

Preliminary communication

PHOSPHORUS DONOR LIGAND SUBSTITUTION IN PENTANUCLEAR OSMIUM CLUSTER CARBONYLS: CRYSTAL AND MOLECULAR STRUCTURES OF $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$ AND $[\text{Os}_5\text{H}_2(\text{CO})_{13}(\text{PEt}_3)\text{P}(\text{OMe})_3]$

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Summary

The complexes $[\text{Os}_5\text{H}_2(\text{CO})_{15}\text{L}]$ ($\text{L} = \text{PPh}_3, \text{PEt}_3, \text{P}(\text{OMe})_3$) undergo decarbonylation at 120°C to give compounds with the general formula $[\text{Os}_5\text{H}_2(\text{CO})_{14}\text{L}]$, which adopt a trigonal bipyramidal arrangement of metal atoms with the phosphorus donor group bonded to one of the equatorial Os atoms. These clusters will also undergo further substitution to give $[\text{Os}_5\text{H}_2(\text{CO})_{13}\text{LL}']$ in which the trigonal bipyramidal metal arrangement is retained.

Some of the most extensively studied reactions of transition metal cluster compounds involve substitution by or addition of phosphine and phosphite ligands [1,2]. In most cases substitution occurs, but in a number of reactions cluster breakdown is observed [3]. Molecular orbital calculations, in these cases, indicate that the highest occupied molecular orbitals (HOMO) are close to being antibonding with respect to direct metal-metal interactions within the cluster framework [4]. This suggests that metal-metal bonds may be broken, for example, by the addition of a donor ligand. With higher clusters (M_n , $n > 4$) it is possible that some metal-metal bonds may be broken without complete cluster fragmentation.

The most reactive starting material for investigating reactions of pentanuclear osmium cluster carbonyls is the hydrido complex $[\text{Os}_5\text{H}_2(\text{CO})_{15}]$. This complex is assumed to have a trigonal bipyramidal metal framework. It reacts with a range of nucleophiles to give addition products $[\text{Os}_5\text{H}_2(\text{CO})_{15}\text{Nu}]$ ($\text{Nu} =$ nucleophile) in which one metal-metal bond is broken, and an edge bridging tetrahedral metal framework results [5]. With $\text{P}(\text{OMe})_3$ this donor ligand occupies an equatorial site on the edge bridging metal atom.

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TABLE 1
SPECTROSCOPIC DATA

	IR ($\nu(\text{CO})$) cm^{-1} (CH_2Cl_2)	Mass spectrum (m/e) based on ^{192}Os
$[\text{Os}_5\text{H}_2(\text{CO})_{15}\text{P}(\text{OMe})_3]$	2116w, 2070s, 2048vs 2036s, 2014sh, 1997w	1499
$[\text{Os}_5\text{H}_2(\text{CO})_{15}(\text{PET}_3)]$	2115w, 2069s, 2047s 2035s, 2020sh, 1999w	1493
$[\text{Os}_5\text{H}_2(\text{CO})_{15}(\text{PPh}_3)]$	2096w, 2070s, 2050s 2037s, 2025sh	1636
$[\text{Os}_5\text{H}_2(\text{CO})_{14}\text{P}(\text{OMe})_3]$	2094m, 2063s, 2041s 2020m	1471
$[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PET}_3)]$	2092m, 2061s, 2041s 2019m, 1997w	1465
$[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PPh}_3)]$ (major product)	2118w, 2074m, 2066s 2043s, 2024w	1609
$[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PPh}_3)]$ (minor product)	2088m, 2058m, 2033s 2009m, 1985w	1609
$[\text{Os}_5\text{H}_2(\text{CO})_{13}\{\text{P}(\text{OMe})_3\}_2]$	2077s, 2032vs, 2007s 1968m	1566
$[\text{Os}_5\text{H}_2(\text{CO})_{13}(\text{PET}_3)\text{P}(\text{OMe})_3]$	2077m, 2027s, 2005s 1969m	1562

When the complex $[\text{Os}_5\text{H}_2(\text{CO})_{15}\text{L}]$ ($\text{L} = \text{P}(\text{OMe})_3, \text{PET}_3$) is heated under reflux for 1 h, in *n*-octane, $[\text{Os}_5\text{H}_2(\text{CO})_{14}\text{L}]$ is obtained in good yield (80%), and has been characterised by spectroscopic techniques (Table 1). With the analogous PPh_3 containing complex under identical conditions two products are obtained. The major product has been characterised by spectroscopic techniques (Table 1) as $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PPh}_3)]$, while the mass spectrum of the low yield product (10%) indicated that it is also a pentanuclear cluster. It is probable that this second product may involve *ortho*-metallation of one of the phenyl rings, as has been observed in a number of other systems [6]. However, with all three phosphorus donor ligands the major reaction pathway is the decarbonylation, and the spectroscopic data for the three products suggests that their structures are similar.

It is important to establish whether the loss of a carbonyl group is concomitant with a change in the geometry of the metal framework. Therefore, it was decided to determine the structure of one of the complexes by X-ray analysis. Good quality crystals of $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PET}_3)]$ were obtained from dichloromethane and this complex has been investigated.

The molecular geometry* of $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PET}_3)]$ is shown in Fig. 1, which includes some important bond parameters. The five Os atoms lie at the vertices of a trigonal bipyramid. The phosphine ligand is bonded to one of the equatorial Os atoms which is also coordinated to two terminal carbonyl ligands. Each of the other four metal atoms is bound to three terminal carbonyl groups. The two hydride ligands were not located directly, but potential energy calculations [7] indicate that one hydride bridges the equatorial Os(2)—Os(3) edge and the other bridges the equatorial—axial Os(2)—Os(5) edge.

* $\text{C}_{20}\text{H}_{15}\text{O}_{14}\text{Os}_5\text{P}$, $M = 1462.97$, orthorhombic, space group $Pbca$, a 15.634(8), b 15.601(11), c 24.671(20) Å, U 6017.4 Å³, D_c 3.23 g cm⁻³, $Z = 8$, $F(000) = 5150$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 211.42 cm⁻¹. 3330 reflections measured on a Syntex P2₁ diffractometer. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by blocked cascade least squares to $R = 0.055$ and $R_w = 0.050$ for 2755 observed reflections [$F > 3\sigma(F)$].

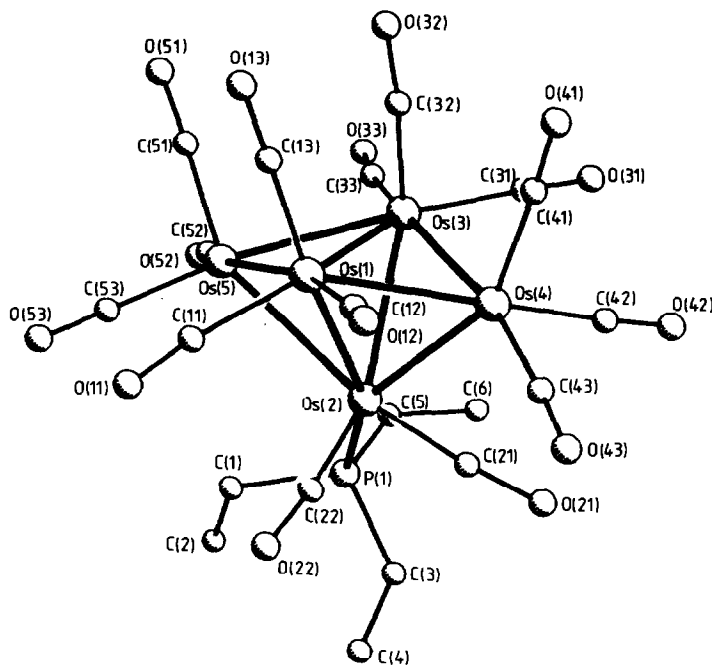


Fig. 1. The molecular structure of $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$. Bond lengths: Os(1)—Os(2), 2.832(3); Os(1)—Os(3), 2.837(2); Os(1)—Os(4), 2.681(2); Os(1)—Os(5), 2.742(2); Os(2)—Os(3), 2.898(3), Os(2)—Os(4), 2.943(3); Os(2)—Os(5), 3.045(2); Os(3)—Os(4), 2.821(2); Os(3)—Os(5), 2.844(2); Os(2)—P(1), 2.380(7) Å.

The observed structure confirms that a carbonyl group has been lost from the $[\text{Os}_5\text{H}_2(\text{CO})_{15}(\text{PEt}_3)]$ addition complex, and that a metal—metal bond has reformed to give the trigonal bipyramidal geometry. The position of the phosphine in $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$ suggests that it is not a simple Os—Os bond formation which has occurred since the phosphine would be coordinated to an apical Os atom (Fig. 2). Either there has been a rearrangement of the metal framework, or ligand migration has occurred, or perhaps both.

The Os—Os bond distances in $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$ 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 [8], are the ones between Os(2) and the two apical metal 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 Os atoms. One of these two bonds, Os(2)—Os(5), is bridged by a hydride, and may be thought of as a delocalised three-centre unit. The equatorial bond, Os(2)—Os(3), which is bridged by the other hydride 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 $[\text{Os}_5\text{H}(\text{CO})_{15}]^-$ anion [9].

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. This electronic imbalance is partially redressed by two incipient bridging carbonyl groups, C(12)O(12) and

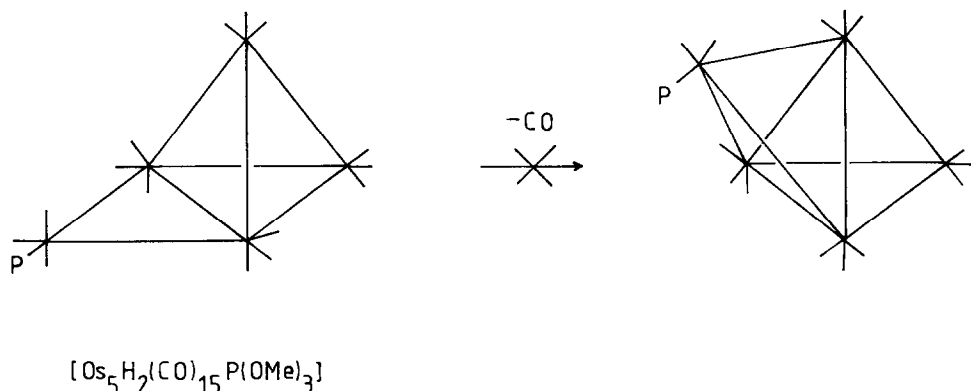


Fig. 2. Simple rearrangement pattern for $[\text{Os}_5\text{H}_2(\text{CO})_{15}(\text{PEt}_3)]$ which does not lead to the geometry observed in the crystal structure of $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$.

C(21)O(21), donating electron-density to the electron-poor Os(4) atom (Os(4)—C(12), 2.73(3) Å; Os(1)—C(12)—O(12), 165(2)°; Os(4)—C(21), 2.89(3) Å; 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 $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ [10], and this suggests 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 [8,9,11]. The Os(2)—P(1) bond length is similar to the value of 2.370(2) Å for the equivalent bond in $[\text{Os}_3\text{H}_2(\text{CO})_{10}(\text{PPh}_3)]$ [12].

Further substitution of carbonyl groups of the $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PR}_3)]$ complexes is possible. When $[\text{Os}_5\text{H}_2(\text{CO})_{14}\text{P}(\text{OMe})_3]$ is heated under reflux with excess $\text{P}(\text{OMe})_3$ for 5 h, the major product is the substituted complex $[\text{Os}_5\text{H}_2(\text{CO})_{13}\{\text{P}(\text{OMe})_3\}_2]$ which has been characterised spectroscopically (Table 1). It is assumed that, from the spectroscopic data, $[\text{Os}_5\text{H}_2(\text{CO})_{14}\text{P}(\text{OMe})_3]$ has a similar structure to that of $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$, and when the former complex is heated in *n*-heptane, under reflux, for 16 h with PEt_3 the major product isolated is the mixed substitution complex $[\text{Os}_5\text{H}_2(\text{CO})_{13}(\text{PEt}_3)\text{P}(\text{OMe})_3]$ (Table 1). In order to establish the arrangement of ligands in the cluster a single X-ray analysis has been undertaken.

The molecular structure* of $[\text{Os}_5\text{H}_2(\text{CO})_{13}(\text{PEt}_3)\text{P}(\text{OMe})_3]$ is shown in Fig. 3, together with some important bond parameters. The trigonal bipyramidal metal framework of the mono-phosphine complex is retained. However, the phosphite ligand which occupies a site on an equatorial Os atom in the mono-substituted complex now occupies a site on an axial Os atom in the di-substituted complex, and the incoming PEt_3 group occupies a site on an equatorial Os atom. Each of the Os atoms bonded to the phosphorus donor ligands is also bonded to two

* $\text{C}_{22}\text{H}_{26}\text{O}_{16}\text{Os}_5\text{P}_2$, $M = 1559.37$, monoclinic, space group $P2_1/c$, a 17.966(3), b 11.564(2), c 18.080(2) Å, β 112.85(1)°, U 3461.5 Å³, D_c 2.99 g cm⁻³, $Z = 4$, $F(000) = 2784$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 184.30 cm⁻¹. 6648 reflections measured on a Stoe—Siemens diffractometer. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by blocked cascade least squares to $R = 0.056$ and $R_w = 0.055$ for 4607 observed reflections [$F > 4\sigma(F)$].

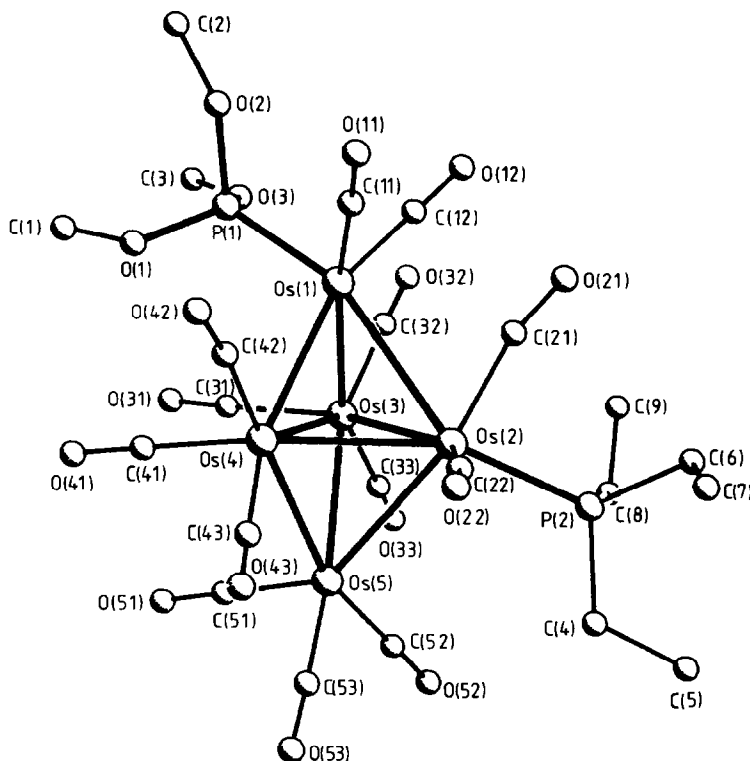


Fig. 3. The molecular structure of $[\text{Os}_5\text{H}_2(\text{CO})_{13}(\text{PEt}_3)\text{P}(\text{OMe})_3]$. Bond lengths: Os(1)—Os(2), 2.990(1); Os(1)—Os(3), 2.879(1); Os(1)—Os(4), 2.684(1); Os(2)—Os(3), 2.897(1); Os(2)—Os(4), 2.821(1); Os(2)—Os(5), 3.045(1); Os(3)—Os(4), 2.824(1); Os(3)—Os(5), 2.847(1); Os(4)—Os(5), 2.737(1); Os(1)—P(1), 2.238(5); Os(2)—P(2), 2.380(5) Å.

terminal carbonyl groups, and the other three metal atoms are bonded to three terminal carbonyls each. Potential energy calculations [7] indicate that the two hydrides bridge the equivalent equatorial Os(2)—Os(3) and equatorial—axial Os(2)—Os(5) edges as in the mono-substituted complex.

The structure shows that the reaction of $[\text{Os}_5\text{H}_2(\text{CO})_{14}\text{P}(\text{OMe})_3]$ with PEt_3 is not a simple substitution of a carbonyl by the PEt_3 group since the $\text{P}(\text{OMe})_3$ ligand is bonded to an axial Os atom. It is apparent that a major rearrangement involving the breaking and subsequent reformation of several Os—Os bonds, or ligand migration, is required to give the observed product. Further studies are currently in progress to determine the nature of the rearrangement.

The structural parameters for $[\text{Os}_5\text{H}_2(\text{CO})_{13}(\text{PEt}_3)\text{P}(\text{OMe})_3]$ are similar to those in the mono-substituted complex. Again the longest Os—Os bonds are associated with the equatorially phosphine substituted metal atom, Os(2). In this structure the apical Os(1) atom is electron-poor with 17 electrons, while one of the equatorial Os atoms is formally electron-rich. The electron imbalance is partially redressed by two incipient carbonyl groups, C(21)O(21) and C(42)O(42), which bridge to Os(1) (Os(1)—C(21), 2.78(3) Å; Os(2)—C(21)—O(21), 166(2)°; Os(1)—C(42), 2.63(3) Å; Os(4)—C(42)—O(42), 167(3)°). The equatorial Os(2)—P(2) phosphine distance is similar in length to the equatorial Os—P phosphine distance in $[\text{Os}_5\text{H}_2(\text{CO})_{14}(\text{PEt}_3)]$, while the axial Os(1)—P(1) phosphite distance is ca. 0.14 Å shorter.

The hydride positions in these two structures are of particular interest. It might be expected that, in order to maintain an electronically balanced structure each apical metal atom would be bonded to a hydride which bridges to an equatorial Os atom. The presence of a hydride bridging an equatorial—equatorial Os—Os bond introduces the electron imbalance, and requires an equatorial—apical Os—Os donor bond to equilibrate the electron balance. If this hydride distribution also occurs in the parent hydrido complex $[\text{Os}_5\text{H}_2(\text{CO})_{15}]$, the presence of a donor bond may be responsible for the increase in reactivity of this cluster over other pentanuclear Os complexes.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

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