Letter

Photochemistry of $Os_3(CO)_{12}$ with $AuPPh_3Cl$: synthesis and structural characterisation of (μ-$AuPPh_3$)(μ-Cl)$Os_3(CO)_{10}$

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Studies showing the potential of photochemistry for the preparation of mixed-metal clusters are presented, the synthesis and molecular structure of (μ-$AuPPh_3$)(μ-Cl)$Os_3(CO)_{10}$ being reported.

The photochemistry of organometallic compounds is a developing research area, being of importance both in synthesis and catalysis as well as proving fascinating in its own right.[1,2] Research in our group has focused on harnessing the synthetic potential of photochemistry to generate known and novel compounds efficiently and in high yields.[3]

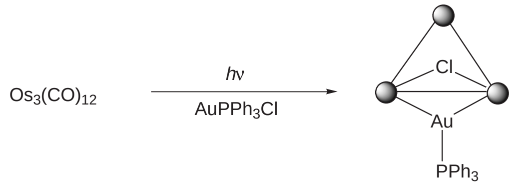
The trinuclear clusters $M_3(CO)_{12}$ [M = Ru (**1a**), Os (**1b**)] can, in principle, undergo either photofragmentation or photosubstitution reactions. The photochemistry of **1a** can be controlled by the solvent in which the reaction is undertaken, solvents such as hexane favouring fragmentation and donor solvents such as ethyl acetate favouring substitution.[4] In the case of **1b**, although substitution dominates the photochemistry in most media, by using a donor solvent it is possible to stabilise the coordinatively unsaturated fragment $[M_3(CO)_{11}]$ formed and, in the presence of a ligand, it is possible to form substitution products.[5] To date, we have used photochemistry to attach organic fragments to organometallic fragments. The work reported here represents an extension of that work to look at the photogeneration of polynuclear mixed-metal complexes. Since we have shown that photochemistry offers a route to the di-hydrido cluster (μ-H)$_2$$Ru_3(CO)_{10}$ and the hydrogen chloride bridged complex (μ-H)(μ-Cl)$Ru_3(CO)_{10}$,[6] it was decided to investigate the photochemistry of $M_3(CO)_{12}$ with the isolobal fragment $AuPPh_3Cl$. Since osmium clusters are often more stable than their ruthenium counterparts, initial studies have focused on the photochemistry of **1b** with the gold fragment.

Broad-band UV irradiation of an ethyl acetate solution of **1b** (30 mg in 100 ml) containing an excess (3 equiv.) of $AuPPh_3Cl$ leads to the formation of the bimetallic cluster (μ-$AuPPh_3$)(μ-Cl)$Os_3(CO)_{10}$ (**2b**) (Fig. 1).† The cluster is not photostable and prolonged irradiation of the reaction mixture leads to decomposition. The optimal photolysis time was found to be 30 min, this producing **2b** in *ca.* 60% yield after chromatographic separation.

Although **2b** has been prepared previously, by refluxing a xylene solution of **1b** with $AuPPh_3Cl$, the yields are significantly lower than by the presented photochemical routes.[7] In addition, in the case of the thermochemical route, a number of by-products are formed, this making separation of the desired product difficult. This is not the case in the photochemical preparation where careful monitoring of the conditions leads to the product being formed with minimal decomposition or by-product formation.

The molecular structure of **2b** was determined by a single-crystal X-ray diffraction study and is shown in Fig. 2 together with selected bond lengths and angles.‡

The solid-state structure of **2b** is consistent with that proposed in solution, the $AuPPh_3$ and Cl moieties bridging one of the Os—Os bonds symmetrically. The doubly-bridged Os(l)—Os(2) bond is slightly longer [2.880(2) Å] and the unbridged Os—Os bonds slightly shorter [mean 2.838(5) Å] than the metal–metal bonds in the parent cluster **1b** [mean 2.867(3) Å].[8] This compares to a doubly bridged Os—Os



(μ-$AuPPh_3$)(μ-Cl)$Os_3(CO)_{10}$

2b

Fig. 1 The photochemical reaction of $Os_3(CO)_{12}$ with $AuPPh_3Cl$

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† All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a nitrogen bubbler, reflux condenser and dry-ice cooling finger. A 125 W mercury arc broad-band UV lamp was used as the irradiation source and reflectors placed around the reaction vessel to maximise efficiency. Photolysis mixtures were kept at between 2 and −2 °C. Product **2b** was separated by thin-layer chromatography (1 : 1 dichloromethane : hexane as eluent). Spectroscopic data for **2b**: IR (cyclohexane): ν(CO) 2097 (m), 2045 (vs), 2014 (vs), 2008 (vs), 1984 (m), 1974 (w), 1996 (m) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 7.65 (m, Ph); negative-ion FAB mass spectrum: *m/z* 1343 (calc. 1345 based on ^{190}Os and ^{197}Au).

‡ Crystal data for (μ-$AuPPh_3$)(μ-Cl)$Ru_3(CO)_{10}$ **2b**: $C_{28}H_{15}O_{10}PClOs_3Au$, $M = 1345.42$, red blocks, crystal dimensions 0.46 × 0.25 × 0.51 mm, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.892(9)$, $b = 16.899(1)$, $c = 16.255(3)$ Å, $\beta = 113.75(1)°$, $U = 3241.46(10)$ Å^3, $D_{calc} = 2.76$ Mg cm^{-3}, $Z = 4$, $F(000) = 2372$, Mo-Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 16.379 mm^{-1}, $T = 298(2)$ K. Stoe-Siemens AED diffractometer, 7019 reflections collected by the ω/θ scan method in the range $2.5° \leqslant \theta \leqslant 25.00°$. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections ($20 < 2\theta < 22.5°$). An analytical absorption correction based on 12 indexed faces was applied. The structure was solved by direct methods followed by Fourier difference synthesis and refined by blocked-cascade least-squares on F (SHELXL-76).[11] All Au, Os, P, Cl and O atoms were treated anisotropically. The hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. The phenyl rings on the triphenylphosphine moiety were refined as rigid groups with the bond lengths and angles fixed at 1.395 Å and 120°, respctively. The refinement converged at $R1 = 0.055$ and $wR1 = 0.0450$ for 4298 observed data [$F > 4\sigma(F)$]. $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $wR1 = [\Sigma w^{1/2}(\| F_o | - | F_c \|)/\Sigma w^{1/2} | F_o |]$, $w = 1/[\sigma^2(F_o)^2 + 0.00080F^2]$. The final difference synthesis showed no Δρ above 2.53 or below −1.91 eÅ^{-3}, the major features lying near the osmium and gold atoms. CCDC reference number 440/040.

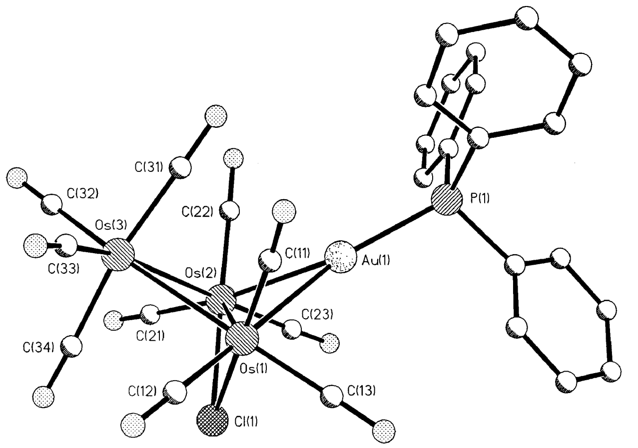

Fig. 2 The molecular structure of (μ-$AuPPh_3$)(μ-Cl)$Os_3(CO)_{10}$ (**2b**) showing the atomic numbering scheme; O, phenyl C and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)—Os(2) 2.880(2), Os(2)—Os(3) 2.835(2), Os(1)—Os(3) 2.841(2), Au(1)—Os(1) 2.766(2), Au(1)—Os(2) 2.765(2), Au(1)—P(1) 2.309(4), Os(1)—Cl(1) 2.450(4), Os(2)—Cl(1) 2.459(4), Os(1)—C(11) 1.881(15), Os(1)—C(12) 1.940(21), Os(1)—C(13) 1.919(20), Os(2)—C(21) 1.942(18), Os(2)—C(22) 1.868(14), Os(2)—C(23) 1.905(21), Os(3)—C(31) 1.961(16), Os(3)—C(32) 1.946(21), Os(3)—C(33) 1.911(21), Os(3)—C(34) 1.936(15), Os(1)—Os(2)—Os(3) 59.6(1), Os(2)—Os(1)—Os(3) 59.4(1), Os(1)—Os(3)—Os(2) 61.0(1), Os(1)—Os(2)—Cl(1) 53.9(1), Os(2)—Os(1)—Cl(1) 54.2(1), Os(3)—Os(2)—Cl(1) 87.2(1), Os(3)—Os(1)—Cl(1) 87.3(1), Os(3)—Os(1)—Cl(1) 87.3(1), Au(1)—Os(1)—Os(2) 58.6(1), Au(1)—Os(2)—Os(3) 96.5(1), Au(1)—Os(1)—Os(3) 96.4(1), Os(1)—Au(1)—Os(2) 62.7(1), Os(1)—Au(1)—P(1) 150.7(1), Os(2)—Au(1)—P(1) 146.6(1), Au(1)—Os(1)—Cl(1) 97.1(1), Au(1)—Os(2)—Cl(1) 96.9(1).

bond length of 2.846(1) Å in the related cluster (μ-H)(μ-Cl) $Os_3(CO)_{10}$ (**3b**)^9 and, although the difference in doubly-bridged Os—Os bond lengths in **2b** and **3b** at 0.034 Å is on the limit of chemical significance, bond lengthening influence induced by a bridging gold atom is greater than the related effect of a bridging hydride ligand. Comparison between the doubly bridged metal–metal bond lengths in (μ-$AuPPh_3$)(μ-Cl)$Ru_3(CO)_{10}$ [2.8742 (6) Å]^{10} and (μ-H)(μ-Cl)$Ru_3(CO)_{10}$ [2.833 (2) Å]^{6b} reveals a similar trend.

The dihedral angles made by the Os(1)—Os(2)—Au(1) and Os(1)—Os(2)—Cl(1) planes with the Os(3) triangle are 120.8° and 110.0°, respectively. As a result, **2b** can be considered as consisting of a 'butterfly' metal framework with the gold atom adopting a wing-tip position.

All the carbonyl ligands in **2b** are terminally bound but their arrangement and bonding are of interest. The bridging gold and chlorine groups force the carbonyl ligands C(12)—O(12), C(13)—O(13), C(21)—O(21) and C(23)—O(23) into semi-axial positions. There is a distinct *trans* influence in the metal-carbonyl distances for the carbonyl groups *trans* to the halogen atom, these being the shortest Os—C(O) bonds [Os(1)—C(11) = 1.881 (15) Å, Os(2)—C(22) = 1.868 (14) Å]. The longest Os—C(O) bonds are found to involve the carbonyl ligands on Os(3) that are *trans* to each other [Os(3)—C(31) = 1.961(16) Å, Os(3)—C(32) = 1.946 (24) Å]. All these bond lengths can be compared to those reported for **1b** [Os—CO(equatorial) = 1.912 (7) Å, Os—CO(axial) = 1.946(6) Å].

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