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High nuclearity clusters of osmium and ruthenium containing the $[Au_2(Ph_2PCH_2PPh_2)]^{2+}$ cation; the X-ray structures of $[Os_4H_4(CO)_{11}Au_2(Ph_2PCH_2PPh_2)]$ and $[Ru_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$[1]

Angelo J. Amoroso *, Michael A. Beswick, Chi-Keung Li, Jack Lewis, Paul R. Raithby, M. Carmen Ramirez de Arellano

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

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Abstract

Treatment of $[Os_4H_4(CO)_{11}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$ and $[Ru_{10}C(CO)_{24}]^{2-}$ with $[Au_2(Ph_2PCH_2PPh_2)Cl_2]$ in the presence of an excess of $TlPF_6$, gave $[Os_4H_4(CO)_{11}(Au_2Ph_2PCH_2PPh_2)]$ **1**, $[Os_{10}C(CO)_{24}(Au_2Ph_2PCH_2PPh_2)]$ **2** and $[Ru_{10}C(CO)_{24}(Au_2Ph_2PCH_2PPh_2)]$ **3**, respectively, all of which were obtained in high yield. The structures of the clusters **1** and **3** have been established by X-ray crystallography, both exhibiting novel coordination modes of the bidentate gold fragments. Cluster **1** contains a tetrahedral Os_4 core with one of the Au atoms of the $Au_2(Ph_2PCH_2PPh_2)$ ligand bridging an edge of the tetrahedron, and the second Au atom coordinated to a third Os atom. In **3** the two Au atoms of the $Au_2(Ph_2PCH_2PPh_2)$ ligand cap two adjacent, vertex sharing, triangular faces of the Ru_{10} tetracapped octahedral core. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Ruthenium; Gold; Phosphine; X-ray structure

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1. Introduction

Recent work has been carried out using bifunctional gold reagents, such as $[Au_2(Ph_2PCH_2PPh_2)]^{2+}$, for the metathetical formation of metal–metal bonds with anionic metal carbonyl clusters. The presence of group II metals introduces a polarity into the metal framework generating novel metal geometries that are only observed in heterometallic clusters and not in homometallic clusters [1]. However, in all the cases to date the bonding mode of the gold phosphine fragment to the cluster is generally μ_2 to a M–M edge, μ_3 to MMM triangle or μ_3 to a MMAu triangle [2–5]. We have recently embarked on the search for novel coordination modes of the gold fragment in cluster compounds and have extended our synthetic study to include higher nuclearity cluster anions. The higher nuclearity cluster core increases the probability of finding a greater variety of coordination modes for the gold phosphine ligands. There are four different core geometries possible for digold fragments interacting with a triangular cluster face (Fig. 1). The four possibilities are (i) the μ_3:μ_2 coordination mode with the generation of a trigonal bipyramid geometry between the digold fragment and the triangular face of the cluster; (ii) the μ_2:μ_2 coordination to give a square-based pyramidal geometry; (iii) the μ_2:μ_2 coordination to give a tetrahedral geometry which can be related to the μ_3:μ_2 type coordination by

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* Corresponding author. Fax: +44 1223 336362; e-mail: prr1@cam.ac.uk

[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday in recognition of his outstanding contributions to inorganic chemistry, with thanks for his friendship and unbounded enthusiasm which has supported us over the years.

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the reformation of a M–Au bond; (iv) the μ_2:μ_1 coordination in which two of the Au–M contacts are absent by comparison to that of the μ_3:μ_2 coordination mode. A summary of the relevant bond lengths for the cluster systems is presented in Table 1.

We have recently reported that in [$Ru_5(CO)_{15}$($Au_2Ph_2PCH_2PPh_2$)] the gold atoms adopt a μ_3:μ_3 coordination mode, capping adjacent edge sharing faces of the Ru_5 trigonal bipyramid [6]. We now report a different μ_3:μ_3 coordination mode for the same gold phosphine ligand. In this case five basal ruthenium atoms of the tetracapped octahedral structure are μ_3:μ_3 capped by the digold phosphine ligand. The two capped metal triangles share only a common vertex, which is in contrast to the situation in the previous example where four ruthenium atoms capped in a μ_3:μ_3 mode, and the two adjacent triangles share a common edge. There are now a number of examples of structures in which either

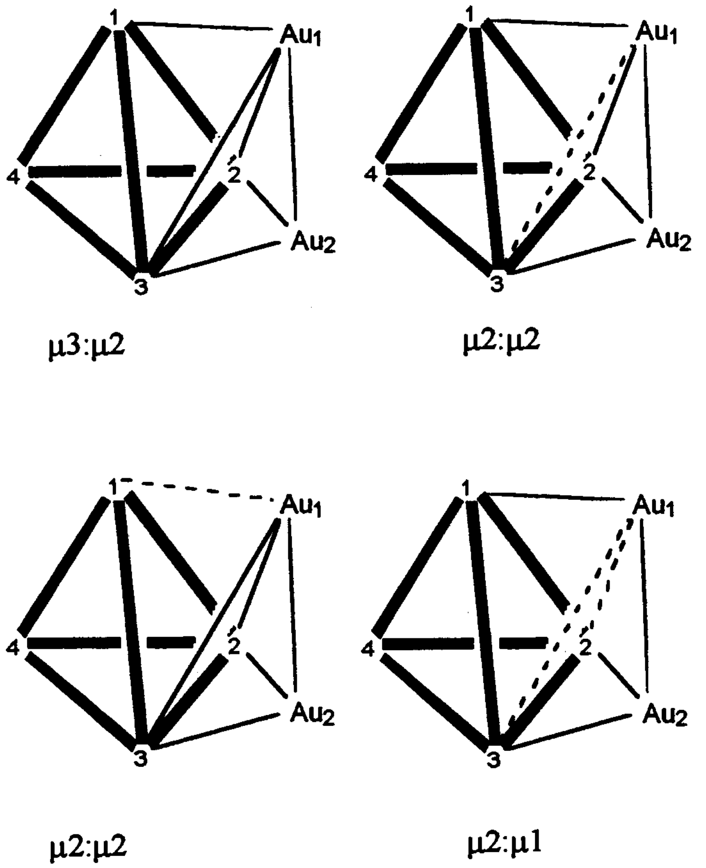

Fig. 1. The four possible modes of coordination of two gold fragments to a triangular face of a cluster.

Table 1
Compounds exhibiting the coordination found on the interaction of two gold atoms with an M_3 triangular face

Coordination Mode	Compound	Au–Au	1–2	1–3	2–3	Au 1–1	Au 1–2	Au 1–3
μ_3:μ_2	$Ru_2Co_2(CO)_{12}(AuPPh_3)_2$	2.890	2.723	2.492	2.954	2.866	2.887	2.651
	$Ru_3CoH(CO)_{12}(AuPPh_3)_2$	2.787			2.989	2.704	2.915	2.953
	$Ru_4H_2(CO)_{12}(AuPPh_3)_2$	2.791	2.984	2.966	3.011	3.091	2.859	2.949
	$Ru(\mu_3\text{-}S)(CO)_9(AuPPh_3)_2$	2.915	2.833	2.883	3.034	2.817	2.859	2.867
μ_2:μ_2	$Os_4(Co)_{13}(AuPEt_3)_2$	3.128	2.887	2.824	2.958		2.947	
	$Ru_4H_2(CO)_{12}$–$Au_2(Ph_2AsCH_2PPh_2)$	2.832	2.969	3.029	3.029	4.111	2.821	3.836
	$Ru_4H_2(CO)_{12}(Au_2dppm)$	2.823	2.932	3.006	3.003	3.799	2.862	4.173
	$Ru_4H_2(CO)_{12}(Au_2dppe)$	2.828	2.947	2.984	3.008	3.446	2.965	
	$Ru_3(\mu_3\text{-}S)(CO)_9(Au_2dppm)$	2.802	2.923	2.773	2.968	3.335	2.836	4.321
μ_2:μ_2	$Os_4H_2(CO)_{12}(AuPPh_3)_2$	2.793	2.968	2.952	2.977			

Metal numbering scheme corresponds to that in Fig. 1.

Table 2
Spectroscopic data for $[Os_4H_4(CO)_{11}Au_2(Ph_2PCH_2PPh_2)]$ **1**, $[Os_{10}C(CO)_{24}Au(PPh_2CH_2PPh_2)]$ **2** and $[Ru_{10}C(CO)_{24}Au(Ph_2CH_2PPh_2)]$ **3**

Cluster	IR/νCO (cm^{-1})[a]	^{1}H-NMR/δ/ppm[b]	^{31}P-NMR/δ/ppm	MS[b]
1	2072s, 2048s, 2021vs, 1986m, 1929w, br	3.79 (t, 2H); 7.2–7.8 (m, 10H) −18.07 (s, 2H); −20.62 (s, 2H)	−68.41(d) −102.44(d)	1858, 1858
2	2091m, 2068s, 2053vs, 2018vs	3.92 (t, 2H); 7.2–7.4 (m, 10H); 2008m	−81.27(s)	—
3	2090m, 2067s, 2053vs, 2019s, 2008m	3.89 (t, 2H), 7.2–7.4 (m, 10H)	−97.64(s)	—

Spectra recorded in [a] CH_2Cl_2 and [b] CD_2Cl_2.

two monogold phosphine liagands or a single digold phosphine ligand μ_3:μ_3 coordinate to cluster anions; these include $[Ru_5(CO)_{15}(Au_2Ph_2PCH_2PPh_2)]$ [6], $[Os_8(CO)_{22}(AuPPh_3)_2]$ [7], $[Os_4(CO)_{12}(AuPMePh_2)_2]$ [8] and $[Ru_{10}C(CO)_{24}(Au_2Ph_2PCH_2PPh_2)]$ **3** from the present work. In this paper we also report the first example of a, μ_2:,μ_1 coordination mode for a digold phosphine fragment bound to a cluster.

2. Results and discussion

The reaction of freshly prepared $[Os_4H_4(CO)_{11}]^{2-}$ with one equivalent of $[Au_2(Ph_2PCH_2PPh_2)Cl_2]$, in the presence of excess $TIPF_6$, in CH_2Cl_2, resulted in the formation of a stable neutral cluster **1** in 60% yield. The cluster was initially characterised by IR, ^{1}H-NMR, ^{31}P-NMR, negative ion FAB mass spectrometry and microanalysis as $[Os_4H_4(CO)_{11}Au_2(Ph_2PCH_2PPh_2)]$ **1**. Spectroscopic data for **1** is presented in Table 2. The IR spectrum confirms the presence of terminal carbonyl ligands, and the ^{1}H-NMR spectrum indicates the presence of bridging hydride ligands and of the $Ph_2PCH_2PPh_2$ unit. The ^{31}P-NMR spectrum for this compound, in CD_2Cl_2, at room temperature, shows two sharp doublets of equal intensity at δ −68.41 and −102.44 which suggests that the two gold atoms are bound differently to the Os_4 cluster unit. The result is consistent with the solid state crystal structure. This spectroscopic result contrasts with the single ^{31}P-NMR resonance at δ −97.8 found for $[Ru_5(CO)_{15}$-$Au_2(Ph_2CH_2PPh_2)]$ [6].

In order to establish the geometry of the cluster an X-ray analysis was undertaken. Single crystals of **1** suitable for the study were obtained by slow evaporation of a CH_2Cl_2/hexane solution of the compound over several days.

The molecular structure of **1** is shown in Fig. 2 and selected bond parameters are presented in Table 4. The molecular structure consists of a distorted Os_4 tetrahedron with one gold atom Au(1) of the $[(Au_2Ph_2PCH_2PPh_2)]^{2+}$ unit asymmetrically bridging the Os(3)–Os(2) edge (Os(2)–Au(1) 2.801(3) Å being longer than Os(3)–Au(1) 2.699(3)Å while the other gold atom Au(2) is bound terminally to Os(1). The four hydrides in **1** were not located directly, but an analysis

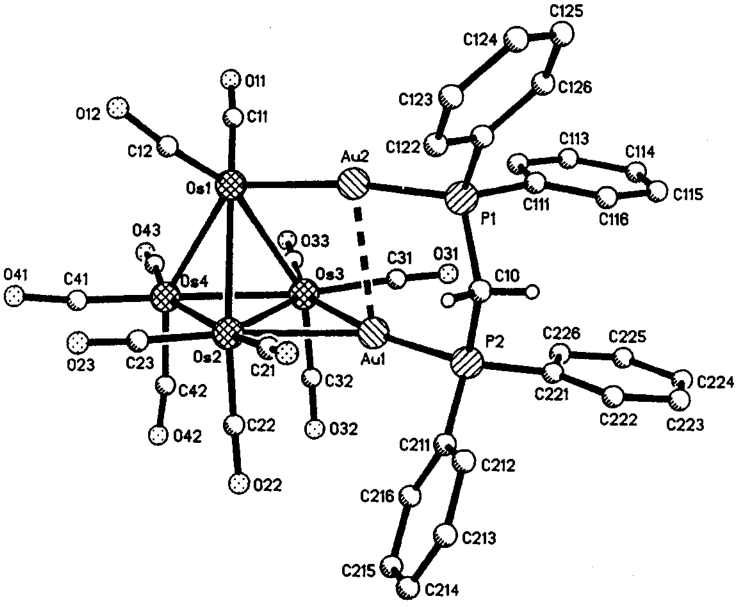

Fig. 2. The molecular structure of $[Os_4H_4(CO)_{11}Au_2(Ph_2PCH_2PPh_2)]$ **1**.

Table 3
Crystal data and structure solutions of **1** and **3**[a]

	1	**3**
Formula weight	1851.2	2473.2
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
Crystal size (mm^3)	$0.20\times0.24\times0.30$	$0.44\times0.38\times0.36$
a (Å)	12.316(3)	26.729(7)
b (Å)	26.420(6)	18.893(3)
c (Å)	14.467(4)	12.213(3)
β (°)	104.05(2)	90
V (Å^3)	4566(2)	6167(2)
Z	4	4
ρ_{calc} (M gm^{-3})	2.693	2.664
F(000)	3288	4568
Absorption coefficient (mm^{-1})	17.608	7.237
θ range	$2.5<\theta<22.5$	$2.5<\theta<22.5$
Reflections collected	6641	4458
Independent reflections	5994	4283
R_{int}	0.019	0.012
Max/min transmission	0.2276, 0.0919	0.126, 0.058
Refinement method	Refined on F data full-matrix least-squares	Refined on all F^2 data full-matrix least-squares
GoF	1.64	1.053
R indices	$[F>4\sigma(F)]$	$[I>2\sigma(I)]$
	$R_1=0.0753$	$R_1=0.0523$
	$wR_1=0.0886$	$wR_2=0.1110$
Largest difference peak and hole (e Å^{-3})	2.66 and −2.89	1.468 and −1.214

[a] Details in common: wavelength λ, 0.71073 Å; T, 293(2) K; $R_1=\Sigma|F_o|-|F_c||/\Sigma|F_o|$, $wR_2=\{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{0.5}$, $w=1/[\sigma^2(F_o^2)+(xP)^2+yP]$, $P=(F_o^2+2F_c\,2/3)^{18}$.

of the Os–Os bond lengths indicates that four of them are significantly longer than the other two. One of these edges, Os(2)–Os(3), is bridged by Au(1), but it is likely that the other three long edges are bridged by three hydrides since similar trends are observed in the related cluster $[Os_4H_2(CO)_{12}(AuPPh_3)_2]$ [9]. The position of the fourth hydride is less clear, and potential energy calculations [10] were not successful in locating it within the Os core. It may be that an Os–Au edge is being bridged by the hydride although this is not entirely consistent with the ^{1}H-NMR data. The novel terminal Os–Au bonding observed in compound **1** is the first example that we are aware of in metal carbonyl clusters. Related Au_2M_4 clusters such as $[Os_4H_2(CO)_{12}(AuPPh_3)_2]$ [9] and $[Ru_4H_2(CO)_{12}(AuPPh_3)_2]$ [11] show the μ_2:μ_2 bonding mode for the two gold atoms. The fact that a chelating ligand and four bridging hydrides are present in compound **1** may well be the reason for the novel coordination of the gold atoms and the osmium metal core. A weak Au–Au interaction is observed in the coordinated $(Au_2Ph_2PCH_2PPh_2)$ ligand which is similar in length to the value of 2.944(2) Å found in $[Ru_5(CO)_{15}Au_2(Ph_2CH_2PPh_2)]$ [6], but this may reflect the requirements of the bite of the chelating ligand.

The reaction of the chelating digold phosphine cation with decanuclear cluster dianions was then investigated. The addition of $[Au_2(Ph_2PCH_2PPh_2)]Cl_2$ to $[M_{10}C(CO)_{24}]^{2-}$ (M = Os or Ru), in the presence of $TlPF_6$, in CH_2Cl_2, resulted in a rapid colour change. The carbonyl infrared spectra showed a large shift in comparison to the parent dianion in accordance with the formation of a neutral cluster. The compounds were purified and characterised as $[M_{10}C(CO)_{24}Au_2(Ph_2CH_2PPh_2)]$ (M = Os(**2**), Ru (**3**)) by IR, ^{1}H-NMR, ^{31}P-NMR and microanalysis (Table 2). The IR spectrum of **2** and **3** showed the presence of terminal carbonyl ligands, and the ^{1}H-NMR spectrum indicated that the $(Ph_2CH_2PPh_2)$ group was present. The ^{31}P-NMR spectrum showed only one resaonance at δ −81.27 for **2** and −97.64 for **3**, in contrast to that observed for **1**, but similar to that found for $[Ru_5(CO)_{15}Au_2(Ph_2CH_2PPh_2)]$ [6] and $[Ru_6C(CO)_{16}Au_2(Ph_2PCH_2PPh_2)]$ [6].

In contrast to the reaction reported here, in the case of $[Os_{10}C(CO)_{24}]^{2-}$, the addition of two equivalents of $[AuPPh_3Cl]$ resulted in the addition of only one gold, forming the monoanion $[Os_{10}C(CO)_{24}(AuPPh_3)]^-$, and the neutral product $[Os_{10}C(CO)_{24}(AuPPh_3)_2]$ was not obtained. In the case of **2** the neutral cluster is only stable in non-polar non-coordinating solvents, and in acetone it dissociates back to the dianion $[Os_{10}C(CO)_{24}]^{2-}$. The addition of nucleophiles, such as

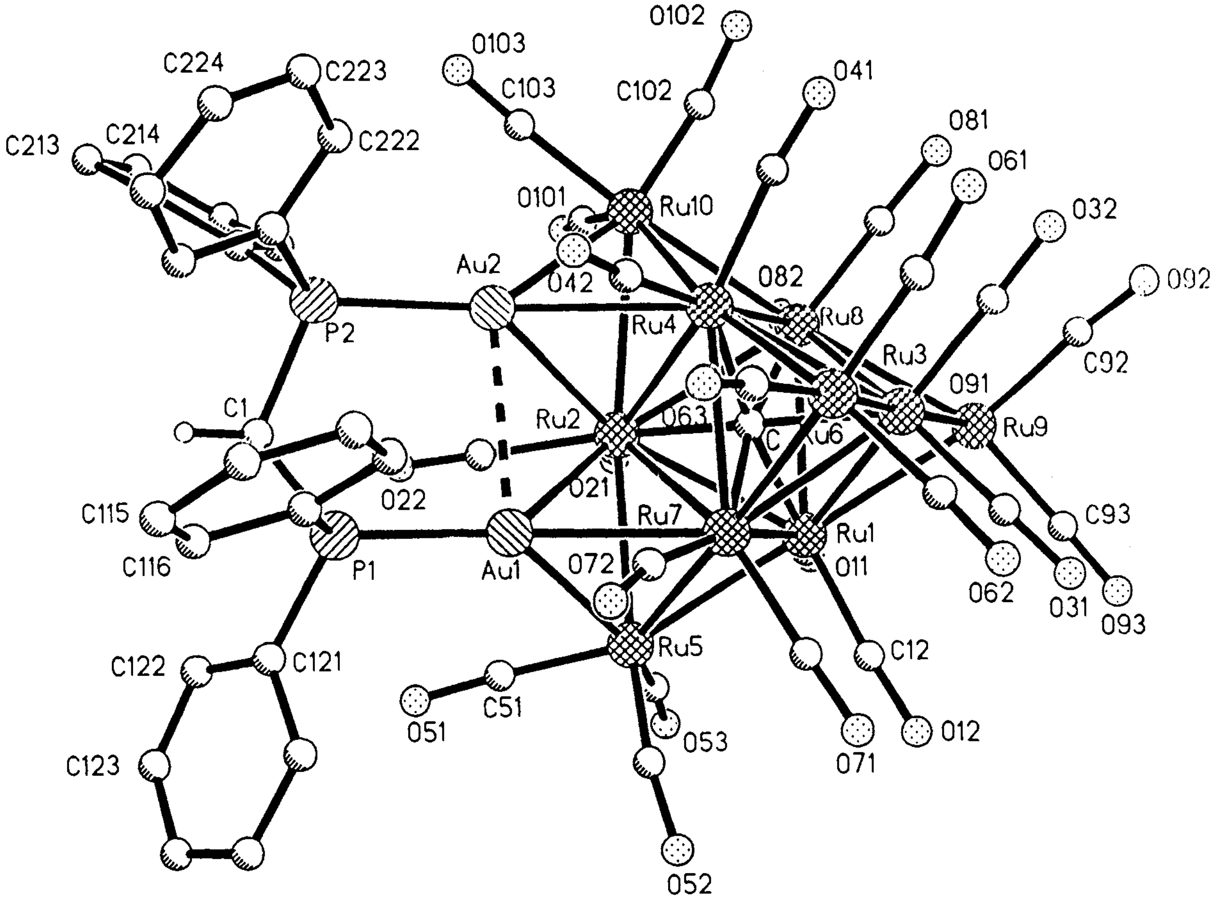

Fig. 3. The molecular structure of $[Ru_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$ **3**.

PR_3, to **2** instead of resulting in the formation of a substitution product the dianion $[Os_{10}C(CO)_{24}]^{2-}$ is again regenerated. Compound **2** is relatively stable to heat and is also stable up to 60 atmospheres pressure of CO with only a little decomposition back to $[Os_{10}C(CO)_{24}]^{2-}$.

Single crystals of **3**, suitable for an X-ray analysis, were grown from by the slow layered diffusion of hexane into a CH_2Cl_2 solution of the compound. As with **2**, compound **3** is relatively unstable for extended periods in polar and coordinating solvents, being slightly more stable than **2**. Poor quality crystals were also obtained for **2**, and preliminary X-ray analysis indicated that the two mixed metal clusters **2** and **3** are isomorphous with the lattice constants being very similar. It was decided to concentrate the crystallographic efforts on the determination of the structure of **3**, since better quality crystals were available. The molecular structure of **3** is shown in Fig. 3, while the molecular core is illustrated in Fig. 4. Selected bond lengths are listed in Table 4.

The metal framework in **3** consists of a tetracapped octahedron of ruthenium atoms, with the two gold atoms capping adjacent triangles (sharing a common vertex) of a Ru_5 face. The Au(l) atom is bonded μ_3 to the triangular face generated by the three metals Ru(2), Ru(5), Ru(7) and Au(2) is bonded μ_3 to the triangular face generated by the three metals Ru(4), Ru(2), Ru(10), Ru(2) is the common metal coordinated to both gold atoms. Both gold caps show significant asymmetry, with the greater range of Au–Os distances found for Au(1). Within the ruthenium core the central Ru_6 octahedron has a carbido carbon at the centre. The 24 carbonyl ligands are all terminal and essentially linear. Overall the ruthenium core geometry is similar to that found in the parent dianion $[Ru_{10}C(CO)_{24}]^{2-}$ [12]. However, two of the Ru–Ru edges of the triangles capped by the gold atoms in **3** are lengthened significantly (Ru(2)–Ru(4) [3.022(4) Å] and Ru(2)–Ru(7) [3.128(3) Å]) by comparison with the other edges in the structure (average Ru–Ru distance of 2.847 Å) and by comparison to all the Ru–Ru edges (average 2.813 Å) in the parent dianion cluster [12]. The Au(1)–Au(2) separation of 2.943(2) Å is similar to that observed in **1**, but this may again reflect the bite requirements of the bidentate ligand. It is worth noting that the μ_3 capping coordination of the gold atoms to the ruthenium core is different to the μ_2 bridging observed in $[Os_{10}C(CO)_{24}(AuPPh_3)]^-$ but is similar to that found for the $Cu(CH_3CN)$ group in $[Os_{10}C(CO)_{24}\{Cu(CH_3CN)\}]^-$ [13]. The μ_3:μ_3 mode of bonding for two gold phosphine fragments have been observed pre-

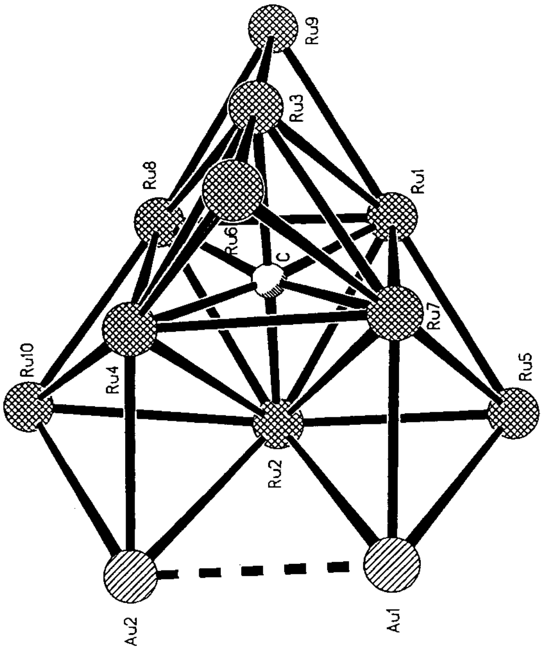

Fig. 4. The metal core structure of $[Ru_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$ **3**.

viously in the structures $[Os_8(CO)_{22}(AuPPh_3)_2]$ [7], $[Os_4(CO)_{12}(AuPMePh_2)_2]$ [8] and $[Ru_5(CO)_{14}(Au_2\text{-}Ph_2PCH_2PPh_2)]$ [6]. In $[Os_8(CO)_{22}(AuPPh_3)_2]$ [8] and $[Os_4(CO)_{12}(AuPMePh_2)_2]$ [7] the Au···Au separation is over 4 Å since the two phosphines are monodentate, and there is obviously no Au···Au interaction, in the case of $[Ru_5(CO)_{12}(Au_2Ph_2PCH_2PPh_2)]$ [6] the separation is 2.99(2) Å, consistent with the chelating nature of the ligand, and some form of interaction may be contemplated.

3. Experimental

3.1. General experimental procedure

All the reactions were performed under an atmosphere of dry, oxygen free nitrogen. Technical grade solvents were purified by standard procedures. The dianions $[Os_4H_4(CO)_{11}]^{2-}$ [14], $[Os_{10}C(CO)_{24}]^{2-}$ [15], and $[Ru_{10}C(CO)_{24}]^{2-}$ [12], and the gold complex $[Au_2(Ph_2PCH_2PPh_2)Cl_2]$ [16] were prepared by literature procedures. Mass spectra were recorded using a Kratos model MS902, IR spectra on a Perkin-Elmer 1710 FT-JR spectrometer, ^1H- and ^{31}P-NMR spectra on a Broker WH 400 MHz spectrometer. Elemental analyses were performed by the microanalytical service in the Department of Chemistry.

3.2. Preparations

3.2.1. *$[Os_4H_4(CO)_{11}Au_2(Au_2(Ph_2PCH_2PPh_2)]$* **1**

To a solution of freshly prepared $[Os_4H_4(CO)_{11}]^{2-}$ (50 mg) in CH_2Cl_2 (20 ml), was added $[Au_2(Ph_2PCH_2PPh_2)Cl_2]$ (one equivalent) and $TIPF_6$ (2.5 equivalents), the solution was stirred for 1 h. After removal of the solvent the orange solid residue was chromatographed by TLC using CH_2Cl_2/hexane (50:50) as eluent. The orange band was identified as $[Os_4H_4(CO)_{11}Au_2(Au_2(Ph_2PCH_2PPh_2)]$ **1**. R_f 0.6, 60% yield. Elemental analysis calculated for $[Os_4H_4(CO)_{11}Au_2(Au_2(Ph_2PCH_2PPh_2)]$: C, 23.3; H, 1.4. Found: C, 23.1; H, 1.4.

3.2.2. *$[Os_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$* **2**

To a solution of $[PPN]_2[Os_{10}C(CO)_{24}]$ (50 mg) in CH_2Cl_2 (20 ml), was added $[Au_2(Ph_2PCH_2PPh_2)Cl_2]$ (one equivalent) and $TIPF_6$ (2.5 equivalents), the

Table 4
Selected bond lengths (Å) for compounds **1** and **3**

Compound **1**					
Os(l)–Os(2)	3.008(3)	Os(l)–Au(2)	2.825(3)	Os(l)–Os(3)	3.006(3)
Os(2)–Au(1)	2.801(3)	Os(l)–Os(4)	2.976(3)	Os(3)–Au(1)	2.699(3)
Os(2)–Os(3)	2.937(3)	Au(1)–Au(2)	2.978(3)	Os(2)–Os(4)	2.813(3)
Au(1)–P(2)	2.298(13)	Os(3)–Os(4)	2.818(3)	Au(2)–P(1)	2.274(13)
Compound **3**					
Ru(l)–Ru(2)	2.860(3)	Ru(l)–Ru(3)	2.824(4)	Ru(l)–Ru(5)	2.778(4)
Ru(l)–Ru(7)	2.870(3)	Ru(l)–Ru(8)	2.836(4)	Ru(l)–Ru(9)	2.790(4)
Ru(2)–Ru(4)	3.022(4)	Ru(2)–Ru(5)	2.801(4)	Ru(2)–Ru(7)	3.128(3)
Ru(2)–Ru(8)	2.864(4)	Ru(2)–Ru(10)	3.012(4)	Ru(3)–Ru(4)	2.851(3)
Ru(3)–Ru(6)	2.710(3)	Ru(3–Ru(7)	2.795(4)	Ru(3)–Ru(8)	2.795(3)
Ru(3)–Ru(9)	2.740(3)	Ru(4)–Ru(6)	2.820(3)	Ru(4)–Ru(7)	2.890(4)
Ru(4)–Ru(8)	2.869(3)	Ru(4)–Ru(10)	2.818(3)	Ru(5)–Ru(7)	2.900(4)
Ru(6)–Ru(7)	2.807(4)	Ru(8)–Ru(9)	2.798(3)	Ru(8)–Ru(10)	2.748(3)
Au(1)–Ru(2)	2.946(3)	Au(1)–Ru(5)	2.906(3)	Au(1)–Ru(7)	2.748(3)
Au(2)–Ru(2)	2.867(3)	Au(2)–Ru(4)	2.822(3)	Au(2)–Ru(10)	2.825(3)
Au(1)–Au(2)	2.943(2)	Au(1)–P(1)	2.317(8)	Au(2)–P(2)	2.315(8)

solution was stirred for 1 h. After removal of the solvent the black solid residue was chromatographed by TLC using CH_2Cl_2 as eluent. The top black band was isolated and identified as $[Os_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$ **2**. Elemental analysis calculated for $[Os_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$: C, 17.8; H, 0.66. Found: C, 18.0; H, 0.70.

*3.2.3. $[Ru_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$ **3***

The same procedure as described for **2** was employed except that the salt $[PPN]_2[Ru_{10}C(CO)_{24}]$ was used. Elemental analysis calculated for $[Ru_{10}C(CO)_{24}Au_2(Ph_2PCH_2PPh_2)]$: C, 24.3; H, 0.89. Found: C, 24.4; H, 0.87.

3.3. Crystallography—data collection and processing

The intensity data for the two structures were collected on a Siemens R3m/V diffractometer using graphite monochromated Mo–K_α radiation. For both data sets intensity data were corrected for Lorentz polaristion effects and for absorption using the Ψ-scan method. The structures were solved by a combination of direct methods and Fourier difference techniques and refined on F (for **1**) and F^2 (for **3**), respectively by full matrix least-squares analysis using the SHELXTL PLUS and SHELXL 93 programs, respectively [17,18]. H-atoms were placed in idealised positions and were allowed to ride on the relevant C-atom for structure **1** but were not included in the model for structure **3**. Details of the structure solutions and refinements for **1** and **3** are listed in Table 3. Atomic coordinates, displacement parameters, and bond lengths and angles for compound **3** have been deposited at the Cambridge Crystallographic Data Centre, hard copies of those for compound **1** are available from the authors.

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