

## Synthesis, Reactivity, and Molecular Structure of the Raft Complex $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$

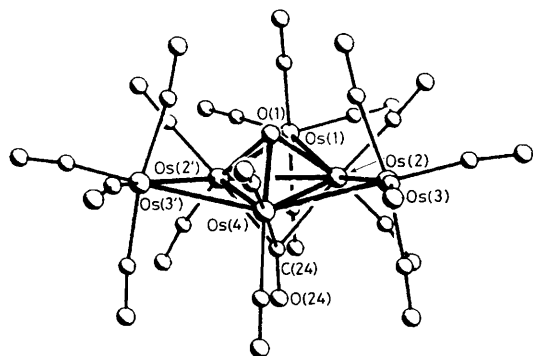
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The cluster  $[\text{Os}_6(\text{CO})_{20}]$  reacts with molecular oxygen to give  $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$ , which has been shown by an X-ray analysis to contain an  $\text{Os}_6$  raft, the central triangle of which is capped on one side by an O atom and on the other by a carbonyl group; this oxygenated cluster reacts with  $\text{P}(\text{OMe})_3$  to yield the clusters  $[\text{Os}_6(\text{CO})_{21-n}\{\text{P}(\text{OMe})_3\}_n]$  ( $n = 1-6$ ) and the cluster  $[\text{Os}_6(\text{CO})_{20}]$  also reacts with acetylene to give  $[\text{Os}_4(\text{CO})_{12}(\text{C}_2\text{H}_2)]$  and  $[\text{Os}_5(\text{CO})_{13}(\text{C}_2\text{H}_2)_2]$  and with hydrogen sulphide to give  $[\text{H}_2\text{Os}_3(\text{CO})_9\text{S}]$ .

We have recently reported the formation of phosphite derivatives of the planar cluster  $[\text{Os}_6(\text{CO})_{21}]$  from the reaction of  $[\text{Os}_6(\text{CO})_{20}]$  with  $\text{P}(\text{OMe})_3$ .<sup>1</sup> There is an appealing analogy between the  $\text{Os}_6$  planar framework in these complexes and a metal surface. Recent theoretical calculations<sup>2</sup> have indicated that there is an empty low-lying molecular orbital in the 'raft' systems which might be expected to interact with donor molecules. In view of this suggestion, and in the hope of gaining information on the modes of co-ordination of reactive species to metal surfaces, we have treated the  $[\text{Os}_6(\text{CO})_{21}]$  derivatives, formed *in situ* in solutions of  $[\text{Os}_6(\text{CO})_{20}]$  under reaction conditions, with a number of small molecules. In this communication we report the reaction between  $[\text{Os}_6(\text{CO})_{20}]$  and dioxygen, acetylene, and hydrogen sulphide.

When  $\text{O}_2$  gas is passed through a toluene solution of  $[\text{Os}_6(\text{CO})_{20}]$ , under reflux, for 3 h, a purple solution is obtained. The solvent is removed under vacuum and the product purified by t.l.c. The i.r. spectrum in the carbonyl region shows absorption bands at 2132(w), 2103(s), 2077(w), 2059(s), 2047(s), 2024(s), 1963(w), and 1765(w)  $\text{cm}^{-1}$  which indicates the presence of bridging as well as terminal ligands in the complex. The mass spectrum exhibits an ion at  $m/z$  1700 and shows sequential loss of 19 carbonyl groups. Purple crystals suitable for a single-crystal X-ray analysis were obtained by recrystallisation from  $\text{CH}_2\text{Cl}_2$ -hexane.

*Crystal data:*  $\text{C}_{19}\text{O}_{20}\text{Os}_6$ ,  $M = 1689.39$ , orthorhombic, space group  $Pnam$ ,  $a = 16.496(4)$ ,  $b = 10.429(2)$ ,  $c = 16.906(2)$  Å,  $U = 2908.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 3.86$   $\text{g cm}^{-3}$ ,  $F(000) = 2918$ , graphite-monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo}-K_\alpha) = 261.94$   $\text{cm}^{-1}$ . A total of 2917 intensities were recorded to a  $2\theta_{\text{max}} = 50.0^\circ$  on a Stoe four-circle diffractometer and were corrected for absorption. 1461 Reflections [ $F > 5\sigma(F)$ ] were used to solve (direct methods and electron-density difference techniques) the structure which was refined by full-matrix least squares (Os,

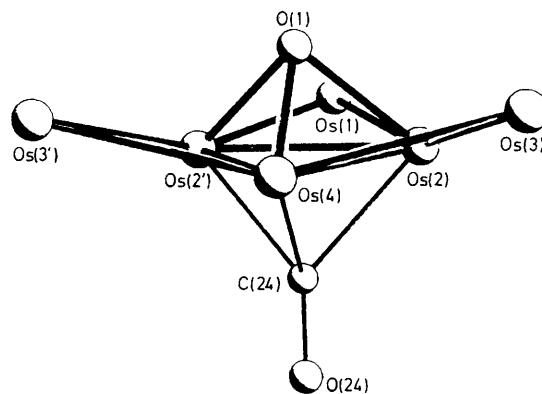


**Figure 1.** The molecular structure of  $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$ . Bond lengths: Os(1)–Os(2), 2.784(2); Os(2)–Os(3), 2.803(2); Os(2)–Os(4), 2.706(2); Os(2)–Os(2'), 2.743(2); Os(3)–Os(4), 2.778(1); Os(2)–O(1), 2.06(2); Os(4)–O(1), 2.07(2); Os(2)–C(24), 2.15(4); and Os(4)–C(24), 2.15(4) Å.

$\mu_3\text{-O}$ ,  $\mu_3\text{-CO}$  anisotropic; C, O isotropic) to  $R = 0.058$  and  $R_w = 0.060$  for the observed data.<sup>†</sup>

The molecular structure of  $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$  is shown in Figure 1 together with some important bond parameters. The molecule contains a crystallographic mirror plane which passes through Os(1), Os(4), and the terminal axial carbonyls associated with these two metal atoms, O(1), C(24), and O(24). The cluster core geometry is illustrated in Figure 2. The hexanuclear metal framework is related to that observed in  $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{OMe})_3\}_4]$ ,<sup>1</sup> but in this case the fused triangles show an increase in puckering: the central Os(2)Os(4)Os(2') triangle makes angles of 8.6 and 16.1° with the Os(1)Os(2)Os(2') and Os(2)Os(3)Os(4) planes, respectively. The three outer triangles all bend towards the oxygen atom which symmetrically caps one side of the central triangle. The other side of this triangle is capped symmetrically by a carbonyl group. The Os(2) and Os(4) atoms each have two terminal carbonyls bonded to them while Os(1) and Os(3) each have two equatorial and two axial carbonyls associated with them. Two of these axial carbonyls, one on Os(1) and one on Os(3), make short contacts with the capping oxygen C(11)  $\cdots$  O(1), 2.86(4); C(31)  $\cdots$  O(1), 2.66(4) Å.

This complex represents the first example of an oxygen atom co-ordinated to an osmium cluster, although a similar mode of co-ordination for an oxygen atom has been observed in the trinuclear ruthenium complex,  $[\text{Ru}_3(\mu_3\text{-O})(\text{CO})_6(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)]$ .<sup>3</sup> Capping  $\mu_3\text{-O}$  atoms have also been observed in a series of trinuclear molybdenum clusters.<sup>4</sup> Capping  $\mu_3\text{-CO}$  ligands are also uncommon in heavy-metal carbonyl clusters, and this would appear to be the first



**Figure 2.** The cluster core in  $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$ .

<sup>†</sup> The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

example that has been characterised crystallographically for an osmium cluster.

In terms of electron counting, assuming that the capping oxygen atom acts as a four-electron donor, the complex  $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$  is a 90 electron system. This is consistent with the effective atomic number rule for a system formally containing nine metal-metal bonds.

The reaction of  $[\text{Os}_6(\mu_3\text{-O})(\mu_3\text{-CO})(\text{CO})_{18}]$  with excess of  $\text{P}(\text{OMe})_3$  in benzene, under reflux, gives a dark blue solution. The solvent was removed under vacuum and the products separated by t.l.c. The products were characterised as  $[\text{Os}_6(\text{CO})_{21-n}\{\text{P}(\text{OMe})_3\}_n]$  ( $n = 1-6$ ) from their i.r. spectra.<sup>1</sup> This indicates that the oxygen cap is readily removed, presumably as a phosphite oxide, although no  $\text{OP}(\text{OMe})_3$  was detected. This reaction is reversible, since  $[\text{Os}_6(\text{O})(\text{CO})_{19}]$  is produced when  $\text{O}_2$  gas is passed through a toluene solution of  $[\text{Os}_6(\text{CO})_{20}\text{P}(\text{OMe})_3]$  under reflux.

When acetylene is passed through a toluene solution of  $[\text{Os}_6(\text{CO})_{20}]$ , under reflux, for 4 h, and the solvent then removed, several acetylenic cluster compounds may be isolated upon separation by t.l.c. The two products which have been fully characterised so far have been found to be the known species  $[\text{Os}_4(\text{CO})_{12}(\text{C}_2\text{H}_2)]^5$  and  $[\text{Os}_5(\text{CO})_{13}(\text{C}_2\text{H}_2)_2]^6$ . No hexaosmium clusters have been isolated, and it appears that the use of acetylene leads to cluster breakdown. Under similar conditions  $[\text{Os}_6(\text{CO})_{20}]$  reacts with  $\text{H}_2\text{S}$  to give

several products, the major one of which has been characterised as the known cluster  $[\text{Os}_3\text{H}_2(\text{CO})_9\text{S}]^7$ .

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