

Preliminary communication

Synthesis and structural characterisation of
 $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$: the first cluster with an Os_4Au_4 core¹

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Abstract

The reaction of the dianion $[\text{Os}_4\text{H}_2(\text{CO})_{11}]^{2-}$ with two equivalents of $\text{Au}_2(\text{DPPM})\text{Cl}_2$ ($\text{DPPM} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$), in the presence of $\text{Ti}[\text{PF}_6]$, affords a digold species which upon treatment with NEt_3 gives the neutral cluster $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$. This cluster has been characterised by ^1H and ^{31}P NMR spectroscopy, mass spectrometry and X-ray crystallography. The metal core consists of an Os_4 tetrahedron, one face of which is capped by three Au atoms while the fourth Au atom caps an OsAu_2 face. © 1997 Elsevier Science S.A.

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1. Introduction

The chemistry of mixed-metal clusters containing gold phosphine units is well established [1]. Much of the initial interest in these clusters stemmed from the perceived isolobal analogy between a hydride and a gold–phosphine group [2]. While this analogy works well for clusters which contain a single gold–phosphine unit, and the observed structures are similar to those of the hydride derivatives, for clusters with more than one gold–phosphine unit, structural differences are commonplace. A case in point is the structural difference between $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ [3] and $[\text{Ru}_4\text{H}(\text{CO})_{12}(\text{AuPPh}_3)_3]$ [4], and their osmium analogues [5,6]. While in the hydrido derivatives the hydrogen atoms span four of the metal–metal edges so that the M_4H_4 core has approximate D_{2d} symmetry, the trigold derivatives consist of a M_4 tetrahedron, one face of which is capped by an Au atom and the other Au atoms then cap two different M_2Au faces, thus forming an M_4Au_3 bi-capped trigonal bipyramidal core. This difference in structure may be attributed to a direct bonding interaction between the gold atoms, which is not possible for the hydrido analogues. Evidence for this $\text{Au} \cdots \text{Au}$

interaction comes from both experimental [1] and theoretical data [7].

Attempts to deprotonate the clusters $[\text{Os}_4\text{H}(\text{CO})_{12}(\text{AuPR}_3)_3]$ in the presence of $[\text{AuPR}_3]^+$ have not produced the tetragold cluster, and the only osmium cluster carbonyls which contain four gold atoms are the high nuclearity species $[\text{Os}_{10}\text{C}(\text{CO})_{24}\text{Au}(\text{AuP}(\text{C}_6\text{H}_{11})_3)_3]$ [8], in which the four Au atoms form a tetrahedron and are only linked to the Os core by an interaction to one gold, and $[\text{Os}_{10}(\text{CO})_{24}\{\text{Au}(\text{PPh}_2\text{R})\}_4]$ [9], in which the Au atoms are not linked together but cap the ends of the Os_{10} tube. In this communication a new strategy for the formation of clusters with an Os_4Au_4 core is presented, which involves the reaction of the anion $[\text{Os}_4\text{H}_4(\text{CO})_{11}]^{2-}$ with the chelated gold salt $\text{Au}_2(\text{DPPM})\text{Cl}_2$ ($\text{DPPM} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$).

2. Results and discussion

The reduction of $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$ with $\text{K}^+/\text{Ph}_2\text{CO}$ at -60°C in THF leads to the formation of the dianion $[\text{Os}_4\text{H}_4(\text{CO})_{11}]^{2-}$ [10]. This solution was brought to room temperature and treated with two equivalents of $\text{Au}_2(\text{DPPM})\text{Cl}_2$ in the presence of $\text{Ti}[\text{PF}_6]$, which acts as a halide abstractor, in dichloromethane solution. After 1 h, the colour of the solution changed to deep yellow, and a neutral species, presumed to be

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¹ Dedicated to the memory of Professor Yuri Struchkov in recognition of his outstanding contributions to structural organometallic chemistry.

$[\text{Os}_4\text{H}_4(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}]$, was formed. This product was not isolated, but a drop of the base NEt_3 was added to the solution and the mixture was stirred for a further 14 h. The resulting solution was concentrated and then chromatographed by TLC using dichloromethane/hexane (60:40) as eluant. A single red product was isolated in near quantitative yield. This product was initially characterised as $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$ from spectroscopic and analytical data.

Spectroscopic and analytical data for $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$: IR ($\nu(\text{CO})$ (cm^{-1}), CH_2Cl_2) 2055(vs), 2012(m), 1990(s), 1959(w), 1918(w,br), 1865(w). Mass spectrum m/z 2636 (2634). Anal. Found: C, 28.10; H, 1.85. Calc.: C, 27.88; H, 1.76%.

As well as the signals due to the DPPM ligand, the ^1H NMR spectrum, run in CDCl_3 , showed two broad singlets at δ -17.43 and -18.64, consistent with the presence of two inequivalent bridging hydride ligands. The ^{31}P NMR spectrum, run in CD_2Cl_2 solution, displayed four sets of poorly resolved doublets at δ -64.65, -77.10, -97.65 and -104.55 ($J_{\text{pp}} = 17\text{ Hz}$), consistent with there being four different environments for the four P atoms from the two DPPM ligands. These data suggest that this cluster is not fluxional at room temperature on the NMR timescale, perhaps because of the constraints of the chelating DPPM ligands. This behaviour contrasts with that in $[\text{M}_4\text{H}(\text{CO})_{12}(\text{AuPPh}_3)_3]$

($\text{M} = \text{Ru}$ [4], Os [6]) and $[\text{Ru}_3(\text{CO})_9(\text{COMe})(\text{AuPPh}_3)_3]$ [11], where the room temperature ^{31}P NMR spectrum shows only one signal for the P atoms, although the X-ray structures show that in the solid state there are two different phosphorus environments.

In order to establish the complete molecular structure of $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$, an X-ray analysis was undertaken.

Crystal data for $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2] \cdot \text{CH}_2\text{Cl}_2$: $\text{C}_{62}\text{H}_{48}\text{Au}_4\text{Cl}_2\text{O}_{11}\text{Os}_4\text{P}_4$, $M = 2712.45$, orthorhombic, space group $Pca2_1$, $a = 25.35(2)$, $b = 11.897(7)$, $c = 23.73(2)\text{ \AA}$, $V = 7155(8)\text{ \AA}^3$, $Z = 4$, $D_c = 2.518\text{ Mg m}^{-3}$, $F(000) = 4888$, Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$, $\mu(\text{Mo K}\alpha) = 15.457\text{ mm}^{-1}$, crystal dimensions $0.25 \times 0.25 \times 0.33\text{ mm}^3$, 7023 independent absorption corrected reflections ($R_{\text{int}} = 0.020$), $2\theta_{\text{max}} = 45.0^\circ$. The structure was solved by direct methods (SHELXTL-PLUS, Program Vers. 4.0, Siemens Analytical X-Ray Instruments, Madison, WI, 1990) and Fourier difference techniques, refined by full-matrix least-squares based on F^2 (Os, Au, P and Cl anisotropic, DPPM H atoms in idealised positions, arene rings and carbonyl ligands restrained) (SHELXL-93, G.M. Sheldrick, Program for crystal structure refinement, University of Göttingen, 1993) to $R_1 = 0.056$ [$I > 2\sigma(I)$] and $wR_2 = 0.187$ (all data), $\text{GOF} = 1.097$, $w^{-1} = [\sigma^2 F^2 + (0.1091P)^2 + 179.7P]$ where $P = [0 \text{ or } F_o^2 + 2F_c^2]/3$.

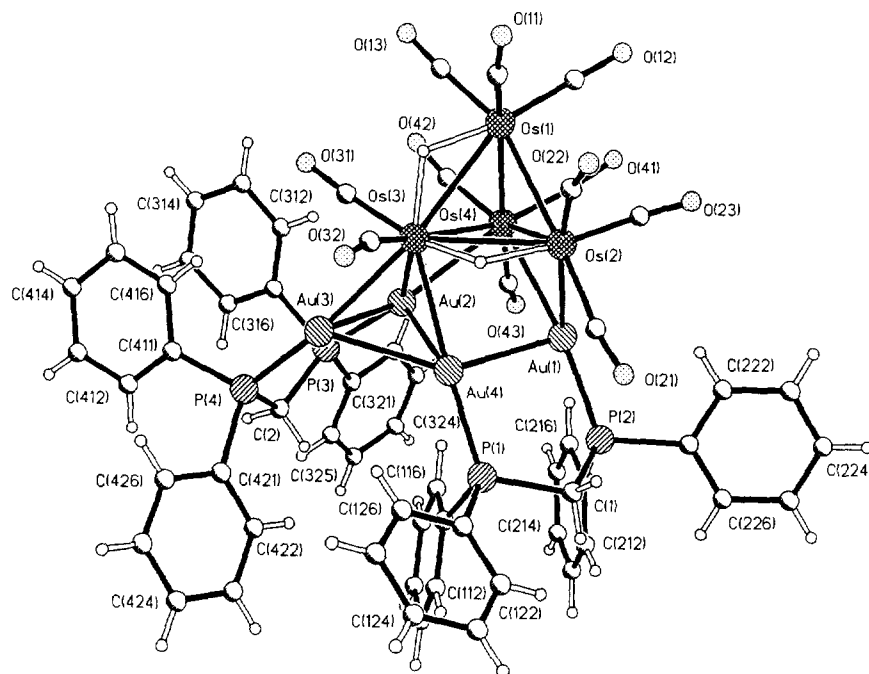


Fig. 1. The molecular structure of $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$ showing the atom numbering scheme adopted. Selected bond lengths (\AA) and angles ($^\circ$): Os(1)–Os(2) 2.793(2), Os(1)–Os(4) 2.858(2), Os(1)–Os(3) 2.924(2), Os(2)–Au(1) 2.794(2), Os(2)–Os(4) 2.931(2), Os(2)–Os(3) 3.008(2), Os(3)–Au(3) 2.733(2), Os(3)–Au(4) 2.749(3), Os(3)–Au(2) 2.930(2), Os(3)–Os(4) 2.980(2), Os(4)–Au(1) 2.734(2), Os(4)–Au(2) 2.762(2), Au(1)–P(2) 2.311(8), Au(1)–Au(4) 2.870(2), Au(2)–P(3) 2.317(9), Au(2)–Au(3) 2.813(2), Au(2)–Au(4) 2.882(2), Au(3)–P(4) 2.264(9), Au(3)–Au(4) 2.769(2), Au(4)–P(1) 2.271(8); P(2)–Au(1)–Os(4) 162.4(2), P(2)–Au(1)–Os(2) 133.5(2), P(3)–Au(2)–Os(4) 153.3(2), P(3)–Au(2)–Os(3) 138.5(2), P(4)–Au(3)–Os(3) 162.0(3), P(1)–Au(4)–Os(3) 172.9(2), Au(3)–Au(2)–Au(4) 58.18(4), Au(4)–Au(3)–Au(2) 62.15(6), Au(3)–Au(4)–Au(2) 59.67(5).

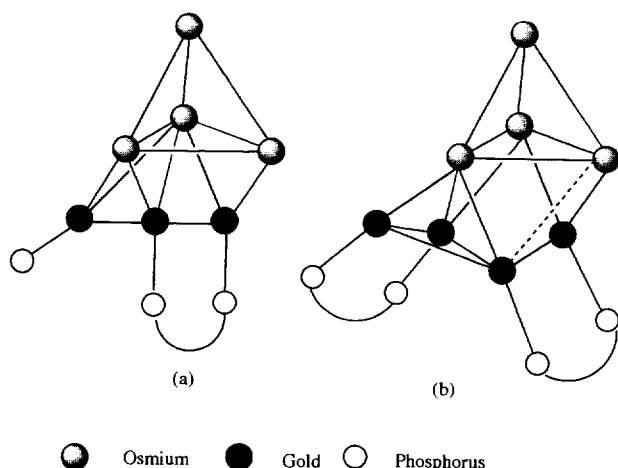


Fig. 2. Comparative metal core geometries for (a) $[\text{Ru}_4\text{H}(\text{CO})_{12}\{\text{Au}_2(\text{DPPM})\}\text{AuPPh}_3]$ and (b) $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

The crystal structure consists of discrete molecules of $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$ separated by normal van der Waals distances, and each asymmetric unit contains two disordered half molecules of CH_2Cl_2 . The molecular structure is shown in Fig. 1, the caption to which includes some important bond parameters. The metal core consists of an Os_4 tetrahedron, the $\text{Os}(2)\text{--Os}(4)$ edge of which is bridged by the $\text{Au}(1)$ atom, while the $\text{Os}(3)$ atom caps the gold triangle $\text{Au}(2), \text{Au}(3), \text{Au}(4)$; there is also a short contact between $\text{Os}(4)$ and $\text{Au}(2)$, so that the $\text{Au}(2)$ atom may be viewed as bridging the $\text{Os}(3)\text{--Os}(4)$ edge. The two hydrides were not located in the X-ray analysis, but were shown by potential energy calculations [12] to bridge the $\text{Os}(1)\text{--Os}(3)$ and $\text{Os}(2)\text{--Os}(3)$ edges. The carbonyl groups are all terminal and essentially linear, although the short contacts between Au atoms and carbonyl C atoms often observed in gold-containing mixed-metal carbonyl clusters [1] are present in this structure ($\text{Au}(1) \cdots \text{C}(43)$ 2.53(4) Å, $\text{Au}(2) \cdots \text{C}(43)$ 2.61(3) Å); these interactions are generally considered to be the result of ligand packing forces and do not indicate any form of bonding interaction. The bond parameters within the two DPPM ligands do not deviate significantly from the expected values.

The metal core geometry in $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$ is novel, and the coordination of the gold atoms to the Os_4 tetrahedron is much less symmetric than the arrangement observed in $[\text{Ru}_4\text{H}(\text{CO})_{12}(\text{AuPPh}_3)_3]$ [4]. It is more closely related

to that observed in $[\text{Ru}_4\text{H}(\text{CO})_{12}\{\text{Au}_2(\text{DPPM})\}\text{AuPPh}_3]$ [13], where the two Au atoms from the $\text{Au}_2(\text{DPPM})$ ligand cap a face of the Os_4 tetrahedron to form an Os_3Au_2 square-based pyramid, one face of which is then capped by the third Au atom (Fig. 2(a)). The core geometry of $[\text{Os}_4\text{H}_2(\text{CO})_{11}\{\text{Au}_2(\text{DPPM})\}_2]$ may then be viewed as derived from that of $[\text{Ru}_4\text{H}(\text{CO})_{12}\{\text{Au}_2(\text{DPPM})\}\text{AuPPh}_3]$ by the insertion of a third gold atom, $\text{Au}(2)$, into the Os_3Au_2 square-based pyramid to form a distorted Os_3Au_3 octahedron, which is then capped by $\text{Os}(1)$ on one face and $\text{Au}(3)$ on another (Fig. 2(b)). In terms of electron counting, it is simplest to consider that each Au atom acts as a one-electron donor, and to ignore tangential gold–gold interactions, then the molecule as a whole has 60 electrons, and is isoelectronic with $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$.

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