Synthesis and Molecular Structure of $[Os_5(CO)_{15}POMe]$

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Summary $[Os_5(CO)_{15}POMe]$ has been isolated as a product of the pyrolysis of $[Os_3(CO)_{11}P(OMe)_3]$; a single-crystal *X*-ray analysis has shown that the metal atoms adopt a square-pyramidal geometry with the phosphite ligand capping the square face.

THE pyrolysis of $[Os_3(CO)_{12}]$ leads to the formation of polynuclear osmium carbonyl species based on five to eight metal atoms.[1] Because of the interest in these compounds as models for metal surfaces, and because of the possibility of studying catalytic reactions thereon, we have extended our investigations to include the pyrolysis reactions of substituted triosmium carbonyl clusters. We now report some preliminary results of our studies on $[Os_3(CO)_{11}P(OMe)_3]$.

The pyrolysis of $[Os_3(CO)_{11}P(OMe)_3]$ at 210 °C for 16 h yielded a red-brown solid, which upon purification (t.l.c.) gave a number of cluster compounds. The mass spectrum of one of these (*m/e* 1433; measured on an AEI MS12 instrument), a red crystalline solid, showed it to be an Os_5 cluster. I.r. and ^1H n.m.r. data [ν_{CO} (cyclohexane) 2 085w, 2 064vs, 2 045w, 2 032vs, 2 021w, and 1 998w,br cm^{-1}; $\tau(CDCl_3)$ 6·57 (d, *J* 17·6 Hz)] indicated the presence of terminal carbonyls and a phosphite species. No hydride resonances were observed. The nature of the phosphite ligand and the overall molecular geometry was established by a single-crystal *X*-ray analysis. Crystals were obtained by crystallization from ethyl acetate–hexane.

Crystal data: $C_{16}H_3O_{16}Os_5P$, M = 1 433·15, monoclinic, a = 15·990(5), b = 9·762(3), c = 16·965(5) Å, β = 107·53(2)°, U = 2 525 Å^3, Z = 4, D_c = 3·769 g cm^{-3}; $\mu(\text{Mo-}K_\alpha)$ = 252·0 cm^{-1}, space group *Cc*. 3 647 intensities ($2\theta_{max}$ = 60·0°) were recorded on a Syntex $P2_1$ four-circle diffractometer, with graphite-monochromated Mo-K_α radiation. The data were corrected for absorption and Lorentz polarisation factors, and averaged to give 3 310 unique observed intensities [$I > 2{\cdot}5\sigma(I)$]. The Os atoms were located by multisolution tangent refinement, and the remaining atoms by difference syntheses. The structure was refined by full-matrix least-squares (Os and P anisotropic, C and O isotropic, and all C–O distances constrained to be equal) to a current R of 0·060, and R_w [$=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|$] = 0·060.

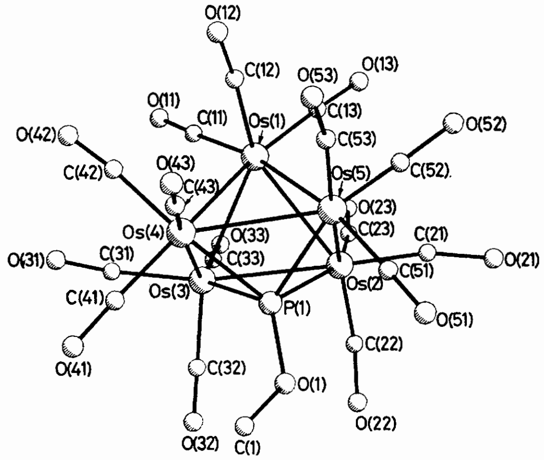

FIGURE. The molecular structure of $[Os_5(CO)_{15}POMe]$. Bond lengths: Os(1)–Os(2), 2·886(3); Os(1)–Os(3), 2·866(3); Os(1)–Os(4), 2·848(3); Os(1)–Os(5), 2·803(3); Os(2)–Os(3), 2·878(3); Os(2)–Os(5), 2·896(3); Os(3)–Os(4), 2·887(3); Os(4)–Os(5), 2·932(3); Os(2)–P(1), 2·338(9); Os(3)–P(1), 2·393(8); Os(4)–P(1), 2·357(8); Os(5)–P(1), 2·381(8) Å; bond angles: Os(2)–P(1)–Os(3), 74·9(3); Os(2)–P(1)–Os(4), 121·0(4); Os(3)–P(1)–Os(4), 74·9(2); Os(2)–P(1)–Os(5), 75·7(3); Os(3)–P(1)–Os(5), 118·9(4); Os(4)–P(1)–Os(5), 76·5(2)°.

The molecular geometry is shown in the Figure, which includes some important bond parameters. The four basal Os atoms are coplanar (maximum deviation 0·029 Å), and the apical metal lies 1·981 Å above this plane. The P atom of the phosphite ligand bonds to the four basal Os atoms, lying 1·185 Å below the square face, and the P–O vector makes an angle of 84·1° to this plane. Each metal atom is also bonded to three terminal carbonyl groups, so that all five Os atoms are seven co-ordinate.†

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† 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.

The square-based pyramidal geometry has not been previously reported for an Os_5 cluster, $[Os_5(CO)_{16}]$[2] and several derivatives[3] have distorted trigonal pyramidal geometries. The two clusters, $[Os_6(CO)_{16}(CMe)_2]$ and $[Os_6(CO)_{16}(MeCCMe)C]$,[4] do, however, contain a square pyramidal unit. A μ_4-capping phosphorus donor ligand has been found in the first row transition metal clusters $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2]$[5] and $[Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6]$.[6] The phosphorus–metal distances show slight variations as in this cluster.

The μ_4-phosphite ligand presumably acts as a four-electron donor. Then, in terms of electron counting, each metal atom obeys the '18 electron rule,' and results in a 74 e system. The cluster is thus isoelectronic with $[Fe_5(CO)_{15}C]$, where the metal cluster geometry is similar.[7]

We thank the S.R.C. for support (to P. R. R.), and Johnson Matthey and Co. Ltd. for the loan of OsO_4. J. M. F. is on leave from Instituto de Quimica, Ciudad Universitaria, Mexico.

(*Received*, 31*st July* 1978; *Com.* 821.)

[1] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1975, 2606.

[2] B. E. Reichert and G. M. Sheldrick, *Acta Cryst.*, 1977, **B33**, 173.

[3] A. G. Orpen and G. M. Sheldrick, *Acta Cryst.*, 1978, **B34**, 1992; J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *ibid.*, p. 1994.

[4] C. R. Eady, J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *J.C.S. Chem. Comm.*, 1978, 421.

[5] G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, 1973, **95**, 2175.

[6] L. D. Lower and L. F. Dahl, *J. Amer. Chem. Soc.*, 1976, **98**, 5046.

[7] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.