

Activation of a Carbonyl Group in the Pentanuclear Carbido Clusters $\text{Os}_5\text{C}(\text{CO})_{15}$ and $\text{I}_2\text{Os}_5\text{C}(\text{CO})_{15}$ by Alcohols: X-Ray Analysis of $\text{HOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{Et})$ and $\text{IOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{Me})$

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The clusters $\text{Os}_5\text{C}(\text{CO})_{15}$ and $\text{I}_2\text{Os}_5\text{C}(\text{CO})_{15}$ react with alcohols under mild conditions to give derivatives of the type $\text{HOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{R})$ and $\text{IOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{R})$, respectively; X-ray analysis has confirmed that in both cases the alkoxy-group has attacked a carbonyl ligand in the parent compound to form an $\eta^2\text{-}\mu_2\text{-CO}_2\text{R}$ group.

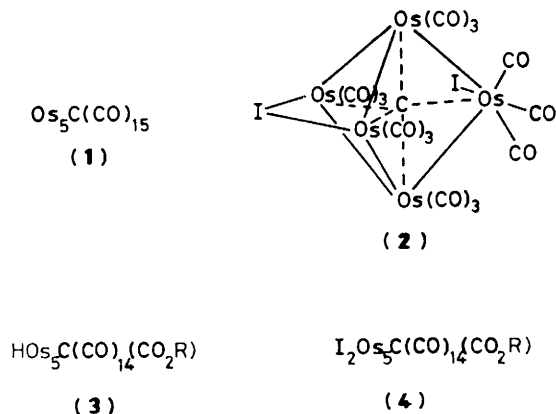
Carbon-oxygen bond scission is an important requirement in certain CO hydrogenation reactions. However, few specific models of intermediates in the conversion of carbon monoxide into separate C and O atoms on a metal surface have been found in clusters with more than four metal atoms. We find that the reaction of the pentanuclear osmium clusters $\text{Os}_5\text{C}(\text{CO})_{15}$ (1) and $\text{I}_2\text{Os}_5\text{C}(\text{CO})_{15}$ (2) with alcohols gives products containing $\eta^2\text{-}\mu_2\text{-CO}_2\text{R}$ groups which may be regarded as models for intermediates of this type.

When $\text{Os}_5\text{C}(\text{CO})_{15}$ (1) is heated under reflux with alcohol (ROH), compounds formulated as $\text{HOs}_5\text{C}(\text{CO})_{15}(\text{OR})$ on the basis of n.m.r. and mass spectrometric data[†] are obtained. However, the similarity of their i.r. spectra to that¹ of $\text{HOs}_5\text{C}(\text{CO})_{14}(\text{C}_5\text{H}_4\text{N})$ indicated that these compounds were

the result of alkoxy-attack on a carbonyl ligand and should be formulated as $\text{HOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{R})$ (3). This was confirmed by an X-ray analysis[‡] of the EtOH derivative (3, R = Et) which has the structure shown in Figure 1. It may be inferred from the characteristic bending back of the carbonyl ligands associated with the 'hinge' bond, Os(1)–Os(4), that the H-ligand is bridging these two atoms. The metal core has the 'bridged-butterfly' or *arachno*-pentagonal bipyramidal geometry expected for M_5 clusters with eight skeletal electron pairs ($S = 8$).^{2,3}

Compounds containing a similar bridging CO_2R ligand, $\text{IOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{R})$ (4)[§] are formed under even milder conditions when the di-iodide derivative $\text{I}_2\text{Os}_5\text{C}(\text{CO})_{15}$ (2) is stirred at room temp. in alcohols. A comparison of the i.r. spectrum of (2) with those of the structurally characterised⁴ derivatives $\text{HXM}_5\text{C}(\text{CO})_{15}$ suggests that (2) has the structure shown. X-ray analysis[‡] of the MeOH derivative (4, R = Me) shows the related structure which is illustrated in Figure 2.

The metal core in (4) is related to that in (3) but with the



[†] For (3, R = Et), ¹H n.m.r. (CDCl_3): 6.25 τ (q), 8.95 τ (t), 34.68 τ (hydride); M^+ at 1438 (¹⁹²Os); i.r. (hexane) 2109 w, 2081 vs, 2061 vs, 2056 s sh, 2028 s, 2015 s, 2008 s, 1984 m, and 1970 w cm^{-1} .

[‡] Crystal data: (3, R = Et), $\text{C}_{17}\text{H}_3\text{IO}_{16}\text{Os}_5$, $M = 1541.11$ orthorhombic, space group $Pna2_1$, $a = 17.019(3)$, $b = 10.063(2)$, $c = 15.810(3)$ Å, $Z = 4$, $I/\sigma(I) \geq 3.0$, θ range 2.7–27°, present R value 0.049 from 2460 absorption corrected data. (4, R = Me), $\text{C}_{18}\text{H}_6\text{O}_{16}\text{Os}_5$, $M = 1429.24$, monoclinic, space group $P2_1/n$, $a = 15.665$, $b = 16.761$, $c = 10.198$ Å, $\beta = 90.4$, $Z = 4$, $I/\sigma(I) \geq 3.0$, θ range 3–27°, present R value 0.041 for 3461 absorption corrected data. Data were collected on a Philips PW1100 diffractometer using $\text{Mo-K}\alpha$ radiation.

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.

[§] For (4, R = Me), ¹H n.m.r. (CD_2Cl_2): 7.09 τ (s); M^+ at 1550 (¹⁹²Os); i.r. (hexane) 2106 w, 2077 s, 2063 vs, 2059 s sh, 2026 s, 2019 m, 2006 m, 1988 w, and 1977 w cm^{-1} .

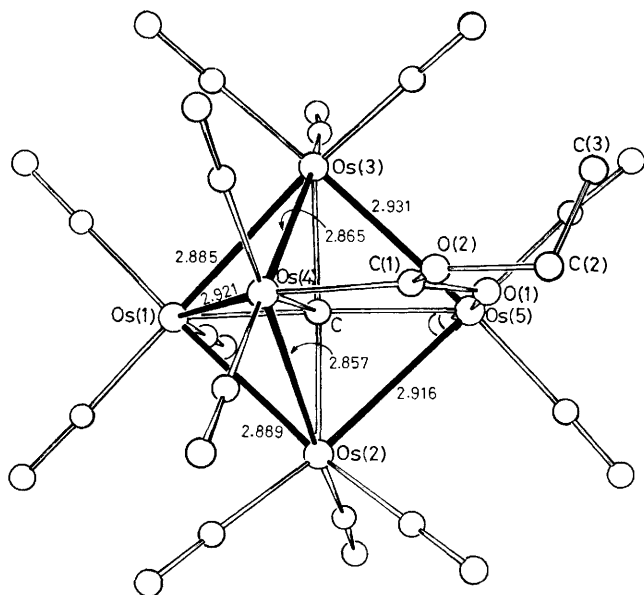


Figure 1. The arachno-pentagonal bipyramidal structure of $\text{HO}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{Et})$ (**3**, $\text{R} = \text{Et}$), showing the Os–Os bond lengths (Å, max. e.s.d.s 0.001 Å). The μ_2 -H ligand bridges Os(1)–Os(4). Other important bond lengths (Å) are Os(4)–C(1) 2.028(15); Os(5)–O(1) 2.118(12); Os–C(carbido) 1.96–2.11(2); Os–CO (mean) 1.91; C(1)–O(1) 1.28(2); C(1)–O(2) 1.34(2); C(2)–O(2) 1.47(2); and C(2)–C(3) 1.35(4).

'hinge' bond broken [Os(1)–Os(4) 3.512(3) Å] by the presence of the μ_2 -I ligand which contributes 2 more electrons than the μ_2 -H ligand in (**3**). The geometry may be described as distorted trigonal bipyramidal with three very long, non-bonded Os . . . Os distances in the equatorial plane, or alternatively as *hypho*-hexagonal bipyramidal ($S = 9$).³

The carbido-atom appears to play an important role in determining the structure adopted by these carbido-cluster compounds as the electron count increases. The differences in geometry between *nido*-octahedral ($S = 7$), arachno-pentagonal bipyramidal ($S = 8$), and *hypho*-hexagonal bipyramidal ($S = 9$) may be regarded as resulting from breaking of Os–Os bonds in such a way that an approximately linear Os–C–Os axis is always maintained with the other three Os atoms swinging round it in the equatorial plane. This contrasts with the behaviour usually observed on addition of electrons to species without carbido-atoms, *i.e.* stepwise fission of metal–metal bonds occurs leading to several possible arrangements of metal atoms.⁵ In (**3**) and (**4**) the CO_2R group lies in the equatorial Os(1), Os(4), Os(5), carbido-plane and it may be significant that in similar Os_5C derivatives substitution or addition of ligands has occurred predominantly in this plane.^{1,6,7}

Formation of (**3**) and (**4**) may be viewed as initial nucleophilic attack by an alkoxide group on the carbon atom of a CO ligand, followed by a bending across of the carbonyl oxygen atom to donate two electrons to an adjacent Os atom. In the case of (**4**), the oxygen donor replaces the terminal iodide ligand present in (**2**), whereas in the formation of (**3**), an Os–Os bond is broken. Conversion of $\text{M}_5\text{C}(\text{CO})_{15}$ ($\text{M} = \text{Ru}, \text{Os}$), which has a square pyramidal metal skeleton, into derivatives of the type $\text{M}_5\text{C}(\text{CO})_{15}\text{L}$, in which the metal atoms adopt a bridged-butterfly arrangement, is a very facile process.^{2,7} It seems therefore that the halogen atoms in (**2**) are in some way responsible for the easier formation of the η^2 - μ_2 - CO_2R group in (**4**), and the activation of the CO group in (**2**) towards alkoxy-attack is not simply a consequence of the 'preformed' metal geometry.

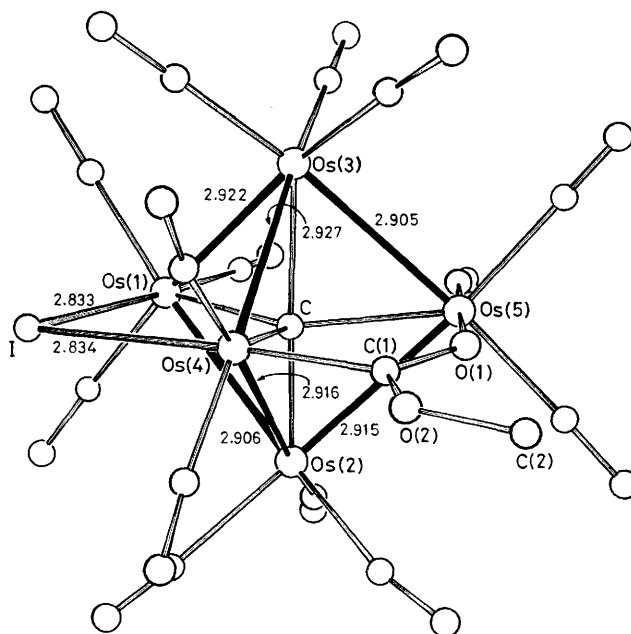


Figure 2. The structure of $\text{IO}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{Me})$ (**4**, $\text{R} = \text{Me}$), showing the Os–Os and Os–I bond lengths (Å, max. e.s.d.s Os–Os 0.002, Os–I 0.004 Å). Other important bond lengths (Å) are Os(4)–C(1) 2.02(4); Os(5)–O(1) 2.17(3); Os–C(carbido) 1.88–2.21(3); Os–CO (mean) 1.91; C(1)–O(1) 1.29(5); C(1)–O(2) 1.28(5); C(2)–O(2) 1.56(7).

Reaction of (**3a**) with H_2 or CO (160 °C, 50 atm) leads to removal of the alkoxy-group and, on the basis of mass spectrometric evidence, formation of the dihydride $\text{H}_2\text{Os}_5\text{C}(\text{CO})_{15}$. A second new cluster, formulated as $\text{Os}_5\text{C}(\text{CO})_{16}$ from mass spectral data, was also isolated from the reaction of (**3**, $\text{R} = \text{Et}$) with CO. The alkoxy-group also appears to be removed by concentrated H_2SO_4 in CH_2Cl_2 ; a cationic species is formed which we believe to be $[\text{HO}_5\text{C}(\text{CO})_{15}]^+$ from a comparison of its i.r. spectrum with that⁸ of the ions $[\text{HM}_5\text{C}(\text{CO})_{15}]^+$ ($\text{M} = \text{Ru}, \text{Os}$), formed by protonation of the parent carbonyl carbido species.

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