Reaction of $[Os_4(\mu\text{-}Cl)(CO)_{13}]^-$ with the $[Au(PPh_3)]^+$ Cation involving Insertion of an $Os(CO)_4$ Fragment into the Gold–Phosphorus Bond

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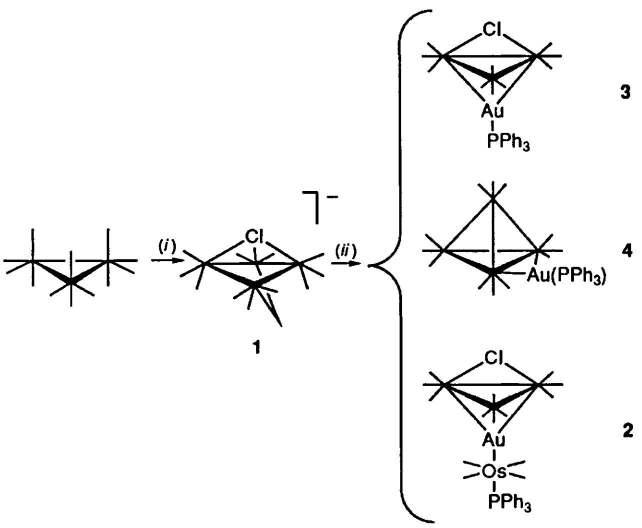
The reaction of the cluster anion $[Os_4(\mu\text{-}Cl)(CO)_{13}]^-$ **1** with $[Au(PPh_3)]^+$ affords the cluster $[Os_3\{\mu\text{-}AuOs(CO)_4(PPh_3)\}(\mu\text{-}Cl)(CO)_{10}]$ **2** which represents the first example in which an $Os(CO)_4$ fragment has been inserted in to a gold–phosphine bond; the structure of **2** has been established by a single-crystal X-ray analysis.

It has been found that the reaction between $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2]Cl$ is the best preparative route to the salt $[N(PPh_3)_2][Ru_4(\mu\text{-}Cl)(CO)_{13}]$.[1] We now report an extension of this mode of synthesis to give the corresponding osmium anion $[Os_4(\mu\text{-}Cl)(CO)_{13}]^-$ **1** as its $[N(PPh_3)_2]^+$ salt in a yield of 50%. The reaction of the cluster **1** (50 mg, 0.029 mol) with $[Au(PPh_3)][NO_3]$ (15.3 mg, 0.029 mmol) yields the new cluster $[Os_3\{\mu\text{-}AuOs(CO)_4(PPh_3)\}(\mu\text{-}Cl)(CO)_{10}]$ **2** (20%) together with the known complexes $[Os_3\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Cl)(CO)_{10}]^2$ **3** (40%) and $[Os_4H_3\{\mu\text{-}Au(PPh_3)\}(CO)_{12}]^3$ **4** (30%) (Scheme 1). The formation of **2** is thought to involve the cleavage of a gold–phosphorus bond of the Au(PPh₃) unit and the novel insertion of an $Os(CO)_4$ fragment. Alternatively **2** may be viewed as arising from the oxidative-addition of the $[Au(PPh_3)]^+$ group to the $Os(CO)_4$ fragment.

The compounds **1**–**4** have been isolated as air stable solids. The mass and IR spectra are consistent with the proposed molecular formulae,† and in the cases of clusters **3** and **4** with the previously reported[2,3] spectroscopic values. The ^{31}P NMR spectra exhibit resonances in the range δ −63.6 to −62.0 which may be assigned to the co-ordinated phosphines. In order to establish the geometry of **2** its crystal structure has been determined.‡



Scheme 1 (*i*) $[N(PPh_3)_2]Cl$, tetrahydrofuran (thf), heat; (*ii*) $[Au(PPh_3)][NO_3]$, thf, heat

The molecular structure of **2** is shown in Fig. 1 together with some important bond parameters. The structure may be described as an osmium triangle with one of the osmium–osmium edges [Os(1)–Os(3)] bridged by both a chlorine ligand and a gold ligand. The fourth osmium atom is incorporated into the gold ligand forming an almost linear Au–Os(4)–P [177.6(2)°] unit. Within the osmium triangle the length of the Os–Os edge that is bridged by the chlorine and the gold ligand is slightly longer [Os(1)–Os(3) 2.908(2) Å] than is observed in the cluster $[Os_3(CO)_{10}\{Au(PPh_3)\}(\mu\text{-}Cl)]$ (Os–Os 2.86 Å).[6] Within the osmium triangle the two osmium atoms involved in the bridged edge are both co-ordinated to three terminal carbonyl ligands while the third osmium atom is co-ordinated to four terminal carbonyl ligands two axial and two equatorial. A similar arrangement of the terminal carbonyl ligands has been found in $[Os_3(CO)_{10}\{Au(PPh_3)\}(\mu\text{-}Cl)]$.[6]

The chlorine ligand is symmetrically bridging the Os(1)–Os(3) edge [Os–Cl 2.457(6) and 2.445(6) Å] and the same is observed for the gold ligand with similar gold–osmium distances [2.746(2) and 2.744(2) Å]. In the cluster $[Os_3(CO)_{10}\{Au(PPh_3)\}(\mu\text{-}Cl)]$ both the chlorine and the gold

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† Spectroscopic data. The $[N(PPh_3)_2]^+$ salt of **1**: IR ν(CO) (*n*-hexane) 2069w, 2034s, 2012s, 1971m, 1805w cm⁻¹; FAB mass spectrum M^+ (obs.) *m*/*z* 1160. (calc.) 1160,**2**: IR ν(CO) (*n*-hexane) 2088w, 2042vs, 2019(sh), 2006s, 1976w cm⁻¹; FAB mass spectrum M^+ (obs.), *m*/*z* 1647 (calc.) 1647; ^1H NMR ($CDCl_3$) δ 6.7 (m, 18 H, PPh₃). **4**: IR ν(CO) (*n*-hexane) 2095m, 2071s, 2034vs, 2008s, 1956m cm⁻¹; FAB mass spectrum M^+ (obs.) *m*/*z* 1558, (calc.) 1559; ^1H NMR ($CDCl_3$) δ 6.4 (m, 18 H, PPh₃), −21.9 (d, 0.8 Hz, 3 H, MH).

‡ Crystal data for **2**. $C_{32}H_{15}AuClO_{14}Os_4P$, M = 1647.6, triclinic, space group $P\bar{1}$ (no. 2), a = 9.553(5), b = 13.499(6), c = 15.693(5) Å, α = 108.29(3), β = 93.18(4), γ = 97.86(4)°, U = 1893.0(14) Å³, Z = 2, D_c = 2.89 g m⁻³, $F(000)$ = 1468, μ(Mo-Kα) = 174.1 cm⁻¹, crystal dimensions 0.10 × 0.18 × 0.25 mm, 4987 unique diffractometer data. Structure solved by direct methods (SHELXTL PLUS[4]) and Fourier difference techniques, refined by full-matrix least-squares analysis on F^2 (all non-hydrogen atoms anisotropic, phenyl-H atoms placed in idealised positions and allowed to ride on the relevant C atoms, U_H = 0.08 Å²) (SHELXL 93[5]) to R_1 = 0.0495 (wR_2 = 0.092) for 4987 reflections [$I > 2\sigma(I)$], $w^{-1} = (\sigma F^2 + 0.035P)$ where $P = [(0$ or $F_o^2) + 2F_c^2]/3$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

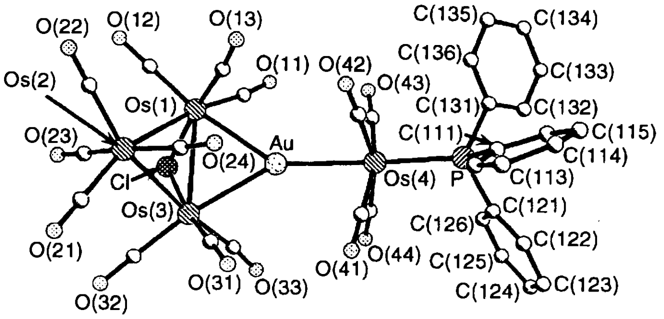

Fig. 1 The molecular structure of $[Os_3\{\mu\text{-}AuOs(CO)_4(PPh_3)\}(\mu\text{-}Cl)(CO)_{10}]$ **2** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.842(2), Os(1)–Os(3) 2.908(2), Os(2)–Os(3) 2.852(2), Os(1)–Cl 2.445(6), Os(3)–Cl 2.457(6), Os(1)–Au 2.746(2), Os(3)–Au 2.744(2), Os(4)–Au 2.706(2), Os(4)–P 2.385(6); Os(1)–Cl–Os(3) 72.8(2), Os(4)–Au–Os(1) 145.25(5), Os(4)–Au–Os(3) 150.75(5), Os(3)–Au–Os(1) 63.97(5), P–Os(4)–Au 177.6(2)

ligand bridges could also be considered symmetric (Os–Au 2.77 and 2.75 Å, Os–Cl 2.41 and 2.43 Å).[6] The Os–Au distances in **2** are slightly shorter than the Os–Au distances [2.802(2)–2.814(2) Å] in the anion $[\{Os_3H(CO)_{10}\}_2Au]^-$ where the central Au atom links two Os_3 triangles by bridging Os–Os edges.[7] The angle subtended at the gold atom by the two bridgehead osmium atoms is 63.97(5)°. The gold atom makes an angle of 54° to the plane of the osmium triangle which is smaller than the equivalent angle of 59° for the $[Os_3(CO)_{10}\{Au(PPh_3)\}(\mu\text{-}Cl)]$ cluster.[6]

Within the gold ligand, Os(4) adopts an approximately octahedral geometry with four terminal carbonyl ligands in the same plane and the gold atom and the triphenylphosphine ligand *trans* to each other. To the best of our knowledge this is the first example of an $Os(CO)_4$ unit co-ordinated in this manner although the osmium triangle is virtually identical to the known compound $[Os_3(CO)_{10}\{Au(PPh_3)\}(\mu\text{-}Cl)]$.[6] Consideration of the 18 electron rule for the Os(4) atom within the gold ligand suggests that it forms a dative bond to the gold atom. The Au–Os(4) bond length [2.706(2) Å] is shorter than the observed osmium–gold distances in the osmium triangle.

The formation of the $Au\text{–}Os(CO)_4\text{–}P$ linkage appears to be unprecedented. There are previous examples of an Au atom linking two metal clusters such as in the anion $[\{Os_3H(CO)_{10}\}_2Au]^-$.[7] Examples are also known where $Au(PR_3)$ groups form terminal gold linkages to a variety of transition metals,[8] such as in the dinuclear complexes $[Mn(CO)_5\{Au(PPh_3)\}]$ and $[V(CO)_6\{Au(PPh_3)\}]$, and in the Au-linked trimetal anion $[Au\{Mn(CO)_5\}_2]^-$.[9] In these systems the Au atom may be viewed as participating in a conventional two-centre two-electron covalent bond, in contrast to **2** where the 18 electron Os(4) centre may donate two electrons to the gold atom forming a dative covalent bond. Work is continuing to understand better the formation of **2** and to explore the chemistry of the new linkage.

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