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Reactivity of the mixed-metal cluster $[Os_6(CO)_{17}(Au_2dppm)]$ towards gold electrophiles (dppm = $Ph_2PCH_2PPh_2$)

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Dedicated to Professor Sheldon G. Shore in recognition of his outstanding contribution to organometallic chemistry.

Abstract

Reduction of the mixed-metal octanuclear cluster $[Os_6(CO)_{17}(Au_2dppm)]$ (**1**) with Na–Hg amalgam and subsequent reaction with one equivalent of $[Au_2dppm][NO_3]$ affords two isomers of the neutral decanuclear cluster $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2a**, **2b**). In a similar reaction between the reduced form of **1** with two equivalents of $[AuPPh_3][NO_3]$ gives two isomers of the related cluster $[Os_6(CO)_{17}(Au_2dppm_2)(AuPPh_3)_2]$ (**3a**, **3b**). All the new clusters have been characterised by IR and NMR spectroscopy and FAB mass spectrometry. The molecular and crystal structure of **2a** has been established by a single-crystal X-ray structure. In **2a** the six Os atoms define an octahedron, in contrast to the bicapped tetrahedral osmium core previously observed for **1**. Two of the Au atoms in **2a** cap adjacent triangular faces of the Os_6 octahedron while the third spans an open $OsAu_2$ triangle, and the fourth caps a closed $OsAu_2$ triangle. Overall the decametal core may be viewed as an octahedron fused with a capped square based pyramid. © 2000 Elsevier Science B.V. All rights reserved.

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

1. Introduction

There is current interest in developing more 'rational' methods for synthesising higher nuclearity transition metal clusters because of their potential applications in nanotechnology [1]. One method that has proved successful for generating clusters that contain up to 30 metal atoms is that of ionic coupling between lower nuclearity cluster anions and mono- or dimetallic cationic fragments [2]. A key step in this process is the generation of the reactive cluster anion, and Shore was among the first to develop a systematic method of preparing these anions from hydrido carbonyl clusters by stepwise deprotonation using potassium hydride in tetrahydrofuran [3]. Since that time it has been shown that potassium/benzophenone or zinc/mercury amalgam can be used to reduce neutral clusters to form anions with the loss of carbonyl groups [4]. We have used this methodology to prepare a series of higher nuclearity mixed-metal clusters by treating reduced osmium cluster anions with a range of cationic fragments including $[Ru(\eta^6\text{-}C_6H_6)]^{2+}$ [5,6], $[Ru(\eta^5\text{-}C_5H_5)]^+$ [7], $[Rh(\eta^5\text{-}C_5Me_5)]^{2+}$ [8], $[AuPR_3]^+$ (R = Ph, Cy) [9], and $[Au_2dppm]^{2+}$ [9,10]. In this paper we report the formation of the novel decanuclear clusters $[Os_6(CO)_{17}(Au_2dppm)_2]$ and $[Os_6(CO)_{17}(Au_2dppm_2)(AuPPh_3)_2]$ that have been prepared by the reduction of $[Os_6(CO)_{17}(Au_2dppm)]$, presumably to form the dianion '$[Os_6(CO)_{17}(Au_2dppm)]^{2-}$', and the subsequent reaction with $[Au_2dppm]^{2+}$ and $[AuPPh_3]^+$, respectively.

2. Results and discussion

The reduction of the mixed-metal cluster $[Os_6(CO)_{17}(Au_2dppm)]$ [11] (**1**) (dppm = $Ph_2PCH_2PPh_2$)

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with an excess of freshly prepared Na–Hg amalgam, in tetrahydrofuran, gives the dianion $[Os_6(CO)_{17}(Au_2dppm)]^{2-}$. This anion was not isolated or fully characterised because of its air-sensitive nature, but was treated in situ with one equivalent of $[Au_2dppm][NO_3]$, in dichloromethane, at room temperature. After work-up and purification by thin layer chromatography using dichloromethane:hexane (60:40) as eluent a yellow (**2a**) and a pink (**2b**) product were isolated in 50 and 30% yields, respectively. The products were characterised initially by IR, ^1H- and ^{31}P-NMR spectroscopies and by negative ion FAB mass spectrometry (Table 1), and were subsequently formulated as two isomers of the neutral decametal cluster $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2**). The ^{31}P-NMR spectrum of the major isomer **2a** exhibited two equal intensity doublets at δ -66.98 and -112.21 ppm with a coupling constant of $J_{PP} = 69.8$ Hz, that can be attributed to two different phosphorus environments, indicating that not all the gold atoms occupy equivalent environments. The signal at δ -112.21 ppm is at quite high field for cluster bound gold phosphine phosphorus nuclei but such high field signals have been reported previously in $[Os_4H_4(CO)_{11}(Au_2dppm)]$ [10], $[Os_4H_2(CO)_{11}(Au_2dppm)_2]$ [12] and $[Os_7C(CO)_{19}(Au_2dppm)]$ [13]. No clear signals were observed in the room temperature ^{31}P-NMR spectrum of **2b**, a feature that may be consistent with a fluxional process occurring at this temperature. A low temperature ^{31}P-NMR investigation was hampered by the low solubility of the compound. The FAB mass spectra of **2a** and **2b** did not show the molecular ion in either case, instead a peak at m/z of 3156 is observed, that corresponds to the loss of one carbonyl group from the expected formulation. The IR spectrum of **2a** displays six bands in the terminal $\nu(CO)$ stretching region while that of **2b** shows only four bands, but the band pattern is somewhat similar.

In order to establish the exact formulation and structure of the two isomers attempts were made to grow single crystals of the two products. Suitable yellow, single crystals of **2a** were obtained by recrystallisation from dichloromethane–hexane at −20°C, but the pink cluster **2b** decomposed during all attempts at recrystallisation.

The overall molecular structure of $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2a**) is illustrated in Fig. 1 while the metal core geometry is shown in Fig. 2. Selected bond parameters are listed in Table 2. The osmium metal framework can be described as an octahedron two adjacent faces of which are capped asymmetrically by two gold atoms, Au(1) and Au(4), one from each of the two $[Au_2dppm]^{2+}$ units. One of the remaining gold atoms, Au(3), caps the *open* triangle, Au(1), Os(1), Au(4), while the second, Au(2), caps the *closed* triangle, Au(1), Os(1), Au(3). Overall, the framework may be viewed as an octahedron fused with a capped square based pyramid. The key point to note is perhaps that there has been a significant structural change in the osmium core from the bicapped tetrahedral arrangement in the precursor complex $[Os_6(CO)_{17}(Au_2dppm)]$ (**1**) [11] to the octahedral arrangement in **2a**. This change is consistent with the formal addition of two electrons, with the inclusion of the second $[Au_2dppm]^{2+}$ unit, as the electron count for **1** is 84 electrons and that for **2a** is 86 electrons, with each digold unit acting as a two-electron donor.

The coordination of the four gold atoms to the osmium cluster core in **2a** is somewhat similar to that observed for the two $[Au_2dppm]^{2+}$ units in $[Os_4H_2(CO)_{11}(Au_2dppm)_2]$ [12]. In the latter cluster two Au atoms, one from each $[Au_2dppm]^{2+}$ unit, are μ_2-bound to the osmium core rather than μ_3-bound, and the other two Au atoms are coordinated to the same Os atom of the tetrahedron so that with the Au–Au bonding present a triangle of Au atoms is generated, similar to the Au(1), Au(2), Au(3) triangle observed in **2a**. Within the cluster **2a** the Au–Au distances lie in the range 2.677(3)–3.188(3) Å, with a mean of 2.851 Å. A similar range has been found in a variety of homonu-

Table 1
Spectroscopic data for $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2a**, **2b**) and $[Os_6(CO)_{17}(Au_2dppm)(AuPPh_3)_2]$ (**3a**, **3b**)

Compound	IR $\nu(CO)$ (cm^{-1}) [a]	^1H-NMR [b] δ (ppm)	^{31}P-NMR [c] δ (ppm)	Mass spectrometry (m/z) [d]
2a	2063(m), 2027(vs), 2012(vs), 1973(w), 1946(w, br), 1913(w)	7.32–7.67(m)	-66.98(d), -112.2(d), $J_{PP} = 69.8$ Hz	3156 (3184)
2b	2064(s), 2038(vs), 2004(s), 1965(m)	7.23–7.71(m)	–	3156 (3184)
3a	2063(s), 2027(vs), 20139(s), 1974(w, br), 1915(w)	7.27–7.75(m)	–	3324 (3324)
3b	2068(m), 2026(vs), 1992(w)	7.31–7.78(m)	–	3324 (3324)

[a] In dichloromethane.

[b] In $CDCl_3$.

[c] Referenced to trimethylphosphite.

[d] Based on ^{192}Os, calculated values in parenthesis.

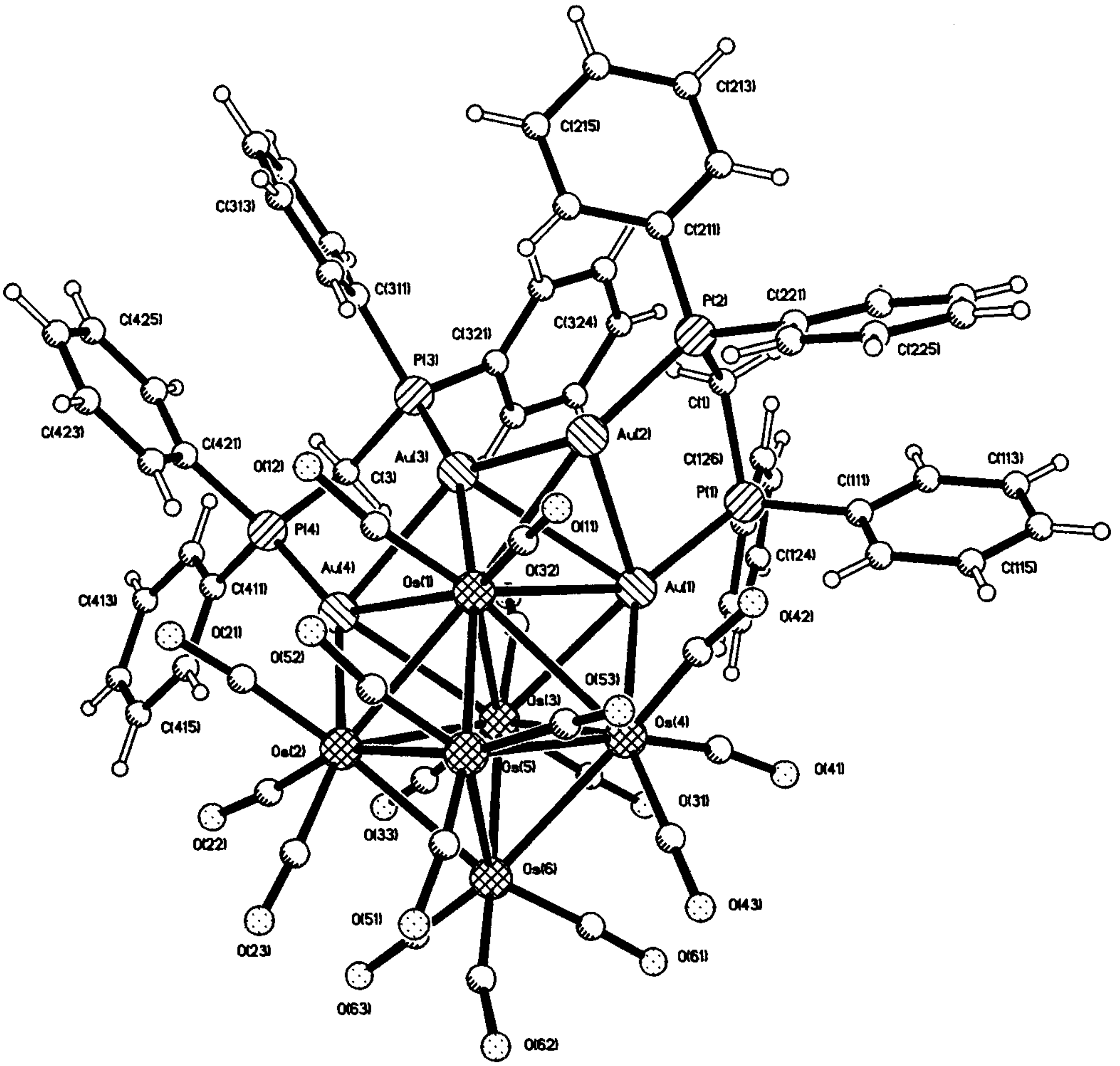


Fig. 1. The molecular structure of $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2a**) showing the atom numbering scheme adopted.

clear poly-gold clusters [14]. The shortest Au–Au distance of 2.677(3) Å is between Au(2) and Au(3), two Au atoms from different $[Au_2dppm]^{2+}$ ligands, a feature that is consistent with a direct bonding interaction and is not dependent on the 'bite' of the chelating phosphine ligand. The two Au–Au distances within the two bidentate ligands are 2.770(2) and 2.767(3) Å are marginally longer than the value of 2.759(1) Å found in **1** [11]. The Au–Os distances lie in the range 2.744(2)–3.095(3) Å with an average of 2.869 Å. The capping gold atoms Au(1) and Au(4) make the longer contacts with Os(1), the metal that has the highest metal–metal connectivity, with four Os–Os and four Os–Au contacts. The Os–Os edge lengths average 2.932 Å, a distance that is ca. 0.07 Å longer than that found in the octahedral cluster $[Os_6(CO)_{18}]^{2-}$ [15], but this increase in length may be attributed to the expansion of the two triangular faces Os(1),Os(2),Os(3) and Os(1),Os(3),Os(4) that are capped by the two gold atoms. These five edges have an average length of 3.003 Å.

All the carbonyl ligands in **2a** are terminally coordinated to the Os atoms, three to each metal except for Os(1) that is linked to only two carbonyls. A number of short Au···C distances are present {Au(1)···C(32), 2.63(4), Au(2)···C(11), 2.46(4) Å}, but as in the case of other mixed-metal clusters that contain gold there is not thought to be a significant bonding interaction between these atoms [16].

The solid-state structure is not completely consistent with the spectroscopic data for **2a** (Table 1). The structure confirms the presence of 17 carbonyl groups, as in the parent cluster **1**. The structure is not consistent with the ^{31}P-NMR data that suggests that there are two

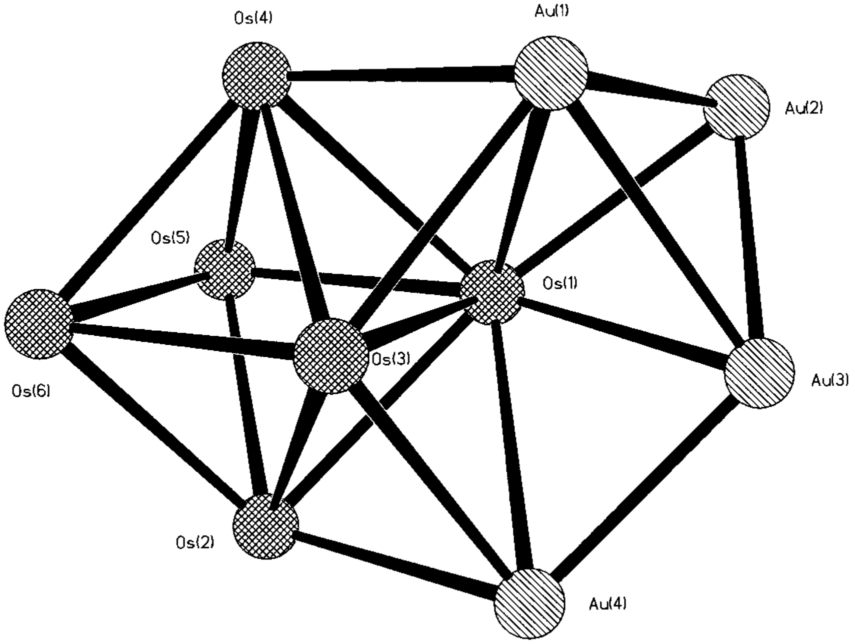


Fig. 2. The metal core geometry in $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2a**).

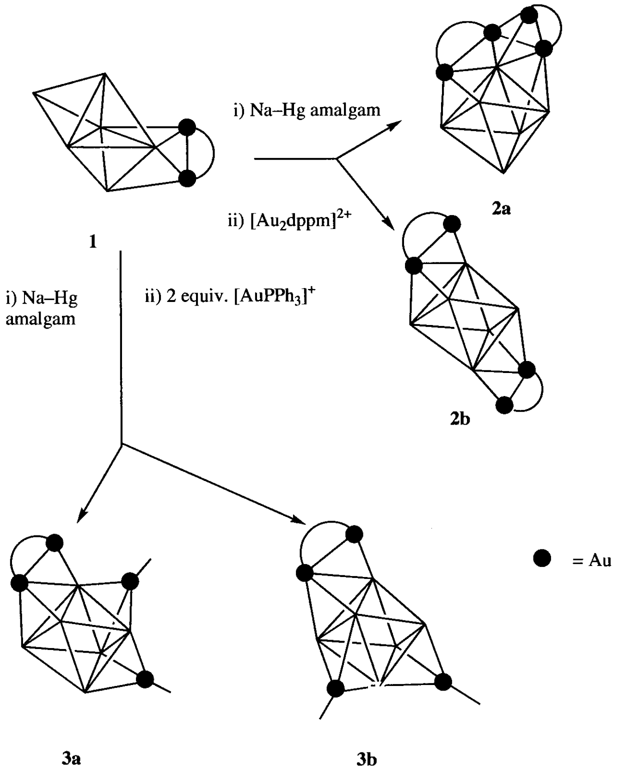
phosphorus environments, but in the structure the four phosphorus atoms are inequivalent. A fluxional process that involves an equilibrium between pairs of phosphorus nuclei must be occurring at room temperature. Again, the insolubility of the cluster precludes a low temperature investigation. A possible explanation for the ^{31}P-NMR spectrum of **2a** is that the two observed phosphorus resonances are from two phosphorus atoms of a single dppm ligand, both dppm ligands being rendered equivalent by the process, with both the P atoms of each dppm remaining inequivalent. The coupling presumably arises through the methylene group. Exchange of the Au(3) and Au(2) positions (Fig. 2), involving Au(3)–Os(3) bond formation and Au(2)–Os(1) bond cleavage, while maintaining the Au(2)–Au(3) bond would achieve this.

From the structure of **2a** and the spectroscopic data for **2b** it is not possible to suggest a structure for the latter. Since the electron count for the two isomers is the same it is likely that **2b** also has an octahedral osmium core, although isomers of the octahedron such as the capped square based pyramid cannot be ruled out (both these frameworks have the same number of skeletal electron pairs). It is also probable that the arrangement of the two $[Au_2dppm]^{2+}$ units on the surface of the osmium core is different.

In a related reaction the reduced cluster anion $[Os_6(CO)_{17}(Au_2dppm)]^{2-}$ can be treated with two equivalents of $[AuPPh_3][NO_3]$, in dichloromethane, and after purification by TLC two products are obtained. The complexes were again characterised by IR and NMR spectroscopies and FAB mass spectrometry (Table 1), and were identified as two isomers of the decanuclear cluster $[Os_6(CO)_{17}(Au_2dppm)(AuPPh_3)_2]$ (**3**). The major yellow isomer **3a** was obtained in 45% yield, and the minor pink isomer **3b** in 25% yield. Both clusters showed a low intensity peak in the FAB mass spectrum at *m*/*z* 3324 that corresponds to the formulation, and since, by analogy with **2**, it is unlikely that the clusters have scavenged carbonyl ligands from the reaction the assignment is thought to be correct. The ^{31}P-NMR spectra for both clusters showed only broad, weak peaks, consistent with a fluxional process, and solubility problems precluded a low temperature investigation. However, the band structure in the terminal

Table 2
Selected metal core dimensions for $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2**); bond lengths (Å) and angles (°)

Os(1)–Os(2)	2.987(3)	Au(1)–Os(4)	2.896(2)
Os(1)–Os(3)	3.038(2)	Au(2)–Os(1)	2.791(2)
Os(1)–Os(4)	3.006(3)	Au(3)–Os(1)	2.768(2)
Os(1)–Os(5)	2.876(2)	Au(4)–Os(1)	3.095(3)
Os(2)–Os(3)	3.005(3)	Au(4)–Os(2)	2.744(2)
Os(2)–Os(5)	2.844(3)	Au(4)–Os(3)	2.905(3)
Os(2)–Os(6)	2.865(3)	Au(1)–Au(2)	2.770(2)
Os(3)–Os(4)	2.980(3)	Au(1)–Au(3)	3.188(3)
Os(3)–Os(6)	2.896(2)	Au(2)–Au(3)	2.677(3)
Os(4)–Os(5)	2.869(3)	Au(3)–Au(4)	2.767(3)
Os(4)–Os(6)	2.856(3)	Au(1)–P(1)	2.327(10)
Os(5)–Os(6)	2.958(3)	Au(2)–P(2)	2.280(10)
Au(1)–Os(1)	2.958(3)	Au(3)–P(3)	2.288(12)
Au(1)–Os(3)	2.796(2)	Au(4)–P(4)	2.295(11)
P(1)–Au(1)–Os(4)	138.1(3)	P(1)–Au(1)–Os(3)	144.5(3)
P(1)–Au(1)–Os(1)	146.0(3)	P(2)–Au(2)–Os(1)	164.7(3)
P(3)–Au(3)–Os(1)	166.4(3)	P(4)–Au(4)–Os(2)	151.5(3)
P(4)–Au(4)–Os(3)	136.9(3)	P(4)–Au(4)–Os(1)	140.6(3)



Scheme 1. The reaction scheme for the formation of **2** and **3** from **1**.

carbonyl stretching region of the IR spectrum for **3a** is very similar to that of **2a**, consistent with a similar symmetry for the two molecules. On this tentative evidence, **3a** can be assigned a structure similar to that of **2a**, with an octahedral osmium core and, perhaps, a similar arrangement of the gold phosphine ligands. The IR spectrum of **3b** is somewhat different from that of **2b** and no structural assignments can be made. It may be of significance that both **2b** and **3b** are pink in colour. From electron counting rules, both **3a** and **3b** might be expected to have octahedral osmium cores since both are 86 electron clusters.

The overall transformations from **1** to **2** and **3** are illustrated in Scheme 1, but the positions of the gold phosphine ligands in the structures of **2b**, **3a** and **3b** must be viewed as completely speculative.

3. Experimental

All reactions were performed under an atmosphere of purified dinitrogen using standard Schlenk and vacuum line techniques [17]. 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 (TLC) using commercially prepared glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60 F_{254}, or using laboratory prepared glass plates coated to 1 mm thickness with Merck Kieselgel 60 F_{254}.

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

The compounds $[Os_6(CO)_{17}(Au_2dppm)]$ [11], $[Au_2dppm][NO_3]_2$ [18], and $[AuPPh_3][NO_3]$ [18] were prepared by literature methods. All other chemicals were used as purchased without further purification.

3.1. Preparation of $[Os_6(CO)_{17}(Au_2dppm)_2]$ (2)

$[Os_6(CO)_{17}(Au_2dppm)]$ [11] (**1**) (50 mg, 2.1×10^{-5} mol) was reduced by fresh Na–Hg amalgam by dissolving the cluster in 20 cm^3 of dry deoxygenated THF and transferring the resulting solution to a flask containing freshly prepared amalgam, with the help of a canula. The reaction mixture was stirred for a few minutes. The stirring was stopped when the reduction was complete, as monitored by IR spectroscopy. The solution was passed through a celite pad using the canula–septum technique to remove the amalgam. The solvent was removed under vacuum and to the resulting residue dry, deoxygenated dichloromethane (20 cm^3) was added. One equivalent of $[Au_2dppm][NO_3]$ (18.8 mg) was dissolved in 10 cm^3 of dichloromethane and added to the suspension, and the mixture stirred for 30 min. The solid residue obtained after removal of the solvent was purified by TLC eluting with a mixture of dichloromethane:hexane (60:40). A yellow product (**2a**) was obtained in 50% yield and a pink product (**2b**) in 30% yield, and characterised as two isomers of $[Os_6(CO)_{17}(Au_2dppm)_2]$. Anal. Calc. for **2a** ($Os_6Au_4P_4O_{17}C_{67}H_{44}$): C, 25.35; H, 1.40. Found: C, 25.10; H, 1.36%; Anal. Calc. for **2b** ($Os_6Au_4P_4O_{17}C_{67}H_{44}$): C, 25.35; H, 1.40. Found: C, 25.70; H, 1.20%.

3.2. Preparation of $[Os_6(CO)_{17}(Au_2dppm)(AuPPh_3)_2]$ (3)

The cluster **1** (50 mg, 2.1×10^{-5} mol) was reduced in the same manner as described above, and the redissolved residue treated with two equivalents of $[AuPPh_3][NO_3]$ (21.9 mg) in dichloromethane (20 cm^3). The resulting solution was worked up as described above, and two compounds, one yellow (**3a**) and one pink (**3b**), were isolated after purification by TLC, and identified as isomers of $[Os_6(CO)_{17}(Au_2dppm)_2(AuPPh_3)_2]$. Anal. Calc. for **3a** ($Os_6Au_4P_4O_{17}C_{78}H_{52}$): C, 28.27; H, 1.60. Found: C, 28.10; H, 1.45%. Anal. Calc.

for **3b** ($Os_6Au_4P_4O_{17}C_{78}H_{52}$): C, 28.27; H, 1.60. Found: C, 28.82; H, 1.30%.

3.3. Crystal structure determination of $[Os_6(CO)_{17}(Au_2dppm)_2]$ (2a)

Yellow crystals of $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**1a**) were obtained by recrystallisation from dichloromethane–hexane at −20°C. A suitable crystal was mounted on a glass fibre 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 $5.08 \leq 2\theta \leq 50.0°$. A semi-empirical absorption correction based on ψ scans was applied. Crystal data, data collection parameters, and details of structure solution and refinement are presented in Table 3. The structure was solved by direct methods (SHELXTL-PLUS [19]) and refined by full-matrix least-squares on F^2 (SHELXL–97 [20]). The Os, Au and P atoms were assigned anisotropic displacement parameters while the remaining non-hydrogen atoms were assigned isotropic displacement parameters. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms. In the final cycles of refinement a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.0807P)^2 + 185.648P]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced. The final converged R factors for 367 refined parameters were $R_1 = 0.0678$ (for 5474 reflections with $I > 2\sigma(I)$) and $wR_2 = 0.483$ (for all data), goodness-of-fit = 1.054.

Table 3
Crystal data and refinement parameters for $[Os_6(CO)_{17}(Au_2dppm)_2]$ (**2a**)

Empirical formula	$C_{67}H_{44}Au_4O_{17}Os_6P_4$
Formula weight	3173.97
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	14.889(5)
b (Å)	19.863(5)
c (Å)	14.478(6)
α (°)	101.37(3)
β (°)	109.74(3)
γ (°)	93.68(3)
Volume (Å^3), Z	3911(2), 2
D_{calc} (Mg m^{-3})	2.695
Absorption coefficient (mm^{-1})	17.313
$F(000)$	2828
Crystal size (mm)	$0.15 \times 0.22 \times 0.25$
θ Range for data collection (°)	2.59–24.99
Limiting indices	$0 \leq h \leq 6$, $-21 \leq k \leq 21$, $-17 \leq l \leq 14$
Max. and min. transmission	1.000, 0.425
Reflections collected	10 219
Independent reflections	10 219
Data/restraints/parameters	10 155/0/367
Goodness-of-fit on F^2	1.054
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0678$, $wR_2 = 0.1505$
R indices (all data)	$R_1 = 0.1592$, $wR_2 = 0.4826$
Largest difference peak and hole (e Å^{-3})	2.366 and −2.015

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142216 for compound **2a**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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