

## Synthesis and X-Ray Crystal Structure of the Cluster [Os<sub>6</sub>(CO)<sub>17</sub>{P(OMe)<sub>3</sub>}<sub>4</sub>], an Example of a Hexa-metal Planar Complex

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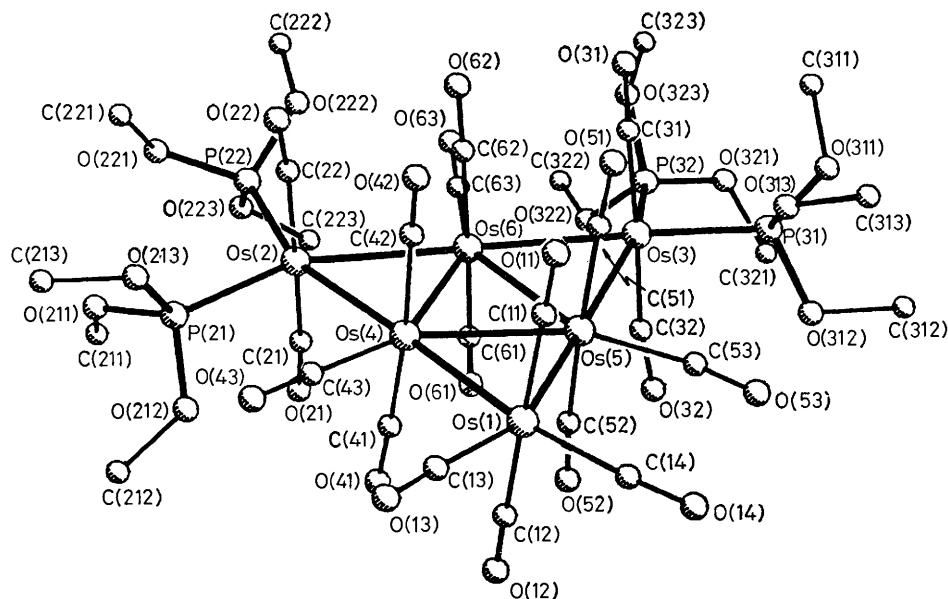
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The cluster [Os<sub>6</sub>(CO)<sub>17</sub>{P(OMe)<sub>3</sub>}<sub>4</sub>] has been obtained by the reaction of [Os<sub>6</sub>(CO)<sub>20</sub>] with P(OMe)<sub>3</sub>; the six Os atoms are approximately coplanar with the central Os<sub>3</sub> triangle having each edge bridged by an Os atom.

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The relevance of metal cluster carbonyls to catalysis is well known. However, there is little information available on the stability of such cluster systems towards CO, H<sub>2</sub>, or donor

ligands. Until recently only one binary carbonyl had been reported for each of the range of polynuclear osmium clusters. A second binary carbonyl, [Os<sub>5</sub>(CO)<sub>16</sub>],<sup>1</sup> having three more



**Figure 1.** The molecular structure of  $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{OMe})_3\}_4]$ . Bond lengths: Os(1)–Os(4), 2.860(2); Os(1)–Os(5), 2.850(2); Os(2)–Os(4), 2.909(2); Os(2)–Os(6), 2.874(1); Os(3)–Os(5), 2.909(2); Os(3)–Os(6), 2.889(1); Os(4)–Os(5), 2.845(1); Os(4)–Os(6), 2.848(2); Os(5)–Os(6), 2.834(2); Os(2)–P(21), 2.268(8); Os(2)–P(22), 2.227(12); Os(3)–P(31), 2.241(8); Os(3)–P(32), 2.241(12) Å. Bond angles: P(21)–Os(2)–P(22), 97.6(3); P(31)–Os(3)–P(32), 96.2(4)°.

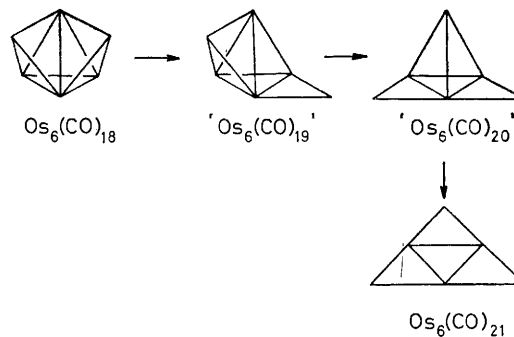
carbonyl ligands than the previously reported parent binary carbonyl,  $[\text{Os}_5(\text{CO})_{16}]$ ,<sup>2</sup> has now been fully characterised. In the same series of reactions on the carbonylation of  $[\text{Os}_6(\text{CO})_{18}]$  a second hexanuclear binary carbonyl,  $[\text{Os}_6(\text{CO})_{20}]$ , was observed.<sup>1</sup> We now report on the reaction of  $[\text{Os}_6(\text{CO})_{20}]$  with  $\text{P}(\text{OMe})_3$  and present structural data which indicate that the systematic cleavage of the *closo*- $\text{Os}_6$  polyhedron is occurring to produce the first example of a planar  $\text{Os}_6$  metal skeleton.

The reaction of  $[\text{Os}_6(\text{CO})_{20}]$  with  $\text{P}(\text{OMe})_3$  in benzene gives a mixture of compounds all of which are based on the  $\text{Os}_6$  central unit. After separation by t.l.c. using  $\text{CH}_2\text{Cl}_2$  as eluant a total of six compounds were obtained. These have the general formula  $[\text{Os}_6(\text{CO})_{21-n}\{\text{P}(\text{OMe})_3\}_n]$  ( $n = 1-6$ ). The title compound  $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{OMe})_3\}_4]$  exhibits i.r. carbonyl absorptions at 2108(w), 2068(m), 2044(w), 2028(s), 2011(w), 2003(w), 1988(w), 1978(w), and 1942(w)  $\text{cm}^{-1}$ . The complex did not give a strong parent peak in the mass spectrum. Dark blue platelets suitable for single-crystal X-ray analysis were obtained by recrystallisation from  $\text{CH}_2\text{Cl}_2$ -hexane.

**Crystal data:**  $\text{C}_{20}\text{H}_{36}\text{O}_{29}\text{Os}_6\text{P}_4$ ,  $M = 2113.61$ , monoclinic, space group  $P2_1/c$ ,  $a = 23.406(11)$ ,  $b = 12.067(4)$ ,  $c = 21.067(10)$  Å,  $\beta = 121.99(2)^\circ$ ,  $U = 5210.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.69$  g  $\text{cm}^{-3}$ ,  $F(000) = 3831$ , graphite-monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo}-K_\alpha) = 147.58$   $\text{cm}^{-1}$ .†

The diffracted intensities were measured to  $2\theta_{\text{max}} = 45.0^\circ$ , on a Syntex  $P2_1$ , four-circle diffractometer and were corrected for absorption. 4352 Reflections [ $F > 5\sigma(F)$ ] were used to solve (direct methods and Fourier difference techniques) the structure which was refined by blocked full-matrix least squares (Os, P, and carbonyl O anisotropic, carbonyl C, phosphite C, and O isotropic) to  $R = 0.057$  and  $R_w = 0.057$ . Some of the phosphite C atoms were positionally disordered, and a disordered solvent molecule remained unresolved.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Scheme 1**

The molecular structure of  $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{OMe})_3\}_4]$  is shown in Figure 1 together with some important bond parameters; only one orientation of the disordered phosphites is shown for clarity. The six Os atoms are approximately coplanar with a maximum deviation of 0.1 Å for the least squares plane. The metal skeleton may be described as a triangle defined by the Os(1), Os(2), and Os(3) atoms with the Os(4), Os(5), and Os(6) atoms at the midpoints of these edges. This results in four triangles sharing common edges. The planar arrangement of six Os atoms has been observed in the basal plane of the pyramidal metal skeleton of  $[\text{Os}_{10}\text{H}(\text{CO})_{24}\text{C}]^-$ .<sup>3</sup> There is a close analogy between the arrangement of metal atoms in these clusters to that of a hexagonal close-packed metal surface. The Os–Os bond lengths around the central Os(4)–Os(5)–Os(6) triangle and those in the Os(1)–Os(4)–Os(5) triangle, where the metal atoms have only carbonyl ligands associated with them, are shorter than the value of 2.877(3) Å in  $[\text{Os}_3(\text{CO})_{12}]$ ,<sup>4</sup> but are larger than all the Os–Os bonds in  $[\text{Os}_6(\text{CO})_{18}]$ .<sup>5</sup> The atoms Os(2) and Os(3) each have two equatorial phosphites and two axial carbonyls bonded to them. The Os–Os bonds *trans* to the phosphite groups are *ca.* 0.05 Å longer than the other metal–metal bonds in the structure. This may reflect the weaker  $\pi$ -acceptor properties of the phosphite ligand over the car-

bonyl, for which the *trans* Os–Os bonds are shorter. Alternatively, the non-bonded contacts between phosphite O atoms and carbonyl ligands on adjacent metal atoms are *ca.* 3.0 Å, a shorter Os–Os bond would result in steric congestion between the ligands. The carbonyl ligands bonded to the metal atoms are all linear.

The structure of  $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{OMe})_3\}_4]$  is the first example of a substituted complex of a new binary carbonyl  $[\text{Os}_6(\text{CO})_{21}]$  which would presumably exhibit the same metal framework. It is possible to obtain the metal geometry observed in the title complex from that of  $[\text{Os}_6(\text{CO})_{18}]^5$  by sequentially breaking three metal–metal donor bonds concomitant with the addition of three carbonyl groups. Scheme 1 illustrates this sequence and shows possible structures for the ' $\text{Os}_6(\text{CO})_{19}$ ' and ' $\text{Os}_6(\text{CO})_{20}$ ' complexes. It is therefore probable that a range of  $\text{Os}_6$  binary carbonyls may exist varying in the number of carbonyls co-ordinated to the cluster.

Clusters with the general formula  $[\text{Os}_6(\text{CO})_{21-n}\text{L}_n]$  ( $n = 3-6$ ) may also be obtained from the reaction of  $[\text{Os}_6(\text{CO})_{18}]$  with  $\text{P}(\text{OMe})_3$ . A product analogous to  $[\text{Os}_6(\text{CO})_{15}\{\text{P}(\text{OMe})_3\}_6]$  has been obtained from the reaction of

$[\text{Os}_6(\text{CO})_{18}]$  with 1,2-bis(diphenylphosphino)ethane (dppe). This is formulated as  $[\text{Os}_6(\text{CO})_{15}(\text{dppe})_3]$  in which each dppe ligand chelates to one vertex of the  $\text{Os}_6$  triangle.

The reactions of  $[\text{Os}_6(\text{CO})_{18}]$  and  $[\text{Os}_6(\text{CO})_{20}]$  with CO have as yet failed to yield the parent carbonyl  $\text{Os}_6(\text{CO})_{21}$ .

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## References

- 1 D. H. Farrar, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1981, 273.
- 2 B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B.*, 1977, **33**, 173.
- 3 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 49.
- 4 M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.
- 5 R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1973, **95**, 3802.