameters. Refinement of both structures continued until convergence was reached. The hydrogen atoms in complex (5a) were not located.

Table 5. Atom co-ordinates ($\times 10^4$) for complexes (1) and (5a)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) Complex (1)							
Os(1)	10 177(1)	8 113(1)	3 246(1)	O(31)	11 538(18)	6 085(16)	1 626(10)
Os(2)	6 813(1)	6 881(1)	3 391(1)	C(32)	7 292(24)	5 687(22)	1 492(12)
Os(3)	8 361(1)	5 201(1)	2 353(1)	O(32)	6 663(18)	6 057(17)	973(9)
Os(4)	5 700(1)	2 452(1)	2 219(1)	C(33)	9 157(22)	4 543(20)	3 240(11)
Os(5)	8 113(1)	2 687(1)	1 135(1)	O(33)	9 774(19)	4 208(16)	3 766(8)
C(11)	12 450(24)	8 583(22)	3 126(12)	C(41)	4 568(28)	2 694(25)	3 165(13)
O(11)	13 794(16)	8 884(19)	3 140(10)	O(41)	3 883(24)	2 722(20)	3 708(11)
C(12)	10 344(25)	9 886(24)	3 901(13)	C(42)	4 287(27)	596(26)	1 670(13)
O(12)	10 528(20)	10 995(18)	4 269(9)	O(42)	3 420(21)	−537(18)	1 344(9)
C(13)	9 750(26)	8 624(23)	2 213(13)	C(43)	4 483(27)	3 295(24)	1 564(13)
O(13)	9 626(19)	8 985(18)	1 598(10)	O(43)	3 688(18)	3 731(19)	1 245(10)
C(14)	10 635(25)	7 408(23)	4 224(13)	C(44)	7 000(27)	1 682(24)	2 862(13)
O(14)	11 067(20)	7 108(17)	4 806(9)	O(44)	7 622(18)	1 216(17)	3 285(10)
C(21)	4 500(27)	5 799(25)	3 211(13)	C(51)	9 758(31)	3 339(28)	455(15)
O(21)	3 171(18)	5 176(20)	3 105(12)	O(51)	10 727(21)	3 663(23)	49(10)
C(22)	6 696(25)	8 372(24)	4 205(13)	C(52)	7 340(28)	726(27)	594(14)
O(22)	6 615(21)	9 276(18)	4 722(10)	O(52)	6 910(24)	−447(17)	294(9)
C(23)	6 510(28)	7 837(26)	2 513(14)	C(53)	6 658(25)	3 094(23)	366(12)
O(23)	6 242(23)	8 411(19)	2 027(10)	O(53)	5 895(21)	3 268(20)	−146(10)
C(24)	7 152(25)	5 831(23)	4 194(12)	C(54)	9 655(27)	2 425(24)	1 909(13)
O(24)	7 341(18)	5 252(19)	4 714(10)	O(54)	10 572(19)	2 253(17)	2 359(9)
C(31)	10 354(28)	5 772(25)	1 919(13)				
(*b*) Complex (5a)							
Os(1)	7 461(2)	7 269(2)	3 963(1)	C(23)	7 438(35)	8 347(33)	2 554(30)
Os(2)	6 078(2)	6 915(2)	2 541(1)	O(23)	8 295(42)	9 302(43)	2 598(23)
Os(3)	7 625(2)	5 349(2)	2 580(1)	C(31)	9 051(33)	5 694(57)	3 266(24)
Os(4)	6 314(3)	3 371(2)	1 107(1)	O(31)	9 981(42)	5 905(45)	3 612(24)
Os(5)	8 731(2)	3 491(3)	1 798(1)	C(32)	8 518(46)	6 535(41)	2 143(30)
P(1)	8 461(17)	7 076(20)	4 999(9)	O(32)	9 230(42)	7 251(44)	1 868(23)
O(1)	8 135(65)	7 581(65)	5 741(39)	C(33)	6 434(40)	4 227(44)	2 948(31)
C(1)	7 216(99)	7 735(99)	6 275(58)	O(33)	5 793(43)	3 543(45)	3 251(23)
O(2)	9 914(67)	8 092(65)	5 273(35)	C(41)	4 796(58)	3 626(58)	994(31)
C(2)	10 956(89)	8 032(99)	5 766(61)	O(41)	3 802(44)	3 698(44)	793(23)
O(3)	8 422(63)	5 659(73)	4 958(34)	C(42)	6 046(55)	2 167(32)	156(14)
C(3)	7 679(99)	4 391(81)	5 003(65)	O(42)	5 861(43)	1 266(26)	−381(13)
C(11)	7 164(64)	8 676(39)	4 555(29)	C(43)	5 485(48)	2 116(39)	1 513(30)
O(11)	7 076(45)	9 675(46)	4 907(25)	O(43)	4 852(43)	1 394(44)	1 791(23)
C(12)	9 071(27)	8 182(58)	3 802(36)	C(44)	7 216(42)	4 648(37)	729(26)
O(12)	10 052(45)	8 859(46)	3 717(25)	O(44)	7 598(36)	5 340(31)	375(21)
C(13)	5 860(28)	6 267(55)	4 083(36)	P(3)	8 841(22)	1 796(21)	894(14)
O(13)	4 871(43)	5 560(47)	4 206(24)	O(7)	8 727(51)	1 700(51)	−52(30)
P(2)	4 855(17)	8 070(21)	2 993(10)	C(7)	10 031(58)	2 390(79)	−180(47)
O(4)	3 754(66)	8 121(64)	2 499(36)	O(8)	7 585(50)	399(55)	718(27)
C(4)	3 038(99)	7 433(99)	1 715(45)	C(8)	7 581(86)	−853(60)	726(46)
O(5)	4 098(65)	7 642(64)	3 636(36)	O(9)	10 020(52)	1 377(51)	949(27)
C(5)	2 933(90)	7 760(99)	3 946(63)	C(9)	11 197(62)	2 215(77)	765(48)
O(6)	5 650(65)	9 492(74)	3 301(36)	C(51)	10 380(22)	3 999(54)	2 311(28)
C(6)	5 419(99)	10 660(92)	3 715(61)	O(51)	11 111(44)	4 094(44)	2 790(23)
C(21)	5 647(53)	6 560(56)	1 505(8)	C(52)	9 652(46)	4 601(44)	1 322(30)
O(21)	5 502(42)	6 509(43)	847(23)	O(52)	10 203(43)	5 238(44)	919(23)
C(22)	4 735(37)	5 505(34)	2 572(31)	C(53)	7 833(46)	2 432(45)	2 312(29)
O(22)	3 966(43)	4 575(43)	2 564(24)	O(53)	7 377(43)	1 800(44)	2 716(23)

Complex neutral-atom scattering factors [19] were employed in both structure solutions and refinements. All computations were performed on an IBM 370/165 computer at the University of Cambridge using programs written by Professor G. M. Sheldrick; [20] Figures 1 and 2 were drawn using the PLUTO program.[21] The final atomic fractional co-ordinates for complexes (1) and (5a) are listed in Table 5.

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