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Preliminary Communication

Isolation and structural characterisation of $Os_5(CO)_{18}$, a postulated intermediate in the conversion of $Os_5(CO)_{19}$ into $Os_5(CO)_{16}$

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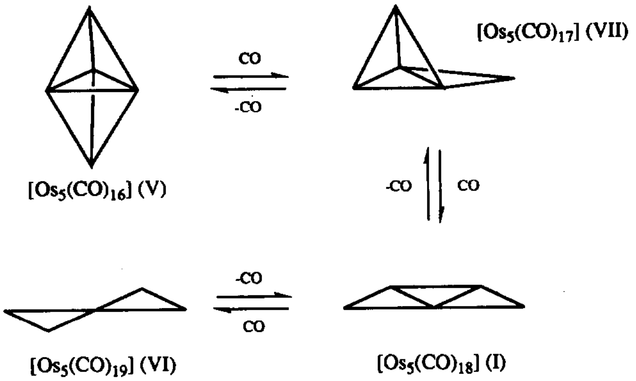
Abstract

The binary carbonyl cluster $Os_5(CO)_{18}$ has been obtained from the room temperature reaction of $Os_3(CO)_{10}(MeCN)_2$ with $H_2Os_3(CO)_{12}$. X-Ray structural analysis of the cluster shows that it has an unusual metal framework, consisting of a five metal planar 'raft'.

Binary carbonyl clusters containing varying ratios of metal to carbonyl groups, for a given nuclearity, are now becoming more common. Here we report the synthesis of the new cluster $Os_5(CO)_{18}$ (I) which provides the third member of a set of pentaosmium clusters with differing numbers of carbonyl ligands [1].

The binary nature of the cluster may be retained, when there is a change in the number of carbonyl ligands, by adjusting the number of metal–metal bonds, as decarbonylation is accompanied by metal–metal bond formation.

For sequential loss of carbon monoxide, structural pathways have been predicted between known clusters differing only in the number of carbonyl ligands. For example, for the binary pentaosmium series [1], we may consider the breaking of bonds via osmium–carbonyl bond formation, leading to the intermediates shown in Scheme 1. The present compound provides the third member of this series, the only remaining member is related to the adduct formed by nucleophilic addition to $Os_5(CO)_{16}$ [2].



Scheme 1.

Treatment of a dichloromethane solution of $Os_3(CO)_{10}(MeCN)_2$ with $H_2Os_3(CO)_{12}$ [3], at room temperature with the exclusion of light, affords an unstable product, tentatively formulated as a hexaosmium adduct. On standing in solution, this compound decomposes, possibly via the known cluster $Os_5(CO)_{19}$ [1] (since trace amounts of this compound were detected) to the new cluster $Os_5(CO)_{18}$ (I).

An X-ray structure analysis established the 'raft' like molecular structure of $Os_5(CO)_{18}$ (I) *, shown in Fig. 1, which is the first example of a planar binary carbonyl pentaosmium species.

The metal skeleton may be described as a triangle defined by the Os(1), Os(2) and Os(3) atoms, with the edges Os(1)–Os(2), and Os(1)–Os(3), bridged by Os(4) and Os(5), respectively. Thus, the five coplanar osmium atoms (maximum deviation 0.03 Å) define three triangles, with two common edges.

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* *Spectroscopic data for I:* IR (CH_2Cl_2): ν(CO) 2097(s), 2076(m), 2044(s), 2020(m), 2000(w), 1927(w), 1825(w.br) cm^{-1}. m/z (FAB) 1459 (M^+).

Crystal data for I: $C_{18}O_{18}Os_5$, $M = 1456.75$, triclinic, $P\bar{1}$ (no. 2), $a = 10.287(3)$, $b = 15.519(4)$, $c = 8.847(2)$ Å, $\alpha = 96.15(2)$, $\beta = 109.11(3)$, $\gamma = 73.62(2)°$, $U = 1279.91$ Å^3, $Z = 2$, $D_c = 3.78$ g cm^{-3}, μ(Mo Kα) = 247.83 cm^{-1}, $F(000) = 1264$, $R = 7.3\%$ for 3120 reflections with $I/\sigma|I| \geq 3.0$.

For intramolecular bond lengths see Figure 1. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, See Notice to Authors, Issue No. 1.

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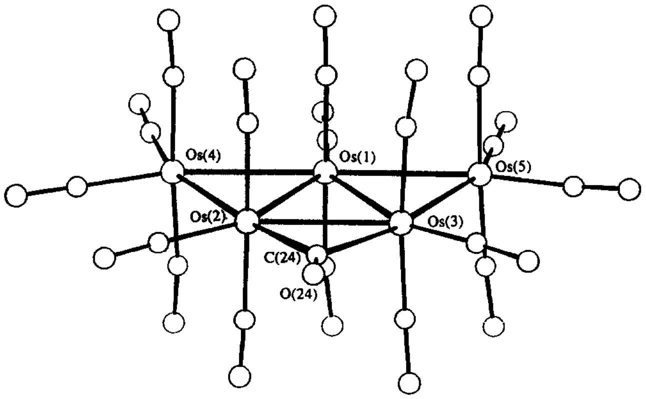

Fig. 1. The molecular structure of the cluster I. Selected bond distances (Å) are: Os(1)-Os(2) 2.848(2), Os(1)-Os(4) 2.843(2), Os(2)-Os(3) 2.841(2), Os(3)-Os(4) 2.840(2), Os(2)-C(24) 2.08(4), Os(1)-Os(3) 2.840(2), Os(1)-Os(5) 2.860(2), Os(2)-Os(4) 2.871(2), Os(3)-C(24) 2.27(4).

The remaining edge of the central triangle [Os(1), Os(2), Os(3)], is bridged by a slightly asymmetric carbonyl ligand. Os(2)-C(24) = 2.08 Å, and Os(2)-C(24) = 2.27 Å, this also lies in the plane of the raft (maximum deviation 0.07 Å).

The remaining seventeen carbonyl ligands are all terminal, with three bonded to each of the central metal atoms (two axial and one equatorial), and of the remaining two [Os(4), and Os(5)], each have two axial and two equatorial carbonyl ligands.

Similar arrangements of five osmium atoms have been observed before in larger clusters, for example in $[Os_6(CO)_{17}(\mu\text{-}H)(C{=}CEt)]$ (**II**) [4], $[Os_6(CO)_{20}(C{=}C(H)Ph)]$ (**III**) [5], and $[Os_6(CO)_{17}(P(OMe)_3)_4]$ (**IV**) [6]. In **II**, the sixth metal forms a tetrahedron by capping an edge triangle of the planar raft.

III is rather similar to **II** in metal framework, but with only two bonds from the sixth osmium to the raft. This yields a six atom 'ladder' complex, however, only five of the osmium atoms are coplanar.

$Os_6(CO)_{17}(\mu\text{-}H)(CCEt)$ (II)

Fig. 2.

$Os_6(CO)_{17}(CC(H)Ph)$ (III)

Fig. 3.

$[Os_6(CO)_{17}(P(OMe)_3)_4]$ (IV)

Fig. 4.

The hexanuclear raft complex $[Os_6(CO)_{17}(P(OMe)_3)_4]$ (**IV**) [6] may be formally derived from **I**, by replacing the bridging carbonyl with an $Os(CO)_4$ unit.

The trigonal bipyramidal complex $Os_5(CO)_{16}$ (**V**) [7] together with the 'bow-tie' cluster $Os_5(CO)_{19}$ (**VI**) [1,8] represented the first example of two strictly binary carbonyl species of the same nuclearity [1]. The characterisation of $Os_5(CO)_{18}$ (**I**) adds to this series, and is the third cluster of a set of four, postulated for the stepwise interconversion of the 'saturated carbonyl cluster', $Os_5(CO)_{19}$ (**VI**) into the parent compound, $Os_5(CO)_{16}$ (**V**) [1].

Present studies are directed at the isolation of $Os_5(CO)_{17}$ (**VII**), completing the series for the stepwise decarbonylation of **VI**, where carbonyl loss is concomitant with metal-metal bond formation [1].

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