Chemical Activation of Pentaosmium Carbonyl Clusters: Synthesis, Structure, and Reactivity of $[Os_5(CO)_{15}(NCMe)]$ and $[Os_5H_2(CO)_{14}(NCMe)]$; Crystal Structures of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ and $[Os_5H_2(CO)_{14}(PEt_3)]$ †

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Simple two-electron oxidation of the salt $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ with $FeCl_3$ in tetrahydrofuran (thf) in the presence of CO produces the neutral binary pentanuclear cluster $[Os_5(CO)_{16}]$ which upon reaction with 1.1 equivalents of anhydrous Me_3NO in the presence of MeCN at room temperature affords the corresponding activated complex $[Os_5(CO)_{15}(NCMe)]$ in 75% yield. The dihydrido pentanuclear cluster $[Os_5H_2(CO)_{15}]$, which is isoelectronic to $[Os_5(CO)_{16}]$, also reacts with 1.1 equivalents of anhydrous Me_3NO in the presence of MeCN at −78 °C to produce the activated complex $[Os_5H_2(CO)_{14}(NCMe)]$ in 70% yield. Both these activated complexes are believed to be based on a trigonal-bipyramidal arrangement of osmium atoms with an acetonitrile ligand associated with one of the equatorial osmium atoms of the bipyramid. The acetonitrile ligand in both these complexes is labile and can be very easily substituted by other simple two-electron phosphorus-donor ligands L = $P(OMe)_3$, PPh_3, or $P(OPh)_3$ to afford $[Os_5(CO)_{15}L]$ and $[Os_5H_2(CO)_{14}L]$ respectively. The structures of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ and $[Os_5H_2(CO)_{14}(PEt_3)]$ have been determined by a single-crystal *X*-ray diffraction analysis and contain trigonal-bipyramidal metal frameworks with the phosphorus-donor ligand attached to one of the equatorial osmium atoms of the bipyramid.

In general, the study of the substitution chemistry of osmium carbonyl clusters is hampered to some extent by the harsh thermolytic reaction conditions which often lead to the formation of a number of products with different metal frameworks.[1,2] Recently, this problem has been overcome by the use of activated clusters containing labile ligands. For example, the reaction of $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2) with ligands L = $P(OMe)_3$, PPh_3, or R_2C_2 affords the corresponding substituted complexes in high yields.[3,4] Trimethylamine *N*-oxide has been used to remove the co-ordinated carbonyl ligand from the parent carbonyl cluster and the vacant co-ordination site is then filled by NMe_3 which is a weakly bound ligand and can be easily displaced by acetonitrile ligand *in situ*. The use of trimethylamine *N*-oxide to remove co-ordinated carbonyl ligands from a cluster has recently been applied to the high-nuclearity cluster $[Os_6(CO)_{18}]$, and the complexes $[Os_6(CO)_{18-n}(NCMe)_n]$ (n = 1 or 2) have been isolated.[5] These two derivatives have been found to be very useful starting materials to study the substitution chemistry. We have extended this approach to study the substitution chemistry of pentaosmium carbonyl clusters, *viz.* $[Os_5(CO)_{16}]$ and $[Os_5H_2(CO)_{15}]$, and isolated the corresponding activated complexes containing labile acetonitrile ligand. In this paper we report the synthesis and structure of the activated clusters $[Os_5(CO)_{15}(NCMe)]$ and $[Os_5H_2(CO)_{14}(NCMe)]$ and describe their reactions with simple phosphorus-donor ligands to produce the monosubstituted Os_5 derivatives containing a trigonal-bipyramidal structure. Part of this work has already been communicated.[6]

Results and Discussion

Synthesis of $[Os_5(CO)_{16}]$ (**1**).—The cluster $[Os_5(CO)_{16}]$ (**1**) was initially obtained in 5—10% yields from the vacuum pyrolysis of $[Os_3(CO)_{12}]$.[7] Since then, efforts have been underway to develop a more systematic and high-yield route to the pentaosmium carbonyl cluster. A major entry into pentaosmium carbonyl clusters comes from the reaction of $[Os_6(CO)_{18}]$ with KOH–MeOH producing $[Os_5(CO)_{15}]^{2-}$ in up to 85% yield.[8] The formation of $[Os_5(CO)_{15}]^{2-}$ in good yield has allowed the development of the chemistry of the corresponding neutral clusters. For example, the dianion $[Os_5(CO)_{15}]^{2-}$ can be successively protonated (reversibly) to give $[Os_5H(CO)_{15}]^-$ and $[Os_5H_2(CO)_{15}]$ in quantitative yields.[8,9] Simple two-electron oxidation of $[Os_5(CO)_{15}]^{2-}$ in thf with $FeCl_3$ in the presence of CO affords the binary carbonyl cluster $[Os_5(CO)_{16}]$ (**1**) in up to 50% yield. The remaining 50% product of the reaction is believed to be an anionic pentaosmium cluster and has been formulated as $[Os_5Cl(CO)_{15}]^-$ on the basis of i.r. and mass spectroscopic data (Table 1). The formation of this anion is further evidenced by the oxidation of $[Os_5(CO)_{15}]^{2-}$ with $FeCl_3$ in thf in the absence of CO, producing mainly $[Os_5Cl(CO)_{15}]^-$. It seems that the initial step is the two-electron oxidation of $[Os_5(CO)_{15}]^{2-}$ by $FeCl_3$ producing a co-ordinatively unsaturated species '$[Os_5(CO)_{15}]$' which then reacts with CO and/or Cl^- (generated *in situ* by the reduction of $Fe^{III}Cl_3$ to $Fe^{II}Cl_2$) to produce (**1**) and/or $[Os_5Cl(CO)_{15}]^-$.

When the solvent is changed from thf to CH_2Cl_2, the oxidation of $[Os_5(CO)_{15}]^{2-}$ with $FeCl_3$ in the presence of CO produces (**1**) in 40—45% yield and the remaining 55% product is an anionic cluster which could not be characterised. The i.r. spectrum of this anionic cluster in the terminal-carbonyl region is different from that of $[Os_5Cl(CO)_{15}]^-$. It seems that in CH_2Cl_2 a more complex side reaction is taking place.

The cluster $[Os_5Cl(CO)_{15}]^-$ does not undergo protonation with acid HBF_4 but does react with $[Au(PPh_3)Cl]$ yielding a neutral hexametallic cluster with a formulation $[Os_5Cl(CO)_{15}(AuPPh_3)]$. This complex has been characterised

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

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

Table 1. Spectroscopic data for pentaosmium clusters

Cluster	I.r.,[a] ν(CO)/cm^{-1}	Mass,[b] *m/z*	^{1}H N.m.r.[c] (δ)
$[Os_5Cl(CO)_{15}]^-$	2 032vs, 2 011w, 1 997m, 1 960w (br)	1 415[d]	—
(2) $[Os_5(CO)_{15}(NCMe)]$	2 090w, 2 054w, 2 031s, 1 980m	*e*	2.71(s)
(3) $[Os_5(CO)_{15}\{P(OMe)_3\}]$[f]	2 091w, 2 056s, 2 030s, 2 017m (sh), 1 982m, 1 942w	1 504	3.84(d)
(3a) $[Os_5(CO)_{15}\{P(OMe)_3\}]$[f]	2 089w, 2 043s, 2 034vs, 2 013(sh), 1 976m	1 504	3.77(d)
(4) $[Os_5(CO)_{15}\{P(OPh)_3\}]$	2 092w, 2 057s, 2 031s, 1 983m, 1 944w	*e*	7.15(m)[g]
(5) $[Os_5(CO)_{15}(PPh_3)]$	2 099w, 2 090m, 2 081vw, 2 065s (sh), 2 058s, 2 033s, 2 018m (sh), 2 007m, 1 985m, 1 948vw	1 642	7.4(m)[g]
(10) $[Os_5H_2(CO)_{14}\{P(OMe)_3\}]$	2 094m, 2 063s, 2 041s, 2 020m, 1 987m (br)	1 478	—
(11) $[Os_5H_2(CO)_{14}(PPh_3)]$	2 118w, 2 074m, 2 066s, 2 043s, 2 024w	1 616	—
(12) $[Os_5H_2(CO)_{14}(PEt_3)]$	2 092m, 2 061s, 2 041s, 2 019m, 1 997w	1 472	—

[a] In CH_2Cl_2. [b] Based on ^{192}Os. [c] In $CDCl_3$. [d] Fast-atom bombardment. [e] Parent peak not observed. [f] ^3J(P–H) 12 Hz. [g] In CD_2Cl_2.

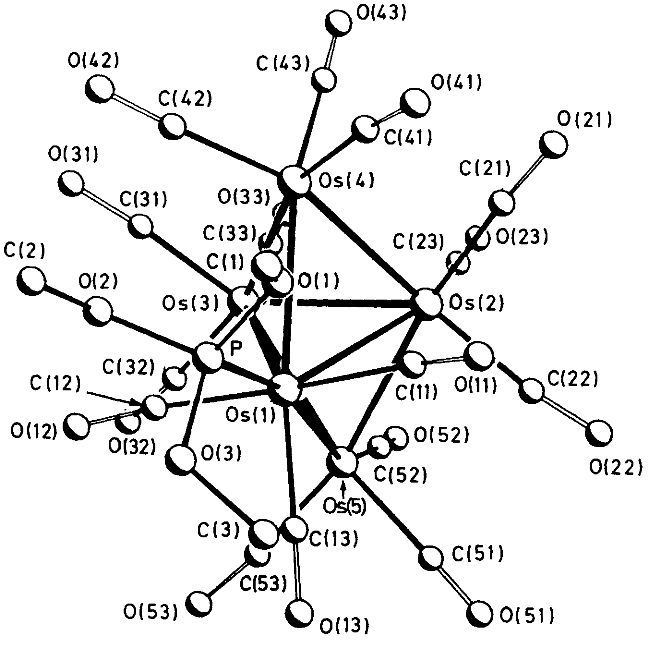


Figure 1. The molecular structure of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ **(3)**

on the basis of i.r. and mass spectroscopy (Table 1). Attempts to obtain suitable single crystals failed and it was not possible to establish the exact geometry of this cluster.

The Cl$^-$ ligand in the complex $[Os_5Cl(CO)_{15}]^-$ could act as a one-electron-donor ligand (terminally bonded) or a three-electron-donor ligand (μ), and depending on this the cluster $[Os_5Cl(CO)_{15}]^-$ could contain a trigonal-bipyramidal structure (72-electron) or an edge-bridged tetrahedron or a square-based pyramidal structure (74-electron). From the data available it is not possible to differentiate between these alternative structures and a single-crystal *X*-ray structure determination is necessary to establish the true structure, but we have not so far been successful in growing suitable single crystals of this cluster.

Synthesis of $[Os_5(CO)_{15}(NCMe)]$ **(2)**.—The reaction of equimolar quantities of $[Os_5(CO)_{16}]$ **(1)** with anhydrous trimethylamine *N*-oxide in CH_2Cl_2 in the presence of a little MeCN, at room temperature, produces a reddish brown cluster tentatively formulated as $[Os_5(CO)_{15}(NCMe)]$ **(2)**. No parent-ion peak was observed in the electron-impact mass spectrum of **(2)**; the only peak observed corresponds to $[Os_5(CO)_{16}]$, indicating that the cluster **(2)** scavenges CO in the spectrometer. Consistent with this observation is the reaction of **(2)** with CO (1 atm, 20 °C) affording **(1)** in quantitative yields. The ^{1}H n.m.r. spectrum of **(2)** exhibits a single resonance at δ 2.71 due to a co-ordinated acetonitrile ligand. Complex **(2)** is very reactive due to the presence of the labile acetonitrile ligand and decomposes to $[Os_5H(CO)_{15}]^-$ on standing CH_2Cl_2 solution (*ca.* 1—2 h). Displacement of the acetonitrile ligand in **(2)** by simple two-electron donor ligands L = $P(OMe)_3$, $P(OPh)_3$, or PPh_3 produces corresponding derivatives $[Os_5(CO)_{15}L]$ **(3)**—**(5)**. It has been noted in the case of L = $P(OMe)_3$ that if the reaction is left stirring at room temperature for longer periods (10—12 h) another isomer $[Os_5(CO)_{15}\{P(OMe)_3\}]$ **(3a)** is obtained. Furthermore, the isomer **(3)** is slowly converted into **(3a)** on standing in CH_2Cl_2 or MeCN solutions and **(3a)** is believed to be the thermodynamically stable product. It is interesting that the i.r. spectrum of either of the isomers, *i.e.* **(3)** and **(3a)**, is different from the reported isomer which was produced as one of the products from the pyrolysis of $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$.[2]

The compounds $[Os_5(CO)_{15}L]$ [L = MeCN, **(2)**; $P(OMe)_3$, **(3)**; $P(OPh)_3$, **(4)**; and PPh_3, **(5)**] exhibit very similar i.r. spectra in the terminal-carbonyl region, implying that substitution has occurred at the same position in each case. Spectroscopic data on these clusters are given in Table 1. In order to establish their geometry and also to ascertain where the substitution has occurred, a single-crystal *X*-ray structure analysis of **(3)** was undertaken. Suitable single crystals were grown by slow evaporation of a $CHCl_3$–hexane solution at −5 °C over a period of 3—4 d.

A view of the molecular structure of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ **(3)** is illustrated in Figure 1, while selected bond parameters are listed in Table 2. The five osmium atoms define a trigonal bipyramid with three carbonyl ligands associated with each osmium atom. A trimethyl phosphite ligand is attached to an equatorial osmium atom in the pseudo-axial site. The structure of **(3)** may be simply viewed as being derived from $[Os_5(CO)_{16}]$ **(1)** by the replacement of a carbonyl ligand on the unique osmium atom by a $P(OMe)_3$ ligand without altering the electronic and carbonyl distributions.[10]

The Os–Os bond distances in **(3)** are similar to those found in the parent carbonyl, $[Os_5(CO)_{16}]$.[10] The longest metal–metal distances are between the unique, formally eight-co-ordinate metal atom Os(1) and the two apical metal atoms Os(4) and Os(5). The shortest metal–metal distances are between the other two equatorial metal atoms Os(2) and Os(3) and the two apical osmium atoms. The presence of the trimethyl phosphite ligand apparently has little influence on the metal-framework distances, although the Os(1)–Os(5) bond which is pseudo-*trans* to the phosphite is marginally longer than Os(1)–Os(4). In terms of electron counting, Os(1) is formally electron rich with 20 electrons, Os(2) and Os(3) are electron precise with 18 electrons each, and Os(4) and Os(5) are electron poor with

Table 2. Selected bond parameters (lengths in A, angles in °) for $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**)

Os(1)–Os(2)	2.862(1)	Os(1)–Os(3)	2.861(1)
Os(1)–Os(4)	2.894(1)	Os(1)–Os(5)	2.904(1)
Os(2)–Os(3)	2.776(1)	Os(2)–Os(4)	2.801(1)
Os(2)–Os(5)	2.761(1)	Os(3)–Os(4)	2.758(1)
Os(3)–Os(5)	2.770(1)	Os(1)–P	2.313(6)
Os(1)–C(11)	1.966(25)	Os(1)–C(12)	1.920(26)
Os(1)–C(13)	1.918(23)	Os(2)–C(21)	1.944(24)
Os(2)–C(22)	1.945(23)	Os(2)–C(23)	1.844(25)
Os(3)–C(31)	1.875(24)	Os(3)–C(32)	1.890(26)
Os(3)–C(33)	1.878(30)	Os(4)–C(41)	1.868(25)
Os(4)–C(42)	1.915(26)	Os(4)–C(43)	1.833(30)
Os(5)–C(51)	1.927(22)	Os(5)–C(52)	1.899(24)
Os(5)–C(53)	1.880(26)		
Os(3)–Os(1)–Os(2)	58.0(1)	Os(4)–Os(1)–Os(2)	58.2(1)
Os(4)–Os(1)–Os(3)	57.3(1)	Os(5)–Os(1)–Os(2)	57.2(1)
Os(5)–Os(1)–Os(3)	57.4(1)	Os(5)–Os(1)–Os(4)	104.3(1)
P–Os(1)–Os(2)	136.1(2)	P–Os(1)–Os(3)	127.5(2)
P–Os(1)–Os(4)	87.5(2)	P–Os(1)–Os(5)	166.6(2)
Os(3)–Os(2)–Os(1)	61.0(1)	Os(4)–Os(2)–Os(1)	61.5(1)
Os(4)–Os(2)–Os(3)	59.3(1)	Os(5)–Os(2)–Os(1)	62.2(1)
Os(5)–Os(2)–Os(3)	60.0(1)	Os(5)–Os(2)–Os(4)	110.8(1)
Os(4)–Os(3)–Os(2)	60.8(1)	Os(5)–Os(3)–Os(1)	62.1(1)
Os(5)–Os(3)–Os(2)	59.7(1)	Os(5)–Os(3)–Os(4)	111.8(1)
Os(2)–Os(4)–Os(1)	60.3(1)	Os(3)–Os(4)–Os(1)	60.8(1)
Os(3)–Os(4)–Os(2)	59.9(1)	Os(2)–Os(5)–Os(1)	60.6(1)
Os(3)–Os(5)–Os(1)	60.5(1)	Os(3)–Os(5)–Os(2)	60.3(1)
O(1)–P–Os(1)	112.3(7)	O(2)–P–Os(1)	113.4(9)
O(3)–P–Os(1)	116.6(9)		

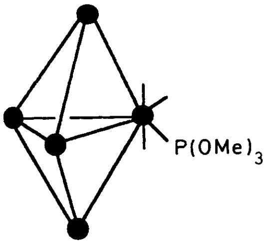


Figure 2. Proposed structure of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3a**)

only 17 electrons each. This formal electron imbalance is partially alleviated by the presence of incipient bridging carbonyl ligands, which donate electron density from the formally electron-rich metal. This type of bridging is observed in all the structurally characterised Os_5 clusters which adopt a trigonal-bipyramidal framework geometry. In the case of compound (**3**), the carbonyls C(11)O(11) and C(12)O(12) bend towards the electron-precise equatorial metals Os(2) and Os(3): Os(2)···C(11) 2.713(27) Å, Os(1)–C(11)–O(11) 165.9(23)°, Os(3)···C(12) 2.707(28) Å, and Os(1)–C(12)–O(12) 169.0(26)°. The remaining carbonyls in (**3**) are terminally co-ordinated to the Os atoms, and the angles at carbon do not deviate significantly from linearity. The Os(1)–P(1) distance in (**3**) is significantly longer than the Os–$P(OMe)_3$ distance of 2.238(5) Å found in $[Os_5H_2(CO)_{13}(PEt_3)\{P(OMe)_3\}]$,[6] but in the latter complex the phosphite is bonded to a metal atom which is formally only six-co-ordinate, and an increase in Os–P distance might be expected with an increase in co-ordination number.

The similarity in the i.r. spectrum of compound (**2**) with that of (**3**) in the terminal-carbonyl region suggests that the acetonitrile derivative (**2**) also possesses a similar metal-core geometry, with an acetonitrile ligand attached to an equatorial osmium atom, and the formation of (**3**) involves a simple substitution of acetonitrile ligand by a $P(OMe)_3$ ligand.

The cluster $[Os_6(CO)_{18}]$ contains a bicapped-tetrahedral metal framwork with three carbonyl ligands attached to each osmium atom.[11] In terms of electron counting, the capping osmium atoms (with co-ordination number 6), are electron deficient with an individual electron count of 17; the other two osmium atoms forming the tetrahedron (with co-ordination number 8) are electron rich with an individual electron count of 19 and the remaining two osmium atoms (with co-ordination number 7) are electron precise with an individual electron count of 18. As the capping osmium atoms are electron deficient, the carbonyl ligands associated with these osmium atoms should be more susceptible towards nucleophilic attack by Me_3NO. This prediction is supported by the fact that the reaction of $[Os_6(CO)_{18}]$ with Me_3NO in the presence of ligand L = MeCN, $P(OMe)_3$, or PPh_3 produces $[Os_6(CO)_{17}L]$, where the incoming ligand L is shown by *X*-ray studies to be attached to the electron-deficient osmium atom.[12]

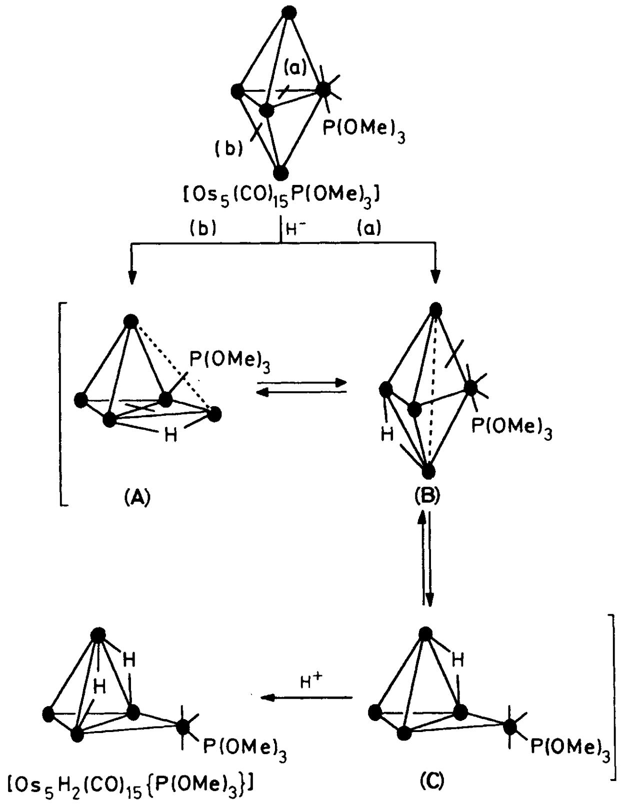
The cluster $[Os_5(CO)_{16}]$ (**1**) contains a trigonal-bipyramidal metal framework with four carbonyl ligands attached to one of the equatorial osmium atoms of the bipyramid whereas the remaining osmium atoms are associated with three carbonyl ligands each.[10] In terms of electron counting, the apical osmium atoms of the bipyramid are electron deficient with an individual electron count of 17 while the unique osmium atom (possessing four carbonyl ligands) is electron rich with an electron count of 20 and the remaining two equatorial osmium atoms are electron precise with an electron count of 18. The apical osmium atoms are electron deficient, and hence the carbonyl ligands attached to these osmium atoms are believed to be more susceptible towards nucleophilic attack by Me_3NO {as found in the case of $[Os_6(CO)_{18}]$} and one would expect the acetonitrile ligand to be associated with the apical osmium atom in (**3**). However, the structure of (**3**) suggests that substitution has occurred at one of the carbonyl ligands associated with the electron-rich unique osmium atom in spite of the fact that the apical osmium atoms in $[Os_5(CO)_{16}]$ are electron deficient. Thus, only on electronic grounds, the site of attack of the amine oxide cannot be predicted with reliability.

Reactivity of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**).—The cluster $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**) is converted into (**3a**) on standing in solution (CH_2Cl_2 or MeCN) over a period of 3—4 d. In an electron-impact mass spectrum the complex (**3a**) exhibits a parent-ion peak at *m*/*z* 1 504 corresponding to the formulation $Os_5(CO)_{15}P(OMe)_3$ and, on the basis of this, (**3a**) is believed to be another isomeric form of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**). It is interesting that the isomer (**3a**) is not converted back into (**3**). Attempts to grow single crystals of (**3a**) have failed, but it is believed that in (**3a**) the phosphite ligand is occupying the equatorial position (Figure 2). The isomerisation of compound (**3**) to form (**3a**) simply involves the migration of a $P(OMe)_3$ ligand from the pseudo-axial position to the equatorial position which is believed to be the most favourable position for bulky, strong σ-donor ligands.[13]

Complex $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**), like $[Os_5(CO)_{16}]$, reacts with CO under pressure (50 atm, 10 h) in toluene at 70 °C to produce the known pentaosmium cluster $[Os_5(CO)_{19}]$, with a bow-tie metal skeleton established by an *X*-ray analysis.[2]

It was thought that the reaction of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**) with molecular hydrogen might produce the known dihydrido complex[1] $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) *via* oxidative addition. Unfortunately, no reaction was observed even under H_2 pressure (60 atm, 120 °C, 40 h) and instead the isomerisation of (**3**) to (**3a**) occurred.

As complex (**3**) is quite resistant to oxidative addition, we have investigated an alternative way of introducing two hydride ligands into it. This alternative route involves the addition of



Scheme 1. Proposed mechanism for the formation of $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) from the reaction of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**) with H^-/H^+

H^- (from NEt_4BH_4) to (**3**) followed by the addition of H^+ (HBF_4). Addition of a small excess of NEt_4BH_4 to a CH_2Cl_2 solution of (**3**) results in an immediate colour change from orange to yellow. The i.r. spectrum of the yellow solution in the terminal carbonyl region [v(CO) 2 038w, 2 018vs, 2 002s, 1 984m, and 1 950w (br) cm^{-1}] shows a shift in the bands by *ca.* 15 cm^{-1} to lower wavenumbers relative to the starting cluster (**3**). A careful protonation of the yellow solution with HBF_4 in the same solvent gives the known orange cluster $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) (50% yield), which exhibits an edge-bridged-tetrahedral metal framework.[1] The cluster (**6**) has previously been obtained[1] from the direct thermolysis of $[Os_5H_2(CO)_{15}]$ (**7**) with excess of $P(OMe)_3$.

The exact mechanism for the formation of compound (**6**) from the reaction of (**3**) with H^-/H^+ is unclear at present. However, it is believed to involve the initial attack of H^- (from $[NEt_4BH_4]$ at the osmium atom (^1H n.m.r. does not support attack at the carbonyl ligand) followed by the opening out of an Os–Os edge (in order to accommodate two electrons provided by H^-) to give an anionic cluster with the formulation $[Os_5H(CO)_{15}\{P(OMe)_3\}]^-$ (**8**) (shown by i.r. spectroscopy). The anionic cluster (**8**) would adopt either an edge-bridged-tetrahedral structure (**A**) or a square-based- pyramidal structure (**B**), depending on which Os–Os edge of the trigonal bipyramid opens up [assuming that no migration of $P(OMe)_3$ takes place]. Both these skeletons could be envisaged on the basis of electron-counting rules for a 74-electron cluster. On the basis of spectroscopic data only, it has not been possible to distinguish between these two structures.

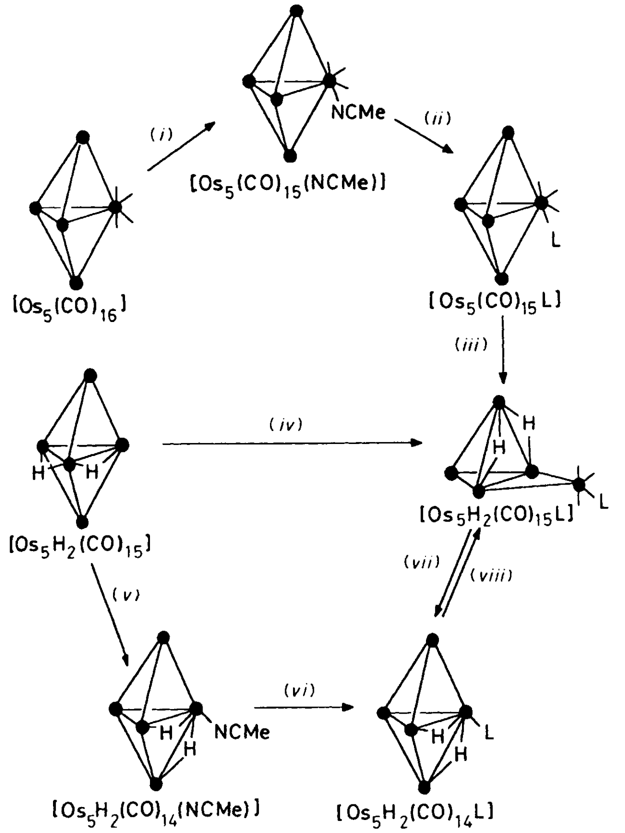
The phosphite ligand in both structures (**A**) and (**B**) is bonded to an equatorial osmium atom whereas in the final product $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) the phosphite ligand is bonded to the bridgehead osmium atom (Scheme 1). In order to explain the formation of (**6**), it is believed that in (**8**) either a metal-polyhedral rearrangement is occurring which would involve the stepwise breaking and making of a polyhedral edge, or ligand migration is occurring, or perhaps both. A similar observation has been noted during the decarbonylation of $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) to $[Os_5H_2(CO)_{14}\{P(OMe)_3\}]$ (**10**), and *vice versa*, where a metal polyhedral rearrangement is believed to be occurring (as shown by ^1H n.m.r. spectroscopy). This will be discussed in detail later in the text.

There is no evidence to rule out any one of the possibilities which would explain the formation of compound (**6**) from (**8**). Based on the observation that the transformation of (**6**) to (**10**) involves a metal polyhedron rearrangement (see text later), it is proposed that a metal polyhedron rearrangement is occurring during the transformation of (**8**) to (**6**). In cluster chemistry, metal framework rearrangements are well known and have been observed in a number of heterometallic clusters containing Group 1B metals and a number of mechanistic pathways have been suggested.[14,15] Johnson[16] has recently proposed a mechanism for the metal polyhedral rearrangements of a five-metal-atom cluster with a trigonal-bipyramidal structure; the rearrangement involves the formation of an edge-bridged-tetrahedral or a square-based-pyramidal geometry, as both these processes involve the successive cleavage of one polyhedral edge at a time. The metal polyhedral rearrangement, shown in Scheme 1, also involves a single-edge cleavage in accordance with Johnson's proposal.[16] Protonation of the anionic cluster $[Os_5H(CO)_{15}\{P(OMe)_3\}]^-$ (**8**) affords the neutral cluster $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**).

Synthesis of $[Os_5H_2(CO)_{14}(NCMe)]$ (**9**).—The reaction of equimolar quantities of $[Os_5H_2(CO)_{15}]$ (**7**) with anhydrous trimethylamine *N*-oxide in CH_2Cl_2 in the presence of a little MeCN at −78 °C followed by warming to room temperature affords a reddish brown cluster tentatively formulated as $[Os_5H_2(CO)_{14}(NCMe)]$ (**9**). No parent-ion peak was observed in the electron-impact mass spectrum of (**9**); the only peak observed corresponds to (**7**). Simple two-electron donor ligands L = $P(OMe)_3$, PPh_3, or PEt_3 displace the acetonitrile ligand in (**9**) to produce corresponding $[Os_5H_2(CO)_{14}L]$ derivatives (**10**)—(**12**). Spectroscopic data for these clusters are given in Table 1. They can also be obtained by thermolysis of (**7**) with ligand L which initially affords $[Os_5H_2(CO)_{15}L]$ with an edge-bridged-tetrahedral structure[1] and decarbonylates on further heating to give $[Os_5H_2(CO)_{14}L]$.[6] The latter reaction is reversible; the cluster $[Os_5H_2(CO)_{14}L]$ reacts with CO (40 atm, 50 °C, 5 h) to produce quantitative yields of $[Os_5H_2(CO)_{15}L]$. All these reactions are summarised in Scheme 2. In order to establish the geometry of these new clusters, suitable single crystals of (**12**) were grown by slow evaporation of CH_2Cl_2 solution over 3—4 d and the structure was determined by *X*-ray diffraction experiments.

The molecular structure of $[Os_5H_2(CO)_{14}(PEt_3)]$ (**12**) is shown in Figure 3, while selected bond parameters are listed in Table 3. The five osmium atoms define a trigonal bipyramid with a phosphine ligand attached to one of the equatorial osmium atoms which is also co-ordinated to other two terminal carbonyl ligands. Each of the remaining four osmium atoms of the bipyramid is associated with three terminal carbonyl ligands. The hydride ligands were not located directly from the *X*-ray studies, but potential-energy calculations suggest that one bridges the equatorial Os(2)–Os(3) edge and the other bridges the equatorial–axial Os(2)–Os(5) edge (Figure 4).

The Os–Os bond distances in compound (**12**) show a large variation. The longer bonds tend to be associated with the Os(2) atom which has the phosphine ligand bonded to it. In fact the two longest bonds in the structure, which are longer than any bonds previously reported in a trigonal-bipyramidal Os_5 cluster, are the ones between Os(2) and the two apical metal



Scheme 2. (*i*) Me_3NO, MeCN, CH_2Cl_2, room temperature (r.t.); (*ii*) L = $P(OMe)_3$, PPh_3, or $P(OPh)_3$, r.t., CH_2Cl_2, 3—4 h; (*iii*) for L = $P(OMe)_3$, H^-/H^+, CH_2Cl_2, r.t.; (*iv*) L = $P(OMe)_3$, PPh_3, or PEt_3, CH_2Cl_2, reflux, 20 h; (*v*) Me_3NO, MeCN, CH_2Cl_2, −78 °C; (*vi*) L = $P(OMe)_3$, PPh_3, or PEt_3, CH_2Cl_2, r.t.; (*vii*) heat, n-octane, 1 h, −CO; (*viii*) CO (40 atm, 50 °C, 5 h)

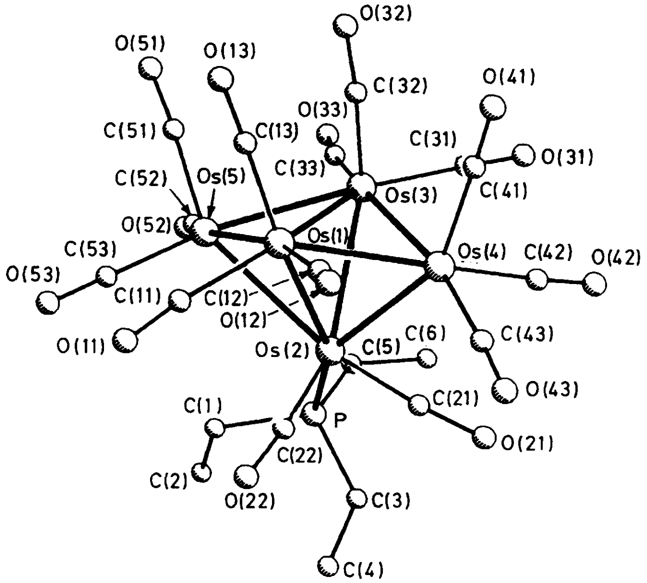


Figure 3. The molecular structure of $[Os_5H_2(CO)_{14}(PEt_3)]$ (**12**)

atoms Os(4) and Os(5). These long distances would be consistent with relatively less direct Os–Os orbital overlap than in the case of shorter metal–metal distances, and indicate a weaker interaction between these osmium atoms. One of these two bonds, Os(2)–Os(5), is bridged by a hydride, and the Os_2H unit

Table 3. Selected bond parameters (lengths in Å, angles in °) for $[Os_5H_2(CO)_{14}(PEt_3)]$ (**12**)

Os(1)–Os(2)	2.832(3)	Os(1)–Os(3)	2.837(2)
Os(1)–Os(4)	2.681(2)	Os(1)–Os(5)	2.742(2)
Os(2)–Os(4)	2.943(3)	Os(2)–Os(5)	3.045(2)
Os(3)–Os(4)	2.821(2)	Os(3)–Os(5)	2.844(2)
Os(2)–Os(3)	2.898(3)	Os(2)–P	2.380(7)
Os(1)–C(11)	1.932(29)	Os(1)–C(12)	1.897(24)
Os(1)–C(13)	1.839(35)	Os(2)–C(21)	1.806(35)
Os(2)–C(22)	1.874(28)	Os(3)–C(31)	1.927(34)
Os(3)–C(32)	1.824(32)	Os(3)–C(33)	1.889(26)
Os(4)–C(41)	1.931(34)	Os(4)–C(42)	1.902(25)
Os(4)–C(43)	1.924(22)	Os(5)–C(51)	1.870(39)
Os(5)–C(52)	1.840(31)	Os(5)–C(53)	1.889(29)

Os(2)–Os(1)–Os(3)	61.5(1)	Os(2)–Os(1)–Os(4)	64.5(1)
Os(3)–Os(1)–Os(4)	61.4(1)	Os(2)–Os(1)–Os(5)	66.2(1)
Os(3)–Os(1)–Os(5)	61.3(1)	Os(4)–Os(1)–Os(5)	116.6(1)
Os(1)–Os(2)–Os(3)	59.3(1)	Os(1)–Os(2)–Os(4)	55.3(1)
Os(3)–Os(2)–Os(4)	57.8(1)	Os(1)–Os(2)–Os(5)	55.5(1)
Os(3)–Os(2)–Os(5)	57.1(1)	Os(4)–Os(2)–Os(5)	100.8(1)
Os(1)–Os(2)–P	152.9(2)	Os(3)–Os(2)–P	115.9(2)
Os(4)–Os(2)–P	148.6(2)	Os(5)–Os(2)–P	98.5(2)
Os(1)–Os(3)–Os(2)	59.2(1)	Os(1)–Os(3)–Os(4)	56.6(1)
Os(2)–Os(3)–Os(4)	61.9(1)	Os(1)–Os(3)–Os(5)	57.7(1)
Os(2)–Os(3)–Os(5)	64.0(1)	Os(4)–Os(3)–Os(5)	109.1(1)
Os(1)–Os(4)–Os(3)	62.0(1)	Os(2)–Os(4)–Os(3)	60.3(1)
Os(1)–Os(4)–Os(2)	60.2(1)	Os(1)–Os(5)–Os(2)	58.3(1)
Os(1)–Os(5)–Os(3)	61.0(1)	Os(2)–Os(5)–Os(3)	58.8(1)
Os(2)–P–C(1)	112.3(10)	Os(2)–P–C(3)	113.7(9)
Os(2)–P–C(5)	113.4(10)		

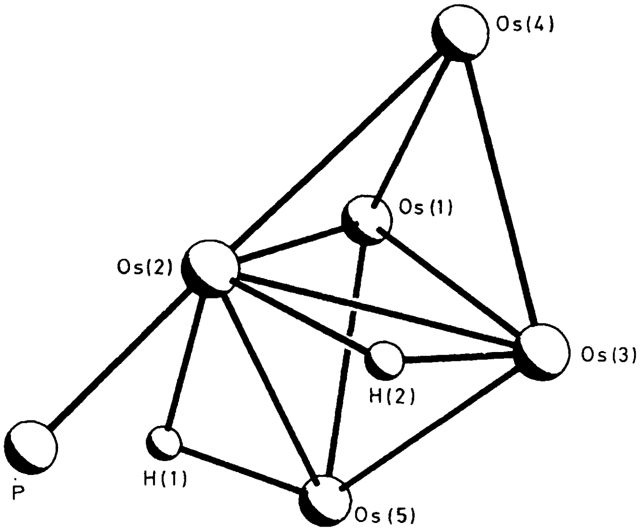


Figure 4. The core geometry of $[Os_5H_2(CO)_{14}(PEt_3)]$ (**12**) showing the calculated positions of the hydrides

may be described as a delocalised three-centre bond. The equatorial bond Os(2)–Os(3), which is bridged by the other hydride ligand, is *ca.* 0.06 Å longer than the other two equatorial bonds in the structure, and slightly longer than the value of 2.867(2) Å for the hydride-bridged bond in the cluster anion $[Os_5H(CO)_{15}]^-$.[17]

In terms of electron counting Os(4) is formally electron poor, with 17 electrons, while either Os(2) or Os(3) may be considered as electron rich, depending on the direction of donation of the bridging hydride ligand. This electronic imbalance is partially redressed by two incipient bridging carbonyl ligands, C(12)O(12) and C(21)O(21), donating electron density to the electron-poor Os(4) atom [Os(4)–C(12)

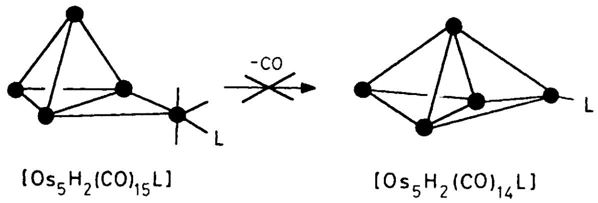
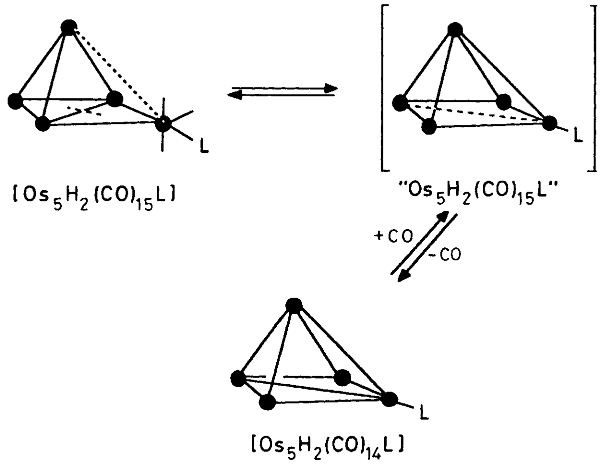


Figure 5. Simple rearrangement pattern for $[Os_5H_2(CO)_{15}L]$ which does not lead to the geometry observed in the crystal structure of $[Os_5H_2(CO)_{14}L]$



Scheme 3. Proposed mechanism for the decarbonylation of $[Os_5H_2(CO)_{15}L]$ to form $[Os_5H_2(CO)_{14}L]$

2.73(3) Å, Os(1)–C(12)–O(12) 165(2)°, Os(4)–C(21) 2.89(3) Å, and Os(2)–C(21)–O(21) 173.6(3)°]. One of these carbonyls, C(12)O(12), bridges the shortest Os–Os bond in the structure. This Os(1)–Os(4) bond length is similar to the value of 2.680(1) Å for the dihydride-bridged Os–Os 'double bond' in $[Os_3H_2(CO)_{10}]$,[18] and may suggest the existence of a metal–metal donor bond to the electron-poor metal atom.

The remaining Os–Os bonds within the metal framework lie in the range observed in other trigonal-bipyramidal Os_5 clusters. The Os(2)–P(1) bond length is similar to the value of 2.370(2) Å for the equivalent bond in $[Os_3H_2(CO)_{10}(PPh_3)]$.[19]

The observed structure confirms that a carbonyl ligand has been lost from the $[Os_5H_2(CO)_{15}(PEt_3)]$ addition complex, and that a metal–metal bond has reformed to give the trigonal-bipyramidal geometry. The position of the phosphine in $[Os_5H_2(CO)_{14}(PEt_3)]$ suggests that it is not a simple Os–Os bond formation which has occurred since the phosphine would be co-ordinated to an apical osmium atom (Figure 5). It is believed that the transformation may have been accompanied either by the migration of the $P(OMe)_3$ ligand from one osmium atom to another, or by a metal polyhedral rearrangement, or both.

In order to resolve this problem, the decarbonylation of compound (**6**) was followed by ^1H n.m.r. spectroscopy. On the n.m.r. time-scale no dissociation of the $P(OMe)_3$ ligand was detected, which minimises the possible migration of the $P(OMe)_3$ ligand from one osmium atom to another. We therefore believe that a rearrangement of the metal polyhedron is occurring during the transformation of (**6**) to (**10**). One of the possible mechanisms involving metal polyhedron rearrangement is given in Scheme 3. This mechanism proceeds *via* the formation of a square-based pyramidal intermediate, which is an alternative geometry for a 74-electron cluster system and is in accordance with Johnson's proposed mechanism for metal polyhedral rearrangement of a five-metal atom cluster with a trigonal-bipyramidal structure.[16]

Experimental

Although none of the clusters reported here is particularly air-sensitive, all the reactions, purifications, *etc.* were carried out under an inert atmosphere of dinitrogen.

Proton n.m.r. spectra were obtained on a Bruker WM250 instrument at 20 °C using deuteriated solvent as internal lock and reference, i.r. spectra on a Perkin-Elmer 983 spectrometer, and mass spectra on an AEI MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17} J) ionising potentials at 100—150 °C. Tris(perfluoroheptyl)-*s*-triazine was used as reference.

The clusters $[Os_3(CO)_{12}]$,[20] $[Os_6(CO)_{18}]$,[7] $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$,[8,9] and $[Os_5H_2(CO)_{15}]$[8,9] were prepared by the literature methods. Trimethylamine *N*-oxide was used freshly sublimed. All the other reagents were commercial grade and used as obtained.

Preparation of $[Os_5(CO)_{16}]$ (**1**).—The salt $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ (100 mg) was dissolved in thf (35 cm^3) and stirred in an ice-cold bath. Carbon monoxide (1 atm) was bubbled through the stirred suspension for 0.5 h. After this time, 2.2 equivalents of $FeCl_3$ were dropped into it and the mixture stirred for about 15—20 min. The progress of the reaction was monitored by analytical t.l.c. and i.r. spectroscopy. After this time, bubbling of CO was stopped and the solvent was removed by a gentle stream of N_2. Purification of the crude mixture by t.l.c. [using CH_2Cl_2–hexane (1:1)] afforded a brownish orange band which was characterised by i.r. spectroscopy to be $[Os_5(CO)_{16}]$ (**1**). The other brown band which did not move on the t.l.c. plate was also collected and removed from silica with acetone. The i.r. spectra of the brown band in CH_2Cl_2 showed it to be an anionic cluster with a formulation $[Os_5Cl(CO)_{15}]^-$.

Preparation of $[Os_5Cl(CO)_{15}]^-$.—The addition of solid $FeCl_3$ (2.2 equivalents) to a thf solution of $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ at room temperature resulted in an immediate colour change from dark orange to dark brown. The i.r. spectrum of the reaction mixture at this stage showed the formation of $[Os_5Cl(CO)_{15}]^-$.

Reaction of $[Os_5Cl(CO)_{15}]^-$ *with* $[Au(PPh_3)Cl]$.—The addition of $[Au(PPh_3)Cl]$ (1.1 equivalents) to a CH_2Cl_2 solution of $[Os_5Cl(CO)_{15}]^-$ at room temperature resulted in an immediate colour change from dark brown to yellowish orange. The contents of the reaction was stirred for about 0.5 h. Work up of the reaction mixture by t.l.c. (50% CH_2Cl_2 in hexane) afforded $[Os_5Cl(CO)_{15}(AuPPh_3)]$ as the major product.

Preparation of $[Os_5(CO)_{15}(NCMe)]$ (**2**).—The compound $[Os_5(CO)_{16}]$ (**1**) (30 mg) was dissolved in CH_2Cl_2 (30 cm^3) and MeCN (1.0 cm^3). A solution of Me_3NO (1.1 equivalents) in CH_2Cl_2 was added dropwise to the stirred suspension at room temperature over a period of 0.5 h. The reaction mixture was gradually warmed to room temperature and left stirring for about 0.5 h. It was then filtered through silica to remove any unreacted amine oxide. The solvent was then removed on a Rotavap. The resulting product formulated as $[Os_5(CO)_{15}(NCMe)]$ (**2**) was used in subsequent reactions without any further purification.

Reaction of $[Os_5(CO)_{15}(NCMe)]$ (**2**) *with* L = $P(OMe)_3$, $P(OPh)_3$, *or* PPh_3.—The cluster $[Os_5(CO)_{15}(NCMe)]$ (**2**) (20 mg) was dissolved in CH_2Cl_2 (25 cm^3) and a two-fold excess of the appropriate ligand L was added. The reaction contents were stirred at room temperature for 4 h. Work up of the reaction mixture by t.l.c. (50% CH_2Cl_2 in hexane) afforded $[Os_5(CO)_{15}L]$ [L = $P(OMe)_3$, (**3**); $P(OPh_3)$, (**4**); or PPh_3, (**5**)] in 60% yield.

Table 4. Atomic co-ordinates (× 10^4) for $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	3 394(1)	2 356(1)	6 147(1)	O(22)	787(21)	3 426(14)	4 088(9)
Os(2)	1 443(1)	3 562(1)	5 808(1)	C(23)	−7(20)	3 859(17)	5 956(13)
Os(3)	1 753(1)	2 397(1)	7 112(1)	O(23)	−873(17)	4 072(18)	6 037(12)
Os(4)	3 023(1)	4 106(1)	7 043(1)	C(31)	2 554(21)	2 574(17)	8 081(14)
Os(5)	1 217(1)	1 483(1)	5 714(1)	O(31)	2 996(19)	2 591(15)	8 712(10)
P	5 262(5)	2 662(5)	6 475(4)	C(32)	1 368(23)	1 065(19)	7 353(15)
O(1)	5 583(13)	3 764(12)	6 270(11)	O(32)	1 207(19)	235(15)	7 546(10)
C(1)	6 708(27)	4 099(24)	6 195(17)	C(33)	433(24)	2 807(19)	7 423(15)
O(2)	5 697(18)	2 464(15)	7 311(11)	O(33)	−377(15)	3 015(14)	7 605(12)
C(2)	6 810(28)	2 630(31)	7 617(30)	C(41)	3 797(21)	5 130(18)	6 635(13)
O(3)	6 070(18)	1 943(17)	6 103(16)	O(41)	4 285(17)	5 708(14)	6 325(12)
C(3)	6 041(28)	1 885(34)	5 305(24)	C(42)	4 153(23)	4 048(19)	7 909(15)
C(11)	3 460(21)	3 414(18)	5 384(14)	O(42)	4 839(20)	4 062(16)	8 421(11)
O(11)	3 710(16)	3 948(14)	4 964(11)	C(43)	2 166(25)	5 023(21)	7 452(16)
C(12)	3 608(23)	1 374(19)	6 944(15)	O(43)	1 551(20)	5 539(16)	7 725(13)
O(12)	3 884(16)	740(15)	7 376(12)	C(51)	1 107(18)	1 217(16)	4 650(12)
C(13)	3 533(20)	1 275(17)	5 455(13)	O(51)	1 041(23)	1 050(15)	4 059(10)
O(13)	3 666(17)	650(15)	5 049(13)	C(52)	−332(20)	1 456(16)	5 697(12)
C(21)	1 735(21)	4 995(18)	5 692(13)	O(52)	−1 209(17)	1 429(17)	5 715(13)
O(21)	1 795(23)	5 821(13)	5 590(13)	C(53)	1 513(22)	94(20)	5 866(14)
C(22)	1 031(20)	3 401(17)	4 724(13)	O(53)	1 673(19)	−758(12)	6 044(13)

Isomerisation of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**).—The cluster $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**) was stirred in CH_2Cl_2 or MeCN at room temperature over a period of 3—4 d. Solvent was removed *in vacuo*. Purification of the resulting reaction mixture by t.l.c. produced $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3a**) in 80% yield.

Reactions of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**).—*With* CO. The cluster $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**) was dissolved in toluene and placed in a Roth autoclave. The autoclave was then charged with 50 atm of CO and heated at 70 °C for 10 h. Work up of the reaction mixture by chromatography afforded $[Os_5(CO)_{19}]$ in 40% yield.

With H^-/H^+. The addition of a dilute solution of NEt_4BH_4 (1.1 equivalents in CH_2Cl_2) to a CH_2Cl_2 solution of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**) produced an immediate colour change from orange to yellow. The i.r. spectrum showed the product to be anionic which on protonation with HBF_4 (1.1 equivalents) produced a neutral orange cluster $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) in 50% yield.

Preparation of $[Os_5H_2(CO)_{14}(NCMe)]$ (**9**).—The cluster $[Os_5H_2(CO)_{15}]$ (**7**) (30 mg) was stirred in CH_2Cl_2 (25 cm^3) in the presence of a little MeCN (0.5 cm^3). A solution of Me_3NO (1.1 equivalents in CH_2Cl_2) was added dropwise to the stirred suspension at −78 °C over a period of 0.5 h. The reaction mixture was stirred for about 0.5 h. The solution was filtered through silica to remove any excess of Me_3NO. The resulting product formulated as $[Os_5H_2(CO)_{14}(NCMe)]$ (**9**) was used in subsequent reactions without any further purification.

Reactions of $[Os_5H_2(CO)_{14}(NCMe)]$ (**9**) *with* L $= P(OMe)_3$, PPh_3, *or* PEt_3.—The cluster $[Os_5H_2(CO)_{14}(NCMe)]$ (**9**) (20 mg) was dissolved in CH_2Cl_2 (25 cm^3) and a two-fold excess of the appropriate ligand L was added. The reaction contents were stirred at room temperature for 4 h. Work up of the reaction mixture by t.l.c. (50% CH_2Cl_2 in hexane) afforded $[Os_5H_2(CO)_{14}L]$[L $= P(OMe)_3$,(**10**);PPh_3,(**11**);orPEt_3,(**12**)].

Reaction of $[Os_5H_2(CO)_{14}\{P(OMe)_3\}]$ (**10**) *with* CO.—The cluster $[Os_5H_2(CO)_{14}\{P(OMe)_3\}]$ (**10**) was dissolved in toluene and placed in a Roth autoclave. The autoclave was then charged with 40 atm of CO and heated at 50 °C for 5 h. Work up of the reaction mixture by chromatography afforded $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ (**6**) in 75% yield.

Crystal Structure Determination of $[Os_5(CO)_{15}\{P(OMe)_3\}]$ (**3**).—Suitable orange plate-shaped crystals of compound (**3**) were grown by slow evaporation of a CH_2Cl_2–hexane solution.

Crystal data. $C_{18}H_9O_{18}Os_5P$, $M = 1\,495.22$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.288(3)$, $b = 13.204(2)$, $c = 17.963(3)$ Å, $\beta = 99.12(2)°$, $U = 2\,877.7$ Å^3 (by least-squares refinement on diffractometer angles from 56 automatically centred reflections in the range $20 < 2\theta < 25°$, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 3.45$ g cm^{-3}, D_m not measured, $F(000) = 2\,684$. Orange plate, crystal dimensions 0.16 × 0.27 × 0.53 mm, $\mu(Mo\text{-}K_\alpha) = 221.20$ cm^{-1}.

Data collection and processing. Stoe STADI-4 four-circle diffractometer, 24-step ω—θ scan mode, ω step width 0.05°, step time 0.5—2.0 s per step, graphite-monochromated Mo-K_α radiation; 10 976 reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $\pm h, \pm k, +l$), on-line profile fitting, 5 072 unique [$R_{int} = 0.067$ after semiempirical absorption connection using 300 azimuthal scan data and a laminar model (transmission factors, minimum, maximum 0.003, 0.023)], 4 052 with $F > 5\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinements. Automated Patterson techniques (Os atoms) followed by Fourier difference techniques (for remaining non-hydrogen atoms). Blocked full-matrix least squares with Os, P, O, and phosphite C anisotropic. Methyl H atoms placed in idealised positions (C–H 1.08 Å) and allowed to ride on relevant C atom; refined common isotropic thermal parameter. The weighting scheme $w = 7.686/[\sigma^2(F) + 0.001|F^2|]$ gave satisfactory agreement analyses. The converged residuals were $R = 0.059$, $R' = 0.061$. A final Fourier difference map showed electron-density ripples of *ca.* 3 e Å^{-3} close to the Os atom positions but no other regions of significant electron density. Final atomic co-ordinates for (**3**) are presented in Table 4.

Crystal Structure Determination of $[Os_5H_2(CO)_{14}(PEt_3)]$ (**12**).—Suitable red crystals of compound (**12**) were grown by slow evaporation of CH_2Cl_2.

Crystal data. $C_{20}H_{17}O_{13}Os_5P$, $M = 1\,462.97$, orthorhombic, space group *Pbca* (no. 61), $a = 15.634(8)$, $b = 15.601(11)$,

Table 5. Atomic co-ordinates (× 10^4) for $[Os_5H_2(CO)_{14}(PEt_3)]$ (**12**)

Atom	x	y	z
Os(1)	5 255(1)	1 636(1)	4 239(1)
Os(2)	4 692(1)	2 375(1)	3 253(1)
Os(3)	3 842(1)	2 775(1)	4 265(1)
Os(4)	5 549(1)	3 320(1)	4 131(1)
Os(5)	3 689(1)	1 053(1)	3 901(1)
P	3 818(4)	2 407(4)	2 463(3)
C(1)	3 465(18)	1 309(19)	2 251(13)
C(2)	3 026(21)	1 233(20)	1 705(13)
C(3)	4 311(16)	2 884(17)	1 904(13)
C(4)	5 133(15)	2 427(20)	1 642(13)
C(5)	2 815(14)	3 024(18)	2 555(13)
C(6)	2 925(22)	3 918(19)	2 621(17)
C(11)	5 582(16)	549(18)	3 925(13)
O(11)	5 821(12)	−33(12)	3 713(10)
C(12)	6 432(15)	1 858(17)	4 363(12)
O(12)	7 141(10)	1 817(13)	4 486(11)
C(13)	5 177(17)	1 224(20)	4 935(15)
O(13)	5 149(11)	942(14)	5 380(9)
C(21)	5 225(20)	3 304(23)	2 977(16)
O(21)	5 526(13)	3 999(13)	2 804(8)
C(22)	5 584(17)	1 742(18)	2 940(13)
O(22)	6 081(13)	1 280(15)	2 737(9)
C(31)	3 666(18)	3 989(22)	4 372(14)
O(31)	3 505(16)	4 700(17)	4 413(16)
C(32)	3 915(15)	2 618(17)	4 996(13)
O(32)	3 877(12)	2 458(17)	5 477(10)
C(33)	2 640(17)	2 680(17)	4 212(12)
O(33)	1 892(12)	2 724(15)	4 189(9)
C(41)	5 734(17)	3 548(19)	4 891(14)
O(41)	5 834(15)	3 663(16)	5 330(11)
C(42)	5 297(14)	4 478(16)	3 949(12)
O(42)	5 168(15)	5 173(15)	3 867(15)
C(43)	6 719(14)	3 539(16)	3 930(11)
O(43)	7 386(11)	3 643(14)	3 778(10)
C(51)	3 376(19)	694(21)	4 597(16)
O(51)	3 140(13)	440(15)	5 006(11)
C(52)	2 577(19)	1 074(20)	3 657(14)
O(52)	1 877(11)	1 067(13)	3 447(9)
C(53)	3 874(16)	−60(19)	3 624(13)
O(53)	3 964(15)	−716(12)	3 455(10)

c = 24.671(20) Å, U = 6 017.4 Å^3 (by least-squares refinement on diffractometer angles from 15 automatically centred reflections in the range $15 < 2\theta < 25°$, λ = 0.710 69 Å), Z = 8, D_c = 3.23 g cm^{-3}, D_m not measured, $F(000)$ = 5 150. Red blocks, dimensions 0.15 × 0.23 × 0.31 mm, μ(Mo-K_α) = 211.42 cm^{-1}.

Data collection and processing. Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo-K_α radiation, 96-step ω—2θ scan mode, scan width from 0.9° below K_{α_1}, to 0.9° above K_{α_2}, scan speed 2.5—29.3° min^{-1}. 3 330 Significant reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $+h,+k,+l$), off-line profile fitting, 2 755 unique, [R_{int} = 0.010 after empirical absorption correction using 320 azimuthal scan data and an ellipsoid model (transmission factors, minimum, maximum 0.269, 1.000)], 2 755 with $F > 3\sigma(F)$. Two standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Centrosymmetric direct methods (Os atoms) followed by Fourier difference techniques (for remaining non-hydrogen atoms). Blocked-cascade least squares with Os, P, O, and phosphine C anisotropic, Ethyl H atoms placed in idealised positions (C–H 1.08 Å) and allowed to ride on the relevant C atom; each type of H atom was assigned a common isotropic thermal parameter. The weighting scheme $w^{-1} = \sigma^2(F) + 0.001|F^2|$ gave satisfactory agreement analyses. The converged residuals were R = 0.055 and R' = 0.050; a final Fourier difference map showed electron-density ripples of *ca.* 2 e Å^{-3} close to the Os atom positions but no other regions of significant electron density. Final atomic co-ordinates for (**12**) are listed in Table 5.

For the solution and refinement of both structures neutral-atom scattering factors were taken from ref. 21. All computations were carried out on the University of Cambridge IBM 3081 computer using modified versions of SHELX 76.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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