Reaction of $[Os_5(CO)_{15}H_2]$ with Acetylenes; *X*-Ray Crystal Structures of $[Os_5(CO)_{15}H_2(CCPh)]$ and $[Os_5(CO)_{13}(PhCCPh)_2]$

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Summary The dihydrido-cluster $[Os_5(CO)_{15}H_2]$ reacts with $R^1C{\equiv}CR^2$ [$R^1 = H$, $R^2 = Ph$; $R^1 = R^2 = Ph$] to produce a number of acetylenic cluster complexes based on the Os_5 unit, two of which have been characterised spectroscopically and by single crystal *X*-ray analyses as $[Os_5(CO)_{15}H_2(CCPh)]$ and $[Os_5(CO)_{13}(PhCCPh)_2]$, containing a 'wing-tip bridged butterfly' and an 'edge-bridged butterfly' metal framework, respectively.

Few reactions between acetylenes and clusters containing five or more metal atoms have been reported.[1,2] Here we report the products of the reaction of the acetylenes $R^1C{\equiv}CR^2$ [$R^1 = H$, $R^2 = Ph$ (**1**); $R^1 = R^2 = Ph$ (**2**)] with $[Os_5(CO)_{15}H_2]$ which is isoelectronic with the parent binary carbonyl $[Os_5(CO)_{16}]$. Phenylacetylene was treated with $[Os_5(CO)_{15}H_2]$ in octane for 5 h under N_2. The solution became light brown and after separation by t.l.c. using 10% ethyl acetate–hexane as eluant, the two main products were isolated and characterised by spectroscopic techniques. Similar products were obtained if the reaction was carried out photochemically for 35 h. The i.r. spectrum of the first product was identical with that reported for a product of the reaction of $[Os_6(CO)_{18}H_2]$ with phenylacetylene and subsequently characterised as $[Os_5(CO)_{13}(HC_2Ph)_2]$.[3] The other major product of the reaction showed a molecular ion peak in the mass spectrum at *m/z* 1475, and also showed a stepwise loss of 15 CO, leaving a peak at *m/z* 1052 that can be assigned to a fragment $Os_5H_2(C_2Ph)$, giving a formulation for the complex of $[Os_5(CO)_{15}H_2(CCPh)]$ (**1**). Details of the i.r. and ^1H n.m.r. spectra are given in the Table. Yellow crystals were obtained from CH_2Cl_2 solution.

Table. Spectroscopic data for $[Os_5(CO)_{15}H_2(CCPh)]$ (**1**) and $[Os_5(CO)_{13}(PhCCPh)_2]$ (**2**).

Complex	I.r. (ν_{CO}/cm^{-1} in CH_2Cl_2)	^1H N.m.r. (δ)
(**1**)	2108 m, 2074 s, 2053 s 2043 sh, 2009 s, 1979 m	6·9—7·2 m −16·6 d, −16·4 d
(**2**)	2096 s, 2071 vs, 2044 s 2026 s, 2013 s	6·7—7·3 m

<u>*Crystal data*</u>: $C_{23}H_7O_{15}Os_5$, $M = 1\,474{\cdot}06$, triclinic, space group $P\bar{1}$, $a = 9{\cdot}948(4)$, $b = 17{\cdot}999(8)$, $c = 19{\cdot}278(9)$ Å, $\alpha = 109{\cdot}10(2)$, $\beta = 110{\cdot}28(2)$, $\gamma = 99{\cdot}08(2)°$, $U = 2912{\cdot}8$ Å^3, $Z = 4$, $D_c = 3{\cdot}36$ g cm^{-3}, graphite monochromated Mo-K_α

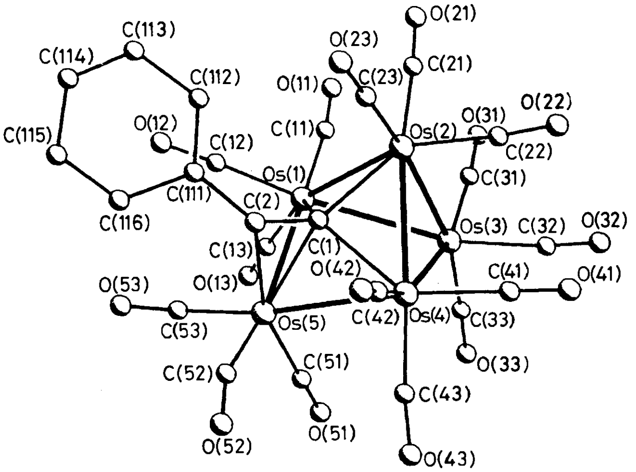

Figure 1. The molecular structure of $[Os_5(CO)_{15}H_2(CCPh)]$ (**1**). Bond lengths: (averaged for two independent molecules) Os(1)–Os(2), 2·894(1); Os(1)–Os(3), 3·049(2); Os(1)–Os(5), 2·865(2); Os(2)–Os(3), 2·834(1); Os(2)–Os(4), 2·842(2); Os(3)–Os(4), 3·017(3); Os(4)–Os(5), 2·887(2); Os(1)–C(1), 2·22(3); Os(2)–C(1), 2·11(3); Os(4)–C(1), 2·21(3); Os(5)–C(1), 2·12(3); Os(5)–C(2), 2·20(3) Å.

radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 217{\cdot}96\ \text{cm}^{-1}$. The diffracted intensities were measured to $2\theta_{\max} = 55°$ on a Stoe four-circle diffractometer and were corrected for absorption. 4376 Reflections $[F > 3\sigma(F)]$ were used to solve (direct methods and Fourier difference techniques) the structure which was refined by blocked-cascade least squares (Os anisotropic, C, O isotropic, phenyl H common isotropic) to R 0·040.†

The molecular structure of (**1**) is shown in Figure 1 together with some important bond parameters while a line diagram of the cluster core is illustrated in Figure 2a. The metal atoms Os(1), Os(2), Os(3), and Os(4) define a 'butterfly' configuration with the two 'wingtip' atoms, Os(1) and Os(4), bridged by the fifth metal atom, Os(5).

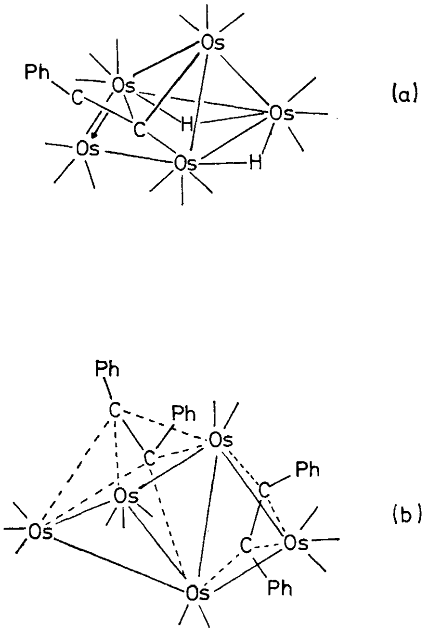

FIGURE 2. Line diagrams of the cluster core of (a), (**1**); (b), (**2**).

A similar geometry has been observed in $[\text{Os}_5\text{C(CO)}_{15}\text{I}]^-$.[4] One carbon atom, C(1), of the acetylene lies over an 'open' face of the metal framework and is co-ordinated to Os(1), Os(2), Os(4), and Os(5). The other acetylenic carbon, C(2), is co-ordinated to Os(5) only. This mode of co-ordination of the acetylenic group may be described as follows: C(1) is involved in a delocalised bond with Os(1), Os(2), and Os(4), while Os(5) is π-bound to the C(1)—C(2) bond. The C(1)–C(2) distance of 1·49(3) Å indicates a reduction in the bond order of this acetylenic bond upon co-ordination to the metal. Closely related modes of bonding of unsaturated organic species have been observed in the structures of $[\text{Ni}(\eta\text{-C}_5\text{H}_5)\text{Ru}_3(\text{CO})_9\text{CC(H)Bu}^\text{t}]$[5] and $[\text{Ru}_4(\text{CO})_{10}\{\text{CC(H)-Pr}^\text{i}\}(\text{OH})(\text{PPh}_2)]$.[6] The two hydride ligands were not located directly but the distribution of the carbonyl ligands suggests that they bridge the two long Os(1)–Os(3) and Os(3)–Os(4) edges; the carbonyls bend away from these bonds because of the steric influence of the hydrides.

In terms of electron counting, the acetylenic ligand is considered to donate four electrons to the cluster which is then a 76 e system having two additional electron pairs to that found in the closed 72 e parent carbonyl $[\text{Os}_5(\text{CO})_{16}]$.

The reaction of $[\text{Os}_5(\text{CO})_{15}\text{H}_2]$ with diphenylacetylene was carried out under the same conditions as for phenylacetylene. There was one major product which exhibited a molecular ion peak at m/z 1672 which could be assigned to a compound with the formula $[\text{Os}_5(\text{CO})_{13}(\text{PhCCPh})_2]$ (**2**). Spectroscopic data for this complex are listed in the Table. Dark red hexagonal plates of (**2**) were crystallised from ethyl acetate–hexane.

Crystal data: $\text{C}_{41}\text{H}_{20}\text{O}_{13}\text{Os}_5$, $M = 1671{\cdot}16$, monoclinic, space group $P2_1/c$, $a = 17{\cdot}893(7)$, $b = 11{\cdot}663(3)$, $c = 19{\cdot}903(9)$ Å, $\beta = 108{\cdot}55(2)°$, $U = 3937{\cdot}7$ Å^3, $Z = 4$, $D_c = 2{\cdot}82\ \text{g cm}^{-3}$, graphite monochromated Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 161{\cdot}29\ \text{cm}^{-1}$. Intensities were recorded on a Stoe four-circle diffractometer to $2\theta_{\max} = 50°$ and were corrected for absorption. 2630 Reflections $[F > 3\sigma(F)]$ were used to solve (direct methods and Fourier difference techniques) the structure which was refined by blocked-cascade least squares (Os anisotropic, C, O isotropic, phenyl H common isotropic) to R 0·038.†

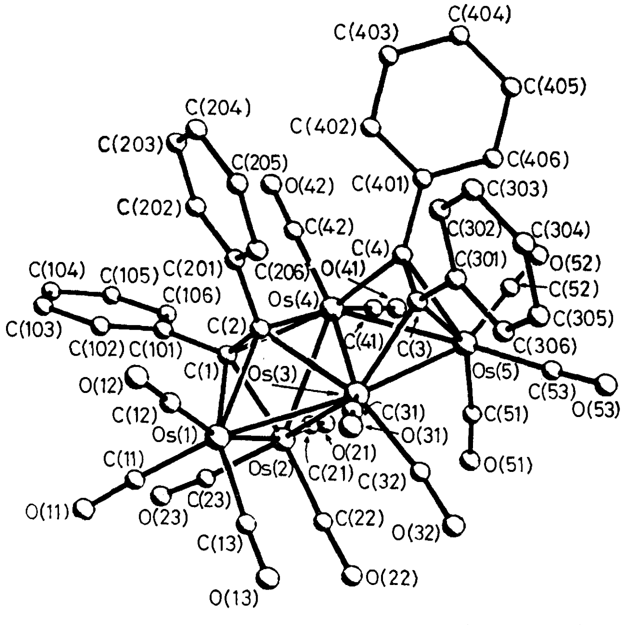

FIGURE 3. The molecular structure of $[\text{Os}_5(\text{CO})_{13}(\text{PhCCPh})_2]$ (**2**). Bond lengths: Os(1)–Os(2), 2·768(2); Os(1)–Os(3), 2·726(2); Os(2)–Os(3), 2·910(2); Os(2)–Os(4), 2·779(2); Os(3)–Os(4), 2·664(2); Os(3)–Os(5), 2·768(2); Os(4)–Os(5), 2·747(2); Os(1)–C(1), 2·27(2); Os(1)–C(2), 2·22(2); Os(2)–C(1), 2·17(2); Os(3)–C(2), 2··22(2); Os(3)–C(3), 2·09(2); Os(4)–C(1), 2·30(2); Os(4)–C(2), 2·23(2); Os(4)–C(4), 2·15(2); Os(5)–C(3), 2·21(2); Os(5)–C(4), 224(2); C(1)–C(2), 1·46(3); C(3)–C(4), 1·39(4) Å.

A line diagram of the cluster core of (**2**) is given in Figure 2b while the full molecular structure is shown in Figure 3 together with some important bond parameters. The atoms Os(1), Os(2), Os(3), and Os(4) define a 'butterfly' metal fragment where Os(1) and Os(4) are the 'wingtip'

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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.

atoms and the 'body' is the Os(2)–Os(3) bond. The short Os(3)–Os(4) edge is bridged by the fifth metal atom, Os(5), to give the 'edge-bridged butterfly' Os framework. This arrangement of metal atoms has not been observed previously in transition metal cluster carbonyl complexes. The dihedral angle between the Os(1)Os(2)Os(3) and Os(2)-Os(3)Os(4) planes is 115°, and that between the planes defined by Os(2)Os(3)Os(4) and Os(3)Os(4)Os(5) is 114°.

The acetylenic bond, C(1)–C(2), of one of the acetylenes lies above and parallel with the Os(2)–Os(3) 'body' bond of the 'butterfly' so that the organic fragment is π-bound to the 'wing-tip' metal atoms, Os(1) and Os(4), and σ-bound to the 'body' atoms, Os(2) and Os(3). A similar mode of bonding has been observed in a number of tetranuclear 'butterfly' clusters.[7] The nature of the interaction between this ligand and the metal framework may involve a four-electron delocalised bond. The other diphenylacetylene ligand is π-bound to Os(5) and σ-bound to Os(3) and Os(4) *via* C(3) and C(4). This type of ligand coordination has been observed in a number of trinuclear clusters,[8] where the C–C unsaturated bond is considered to have formal double bond character. The difference in the C–C distances of the unsaturated bonds in the two coordinated organic ligands in this cluster indicates that the electronic contribution of the former acetylene is greater than that of the latter.

The observed metal geometries in (**1**) and (**2**) may each be considered as derived from the edge-bridged tetrahedral arrangement of Os atoms in [$Os_5(CO)_{16}H_2$][9] by breaking a different metal–metal bond. The metal geometry in [$Os_5(CO)_{16}H_2$] is itself derived from the trigonal bipyramidal arrangement in the parent carbonyl [$Os_5(CO)_{16}$][10] by breaking an Os–Os bond (Figure 4). Thus the two structures reported here are derived from a trigonal bipyramid by the stepwise fission of metal–metal bonds, and of the three possible arrangements of five metal atoms linked by seven metal–metal bonds the only one so far not observed in Os_5 cluster chemistry is that of three triangles sharing a common edge.

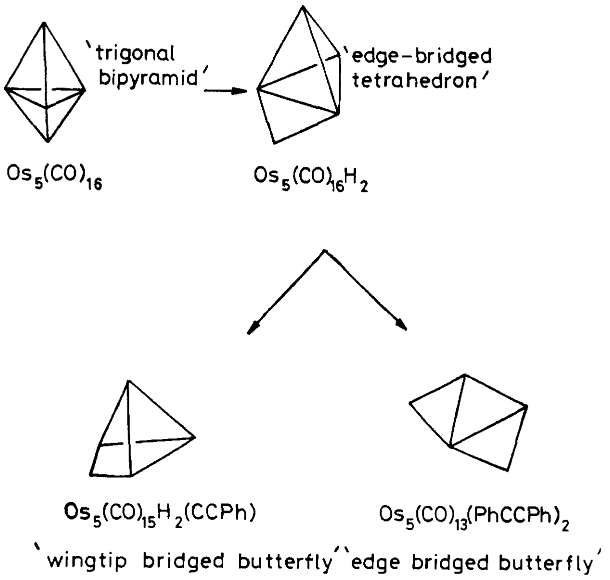

FIGURE 4. Geometrical transformations during the conversions.

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