

Preliminary communication

A TRINUCLEAR CLUSTER OF OSMIUM AND MOLYBDENUM. CRYSTAL STRUCTURE OF THE CO-CRYSTALLIZED MOLECULES $\text{MoOs}_2(\text{CO})_{11}[\text{P}(\text{OMe})_3]_2$ AND $[(\text{MeO})_3\text{P}](\text{OC})_4\text{OsMo}(\text{CO})_5$

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Summary

The crystal structure of $\text{MoOs}_2(\text{CO})_{11}[\text{P}(\text{OMe})_3]_2 \cdot [(\text{MeO})_3\text{P}](\text{OC})_4\text{OsMo}(\text{CO})_5$ is comprised of a slightly disordered, triangular cluster with a $\text{Mo}(\text{CO})_5$ and two $\text{Os}(\text{CO})_3[\text{P}(\text{OMe})_3]$ moieties (Os–Mo bond lengths are 3.041(2) and 3.079(2) Å) together with a $[(\text{MeO})_3\text{P}](\text{OC})_4\text{OsMo}(\text{CO})_5$ molecule having a donor–acceptor Os–Mo bond of length 3.075(2) Å.

Recent studies in these laboratories have shown that neutral 18-electron organometallic compounds can act as ligands to give complexes with unbridged donor–acceptor metal–metal bonds [1,2]. One such complex for which we have reported the synthesis and structure is $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ [2]. We have prepared a number of analogues of this compound of the type $\text{L}(\text{OC})_4\text{OsM}(\text{CO})_5$ (M = Cr, Mo, W; L = phosphorus donor ligand) [3]. In the preparation of some of the molybdenum and tungsten complexes an intensely colored byproduct was formed although the quantities were insufficient for characterization. However, in one preparation of $[(\text{MeO})_3\text{P}](\text{OC})_4\text{OsMo}(\text{CO})_5$ (**2**), from $\text{Os}(\text{CO})_4[\text{P}(\text{OMe})_3]^*$ and $\text{Mo}(\text{CO})_5(\text{THF})$ in hexane, three deep-red crystals were obtained in the crude product. Here we report the X-ray structure analysis of one of those crystals that reveal it to be a 1/1 mixture of **2** and the novel triangular cluster $\text{MoOs}_2(\text{CO})_{11}[\text{P}(\text{OMe})_3]_2$ (**1**).

Crystal data: $\text{C}_{17}\text{H}_{18}\text{MoO}_{17}\text{Os}_2\text{P}_2 \cdot \text{C}_{12}\text{H}_9\text{MoO}_{12}\text{OsP}$, triclinic, $P\bar{1}$, a 8.788(1), b 16.901(2), c 18.456(2) Å, α 68.88(1), β 81.75(1), γ 77.01(1)°, $Z = 2$. The structure was solved by heavy atom methods and refined to $R = 0.0395$ by least-squares using 2886 reflections with $I > 2.5\sigma(I)$ measured on a CAD4 diffractometer with Mo- K_α radiation. The triangular cluster showed a small degree of “Star of David” disorder.

* Prepared from $\text{Os}(\text{CO})_5$ and $\text{P}(\text{OMe})_3$ [4].

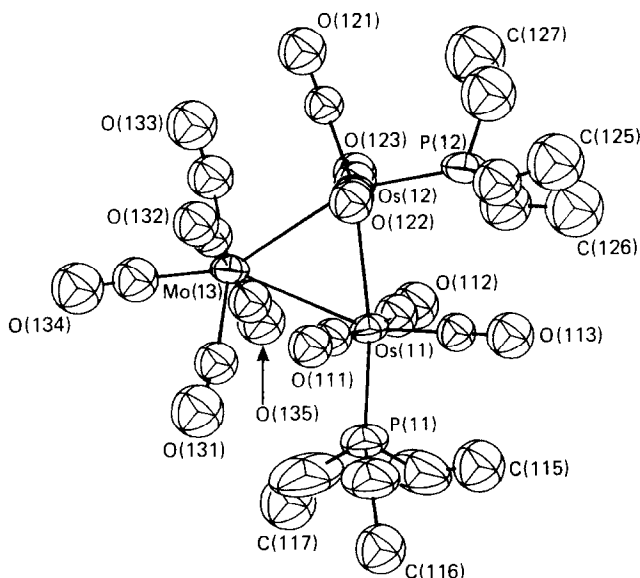


Fig. 1. The molecular structure of $\text{MoOs}_2(\text{CO})_{11}[\text{P}(\text{OMe})_3]_2$. Selected bond lengths (Å): Mo(13)–Os(11) 3.079(2), Os(12)–Mo(13) 3.041(2), Os(11)–Os(12) 2.854(1), Os(11)–P(11) 2.300(7), Os(12)–P(12) 2.271(7).

A view of **1** is shown in Fig. 1. As can be seen, it consists of a $\text{Mo}(\text{CO})_5$ and two $\text{Os}(\text{CO})_3[\text{P}(\text{OMe})_3]$ units bonded in a triangular array; the geometry about the molybdenum atom is approximately pentagonal bipyramidal. The cluster may be considered as a phosphite-substituted derivative of the, as yet, unknown cluster $\text{MoOs}_2(\text{CO})_{13}$. The only other clusters containing Mo–Os bonds in the literature are $(\mu\text{-H})_2(\eta^5\text{-C}_3\text{H}_5)_2\text{Mo}_2\text{Os}_3(\text{CO})_{12}$ (**3**), $(\mu\text{-H})_3(\eta^5\text{-C}_3\text{H}_5)\text{MoOs}_3(\text{CO})_{11}$ (**4**), and $(\mu\text{-H})(\eta^5\text{-C}_3\text{H}_5)\text{MoOs}_3(\text{CO})_{14}$ recently reported by Shore and coworkers [5]. The unbridged Os–Mo distances in **3** and **4** are significantly shorter (range 2.830(1)–2.952(1) Å) than the Os–Mo distances in **1** (3.041(2) and 3.079(2) Å). This

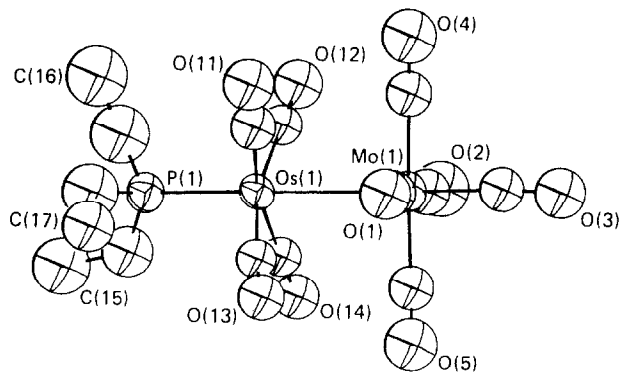


Fig. 2. The molecular structure of $[(\text{MeO})_3\text{P}](\text{OC})_4\text{OsMo}(\text{CO})_5$. Selected bond lengths (Å): Os(1)–Mo(1) 3.075(2), Os(1)–P(1) 2.299(6).

may be a consequence of the more highly condensed nature of clusters **3** and **4**; the Os–Os bond lengths in Os_n ($n > 3$) clusters are generally shorter than those in $\text{Os}_3(\text{CO})_{12}$ [6].

The crystal structure described here has the unusual feature of two chemically different molecules present in the unit cell in a 1/1 ratio; there is no obvious chemical interaction between them. A view of the second molecule, **2**, is given in Fig. 2. It has a configuration similar to that previously found for $(\text{Me}_3\text{P})(\text{OC})_4\text{-OsM}(\text{CO})_5$ ($\text{M} = \text{Cr}$ [3], W [2]) i.e., the 18-electron osmium complex acts as a ligand toward the Group VI metal via an unbridged, donor–acceptor bond. It is of interest that the dative Os–Mo bond in **2** is not significantly different from the covalent Os–Mo bonds in **1**.

We are currently investigating rational syntheses of **1** and related complexes. Prolonged reaction of **2** with excess $\text{Os}(\text{CO})_4[\text{P}(\text{OMe})_3]$ does not yield **1**. However, ultraviolet irradiation of a hexane solution of $\text{Mo}(\text{CO})_4(\text{norbondadiene})$ and $\text{Os}(\text{CO})_4[\text{P}(\text{OMe})_3]$ does produce **1** although still in low yield (~ 5%). From this reaction **1** was isolated after chromatography as deep-red, air-stable crystals that were analytically pure ($\nu(\text{CO})$ 2084w, 2027s, 2016m, 2001vs, 1982w, 1974w, 1964w, 1951m, 1936m, cm^{-1} , hexane solution).

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