High Nuclearity Clusters Containing Methyl Groups.

Synthesis and Structures of Pentaosmium-Gold Carbonyl Cluster Compounds[†]

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[†]Dedicated to the memory of Professor Jack Lewis, the Lord Lewis of Newnham, a pioneer in the chemistry of polynuclear metal carbonyl cluster complexes.

Introduction

Interest in the organometallic chemistry of gold has grown greatly following the discoveries that gold clusters [1] and nanoparticles [2] can catalyze a variety of important organic reactions. Recent studies have shown that gold complexes can also catalyze interesting organic reactions homogeneously [3]. A number of bimetallic transition metal-gold catalysts have been found to exhibit even better activity and product selectivity than that of the individual metals [4].

Over the years there has been considerable interest in the synthesis, structures, bonding and reactivity of polynuclear transition metal carbonyl complexes containing gold-ligand groupings [5]. Jack Lewis was a pioneer in the field of transition metal – gold chemistry. He and his coworkers led the field by synthesizing many of the first examples of metal carbonyl

complexes containing gold-ligand groupings [6] and then expanded it into a range of higher nuclearity transition metal-gold bimetallic carbonyl complexes [7].

Our group has recently shown that complexes containing the gold – carbon bond can be “oxidatively added” to certain polynuclear metal carbonyl complexes to introduce σ and even σ – π coordinated organic ligands into metal cluster ensembles e.g. Eq. (1) – (3) [8-10].

Multiple additions of RAuL , $\text{R} = \text{Me}$ or Ph can yield cluster complexes with several gold groupings with one or more alkyl or aryl ligands, e.g. Eq. (4) [11].

In 1989, Lewis and Johnson reported on the reaction of $[\text{PPN}]_2\text{Os}_5(\text{CO})_{15}$, $\text{PPN} = [\text{Ph}_3\text{PNPPh}_3]^+$, with $[\text{Au}(\text{PPh}_3)\text{Cl}]$ [12]. They obtained the complexes $[\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)]^-$, **1** and $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$, **2** depending on the amount of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ that was used in the reaction. We have now investigated the reaction of $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ with $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ in the presence and absence of $\text{MeAu}(\text{PPh}_3)$. Two products $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$, **2** [12], and the new tetragold compound $\text{Os}_5(\text{CO})_{14}[\mu_4\text{-Au}_3(\text{PPh}_3)_3](\mu_3\text{-AuPPh}_3)$, **3** were obtained in the absence of $\text{MeAu}(\text{PPh}_3)$, but when the reaction was performed in the presence of $\text{MeAu}(\text{PPh}_3)$, the new methyl-containing trigold compound $\text{Os}_5(\text{CO})_{14}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_3$, **4** was also obtained. With the exception of a few complexes containing the Group 12-Me group, there are very few examples of high nuclearity transition metal cluster complexes, M_n , $n \geq 5$, that contain methyl ligands [11,13]. The transformations of methyl groups in high nuclearity complexes could have implications for the transformations of methyl groups on metal surfaces [14] which is important for industrial processes such as Fischer Tropsch synthesis [15].

Experimental Section

General Data. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR

spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument, Positive/negative ion mass spectra were recorded on a Micromass Q-TOF instrument by using electrospray (ES) ionization. $\text{CH}_3\text{Au}(\text{PPh}_3)$ and $\text{Os}_3(\text{CO})_{12}$ were obtained from STREM and were used without further purification. $\text{Os}_6(\text{CO})_{18}$ was prepared from $\text{Os}_3(\text{CO})_{12}$ according to the reported procedure [16]. $[\text{PPN}]_2\text{Os}_5(\text{CO})_{15}$, $\text{PPN} = [\text{Ph}_3\text{PNPPh}_3]^+$, was prepared according to a previously reported procedure [16]. Product separations were performed by TLC in air on Analtech 0.50mm silica gel 60 Å F254 glass plates.

Synthesis of $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$, **2 and $\text{Os}_5(\text{CO})_{14}[\mu_4\text{-Au}_3(\text{PPh}_3)_3](\mu_3\text{-AuPPh}_3)$, **3****

18.5 mg (0.035 mmol) of $[(\text{PPh}_3)\text{Au}]\text{NO}_3$ was added to 22.4 mg (0.0092 mmol) of $[\text{PPN}]\text{Os}_5(\text{CO})_{15}$, in 30 mL of dichloromethane. The reaction solution was stirred for 1 h at 25 °C, and the color changed from brown to deep purple. The solvent was removed *in vacuo*, and the product was then isolated by TLC by using a 3:1 hexane/methylene chloride solvent mixture. This workup yielded in order of elution 3.5 mg (16 % yield) of orange $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$, **2** and 15 mg (67 % yield) of purple $\text{Os}_5(\text{CO})_{14}[\mu_4\text{-Au}_3(\text{PPh}_3)_3](\mu_3\text{-AuPPh}_3)$, **3**. Spectral data for **2**: IR $\nu_{\text{CO}}(\text{cm}^{-1})$ in methylene chloride): 2072(m), 2038(s), 2015(s), 1970(w), 1961(w). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, ref. 85% ortho- H_3PO_4) $\delta = 82.86$ (s, 1P, P-Au). Pos. Ion ES/MS $m/z = 2292$ (M^+); Spectral data for **3**: IR $\nu_{\text{CO}}(\text{cm}^{-1})$ in methylene chloride): 2049(m), 2011(s), 1996(s), 1970(w), 1950(w). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, ref. 85% ortho- H_3PO_4) $\delta = 92.19$ (s, 1P, P-Au), 49.98 (s, 1P, P-Au) and 88.89 (s, 2P, P-Au). Pos. Ion ES/MS $m/z = 3179$ (M^+)

Synthesis of $\text{Os}_5(\text{CO})_{14}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_3$, **4**

a) 30 mg (0.06 mmol) of $\text{CH}_3\text{Au}(\text{PPh}_3)$ was added to 35 mg (0.015 mmol) of $\text{Os}_5(\text{CO})_{15}(\text{PPN})_2$ in 30 mL of dichloromethane and stirred for 3 h at 25 °C. 30 mg (0.057 mmol) of $[(\text{PPh}_3)\text{Au}]\text{NO}_3$ was added to the above mixture solution. The solution color changed immediately from brown to deep purple. The reaction was stirred for another 15 mins. The solvent was removed *in vacuo*, and the product was then isolated by TLC using a 3:1 hexane/methylene chloride solvent mixture. In order of elution they gave 8 mg (23% yield) of orange $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$, **2**, 9.0 mg (26% yield) of purple $\text{Os}_5(\text{CO})_{14}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_3$, **4**, and 5.4 mg (15% yield) of purple $\text{Os}_5(\text{CO})_{14}(\mu_4\text{-Au}_3(\text{PPh}_3)_3)(\mu_3\text{-AuPPh}_3)$, **3**. Spectral data for **4**: IR $\nu_{\text{CO}}(\text{cm}^{-1})$ in methylene chloride: 2058(m), 2012(s), 1974(w), 1943(w). ^1H NMR (CD_2Cl_2 , 25 °C, TMS, δ in ppm) 1.46. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, ref. 85% ortho- H_3PO_4 in ppm): 83.74 (s, 3P, P-Au); at -75 °C CD_2Cl_2 : 82.30 (s, 2P, P-Au) and 81.15 (s, 1P, P-Au). Pos. Ion ES/MS $m/z=2736$ (M^+). Attempts to obtain compound **4** from compound **2** by reaction with $\text{CH}_3\text{Au}(\text{PPh}_3)$ at 40 °C or 60 °C for several hours yielded no product.

b) From $\text{Os}_6(\text{CO})_{18}$: 36 mg (0.022 mmol) of $\text{Os}_6(\text{CO})_{18}$ is dissolved in 30 mL of dichloromethane and 5 mL of acetonitrile solution. 2.2 mg (0.03 mmol) of Me_3NO was added and the solution was stirred at 25 °C for 3 h. The solvent was removed *in vacuo*, and the product was then purified by filtering through a silicon plug with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ elution, (V/V=19). 23.8 mg of product was recovered. It was then dissolved in 30 mL of dichloromethane and 15 mg of $\text{CH}_3\text{Au}(\text{PPh}_3)$ was added. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed *in vacuo*, and the product was then isolated by TLC by using a 3:1 hexane/methylene chloride solvent mixture. In order of elution they gave 3 mg of unreacted $\text{Os}_6(\text{CO})_{18}$, 2.0 mg (9.6 % yield) of the known compound, $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)(\mu\text{-H})$, 5.0 mg (24 % yield) of compound **2** and 3.0 mg of purple **4** (14 % yield).

Crystallographic Analyses. Black crystals **2** and red crystals **3** were obtained by slow evaporation of solvent from a solution of the pure compounds in a hexane/benzene solvent mixtures at room temperature. Purple crystals of **4** were obtained by slow evaporation of the hexane/dichloromethane solution at 5°C. The data crystals were glued onto the end of thin glass fibers. X-ray intensity data for compound **2** were collected at 100(2) K by using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å). For compounds **3** and **4**, the X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [17]. Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS [17]. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 by using the SHELXTL software package [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established by the systematic absences in the data and further confirmed by the successful solution and refinement for the structure. Compounds **3** and **4** crystallized in the triclinic crystal system. The space group is $P-1$ was assumed and confirmed by the successful solution and refinement of the structure. Compound **4** crystallized with two independent formula equivalents of the complex in the asymmetric unit of the cell. A large region of heavily disordered solvent molecules remained. No stable and reasonable disorder model could be achieved for these species despite much model

effort. The contribution of these diffusely scattering species was therefore subtracted from the structure factors by using the Squeeze treatment [19]. Squeeze calculated a solvent-accessible volume of 1435.1 Å³ (18.3% of the total unit cell volume), corresponding to 450 electrons per unit cell. Based on trial disordered modeling attempts, the solvents are a mixture of methylene chloride and hexanes. Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Results and Discussion

The reaction of [PPN]₂[Os₅(CO)₁₅] with [Au(PPh₃)] [NO₃] yielded two products the digoldpentaosmium compound Os₅(CO)₁₅(μ₃-AuPPh₃)₂, **2** in 16% yield [12], and the tetragoldpentaosmium compound Os₅(CO)₁₄[μ₄-Au₃(PPh₃)₃](μ₃-AuPPh₃), **3** in 67 % yield. Johnson and Lewis previously reported the compound **2** obtained from the reaction of [PPN]₂[Os₅(CO)₁₅] with ClAu(PPh₃) and also from the reactions of Os₅(CO)₁₅(μ-H)₂ or Os₅(CO)₁₅[μ₃-Au(PPh₃)](μ-H) with an excess of ClAu(PPh₃) [12]. Compound **2** was not previously characterized structurally, so we proceeded to perform that analysis in this study. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. Compound **2** contains a trigonalbipyramidal cluster of five osmium atoms with two triply bridging AuPPh₃ groups. It is structurally similar to the compound Os₅(CO)₁₅[μ₃-Au(PPh₃)](μ-H), **5** which has an edge bridging hydrido ligand in place of one of the triply bridging AuPPh₃ groups. The Os – Os bond distances in **2** range from 2.7981(2) Å to 2.9939(2) Å and are similar to those observed in **5**. The Au(PPh₃) groups bridge adjacent Os₃ triangles and share the apical – equatorial Os(1) – Os(2) bond which is the longest Os – Os bond in the molecule. This is one of five possible isomers for **2** that were previously enumerated for the structure of **2** [12]. The Au – Os bond distances are somewhat uneven over a range from 2.7724(2) Å to 3.1663(2) Å, but are similar to those found

in **5**. The two longest Au – Os distances share the apical osmium atom Os(1), Au(1) – Os(1) = 2.9046(2) Å and Au(2) – Os(1) = 3.1662(2) Å. Assuming that each AuPPh₃ group donates one electron to the Os₅ cluster, compound **2** contains a total of 72 cluster valence electrons and is electron precise, i.e. all of the osmium atoms have 18 electron configurations.

An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. Compound **3** also contains a trigonalbipyramidal cluster of five osmium atoms. There are four Au(PPh₃) groups in compound **3**. One Au(PPh₃) group is a triple bridge on the Os(3), Os(4), Os(5) triangular face. The other three AuPPh₃ groups bridge the two triangular faces Os(2), Os(3), Os(5) and Os(2), Os(4), Os(5) as joined quadruply-bridging trigold group. In particular, Au(1) is joined to Au(2) by a long bond, Au(1) – Au(2) = 3.1203(8) Å and Au(2) is joined to Au(3) by another long bond, Au(2) – Au(3) = 3.1709(9) Å. Au(2) is bond bonded only to Os(2), Os(2) – Au(2) = 2.6710(7) Å while Au(1) is bonded to Os(2), Os(4) and Os(5); Au(1) – Os(2) = 2.7915(8) Å, Au(1) – Os(4) = 2.9914(8) Å, Au(1) – Os(5) = 2.8208(7) Å, and Au(3) is bonded to Os(3) and Os(2), Os(3) and Os(5), Au(3) – Os(2) = 2.7573(8) Å, Au(3) – Os(3) = 3.1503(8) Å, Au(3) – Os(5) = 2.8290(7) Å. The Au(1) – Au(2) – Au(3) bond angle is 90.53(2)°. The ³¹P{¹H} NMR spectrum of **3** exhibits three resonances at δ = 92.19 (s), 49.98 (s) and 88.89 (s) in a 1:1:2 ratio, respectively which is consistent with the structure as observed in the solid state. Assuming that each Au(PPh₃) group donates one electron to the Os₅ cluster, compound **3** contains a total of 72 cluster valence electrons and like compound **2** is electron precise, however this leaves no electrons for the formation of two-center:two electron Au – Au bonds as observed in the quadruply-bridging trigold group. Indeed, these two Au – Au “bonds” trigold group are long and the attractive forces in them may be dominated by “aurophilic” interactions [20].

The reaction of [PPN]₂[Os₅(CO)₁₅] with [Au(PPh₃)] [NO₃] in the presence of CH₃Au(PPh₃) yielded the two products **2** and **3** in 23% and 15% yields, respectively, and the new

compound $\text{Os}_5(\text{CO})_{14}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_3$, **4** in 26% yield. Compound **4** was characterized crystallographically and an ORTEP diagram of its molecular structure is shown in Figure 3. Compound **4** contains a trigonalbipyramidal cluster of five osmium atoms with three triply bridging $\text{Au}(\text{PPh}_3)$ groups. There is one $\text{Au}(\text{PPh}_3)$ bridging group on each of the triangular faces associated with the apical osmium atom $\text{Os}(2)$. The Os – Os and Os – Au bond distances are similar to those observed in compounds **2** and **3**. An interesting feature of the structure of compound **4** is the presence of a methyl group C(1) on the apical osmium atom $\text{Os}(2)$, $\text{Os}(2) - \text{C}(1) = 2.194(19) \text{ \AA}$, $\delta = 1.46$ in the ^1H NMR spectrum. The ^{31}P NMR spectrum of **4** exhibits only one resonance at $\delta = 83.74$ which is not consistent with the observed structure in the solid state, so suspecting dynamical averaging, low temperature measurements were performed. As the temperature was lowered the single ^{31}P resonance broadened and then reformed as two sharp resonances at 82.30 (2P) and 81.15 (1P) in a 2/1 ratio which is consistent with the structure of **4** as found in the solid state. The coalescence temperature was approx. -25°C . The mechanism for the dynamical averaging of the PPh_3 ligands in **4** has not been uniquely established, but we can say that PPh_3 dissociative processes can be ruled out because a ^{31}P NMR spectrum of **4** in the presence of free PPh_3 showed no exchange between the complex and that of the free PPh_3 . It is known that bridging AuPPh_3 groupings can intramolecularly migrate about the surface of metal cluster complexes and we believe that such processes are going on in **4** which could lead to the averaging of the $\text{Au}(\text{PPh}_3)$ groupings at room temperature [5b, 23]. Overall, compound **4** also contains 72 cluster valence electrons and is thus electron precise.

It would seem like compound **4** is an obvious product of a reaction of compound **2** with $\text{CH}_3\text{Au}(\text{PPh}_3)$, but attempts to obtain **4** by a direct reaction of **2** with $\text{CH}_3\text{Au}(\text{PPh}_3)$ failed completely. Thus, it appears that the $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ might in some way be responsible for the

activation of the $\text{CH}_3\text{Au}(\text{PPh}_3)$ toward addition to $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ in the $[\text{Au}(\text{PPh}_3)][\text{NO}_3] / \text{CH}_3\text{Au}(\text{PPh}_3)$ mixture. Studies have shown that cationic digold species, such as $[\text{RAu}_2(\text{PPh}_3)_2]^+$, are formed in mixtures of cationic phosphine complexes $[\text{Au}(\text{PPh}_3)]^+$ with ArylAu(PPh₃) complexes [21, 22]. It is likely that cationic digold species could be formed in mixtures of $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ and $\text{CH}_3\text{Au}(\text{PPh}_3)$. In Scheme 1, we have presented three plausible pathways for the formation of compound **4** in the reaction of $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ with the $[\text{Au}(\text{PPh}_3)][\text{NO}_3] / \text{CH}_3\text{Au}(\text{PPh}_3)$ mixture. Pathway (1) would proceed via the complex **2**, which we have already obtained independently from the reaction of $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ with $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$, followed by the reaction of **2** with $\text{CH}_3\text{Au}(\text{PPh}_3)$. Unfortunately, pathway (1) has been ruled out because, as we have pointed out above, we have been unable to obtain any **4** by the independent reaction of **2** with $\text{CH}_3\text{Au}(\text{PPh}_3)$. Pathway (2) is a two-step process that would involve the reaction $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ with one equivalent of $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ to yield the complex monoanion $[\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)]^-$, **6**. Indeed, this monoanion has already been obtained by Lewis through the reaction of $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ with $\text{ClAu}(\text{PPh}_3)$ [12]. A reaction of anion **6** with a digold cation, such as $[\text{CH}_3\text{Au}_2(\text{PPh}_3)_2]^+$, could produce compound **4** directly. Another possible two-step process is shown by pathway (3). An initial reaction of $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ with the digold cation $[\text{CH}_3\text{Au}_2(\text{PPh}_3)_2]^+$ could lead to a pentaosmium monoanion such as $[\text{Os}_5(\text{CO})_{15}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_2]^-$, **7**, which could then react directly with some $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ still available in solution to yield **4**. Pathway (3) is simply the reverse order of addition of the gold complexes to that of pathway (2). At this point in time, we cannot distinguish between pathways (2) and (3) with the available data and indeed, there may be still other possible pathways from $[\text{PPN}]_2[\text{Os}_5(\text{CO})_{15}]$ to **4** with other species that might be formed in the $[\text{Au}(\text{PPh}_3)][\text{NO}_3] / \text{CH}_3\text{Au}(\text{PPh}_3)$ mixtures. Compound **4** was also obtained albeit in a lower yield (14%) in combination with compound **2** (24%) and a small amount of another known Os_5Au

compound, $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)(\mu\text{-H})$, (9.6%) [12] from the reaction of $\text{Os}_6(\text{CO})_{18}$ with $\text{MeAu}(\text{PPh}_3)$ following treatment with Me_3NO .

Scheme 1

Summary and Conclusions

The reactions of the anion $[\text{Os}_5(\text{CO})_{15}]^{2-}$ with $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ yielded the digoldpentaosmium compound **2** and the tetragoldpentaosmium compound **3**. When this same reaction was performed in the presence of $\text{CH}_3\text{Au}(\text{PPh}_3)$, the new compound **4** was formed which contains a methyl group terminally coordinated to the apical osmium atom of the tri- $\text{Au}(\text{PPh}_3)$ capped trigonalbipyramidal Os_5 cluster. The lack of a reaction of **2** with $\text{CH}_3\text{Au}(\text{PPh}_3)$ to yield **4** in the absence of $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ implies that the $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$ is able to activate the

$\text{CH}_3\text{Au}(\text{PPh}_3)$ when it is present. The formation of a cationic digold species $[\text{CH}_3\text{Au}_2(\text{PPh}_3)_2]^+$ has been proposed as a possible mechanism for this activation process.

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Supplementary Material. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1403699 for compound **2**, CCDC 1403701 for compound **3** and CCDC 1403825 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZUK [Fax. (int code) +44(1223)336-033, or Email: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)].

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Figure 1. An ORTEP diagram of the molecular structure of $\text{Os}_5(\text{CO})_{15}(\mu_3\text{-AuPPh}_3)_2$, **2** showing 55% thermal ellipsoid probability. The phenyl rings on the triphenylphosphine ligands were omitted for clarity. Selected interatomic bond distances ($\text{\AA}$) are as follow: $\text{Au}(1) - \text{Os}(1) = 2.9046(2)$, $\text{Au}(1) - \text{Os}(2) = 2.7973(2)$, $\text{Au}(1) - \text{Os}(4) = 2.8618(2)$, $\text{Au}(2) - \text{Os}(1) = 3.1663(2)$, $\text{Au}(2) - \text{Os}(2) = 2.7724(2)$, $\text{Au}(2) - \text{Os}(3) = 2.7994(2)$, $\text{Os}(1) - \text{Os}(2) = 2.9939(2)$, $\text{Os}(1) - \text{Os}(3) = 2.7981(2)$, $\text{Os}(1) - \text{Os}(4) = 2.8181(2)$, $\text{Os}(2) - \text{Os}(3) = 2.9176(2)$, $\text{Os}(2) - \text{Os}(4) = 2.8760(2)$, $\text{Os}(2) - \text{Os}(5) = 2.8455(2)$, $\text{Os}(3) - \text{Os}(4) = 2.8507(2)$, $\text{Os}(3) - \text{Os}(5) = 2.8129(2)$, $\text{Os}(4) - \text{Os}(5) = 2.8101(2)$.

Figure 2. An ORTEP molecular structure of $\text{Os}_5(\text{CO})_{14}[\mu_4\text{-Au}_3(\text{PPh}_3)_3](\mu_3\text{-AuPPh}_3)$, **3** showing 10% thermal ellipsoid probability. The phenyl rings on the triphenylphosphine ligands were omitted for clarity. Selected interatomic bond distances (Å) and angles (°) are as follow: $\text{Au}(1) - \text{Os}(2) = 2.7915(8)$, $\text{Au}(1) - \text{Os}(4) = 2.9914(7)$, $\text{Au}(1) - \text{Os}(5) = 2.8208(7)$, $\text{Au}(2) - \text{Os}(2) = 2.6710(7)$, $\text{Au}(3) - \text{Os}(2) = 2.7573(8)$, $\text{Au}(3) - \text{Os}(3) = 3.1503(8)$, $\text{Au}(3) - \text{Os}(5) = 2.8290(8)$, $\text{Au}(4) - \text{Os}(5) = 2.9584(8)$, $\text{Au}(4) - \text{Os}(3) = 2.7957(8)$, $\text{Au}(4) - \text{Os}(4) = 2.8040(8)$, $\text{Au}(1) - \text{Au}(2) = 3.1203(8)$, $\text{Au}(2) - \text{Au}(3) = 3.1709(9)$, $\text{Os}(1) - \text{Os}(2) = 2.7176(7)$, $\text{Os}(1) - \text{Os}(3) = 2.8470(8)$, $\text{Os}(1) - \text{Os}(4) = 2.8710(8)$, $\text{Os}(2) - \text{Os}(3) = 2.8691(7)$, $\text{Os}(2) - \text{Os}(4) = 2.8837(8)$, $\text{Os}(2) - \text{Os}(5) = 2.8700(8)$, $\text{Os}(3) - \text{Os}(4) = 2.9124(7)$, $\text{Os}(3) - \text{Os}(5) = 2.9574(7)$, $\text{Os}(4) - \text{Os}(5) = 2.9778(7)$; $\text{Au}(1) - \text{Au}(2) - \text{Au}(3) = 90.53(2)$

Figure 3. An ORTEP diagram of the molecular structure of $\text{Os}_5(\text{CO})_{14}(\text{CH}_3)(\mu_3\text{-AuPPh}_3)_3$, **4** showing 30% thermal ellipsoid probability. The phenyl rings on the triphenylphosphine ligands were omitted for clarity. Selected interatomic bond distances ($\text{\AA}$) and angles ($^\circ$) are as follows: $\text{Os}(2) - \text{C}(1) = 2.194(19)$, $\text{Au}(1) - \text{Os}(1) = 2.8446(9)$, $\text{Au}(1) - \text{Os}(2) = 2.8400(11)$, $\text{Au}(2) - \text{Os}(1) = 2.8683(10)$, $\text{Au}(2) - \text{Os}(2) = 2.8368(9)$, $\text{Au}(2) - \text{Os}(4) = 2.8423(10)$, $\text{Au}(3) - \text{Os}(2) = 2.8557(10)$, $\text{Au}(3) - \text{Os}(3) = 2.8276(11)$, $\text{Au}(3) - \text{Os}(4) = 2.8446(9)$, $\text{Os}(1) - \text{Os}(2) = 2.9631(10)$, $\text{Os}(1) - \text{Os}(3) = 2.9358(9)$, $\text{Os}(1) - \text{Os}(4) = 2.9462(10)$, $\text{Os}(1) - \text{Os}(5) = 2.8563(10)$, $\text{Os}(2) - \text{Os}(3) = 2.9702(10)$, $\text{Os}(2) - \text{Os}(4) = 2.9712(9)$, $\text{Os}(3) - \text{Os}(4) = 2.9640(9)$, $\text{Os}(3) - \text{Os}(5) = 2.8248(10)$, $\text{Os}(4) - \text{Os}(5) = 2.8599(11)$.

Table 1. Crystallographic Data for Compounds 2, 3 and 4.

Compound	2	3	4
Empirical formula	Os ₅ Au ₂ P ₂ O ₂₅ C ₅₁ H ₃₀ · 2 C ₆ H ₆	Os ₅ Au ₄ P ₄ O ₁₄ C ₈₆ H ₆₀ · 1.5 C ₆ H ₆	Os ₅ Au ₃ P ₃ O ₁₄ C ₆₉ H ₄₈
Formula weight	2446.00	3297.25	2736.05
Crystal system	Monoclinic	Triclinic	Triclinic
Lattice parameters			
<i>a</i> (Å)	13.9991(7)	14.1588(12)	13.4578(11)
<i>b</i> (Å)	25.8034(13)	14.6336(13)	24.212(2)
<i>c</i> (Å)	17.4479(9)	24.289(2)	26.750(2)
α (°)	90.00	77.114(2)	107.594(2)
β (°)	96.151(2)	85.708(2)	95.645(2)
γ (°)	90.00	70.422(2)	105.639(2)
<i>V</i> (Å ³)	6266.3(5)	4622.1(7)	7846.0(11)
Space group	P2 ₁ /c (#14)	P-1 (#2)	P-1 (#2)
Z value	4	2	4
ρ_{calc} (g / cm ³)	2.562	2.369	2.316
μ (Mo K α) (mm ⁻¹)	0.71073	0.71073	0.71073
Temperature (K)	100(2)	294(2)	294(2)
2 Θ_{max} (°)	55.16	56.58	50.06
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	13358	12053	16187
No. Parameters	784	1054	1635
Goodness of fit (GOF)	1.122	1.038	0.957
Max. shift in cycle	0.005	0.007	0.019
Residuals*: R1; wR2	0.0182; 0.0358	0.0509; 0.1109	0.0605; 0.1460
Absorption Correction,	Multi-scan	Multi-scan	Multi-scan
Max/min	1.000/ 0.576	1.000 / 0.390	1.000 / 0.339
Largest peak in Final Diff.	1.77		3.43
Map (e ⁻ / Å ³)		2.41	

* $R = \sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|$; $R_w = [\sum_{\text{hkl}} w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$;
 $\text{GOF} = [\sum_{\text{hkl}} w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.

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