

Systematic formation of mixed-metal high-nuclearity clusters: the synthesis and characterisation of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ and $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$)

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Dedicated to Professor F. Albert Cotton in recognition of his seminal contribution to organometallic chemistry

Abstract

Reaction of the hexaosmium cluster $[\text{Os}_6(\text{CO})_{18}]$ with 1.1 equivalents of Me_3NO , in CH_2Cl_2 , in the presence of one equivalent of $[\text{Au}_2\text{dppm}]\text{Cl}_2$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), at room temperature, affords the new mixed-metal cluster $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**), in high yield. Subsequent reduction of **1** with Na–Hg amalgam, and subsequent treatment with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3][\text{PF}_6]$ (**2**) afforded two decanuclear clusters $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**3**) and $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**4**) in moderate yield. Cluster **3** loses CO under reflux in toluene to produce **4**. The new clusters have been fully characterised by IR, ¹H- and ³¹P-NMR spectroscopies, and mass spectrometry. The molecular and crystal structures of **1** and **3** have been established by single-crystal X-ray analyses. In **1**, the bicapped tetrahedral osmium core of $[\text{Os}_6(\text{CO})_{18}]$ is retained and the two Au atoms of the Au_2dppm group cap one Os_3 face in a $\mu_3\text{-}\eta^2$ bonding mode. In **3** the metal core consists of a capped square-based pyramidal arrangement of Os atoms that is capped over the square face by the Au_2dppm group. One Ru atom caps another face of the Os_5 square-based pyramid, and the second Ru atom caps the Ru atom, two Os atoms and an Au atom to form a trigonal bipyramidal arrangement. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ionic coupling; Osmium; Ruthenium; Gold; X-ray structure; Carbonyl cluster

1. Introduction

Since the pioneering work of Cotton [1], Chini et al. [2], Johnson and Lewis [3] and others [4] in the 1950s and 1960s, polynuclear organometallic chemistry has been a major research area in inorganic chemistry. Now, at the beginning of the 21st century, the subject continues to grow and develop into new areas [5]. Throughout this period one of the main challenges of the subject has been to prepare specific high-nuclearity clusters in good yield. Until recently, the most common synthetic routes used have involved thermolysis or pyrolysis techniques, and these methods favour a wide

product distribution, with no specific clusters being prepared in high yield [6]. However, during the last decade a number of research groups have developed a synthetic methodology that involves the ionic coupling between a pre-formed cluster anion and a mono- or dinuclear cationic metal complex. This method leads to a systematic increase in cluster nuclearity by one or two metal units [7,8], and since the coupling reactions generally occur at room temperature it is much easier to control the product distribution, thereby permitting specific clusters to be targeted. Using a range of precursor cationic species, it has been possible to prepare a range of novel high-nuclearity mixed-metal clusters [9].

The group in Cambridge has concentrated on developing the chemistry of coupling reactions between cluster anions and cationic species that contain either metal-arene or metal-cyclopentadienyl fragments such

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as $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)]^{2+}$, $[\text{Os}(\eta^6\text{-C}_6\text{H}_5\text{Me})]^{2+}$, $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)]^{2+}$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)]^+$ [10–14]. These groups either cap triangular faces of the cluster anions or bridge metal–metal edges of the metal cores. In a similar manner we have used mono- and digold species such as $[\text{AuPPh}_3]^+$ [15], $[\text{Au}_2\text{dppm}]^{2+}$ and $[\text{Au}_2\text{dppe}]^{2+}$ [16–19], to build high-nuclearity clusters that display a range of novel geometries [20]. We now report the combination of these two reactions leading to the formation of the novel triheterometallic clusters $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**3**) and $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**4**) (dppm = $\text{Ph}_2\text{PCH}_2\text{-PPh}_2$) by the coupling of the new $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]^{2-}$ dianion with two equivalents of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3]^+$.

2. Results and discussion

The reduction of the hexaosmium cluster $[\text{Os}_6(\text{CO})_{18}]$ with 1.1 equivalents of Me_3NO , in CH_2Cl_2 , at ambient temperature, afforded a reddish–brown anionic cluster [21], which, if immediately treated with one equivalent of $[\text{Au}_2\text{dppm}]\text{Cl}_2$, in CH_2Cl_2 , at room temperature, in the presence of $\text{Ti}[\text{PF}_6]$ (which acts as a halide abstractor), gives an 80% yield of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) after chromatographic work-up. This cluster was initially characterised by spectroscopic and mass spectrometric techniques (Table 1). The IR spectrum in the carbonyl region indicated the presence of terminal carbonyls, and the band pattern was reminiscent of that observed for $[\text{Os}_6(\text{CO})_{18}]$ [22], suggesting that the bicapped tetrahedral osmium core framework had been retained. The $^1\text{H-NMR}$ spectrum confirmed the presence of the dppm ligand. The $^{31}\text{P-NMR}$ spectrum displayed only one signal, indicating that the two P nuclei were in equivalent environments or that a fluxional process, which made the two nuclei equivalent on the NMR timescale, was occurring. The mass spectrum displayed a molecular ion that was consistent with the addition of an $[\text{Au}_2\text{dppm}]^{2+}$ ligand to the

$[\text{Os}_6(\text{CO})_{17}]^{2-}$ dianion to form $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**).

The molecular structure of **1** was established and the crystal structure determined by means of a single-crystal X-ray diffraction experiment. The molecular structure of **1** is illustrated in Fig. 1, while the $\text{Os}_6\text{Au}_2\text{P}_2$ core geometry is presented in Fig. 2. Selected bond parameters are listed in Table 2. In **1** the bicapped tetrahedral Os_6 core of the parent $[\text{Os}_6(\text{CO})_{18}]$ [22] is retained and the ‘ $\text{Au}_2(\text{dppm})$ ’ fragment $\mu_3\text{:}\eta^2$ caps a triangular face of the osmium core to form an Os_3Au_2 square-based pyramid. This coordination mode has been previously reported in the structures of $[\text{Ru}_4\text{H}_4(\text{CO})_{12}(\text{Au}_2\text{dppm})]$ [23] and $[\text{Ru}_4\text{H}_2(\text{CO})_{12}(\text{Au}_2(\text{Ph}_2\text{AsCH}_2\text{AsPPh}_2))]$ [24]. All the carbonyl ligands in the cluster are terminal and essentially linear [mean Os-C-O 175°]. Each Os atom is coordinated to three carbonyls, except Os(3), which is linked to only two. There are, however, two short $\text{Au}\cdots\text{C}$ contacts ($\text{Au}(1)\cdots\text{C}(302)$ 2.68(3) Å and $\text{Au}(2)\cdots\text{C}(403)$ 2.58(3) Å) between the Au atoms and the carbonyl ligands. This is a common feature in mixed osmium and ruthenium clusters that contain coinage metals [25]. It is not entirely clear whether these short $\text{Au}\cdots\text{C}$ contacts represent some degree of long-range interaction [25] or whether they are the result of steric effects in the solid state [26].

In terms of electron counting, if each of the Au atoms in the Au_2dppm group donates one electron to the cluster, then as a whole the cluster is an 84 e^- system, which is consistent with the observed bicapped tetrahedral osmium core geometry, similar to that observed in $[\text{Os}_6(\text{CO})_{18}]$ [22]. However, there is some distortion of the metal core that may reflect the introduction of the heteroatoms. The longest Os–Os edge ($\text{Os}(3)\text{–Os}(4)$, 2.9399(13) Å) is in the central tetrahedron and is bridged by the Au(2) atom. The second edge ($\text{Os}(1)\text{–Os}(3)$, 2.7193(14) Å) that is bridged by Au(1) is the shortest Os–Os distance in the structure. The third bridged edge ($\text{Os}(1)\text{–Os}(4)$, 2.8843(14) Å) is intermediate in length. The Os–Au distances also show significant asymmetry, with the two longer distances being

Table 1
Spectroscopic data for $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**), $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**3**) and $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**4**)

Compound	IR $\nu(\text{CO})$ (cm^{-1}) ^a	$^1\text{H-NMR}$ δ (ppm) ^b	$^{31}\text{P-NMR}$ δ (ppm) ^c	Mass spectroscopy m/z ^d
1	2083(m), 2053(s), 2039(vs), 2015(vs), 1981(vw)	7.30–7.77(m)	–86.01(s)	2407 (2406)
3	2067(s), 2020(vs), 2006(s), 1961(m, br), 1788(m)	7.22–7.67(m), 4.78(s), 5.07(s)	–58.23(d), –67.88(d), $J_{\text{PP}} = 137.7$ Hz	2738 (2738)
4	2060(s), 2036(s), 2006(vs), 1984(s, br), 1971(m), 1928(w, br), 1790(m, br)	7.25–7.76(m), 5.16(s), 5.42(s)	–86.51(d), –80.87(d), $J_{\text{PP}} = 65.5$ Hz	2710 (2710)

^a In CH_2Cl_2 .

^b In CDCl_3 .

^c Ref. TMP.

^d Based on ^{192}Os , calculated values in parentheses.

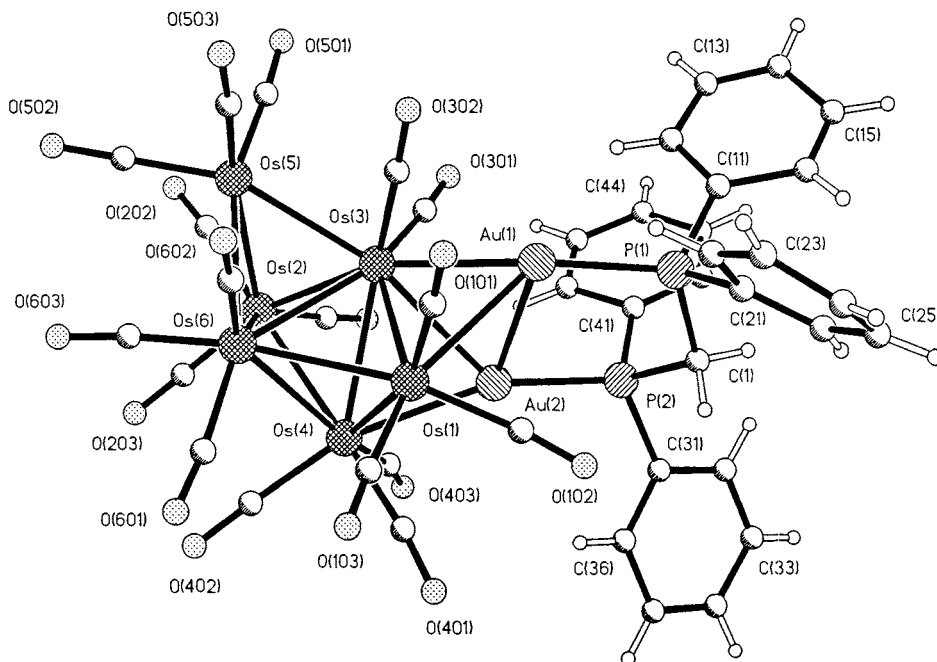


Fig. 1. The molecular structure of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) showing the atom numbering scheme adopted.

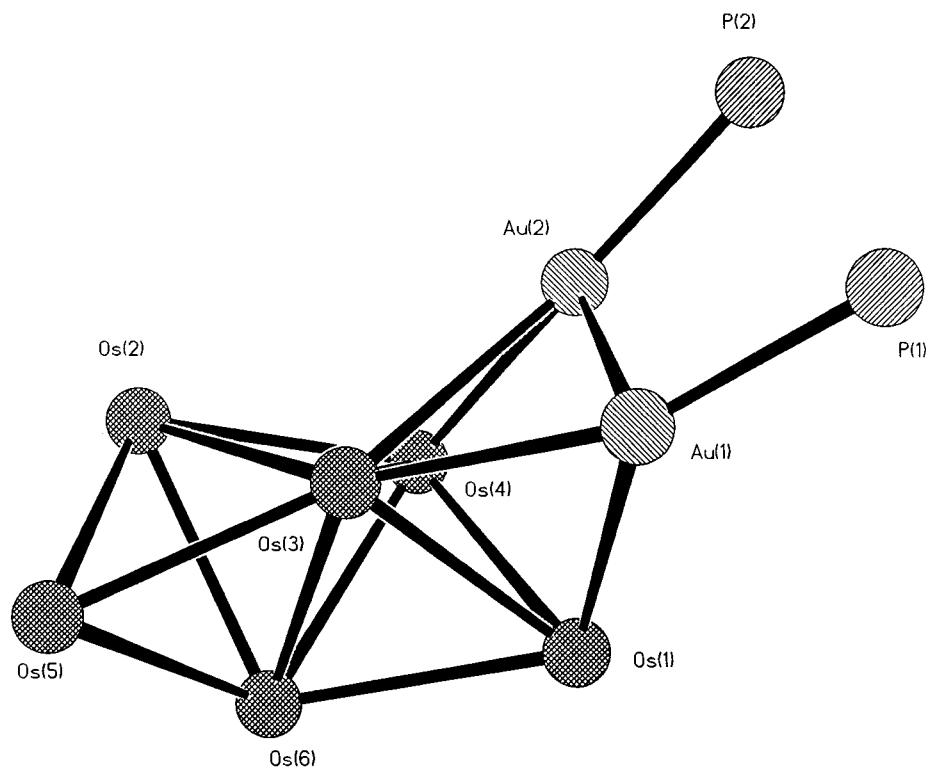


Fig. 2. The core geometry in $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**).

$\text{Au}(1)\text{--Os}(1)$ (2.9781(14) Å) and $\text{Au}(2)\text{--Os}(3)$ (2.9415(13) Å). The $\text{Au}\cdots\text{Au}$ separation is 2.7587(14) Å, but this may not be indicative of a direct metal–metal bond since the distance is a function of the ligand bite.

It has been established that reduction of high-nuclearity osmium–gold neutral clusters with either Na–Hg

amalgam or K– Ph_2CO leads to the formation of mixed-metal anions that are susceptible to attack by metal-containing cationic species [20]. The reactivity of **1** follows the expected path, and reduction with Na–Hg amalgam, in tetrahydrofuran (THF), at room temperature results in the formation of anionic species that

were not isolated. The immediate in situ reaction of the anion with an excess of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3][\text{PF}_6]$ (**2**), acting as the source of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)]^+$, affords two neutral deca-metal clusters $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**3**) and $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**4**) after purification by thin-layer chromatography (TLC).

Clusters **3** and **4** were initially characterised by IR, ^1H - and ^{31}P -NMR spectroscopies and also by mass spectrometry (Table 1). Both clusters showed medium-intensity IR bands around 1790 cm^{-1} , suggesting the presence of capping carbonyl groups, in addition to a number of bands in the region $2070\text{--}1920\text{ cm}^{-1}$ that are readily assigned to terminal carbonyl ligands. Similar signals are observed for the μ_3 -carbonyl groups in $[\text{Os}_5\text{Ru}_2(\text{CO})_9(\mu_3\text{-CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ [27]. Two sharp singlets at δ 4.78 and δ 5.07 in the ^1H -NMR spectrum of **3** can be assigned to two η^5 -coordinated cyclopentadienyl ligands in different chemical environments. The chemical shifts are comparable to those observed for the two non-equivalent cyclopentadienyl groups in $[\text{Os}_5\text{Ru}_2(\text{CO})_9(\mu_3\text{-CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ [27]. Similar chemical shift values are also observed in the ^1H -NMR spectrum of **4**, for which two singlets at δ 5.16 and δ 5.42 are observed, and again, these are assigned to non-equivalent η^5 -cyclopentadienyl rings. The ^{31}P -NMR spectrum of **3** displays two doublets at -67.88 and -58.2 ppm, with a large coupling constant of 137.7 Hz, and these signals are assigned to two non-equivalent phosphorus nuclei bonded to two chemically different gold atoms of the Au_2dppm ligand. Again, in **4**, a similar pattern of signals is observed, with two doublets at -86.51 and -80.87 ppm with a coupling constant of 65.5 Hz, and similar assignments can be made. The observed coupling constant in **4** is similar to the value of 68.6 Hz observed in $[\text{Os}_7(\text{CO})_{20}(\text{Au}_2\text{dppm})]$ and lower than the value of 83.3 Hz reported for

$[\text{Os}_7\text{C}(\text{CO})_{19}(\text{Au}_2\text{dppm})]$ [19]. The mass spectra of the two clusters gave molecular ion peaks that are consistent with the proposed formulae for **3** and **4**.

From the spectroscopic data, cluster **4** can be viewed as derived from **3** by the loss of a carbonyl group. This has been proven experimentally, since **4** is generated from **3** if the latter cluster is heated in toluene, under reflux, for 8 h. This is consistent with a reduction in the formal electron count of two electrons, from 110 e^- in **3** (if the Au_2dppm ligand is considered to be a 2 e^- donor ligand) to 108 e^- in **4**. A loss of electrons is often accompanied by a metal framework rearrangement [20], and this may be the case here since the symmetry of the two molecules from the IR spectral data is different. The decarbonylation reaction is irreversible.

In order to establish the molecular structures of the two clusters, attempts were made to grow single crystals suitable for X-ray analyses. Unfortunately only suitable crystals could be obtained for **3**. These were obtained by slow diffusion of hexane into a dichloromethane solution of the compound, and a full structure determination was carried out on this cluster. The molecular structure of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**3**) is shown in Fig. 3, while a diagram of the metal core arrangement is presented in Fig. 4. Selected bond lengths and angles are presented in Table 3.

The crystal structure of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ (**3**) consists of discrete molecular units with the shortest intermolecular contacts involving carbonyl oxygens on adjacent molecules. The osmium metal core within the molecular structure of **3** may be described as a capped square-pyramid, where the triangular face opposite the Os cap is capped by a ruthenium atom $\{\text{Ru}(1)\}$, and this Ru atom and the two adjacent Os atoms $\{\text{Os}(1)$ and $\text{Os}(2)\}$ are capped by the second ruthenium atom $\{\text{Ru}(2)\}$. This generates a trigonal bipyramid defined by Ru(1), Ru(2), Os(1), Os(2) and Os(3) (Fig. 4), which is further fused with the capped square-pyramidal osmium core. The two Au atoms of the Au_2dppm ligand asymmetrically bridge opposite edges of the square base of the osmium square-based pyramid, with Au(1) also coordinating to Ru(2), thus adopting a μ_3 -bonding mode. The arrangement of a digold chelating ligand spanning a square face of the cluster has been previously observed in several high-nuclearity clusters of osmium and ruthenium [20]. The $\text{Au}\cdots\text{Au}$ separation of $2.874(2)\text{ \AA}$ in **3** is significantly longer than the value of $2.811(1)\text{ \AA}$ found in the closely related $[\text{Os}_6(\text{CO})_{18}(\text{Au}_2\text{dppm})]$, but in neither case is there thought to be significant direct Au–Au bonding, the distance being a function of the ligand bite [28]. The shortest Au–Os contact is $2.715(2)\text{ \AA}$ between Au(2) and Os(5) and the longest is $2.846(2)\text{ \AA}$ between Au(1) and Os(1). These values compare with the average Au–Os distance in the cluster of 2.825 \AA . The single Au–Ru contact of $2.877(3)\text{ \AA}$ is significantly

Table 2
Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**)

Bond lengths			
Os(1)–Os(3)	2.7193(14)	Os(1)–Os(4)	2.8843(14)
Os(1)–Os(6)	2.9352(14)	Os(1)–Au(1)	2.9781(14)
Os(1)–Au(2)	3.2801(14)	Os(2)–Os(3)	2.7465(13)
Os(2)–Os(4)	2.8041(13)	Os(2)–Os(5)	2.7697(14)
Os(2)–Os(6)	2.8428(14)	Os(3)–Au(1)	2.7118(13)
Os(3)–Os(4)	2.9399(13)	Os(3)–Os(5)	2.7294(13)
Os(3)–Os(6)	2.7896(13)	Os(3)–Au(2)	2.9415(13)
Os(4)–Au(2)	2.7247(13)	Os(4)–Os(6)	2.8127(13)
Os(5)–Os(6)	2.8590(13)	Au(1)–Au(2)	2.7587(14)
Au(1)–P(1)	2.264(6)	Au(2)–P(2)	2.300(6)
P(1)–C(1)	1.86(2)	P(2)–C(1)	1.85(2)
Bond angles			
C(1)–P(1)–Au(1)	108.0(8)	C(1)–P(2)–Au(2)	113.0(8)
P(1)–C(1)–P(2)	114.4(12)		

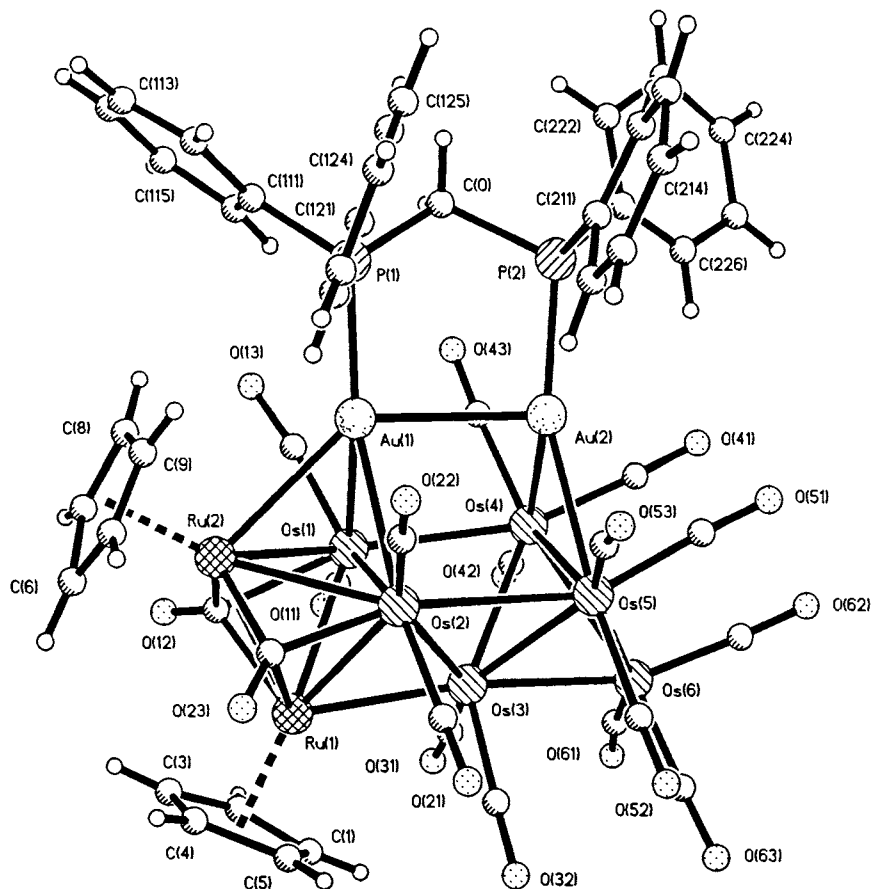


Fig. 3. The molecular structure of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (3) showing the atom numbering scheme adopted.

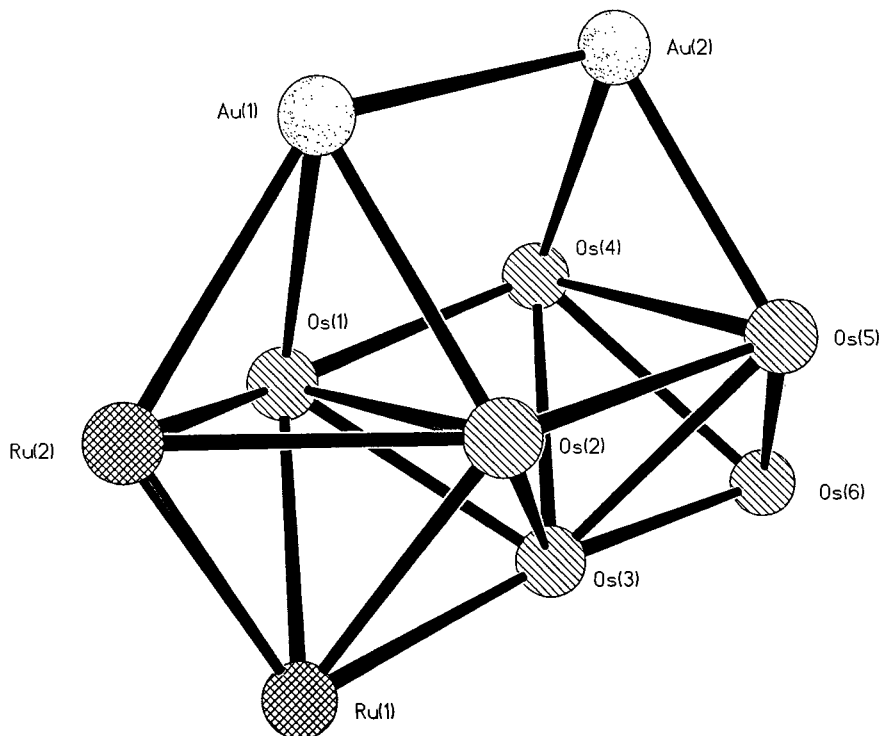


Fig. 4. The metal core geometry in $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (3).

longer. The Os–Os contacts within the core lie in the range 2.734(2)–2.953(2) Å as has been found previously in other high-nuclearity osmium cluster systems [8,9]. The two ruthenium atoms are separated by a relatively short metal–metal distance of 2.730(3) Å, but which is longer than the related Ru–Ru distance of 2.691(3) Å in $[\text{Os}_5\text{Ru}_2(\text{CO})_9(\mu_3\text{-CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ [27]. As in the Os_5Ru_2 cluster, each Ru in **3** is bonded to a η^5 -terminally bonded cyclopentadienyl ligand and to two μ_3 -carbonyls; these two carbonyls cap the Ru(1), Ru(2), Os(1) and Ru(1), Ru(2), Os(2) faces. The presence of the capping carbonyls is consistent with the view that the ‘Ru($\eta^5\text{-C}_5\text{H}_5$)’ centres are electron rich, and that the capping carbonyls help to distribute the ‘excess’ electron density over the cluster framework. In terms of metal connectivity, each ruthenium atom is coordinated to four other metals. All the other carbonyls in the cluster are terminally coordinated, three to each Os atom except Os(3) which is bonded to only two terminal carbonyl groups.

In the structure of **3** there has been a change in metal framework geometry compared with that in the parent pre-reduced cluster $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) where the osmium framework adopts the bicapped tetrahedral core, but it is similar to the capped square-based pyramidal arrangement found in $[\text{Os}_6(\text{CO})_{18}(\text{Au}_2\text{dppm})]$ [28]. Thus the addition of a ‘ $\{\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2\}$ ’ fragment is equivalent, from the structural viewpoint, to adding a carbonyl ligand, so that simplistically, the ‘ $\{\text{Ru}_2(\eta^5\text{-C}_5\text{H}_5)_2\}$ ’ fragment can be considered as a $2 e^-$ donor.

Table 3
Selected bond lengths (Å) and angles (°) for $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**3**)

Bond lengths			
Os(1)–Os(3)	2.737(2)	Os(1)–Ru(1)	2.750(3)
Os(1)–Ru(2)	2.785(3)	Os(1)–Os(2)	2.828(2)
Os(1)–Au(1)	2.845(2)	Os(1)–Os(4)	2.897(2)
Os(2)–Os(3)	2.734(2)	Os(2)–Ru(1)	2.768(3)
Os(2)–Au(1)	2.800(2)	Os(2)–Ru(2)	2.835(3)
Os(2)–Os(5)	2.943(2)	Os(3)–Ru(1)	2.736(3)
Os(3)–Os(6)	2.744(2)	Os(3)–Os(5)	2.774(2)
Os(3)–Os(4)	2.784(2)	Os(4)–Au(2)	2.828(2)
Os(4)–Os(6)	2.857(2)	Os(4)–Os(5)	2.953(2)
Os(5)–Au(2)	2.715(2)	Os(5)–Os(6)	2.873(2)
Ru(1)–Ru(2)	2.730(3)	Ru(2)–Au(1)	2.877(3)
Au(1)–P(1)	2.316(8)	Au(1)–Au(2)	2.874(2)
Au(2)–P(2)	2.302(8)	P(1)–C(0)	1.78(3)
P(2)–C(0)	1.89(3)	Os(1)–C(12)	2.22(4)
Ru(1)–C(12)	2.16(4)	Ru(2)–C(12)	2.14(4)
Os(2)–C(23)	2.03(3)	Ru(1)–C(23)	2.38(4)
Ru(2)–C(23)	1.98(3)		
Bond angles			
C(0)–P(1)–Au(1)	110.1(11)	C(0)–P(2)–Au(2)	110.4(10)
P(1)–C(0)–P(2)	114(2)	Ru(2)–C(12)–Ru(1)	78.7(13)
Ru(2)–C(12)–Os(1)	79.2(13)	Ru(1)–C(12)–Os(1)	77.7(12)
Ru(2)–C(23)–Os(2)	90.1(14)	Ru(2)–C(23)–Ru(1)	76.9(12)
Os(2)–C(23)–Ru(1)	77.2(11)		

The structure of **3** may be rationalised successfully in terms of the Mingos Condensed Polyhedral counting scheme [29], as a $110 e^-$ cluster, as the condensation of an Os_6 capped square-based pyramid ($86 e^-$) with an Os_3Ru_2 trigonal bipyramid ($72 e^-$) less $48 e^-$ for the common triangular face; the (Au_2dppm) fragment is taken to be a $2 e^-$ donor in this scheme. A consequence of the reasoning put forward in these last two paragraphs is that the metal framework structure of $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**4**) must have a higher level of condensation (more metal–metal contacts) than **3** since it has two electrons fewer.

3. Experimental

All reactions were performed under an atmosphere of purified dinitrogen using standard Schlenk and vacuum line techniques [30]. Subsequent work-up of products was carried out without precautions to exclude air. Solvents used were distilled from appropriate drying agents under dinitrogen. Routine separations of products were performed by thin-layer chromatography using commercially prepared glass plates, precoated to 0.25 mm thickness with E. Merck Kieselgel 60 PF₂₅₄, or using laboratory prepared glass plates coated to 1 mm thickness with E. Merck Kieselgel 60 PF₂₅₄.

IR spectra were recorded as dichloromethane solutions on a Perkin–Elmer 1710 Fourier Transform spectrometer. ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker AM-400 spectrometer and were referenced to external tetramethylsilane and trimethylphosphite, respectively. Mass spectral data were obtained by negative ion FAB mass spectrometry on a Kratos MS902 mass spectrometer.

The compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3][\text{PF}_6]$ [31] and $[\text{Au}_2(\text{dppm})\text{Cl}_2]$ [32] were prepared by literature methods. All other chemicals were used as purchased without further purification.

3.1. Preparation of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**)

To a solution of $[\text{Os}_6(\text{CO})_{18}]$ (50 mg, 3.04×10^{-5} mol) in CH_2Cl_2 were added 1.1 equivalents Me_3NO (2.28 mg) and the reaction mixture was stirred for 3 min under an atmosphere of N_2 at room temperature (r.t.). The reaction mixture was passed through Celite to remove the excess amine oxide and then reacted with one equivalent of $[\text{Au}_2\text{dppm}]\text{Cl}_2$ (25.8 mg) and an excess of $\text{Ti}[\text{PF}_6]$ (26.5 mg). After stirring for 30 min the solvent was removed in vacuo and the residue was dissolved in a small quantity of CH_2Cl_2 and purified by TLC using 60:40 CH_2Cl_2 –hexane as eluent. The reddish–brown product was isolated as the main product in 70–80% yield. Anal. Calc. for $\text{Os}_6\text{Au}_2\text{P}_2\text{O}_{17}\text{C}_{42}\text{H}_{22}$ (**1**): C, 21.05; H, 0.93. Found: C, 21.18; H, 0.92%.

Table 4

Crystal data and refinement parameters for $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) and $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**3**)

	1	3
Empirical formula	$\text{C}_{42}\text{H}_{22}\text{Au}_2\text{O}_{17}\text{Os}_6\text{P}_2$	$\text{C}_{52}\text{H}_{32}\text{Au}_2\text{O}_{17}\text{Os}_6\text{P}_2\text{Ru}_2$
Formula weight	2395.67	2727.99
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pna</i> ₂₁
Unit cell dimensions		
<i>a</i> (Å)	20.124(4)	25.573(7)
<i>b</i> (Å)	18.264(4)	12.184(4)
<i>c</i> (Å)	26.629(5)	17.993(5)
Volume (Å ³)	9787(3)	5606(3)
<i>Z</i>	8	4
<i>D</i> _{calc} (Mg m ⁻³)	3.252	3.232
Absorption coefficient (mm ⁻¹)	21.617	19.398
<i>F</i> (000)	8432	4848
Crystal size (mm)	0.35 × 0.35 × 0.29	0.22 × 0.21 × 0.10
θ Range for data collection (°)	2.54–22.50	2.57–22.50
Limiting indices	$-21 \leq h \leq 0,$ $0 \leq k \leq 19,$ $0 \leq l \leq 28$	$-27 \leq h \leq 27,$ $-13 \leq k \leq 1,$ $0 \leq l \leq 19$
Max and min transmission	1.000, 0.270	1.000, 0.625
Reflections collected	6384	8206
Independent reflections	6384	3802 (<i>R</i> _{int} = 0.147)
Data/restraints/parameters	6384/0/327	3799/190/384
Goodness-of-fit on <i>F</i> ²	1.061	1.074
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0562, <i>wR</i> ₂ = 0.1508	<i>R</i> ₁ = 0.0409, <i>wR</i> ₂ = 0.0721
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0740, <i>wR</i> ₂ = 0.1628	<i>R</i> ₁ = 0.0745, <i>wR</i> ₂ = 0.0824
Absolute structure parameter	–	–0.005(14)
Largest difference peak and hole (e Å ⁻³)	3.575 and –2.626	1.518 and –1.570

3.2. Preparation of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**3**) and $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**4**)

$[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) (50 mg, 2.08×10^{-5} mol) was reduced by Na–Hg amalgam by dissolving the cluster in 20 cm³ of dry deoxygenated THF and transferring the resulting solution to a flask containing freshly prepared amalgam, with the help of a cannula. The reaction mixture was stirred for a few minutes. The stirring was stopped when the reduction had occurred, as monitored by IR spectroscopy. The solution was passed through a Celite pad using the cannula–septum technique to remove the amalgam. The resulting solution was treated with an excess of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3][\text{PF}_6]$ (27 mg, 6.24×10^{-5} mol). After removal of solvent, the solid residue was chromatographed by TLC using 60:40 CH₂Cl₂–hexane as eluent. Two products, $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**3**) and $[\text{Os}_6(\text{CO})_{16}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**4**), were obtained in 30 and 10% yield, respectively. Anal. Calc. for **3**, Os₆Au₂Ru₂P₂O₁₇C₅₂H₃₂: C, 23.50; H, 1.43; P, 2.24. Found: C, 23.21; H, 1.60; P, 1.96%.

3.3. Crystal-structure determinations of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) and $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**3**)

Red crystals of $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})]$ (**1**) and $[\text{Os}_6(\text{CO})_{17}(\text{Au}_2\text{dppm})\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\}]$ (**3**) were obtained by recrystallisation from dichloromethane–hexane at –20°C. Suitable crystals were mounted on glass fibres with epoxy resin and transferred to a Rigaku AFC7R diffractometer. Intensity data were recorded using graphite monochromated Mo–K_α radiation and an ω–2θ technique in the range 5 ≤ 2θ ≤ 45°. Absorption corrections were applied using a semi-empirical method based on ψ scans. Crystal data, data collection parameters, and details of structure solution and refinement for the two structures are listed in Table 4. The structures were solved by direct methods (SHELXTL-PLUS [33]) and refined by full-matrix least-squares on *F*² (SHELXL-97 [34]). The Os, Au and P atoms for **1** and the Os, Au, Ru and P atoms for **3** were assigned anisotropic displacement parameters, while the remaining non-hydrogen atoms in each structure were refined with isotropic displacement parameters. For **3**, weak restraints were placed on the phenyl rings that required them to be flat. Hydrogen atoms in both structures were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement for **1** a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.0991P)^2 + 128.00P]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced. The final converged *R* factors for 327 refined parameters were *R*₁ = 0.056 (for 5071 reflections with *I* > 2σ(*I*)) and *wR*₂ = 0.163 (for all data), Goodness-of-fit = 1.061. In the final cycles of refinement for **3** a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 32.00P]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced. The final converged *R* factors for 384 refined parameters were *R*₁ = 0.041 (for 3041 reflections with *I* > 2σ(*I*)) and *wR*₂ = 0.082 (for all data), Goodness-of-fit = 1.074. The function minimised was Σw(*F*_o² – *F*_c²).

4. Supplementary material

Crystallographic data for compounds **1** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 136781 and 135276, respectively. Copies of this information may be obtained free of charge from, The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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