

Multiple Carbon–Carbon Bond Cleavage on a Heptaosmium Cluster: Synthesis and Molecular Structure of $[\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4]$

Brian F. G. Johnson,^a Jack Lewis,^{a*} Julie A. Lunniss,^a Dario Braga,^{b*} and Fabrizia Grepioni^b

^a University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

^b Università Degli Studi di Bologna, Dipartimento di Chimica, 40126 Bologna, Italy

The heptaosmium cluster $[\text{H}_2\text{Os}_7(\text{CO})_{20}]$ reacts with Ph_2C_2 to yield the organometallic cluster $[\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4]$, which has been shown by X-ray crystallographic analysis to possess an unprecedented metal core geometry based on a bicapped square pyramidal arrangement of osmium atoms.

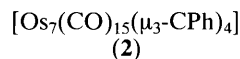
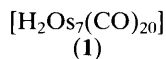
We are currently exploring the interactions of alkynes with a series of cluster compounds containing from three to eight osmium atoms. Our interest is simply to examine the bonding modes adopted by CR fragments and their dependence on the number and type of metal atoms present. In earlier communications we reported on the derivatives obtained from Os_{3-6} precursors;^{1,2} we now report an extension of this work to an Os_7 system.

The dihydrido cluster $[\text{H}_2\text{Os}_7(\text{CO})_{20}]$ (**1**) reacts with Ph_2C_2 in toluene under reflux to produce initially a brown compound, then a green compound and finally, after an extended

period (*ca.* 3 days), a purple compound (**2**). Some difficulty has been experienced in identifying the true formulae of these compounds. Neither ^1H n.m.r. nor mass spectral data were particularly informative, save for verifying the presence of phenyl ligands in all three complexes[†] and, in the case of (**2**),

[†] I.r. $\text{CH}_2\text{Cl}_2[\nu(\text{CO})/\text{cm}^{-1}]$: brown compound 2072vs, 2061s, 2058m, 2028s, 2013m, and 1939w; green compound 2101wm, 2073s, 2065vs, 2027m, 1965w, and 1955w; purple compound (**2**) 2101vw, 2072w, 2063s, 2048s, 2029vs, 2011s, 1980w, and 1945w.

confirming that no hydrido ligands are present. However, we were able to obtain X-ray-quality crystals of (2) by slow evaporation of a solution in tetrahydrofuran at room temperature.‡



The X-ray diffraction study identified compound (2) as $[\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4]$. Its molecular structure is shown in Figure 1 along with relevant bond lengths and angles. The metal core geometry consists of a square pyramid capped on opposite triangular faces by two Os atoms. Each of the four $\mu_3\text{-CPh}$ groups triply bridges a deltahedral face: two of these cap the remaining two faces of the square pyramid, while two more occupy the outer triangular faces generated by the capping Os atoms. All fifteen carbonyl ligands are terminally bonded, with three on each capping atom, two on the Os atoms on the square base, and one on the pyramid vertex. The resulting idealized molecular symmetry is C_{2v} ($mm2$).

With a three-electron donation from each benzylidyne ligand, the molecular electron count for (2) is 98 electrons, making it isoelectronic with $[\text{Os}_7(\text{CO})_{21}]^4$ (a monocapped octahedron) and the parent cluster $[\text{H}_2\text{Os}_7(\text{CO})_{20}]$ (1)⁵ (an edge-bridged polytetrahedron). Thus, the molecular geometry of (2) represents a third of many alternative polyhedra which can be derived by face-capping aggregation (+12 electrons) on 86-electron clusters⁶ such as the related compound $[\text{Os}_6(\text{CO})_{16}(\text{CPh})_2]$ ⁷ (a mono-capped square pyramid).

It is noteworthy that the square base of the square pyramid in structure (2) is unsupported. With the exception of $[\text{H}_2\text{Os}_7(\text{CO})_{21}]^8$ and $[\text{H}_2\text{Os}_6(\text{CO})_{18}]^9$ (both of which are based on a mono-capped square pyramid), all known clusters having a square pyramidal core contain either organic ligands or semi-interstitial atoms quadruply bridging the square base: $[\text{Os}_6(\text{CO})_{16}(\text{CPh})_2]$,⁷ $[\text{Os}_6(\text{CO})_{17}(\text{HCCEt})_2]$,² and $[\text{Os}_5\text{C}(\text{CO})_{15}]^{10}$ are typical examples with $\mu_4\text{-benzylidyne}$, $\mu_4\text{-alkyne}$, and $\mu_5\text{-carbide}$ ligands, respectively.

Interestingly, the square pyramidal core of (2) is slightly 'squeezed' along its axis, with shorter basal-apex bonds [mean 2.647(1) Å] and longer intra-basal bonds [mean 2.792(1) Å]. The opposite effect was observed for the related species $[\text{Os}_6(\text{CO})_{16}(\mu_4\text{-CPh})(\mu_3\text{-CPh})]$,⁷ with basal-apex and intra-basal bond distances of 2.859(3) and 2.743(3) Å, respectively.

The structural parameters determined for the $\mu_3\text{-CPh}$ groups [mean Os-C 2.12(1) Å, C-C_{Ph} 1.45(1) Å, and Os-C-Os 81.4(5)°] agree with those reported for

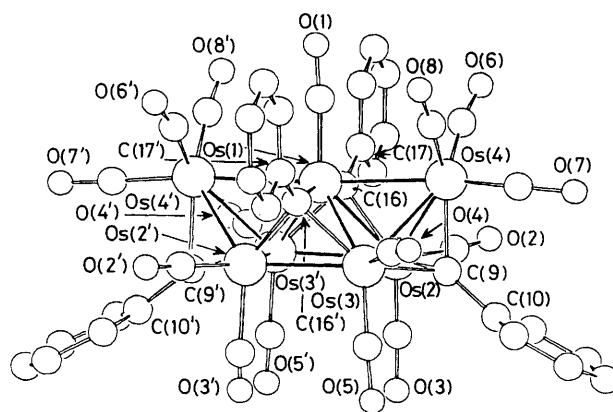


Figure 1. The molecular structure of $[\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4]$ (2). The C atoms of the CO groups bear the same numbering as the corresponding O atoms. Primed atoms are so designated with reference to the crystallographic two-fold axis passing through Os(1) and the centre of the opposite square base. Hydrogen atoms of the phenyl groups are omitted for clarity. Relevant bond distances and angles include: Os(1)-Os(2) 2.645(1); Os(1)-Os(3) 2.650(1); Os(1)-Os(4) 2.856(1); Os(2)-Os(3) 2.729(1); Os(2)-Os(4) 2.780(1); Os(3)-Os(4) 2.775(1); mean Os-C_{CO} 1.90(2); C-O 1.14(2); C_{Ph}-C_{Ph} 1.39(2) Å; Os-C-O 178(2)°; Os-C-Os 81.4(5)°.

$[\text{Os}_3(\text{CO})_9(\mu_3\text{-COMe})(\mu_3\text{-CPh})]^{11}$ [mean Os-C 2.13(1) Å, C-C_{Ph} 1.46(2) Å, and Os-C-Os 82.5(5)°] and $[\text{Os}_6(\text{CO})_{16}(\mu_4\text{-CPh})(\mu_3\text{-CPh})]$ ⁷ [for $\mu_3\text{-CPh}$: Os-C 2.09(3) Å, C-C_{Ph} 1.46(4) Å, and Os-C-Os 81.2(12)°].

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‡ Crystal data: $\text{C}_{43}\text{H}_{20}\text{O}_{15}\text{Os}_7$, $M = 2108$, monoclinic, space group $C2/c$, $a = 15.953(5)$, $b = 19.816(4)$, $c = 14.383(2)$ Å, $\beta = 94.51(6)^\circ$, $U = 4532.9$ Å³, $Z = 4$, $D_c = 3.09$ g cm⁻³, $F(000) = 3535$, $\mu(\text{Mo-K}\alpha) = 196.2$, θ range 2.5–27°, final R value 0.033, $R_w = 0.035$, for 2881 out of 4490 independent reflections [$F_o > 4\sigma(F_o)$]. Absorption correction was applied by the Walker and Stuart method^{3a} (correction range 0.86–1.23). Intensity data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer by the ω -2 θ scan method. All non-H atoms were allowed to vibrate anisotropically. The H atoms of the phenyl groups were added in calculated positions [C-H 1.08 Å] and refined 'riding' on their respective C atoms; a single isotropic thermal parameter was also refined for the H atoms [0.07(1) Å²]. The structure was solved by direct methods.^{3b} Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre; see Notice to Authors, Issue 1.