Products of the Reaction of Carbon Monoxide with [Os₆(CO)₁₈]; X-Ray Crystal Structure of [Os₅(CO)₁₉]

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Summary The new clusters $[Os_5(CO)_{19}]$ and $[Os_6(CO)_{20}]$ have been prepared from the reaction of $[Os_6(CO)_{18}]$ with CO; the Os atom arrangement in the former has been found to be two isosceles triangles sharing the vertex.

THIS work stems from an interest in the reactions of carbonyl clusters with carbon monoxide and hydrogen. An understanding of the chemistry that such clusters undergo with carbon monoxide is essential for any evaluation of their potential as catalysts.

The hexa-osmium cluster, $[Os_6(CO)_{18}]$, has been found to react with carbon monoxide under moderate conditions to produce the new penta-osmium cluster $[Os_5(CO)_{19}]$. This has been identified and characterised on the basis of its spectroscopic data (Table) and by a full, single-crystal

TABLE. Spectroscopic data for $[Os_5(CO)_{19}]$ and $[Os_6(CO)_{20}]$.

Compound	Mass[a] spectrum (m/e)	ν_{CO}/cm^{-1}
$[Os_5(CO)_{19}]$	1484	2099(m) 2073(s) 2068(w, sh) 2040(s, br) 2035(m, sh) 2027(w, sh) 2000(w, br) 1980(w, br) (heptane soln.)
$[Os_6(CO)_{20}]$	1702	2103(s, sh) 2092(s) 2064(m, sh) 2035(s, br) 2018(s) 1997(s, br) 1983(w) 1967(m) 1964(w, sh) 1957(w) 1895(w) (Nujol mull).

[a] The parent ions and ions corresponding to the loss of three $[Os_5(CO)_{19}]$ or two $[Os_6(CO)_{20}]$ CO groups are weak. Ions corresponding to $Os_5(CO)_{16-n}$ $(n = 0—16)$ and $Os_6(CO)_{18-m}$ $(m = 0—18)$ are strong.

X-ray analysis. In a typical preparation $[Os_6(CO)_{18}]$ in heptane was allowed to react with carbon monoxide in a high-pressure vessel at 160 °C and 90 atm for ca. 1 h. The product, an orange crystalline solid, was obtained in yields approaching 80%. The other product of this reaction was identified (on the basis of its i.r. spectrum and properties) as $[Os(CO)_5]$.

$$[Os_6(CO)_{18}](soln.) + 6CO \rightarrow [Os_5(CO)_{19}] + [Os(CO)_5] \quad (1)$$
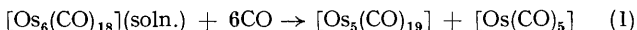
This reaction has also been followed by monitoring the change in i.r. spectrum with time. At no stage were we able to detect other intermediate compounds. Crystals of $[Os_5(CO)_{19}]$ were isolated as orange blocks from dichloromethane solution.

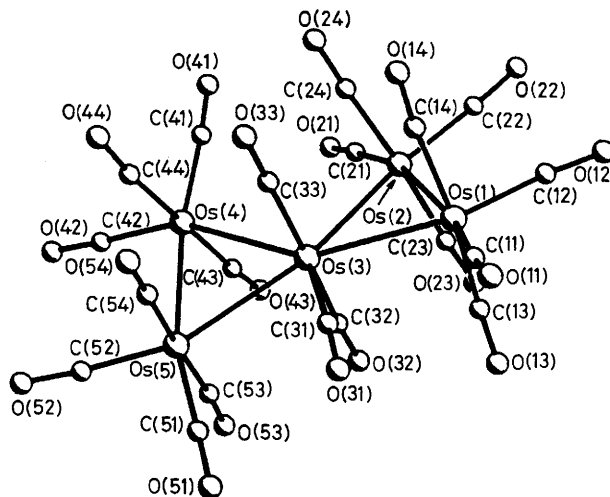FIGURE. The molecular structure of $[Os_5(CO)_{19}]$. Bond lengths: Os(1)–Os(2), 2·853(2); Os(1)–Os(3), 2·918(2); Os(2)–Os(3), 2·950(2); Os(3)–Os(4), 2·940(2); Os(3)–Os(5), 2·913(1); Os(4)–Os(5), 2·848(2) Å.

The molecular structure† of $[Os_5(CO)_{19}]$ is shown in the Figure together with some important bond parameters. The five Os atoms define two triangles sharing a vertex. The two triangles are not coplanar but skewed so that the dihedral angle between the planes Os(1)Os(2)Os(3) and Os(3)Os(4)Os(5) is 21·2°, and Os(4) lies 0·74(1) Å above the Os(1)Os(2)Os(3) triangle and Os(5) 0·26(1) Å below it. The metal framework may be described as a 'bow-tie' cluster. The Os(1)–Os(2) and the Os(4)–Os(5) bonds are ca. 0·03 Å shorter than the metal distances in the triangular cluster $[Os_3(CO)_{12}]$,[1] while all the bonds involving Os(3) are significantly longer. The longest metal–metal bonds Os(2)–Os(3) and Os(3)–Os(4) are associated with the narrowest Os(2)–Os(3)–Os(4) angle of 95·2(1)°, and this asymmetry of the metal bonds to Os(3) may result from steric interactions of the carbonyls on Os(2) and Os(4) [O(21) . . . C(41) 3·206(19) Å] or from an electronic effect of the carbonyl ligands bound to the seven-co-ordinate Os(3) atom. The other four Os atoms are six-co-ordinate, each being bound to four terminal carbonyls. The trend in the Os–C(carbonyl) bond lengths for these atoms is that the axial Os–C bonds [mean 1·949(25) Å] are longer than the equatorial [mean 1·914(23) Å]. This reflects the greater

competition between two *trans* carbonyls for back donation from the filled metal orbitals.

This is the first example of two neutral binary carbonyl clusters with the same nuclearity. $[Os_5(CO)_{16}]$ is a 72-electron system and from its structure[2] it may be considered as the parent of the 78-electron $[Os_5(CO)_{19}]$ binary carbonyl by the breaking of three metal–metal bonds not involving the unique Os atom, which is co-ordinated to four carbonyl groups; this bond cleavage is accompanied by rearrangement of the carbonyl ligands. The average metal–metal bond distance in $[Os_5(CO)_{16}]$ is shorter than in $[Os_5(CO)_{19}]$ with the longest bonds [2·867(3) and 2·889(3) Å] in the former associated with the eight-co-ordinate metal atom.

The 'bow-tie' metal geometry has been observed previously in the structures of $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt).[3] In these species the central metal has a square planar geometry but is involved in incipient bridge bonding with carbonyl groups co-ordinated to the Fe atoms. In $[Os_5(CO)_{19}]$ the central metal may be considered as distorted square planar with regard to Os–Os bonding but has, in addition, three terminal carbonyls bonded to it.

The conditions employed for reaction (1) are critical. Over longer periods of time (*ca.* 2·5 h) or at higher temperatures (*ca.* 170 °C) or pressures (*ca.* 100 atm) a range of products are observed including $[Os(CO)_5]$, $[Os_3(CO)_{12}]$, $[Os_5(CO)_{16}]$, $[Os_5(CO)_{19}]$, $[Os_6(CO)_{20}]$, and $[Os_7(CO)_{21}]$. Of particular interest is the new hexa-nuclear compound $[Os_6(CO)_{20}]$. Although a minor product under the conditions outlined above, reaction of $[Os_6(CO)_{18}]$ in the solid state[4] with CO produces almost quantitative amounts of this compound (equation 2).

$$[Os_6(CO)_{18}](solid) + 2CO \rightarrow [Os_6(CO)_{20}] \qquad (2)$$
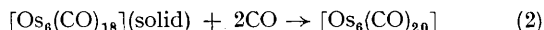
Obtained as a purple solid, $[Os_6(CO)_{20}]$ has been fully characterised from its analytical and spectroscopic properties (Table). On heating, the cluster liberates exactly 2 equiv. of carbon monoxide regenerating $[Os_6(CO)_{18}]$. Crystals of $[Os_6(CO)_{20}]$ suitable for *X*-ray analysis have not been obtained.

As previously noted the penta-osmium clusters bear a close structural relationship. The two triangles sharing a vertex may be derived simply from the trigonal bipyramid

by selective polyhedral-edge fission. We have established the $[Os_5(CO)_{16}]$ undergoes reversible addition of CO to produce $[Os_5(CO)_{19}]$ according to the equation (3).

$$[Os_5(CO)_{16}] \underset{ii}{\overset{i}{\rightleftharpoons}} [Os_5(CO)_{19}] \qquad (3)$$
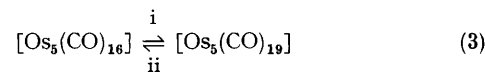
i, CO, 155 °C, 50 atm, heptane; ii, 120 °C, 1 atm, octane.

Carbonylation of $[Os_5(CO)_{19}]$ results in the formation of $[Os_3(CO)_{12}]$ presumably eliminating $[Os_2(CO)_9]$. While $[Os_2(CO)_9]$ cannot be unambiguously identified this provides a means of explaining the $[Os_7(CO)_{21}]$ production, by a simple condensation reaction of $[Os_5(CO)_{19}]$ and $[Os_2(CO)_9]$. Thus, we find that $[Os_5(CO)_{19}]$ readily reacts with $[Os_2(CO)_9]$ to produce the cluster $[Os_7(CO)_{21}]$. The complete reaction pathway is summarised in the Scheme. $[Os_5(CO)_{19}]$ has also been found to react with $[Fe_2(CO)_9]$ resulting in the new mixed cluster $[Fe_2Os_5(CO)_{21}]$.
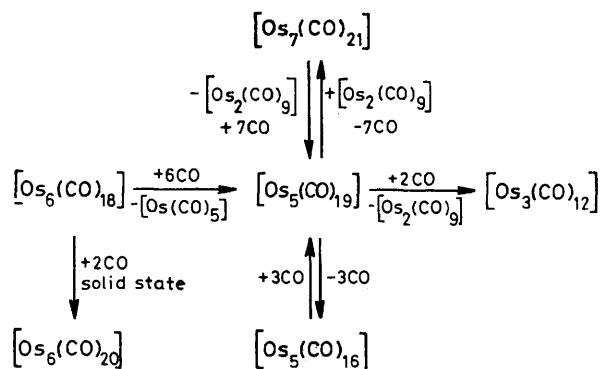
SCHEME. Pathway for the carbonylation of $[Os_6(CO)_{18}]$.

[1] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, 16, 878.
[2] B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1977, 33, 173.
[3] G. Longoni, M. Manassero, and M. Sansone, *J. Am. Chem. Soc.*, 1980, 102, 3242.
[4] A. L. Mann, personal communication.