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# Isolation, characterisation, and crystal and molecular structure of $[Os_6AuC(CO)_{20}(\mu\text{-}OMe)]$

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### Abstract

Treatment of $[Os_3(CO)_{10}(\mu\text{-}AuPEt_3)(\mu\text{-}COMe)]$ with $[Os_3(CO)_{10}(NCMe)_2]$ in refluxing toluene affords the new carbido compound $[Os_6AuC(CO)_{20}(\mu\text{-}OMe)]$ (**1**). A single-crystal X-ray structure analysis of **1** shows that an $Os_2$ fragment and an $Os_4$ carbido fragment are linked together by a gold atom.

The chemistry of heterometallic osmium and ruthenium clusters containing Group IB metals is well established for systems with up to four osmium or ruthenium atoms [1], but for higher nuclearity systems there are relatively few examples [2]. Much of the work involving the use of Group IB metals stems from the isolobal relationship between a hydride ligand and a $MPR_3$ fragment ($M = Cu$, Ag and Au), but for clusters with nuclearities of four and above there are a number of examples where the isolobal analogy breaks down [3] and the structures adopted by the hydrido clusters and the Group IB analogues differ [4]. In the context of this general area, it is of interest to study the interaction between cluster-bound hydrogen atoms, or Group IB metal-ligand fragments, and carbido-carbon atoms, since the formation of C–H or C–M bonds mimics the process which occur on metal surfaces in catalytic reactions. Reactions between hydrogen-containing ligands and the semi-exposed carbide in "butterfly" clusters of iron and ruthenium have been reported [5], but there are few examples of analogous Group IB metal chemistry where a product is formed in which there is an interaction between the carbide and the Group IB metal atom or atoms [6,7]. We now report the preparation of a new hexaosmium carbido cluster $[Os_6AuC(CO)_{20}(\mu\text{-}OMe)]$ (**1**) in which there is a direct interaction between the carbide a "bare" gold atom.

Treatment of $[Os_3(CO)_{10}(\mu\text{-}AuPEt_3)(\mu\text{-}COMe)]$ with $[Os_3(CO)_{10}(NCMe)_2]$ in refluxing toluene affords a brown-red solution after 3 h, which after chromatography on silica gave a brown compound, formulated as $[Os_6AuC(CO)_{20}(\mu\text{-}OMe)]$ (**1**), on the basis of spectroscopic data [MS: $m/z = 1940$ ($^{190}Os$); IR ($\nu(CO)$, $cm^{-1}$, $CH_2Cl_2$): 2117w, 2086m, 2072vs, 2050s, 2035m, 2012m,sh, 2000m; $^1H$ NMR

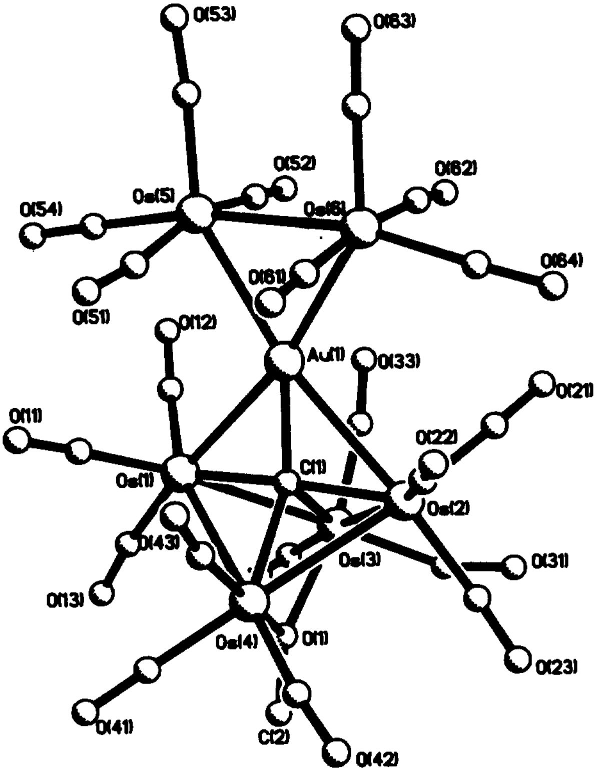

Fig. 1. The molecular structure of $[Os_6AuC(CO)_{20}(\mu\text{-}OMe)]$ (1). Bond lengths: Os(1)–Os(3), 2.802(3); Os(1)–Os(4), 2.862(3); Os(2)–Os(3), 2.864(4); Os(2)–Os(4), 2.799(3); Os(5)–Os(6), 2.727(3); Os(1)–Au(1) 2.839(3); Os(2)–Au(1), 2.822(3); Os(5)–Au(1), 2.664(3); Os(6)–Au(1), 2.669(3); Os(3) ··· Os(4), 3.306(3); Os(1)–C(1), 1.83(5); Os(2)–C(1), 1.95(5); Os(3)–C(1), 2.13(5); Os(4)–C(1), 2.16(4); Au(1)–C(1), 2.06(4); Os(4)–O(1), 2.15(4); Os(3)–O(1), 2.09(3); O(1)–C(2), 1.32(8) Å. Bond angles: Os(1)–Os(3)–Os(2), 83.5(1); Os(3)–Os(2)–Os(4), 71.4(1); Os(3)–Os(1)–Os(4), 71.4(1); Os(1)–Au(1)–Os(2), 83.6(1); Au(1)–Os(1)–Os(3), 84.8(1); Au(1)–Os(2)–Os(3), 84.0(1); Os(1)–Au(1)–Os(6), 169.1(1); Os(2)–Au(1)–Os(5), 168.7(1); Os(2)–Au(1)–Os(6), 107.2(1); Os(1)–Au(1)–Os(5), 107.7(1); Os(5)–Au(1)–Os(6), 61.5(1); Au(1)–Os(6)–Os(5), 59.2(1); Au(1)–Os(5)–Os(6), 59.3(1); Os(1)–C(1)–Os(2), 177(2); Os(4)–C(1)–Os(3), 101(2); Os(3)–C(1)–Au(1), 130(2); Os(4)–C(1)–Au(1), 129(3); Os(3)–O(1)–Os(4), 103(2)°.

$\delta(CDCl_3)$; 2.90 (s,$OCH_3$)]. Single crystals of **1** were obtained from a solution of **1** in $CH_2Cl_2$/n-hexane mixture at −25 °C. The molecular structure of **1**, established by X-ray crystallography, is shown in Fig. 1 together with some important bond parameters *. The molecule consists of an $Os_2$ fragment linked to an $Os_4$ carbido fragment via a bare Au atom. The $Os_2(CO)_8$ fragment is symmetrically bridged by the Au atom with a short Os–Os distance of 2.727(3) Å. The $Os_4$ fragment adopts a pseudo-butterfly arrangement with the gold atom spanning the two "wingtip" Os atoms. The carbido-carbon atom is semi-encapsulated within this $Os_4Au$ metal framework, which is likely to originate from $\mu$-COMe group. The description of the $Os_4$ framework as a butterfly is not completely accurate, as the "hinge" Os(3)–Os(4) separation of 3.306(3) Å is too long to be considered as a formal bond. This edge breaking is expected as a three-electron donor ligand ($\mu$-OMe) is bridging this Os–Os edge. Similarly, in $[Os_5C(CO)_{14}(CO_2Me)(\mu\text{-}I)]$ [8] the hinge of the bridged butterfly is broken by the ($\mu$-I) ligand contributing three electrons. The average Os–Os bond length within the butterfly is 2.83(3) Å, which is similar to the average Os–Os length of 2.87(1) Å in $[Os_5C(CO)_{14}(\mu\text{-H})(CO_2Et)]$ [8] and shorter than the average 2.918(9) Å in $[Os_5C(CO)_{14}(CO_2Me)(\mu\text{-I})]$ [8]. The Au atom displays a very unusual five-fold formal coordination geometry. The two long [average 2.831(3) Å] and two short [average 2.666(3) Å] Os–Au distances are associated with the butterfly fragment and $Os_2$ unit, respectively. The Au–C(carbido) distance [2.06(4) Å] is similar to those in $[Ru_4C(CO)_{12}(AuPPh_3)I]$ [6] and $[HFe_4C(CO)_{12}(AuPPh_3)]$ [7]. The best description of the bonding of the Au atom is to consider that it has $\sigma$-lobes pointing towards the carbide and the mid-point of the Os(5)–Os(6) edge, while the bonding to Os(1) and Os(2) is through tangential orbitals. All Os–C(carbido) distances are within the expected range.

Whilst the mechanism for the formation of **1** is unclear, it is evident that the $[Os_3(CO)_{10}(NCMe)_2]$ acts as an acceptor for the phosphine ligands as small amounts of $[Os_3(CO)_{10}(PEt_3)_2]$ and $[Os_3(CO)_{11}PEt_3]$ are isolated from the reaction mixture. Under similar reaction conditions $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-COMe})]$, the corresponding hydrido cluster of $[Os_3(CO)_{10}(\mu\text{-AuPEt}_3)(\mu\text{-COMe})]$, failed to react with $[Os_3(CO)_{10}(NCMe)_2]$.

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[*] *Crystal data*: $[Os_6AuC(CO)_{20}(\mu\text{-OMe})]\cdot CH_2Cl_2$, $C_{23}H_5AuCl_2O_{21}Os_6$, $M = 2026.4$, Triclinic, space group $P\bar{1}$, $a = 9.724(2)$, $b = 11.807(2)$, $c = 16.578(4)$ Å, $\alpha = 94.68(2)$, $\beta = 95.21(3)$, $\gamma = 91.17(2)°$, $V = 1888.4$ Å$^3$, $D_c = 3.563$ g cm$^{-3}$, $Z = 2$, F(000) = 1760, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 242.03$ cm$^{-1}$. Red irregular block, crystal dimensions: $0.08 \times 0.33 \times 0.56$ mm. 5290 reflections measured on Stoe-Siemens four circle diffractometer ($5.0 \leqslant 2\theta \leqslant 45.0°$), corrected for absorption, 4942 unique reflections and 3320 observed with $F > 4\sigma(F)$, structure solved by a combination of direct methods and difference Fourier techniques and refined by blocked full-matrix least-squares analysis, with Os and Au atoms assigned anisotropic displacement parameters. The asymmetric unit contains a solvent molecule of $CH_2Cl_2$ which has been confirmed by $^1$H NMR of a crystallised sample of **1** [$\delta(CDCl_3)$: 5.32 (s, $CH_2Cl_2$)]. The weighting scheme employed was $w = 6.3428/[\sigma^2(F) + 0.0012F^2]$. The final residuals were $R = 0.086$ and $R_w = 0.088$. The atomic coordinates for this work have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK).