

Synthesis and Molecular Structure of $[\text{Os}_6(\text{CO})_{16}(\text{CMe})_2]$ and $[\text{Os}_6(\text{CO})_{16}(\text{MeC}:\text{CMe})\text{C}]$, Derivatives of Ethylene and $[\text{Os}_6(\text{CO})_{18}]$

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Summary The reaction of ethylene with $[\text{Os}_6(\text{CO})_{18}]$ yields $[\text{Os}_6(\text{CO})_{16}(\text{CMe})_2]$ (**1**) and $[\text{Os}_6(\text{CO})_{16}(\text{MeC}:\text{CMe})\text{C}]$ (**2**), the structures of which have been determined by single-crystal *X*-ray analysis.

TRANSITION metal carbonyl clusters have been considered as models for surface reactivity.¹ As part of our studies of clusters containing three or more metal atoms we have investigated the reaction of $[\text{Os}_6(\text{CO})_{18}]$ with ethylene. Ethylene was passed through a solution of $[\text{Os}_6(\text{CO})_{18}]$ in *n*-decane at 165 °C for 12 h. After purification (t.l.c.) a green product (*ca.* 10%) was obtained. When the reaction was continued for a further 60 h at 175 °C, the colour of the solution darkened, and a red crystalline solid (*ca.* 5%) was isolated. The green and red products were found to be organometallic clusters based on the Os_6 unit, and were characterised as $[\text{Os}_6(\text{CO})_{16}\text{C}_4\text{H}_6]$ (**1**) and $[\text{Os}_6(\text{CO})_{16}\text{C}_5\text{H}_6]$ (**2**), respectively, on the basis of i.r., ¹H n.m.r., and mass spectroscopic data (Table). The nature of the organic

TABLE. Spectroscopic properties of (**1**) and (**2**).

Complex	<i>m/e</i> ^a	¹ H N.m.r. (<i>τ</i>) ^b	<i>ν</i> _{CO} ^c /cm ⁻¹
(1)	1644	6.28 (s), 6.60 (s)	2068vs, 2056s, 2030s, 2023s, 2003br, 2000w, 1963w
(2)	1656	6.91 (s)	2077s, 2067w, 2058m, 2036s, 2020vs, 2005w br, 2001w, 1957w

^a Measured on AEI MS12. ^b CDCl₃ solvent. ^c Cyclohexane solvent.

units, and the overall molecular geometries of (**1**) and (**2**) were established by single-crystal *X*-ray analysis. Both compounds were recrystallised from ethyl acetate-cyclohexane.

Crystal data: (**1**) C₂₀H₆O₁₆Os₆, *M* 1643.5, orthorhombic, *a* = 16.647(6), *b* = 16.353(8), *c* = 20.134(8) Å, *U* = 5481.0 Å³, *Z* = 8, *D*_c = 3.98 g cm⁻³; *μ* (Mo-*K*_α) = 267.0 cm⁻¹, space group *Pbca*. 5686 intensities were recorded (*2θ*_{max} =

55.0°) and averaged to give 1941 unique, observed reflections [$I > 2\sigma(I)$]. Currently $R = 0.105$, $R_w [= \sum w^{\frac{1}{2}} \Delta / \sum w^{\frac{1}{2}} |F_o|] = 0.091$. (2), $C_{21}H_6O_{16}Os_6$, M 1655.5, monoclinic, $a = 11.855(5)$, $b = 13.234(5)$, $c = 19.297(9)$ Å, $\beta = 108.27(3)^\circ$, $U = 2874.9$ Å³, $Z = 4$. $D_c = 3.82$ g cm⁻³; $\mu(Mo-K\alpha) = 264.9$ cm⁻¹, space group $P2_1/c$. 7646 intensities were recorded ($2\theta_{max} = 60.0^\circ$) and averaged to give 4007 unique, observed reflections [$I > 2.5\sigma(I)$]. Currently $R = 0.039$, $R_w = [\sum w^{\frac{1}{2}} \Delta / \sum w^{\frac{1}{2}} |F_o|] = 0.044$.

Data were measured on a Syntex $P2_1$ four-circle diffractometer, using graphite-monochromated Mo- $K\alpha$ radiation, and a θ - 2θ scan technique. Both data sets were corrected for absorption and for Lp factors, and the Os atoms were located by multiresolution Σ_2 sign expansion. The light atom positions were located from subsequent electron-density difference syntheses. Structure (1) was refined by full-matrix least-squares [Os anisotropic, all C(carbonyl) isotropic, temperature factors constrained to be equal, and O(carbonyl) temperature factors 1.333 times this value, and all ethylidinic C atom temperature factors equal], while structure (2) was refined by blocked cascade least-squares (Os anisotropic, C and O isotropic). Weighting schemes of the form $w = 1/[\sigma^2(F) + gF^2]$ [(1), $g = 0.0014$; (2), $g = 0.004$] were employed.†

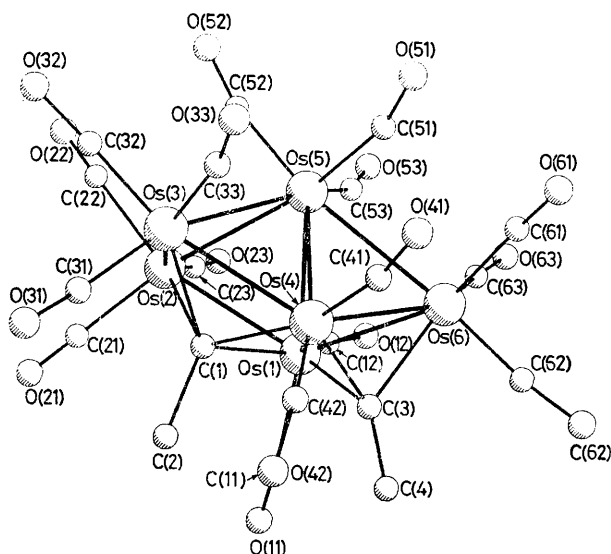


FIGURE 1. The molecular geometry of $[Os_6(CO)_{16}(CMe)_2]$, including the atom numbering scheme. Bond lengths: Os(1)-Os(2), 2.739(6); Os(1)-Os(4), 2.672(6); Os(1)-Os(5), 2.825(5); Os(1)-Os(6), 2.730(6); Os(2)-Os(3), 2.807(6); Os(2)-Os(5), 2.904(6); Os(3)-Os(4), 2.726(6); Os(3)-Os(5), 2.907(6); Os(4)-Os(5), 2.809(6); Os(4)-Os(6), 2.722(6); Os(5)-Os(6), 2.960(6); Os(1)-C(1), 2.13(7); Os(2)-C(1), 2.19(7); Os(3)-C(1), 2.24(7); Os(4)-C(1), 2.17(7); Os(1)-C(3), 2.10(7); Os(4)-C(3), 1.95(7); and Os(6)-C(3), 2.14(7) Å.

The molecular geometries of (1) and (2) are shown in Figures 1 and 2, respectively, which include important bond lengths.

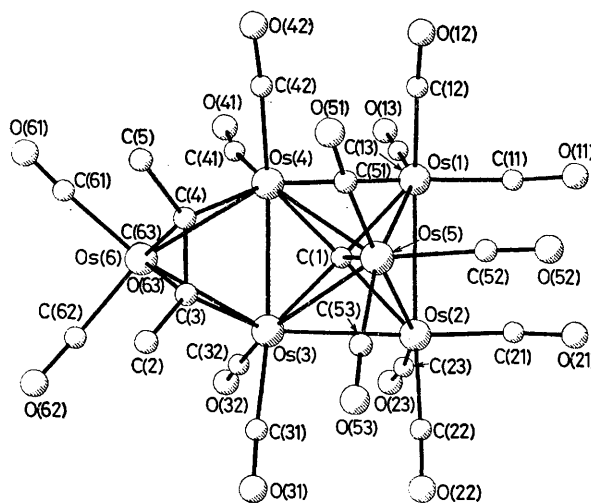


FIGURE 2. The molecular geometry of $[Os_6(CO)_{16}(MeC:CMe)C]$, including the atom numbering scheme. Bond lengths: Os(1)-Os(2), 2.964(4); Os(1)-Os(4), 2.881(4); Os(1)-Os(5), 2.823(4); Os(2)-Os(3), 2.893(4); Os(2)-Os(5), 2.828(4); Os(3)-Os(4), 2.745(4); Os(3)-Os(5), 2.847(4); Os(3)-Os(6), 2.769(4); Os(4)-Os(5), 2.881(4); Os(4)-Os(6), 2.806(4); Os(1)-C(1), 2.05(2); Os(2)-C(1), 2.05(2); Os(3)-C(1), 2.02(2); Os(4)-C(1), 2.04(2); Os(5)-C(1), 2.20(2); Os(3)-C(3), 2.13(2); Os(4)-C(4), 2.13(2); Os(6)-C(3), 2.20(2); Os(6)-C(4), 2.18(2); C(2)-C(3), 1.55(3); C(3)-C(4), 1.36(2); and C(4)-C(5), 1.60(4) Å.

In (1), the Os atoms define a monocapped square-based pyramid, similar to that reported for $[H_2Os_6(CO)_{18}]$.² The structure may be considered as derived from the dihydride, by the replacement of the hydrogen atoms and two carbonyl ligands (one from each Os atom in the basal plane, which is bonded to the face capping metal) by two C_2H_3 groups. One of these organic species caps the Os_4 square plane while the other caps the adjacent Os_3 triangular face involving the capping Os(6) atom. From the 'end-on' orientation of these two fragments, and in view of the spectroscopic evidence (Table), they may be formulated as ethylidene ($>CMe$) ligands. The geometry of the ligand capping the triangular face is similar to that found for the CMe group in $[H_3Ru_3(CO)_6(CMe)]$,³ and both ligands in this Os_6 cluster should be considered as 3-electron donors, although C(1) co-ordinates to four metal atoms.

In (2), the Os atoms define an edge-bridged square-based pyramid, a previously unreported geometry. The Os(6) atom bridges the Os(3)-Os(4) edge and lies on the opposite side of the square-basal plane to the apical atom, Os(5). The angle between the Os(3), Os(4), Os(6) triangle and the Os(1), Os(2), Os(3), Os(4) plane is 25.3° . A single carbon atom lies *ca.* 0.20 Å below the centre of the basal plane, co-ordinating symmetrically to the four basal Os atoms, and also interacting with the apical metal. As in $[Fe_5(CO)_{15}C]$,⁴ where the configuration around the C atoms is the same, the carbide should be considered as a 4-electron donor. The C_4H_6 unit may be formulated as a but-2-yne (MeC:CMe) ligand. The C(2), C(3), C(4), and C(5) atoms are coplanar (maximum deviation 0.01 Å), and the group

† 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.

sits above the $\overline{\text{Os}(3)\text{--Os}(4)\text{--Os}(6)}$ triangle, making an angle of 70.2° with it. It is π -bonded to Os(6), and σ -bonded to Os(3) and Os(4). The central C(3)–C(4) distance is in good agreement with the olefinic C–C bond length [$1.33(3)$ Å] of the bridging diphenylacetylene group in $[\text{Os}_3(\text{CO})_7(\text{C}_6\text{H}_5)_2(\text{C}_2\text{Ph}_2)]$,⁵ while the C(2)–C(3) and C(4)–C(5) bonds are essentially single. The assignments of the organic species as a carbide and a but-2-yne ligand are in agreement with the spectroscopic data.

In terms of 'electron counting,' (1) is an 86-electron system, although not every metal obeys the '18-electron rule,' while (2) is an 88-electron system. The inclusion of

an additional electron-pair has broken an Os–Os bond, and the metal cluster geometries observed are in agreement with the 'expected' structures formulated using the extension of Wade's skeletal electron-counting scheme proposed by Eady, Johnson, and Lewis.⁶

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¹ R. Ugo, *Catalysis Rev.*, 1975, **11**, 225; E. L. Muetterties, *Bull. Soc. chim. belg.*, 1975, **84**, 959.

² M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1976, 883.

³ G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 873.

⁴ E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.

⁵ G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1973, 1933.

⁶ C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1975, 2606.