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Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF $[Pt_3Au(\mu_2\text{-}CO)_3(PCy_3)_4]PF_6$; A TETRAHEDRAL PLATINUM–GOLD CLUSTER

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Summary

$[Pt_3Au(\mu_2\text{-}CO)_3(PCy_3)_4](PF_6)$ (Cy = cyclohexyl) has been synthesised from $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$, and $AuClPCy_3$ in benzene and characterised by IR, NMR ($^{31}P\{^1H\}$) and a single crystal X-ray crystallographic analysis. It represents the first example of a tetrahedral platinum–gold cluster compound, with the $AuPCy_3$ fragment occupying an apical site above the $Pt_3(CO)_3(PCy_3)_3$ triangle.

As early as 1967 Layton et al. [1] proposed, largely on the basis of analytical data, the formation of a compound with a platinum–gold bond from the oxidative-addition reaction of $Pt(PPh_3)_3$ with $AuCl(PPh_3)$. Since that time a large number of heteronuclear metal clusters of Group VIII metals and gold have been synthesised, but surprisingly no examples of structurally characterised platinum–gold clusters have appeared in the literature [2]. Furthermore, the recent report that $Ph_3PAuC_6Cl_5$ prefers to undergo oxidative-addition reactions with $Pt(PPh_3)_3$ involving an *ortho*-C–Cl bond rather than the Au–C bond [3,4] has raised some doubts about the stabilities of gold–platinum cluster compounds. In this and the subsequent communication we report the structural characterisation of two distinct types of tetranuclear platinum–gold cluster compounds.

The synthesis of mixed metal gold cluster compounds has depended primarily on the isolobal relationship between $AuPPh_3$ and the hydrido ligand [5,6] and involved either the addition of $AuPPh_3^+$ to metal carbonyl cluster anions [7], or the elimination of methane from a metal carbonyl hydrido cluster and CH_3AuPPh_3 [8]. We have found that the neutral triangulo cluster of platinum $[Pt_3(CO)_3(PCy_3)_3]$ [9] is sufficiently nucleophilic to react with $AuPCy_3^+$, when formed in situ from $AuClPCy_3$ and $TlPF_6$ [7]. No reaction was observed between $AuClPCy_3$ and $[Pt_3(CO)_3(PCy_3)_3]$ (I) in benzene, but on stirring for

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one hour with $TlPF_6$ an orange-red powder separated. Recrystallisation of the solid from CH_2Cl_2/hexane gave small red crystals of $[Pt_3Au(CO)_3(PCy_3)_4](PF_6)$ (II) in 80% yield.

The infrared spectrum of II (ν(CO) 1775vw, 1805s and 1875vw cm^{-1}; as Nujol mull) is almost identical to that for I, but shifted to higher frequency by ca. 30 cm^{-1}. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of II in CD_2Cl_2 also indicated the retention of the triangular $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ fragment and a symmetrical disposition of the $AuPCy_3$ fragment above this triangle. $^{31}P\{^1H\}$ (to high frequency of trimethylphosphate), δ 51.9 ppm (m, 3P, $PtPCy_3$, $^1J(Pt-P)$ 4898.5, $^2J(Pt-P)$ 282.4, $^1J(Pt-Pt)$ 2100, $^3J(P_{Pt}-P_{Pt}) = {}^3J(P_{Au}-P_{Pt}) = 24.8$ Hz); 82.7 ppm (m, 1P, $AuPCy_3$, $^2J(Pt-P)$ 176.8, $^3J(P_{Au}-P_{Pt})$ 24.8 Hz). $^{195}Pt\{^1H\}$ δ −4583 ppm (to low frequency of Na_2PtCl_6). In I the $^1J(Pt-P)$ and $^1J(Pt-Pt)$ coupling constants are somewhat lower viz. 4412 and 1571 Hz. In order to confirm that the $AuPCy_3$ fragment had capped the parent platinum triangle and formed a tetrahedral cluster a single crystal X-ray crystallographic analysis of II was undertaken.

Crystal data. $C_{75}H_{132}AuF_6O_3P_5Pt_3$ (II), $M = 2132.7$, monoclinic, a 19.149(6), b 18.567(5), c 50.968(12) Å, β 95.96(2)°, U 18023 $Å^3$, space group $C2/c$, $Z = 8$, D_c 1.57 g cm^{-3}, $F(000)$ 8384 electrons, $\mu(Cu\text{-}K_\alpha)$ 129.8 cm^{-1}. Intensity data were collected on a small crystal of approximate dimensions 0.23 × 0.28 × 0.10 mm at ca. 291 K on an Enraf—Nonius CAD4F diffractometer using graphite monochromated $Cu\text{-}K_\alpha$ (λ 1.5418 Å) X-radiation. Of 3386 reflections measured

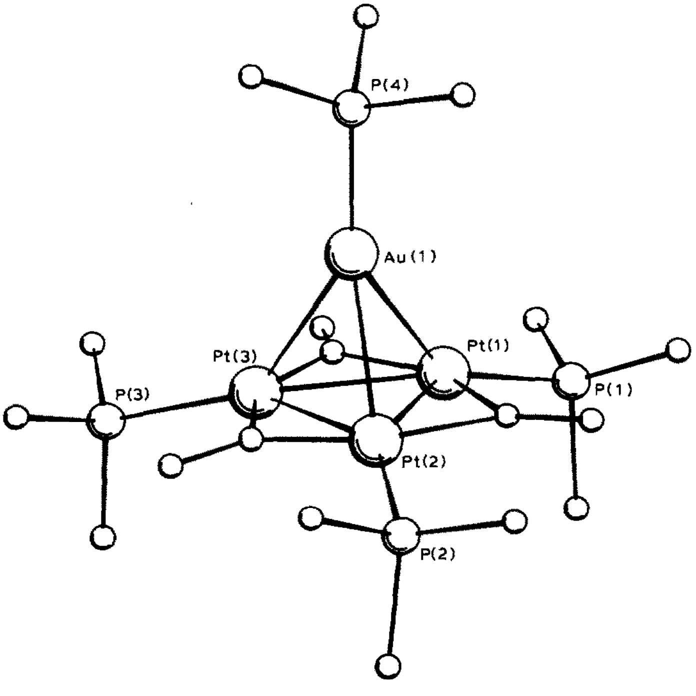

Fig. 1. Structure of the $[Pt_3Au(CO)_3(PCy_3)_4]^+$ cation. For reasons of clarity the cyclohexyl rings have been omitted except for the *ipso* carbon atoms. Important bond lengths include: Pt(1)—Pt(2) 2.705(6), Pt(2)—Pt(3) 2.678(5), Pt(1)—Pt(3) 2.704(6), Pt(1)—Au(1) 2.768(5), Pt(2)—Au(1) 2.757(5), Pt(3)—Au(1) 2.750(5), Pt(1)—P(1) 2.24(3), Pt(2)—P(2) 2.29(3), Pt(3)—P(3) 2.29(3) and Au(1)—P(1) 2.27(3) Å.

in the θ range 1.0 to 35°, 2028 with $I \geqslant 3\sigma(I)$ were used to solve (Patterson and Fourier methods) the structure. The carbonyl atoms were located in a difference Fourier synthesis, but the carbon atom positions were not refined due to instability. This was attributed either to the poor quality of the X-ray data (unsatisfactory absorption correction) or partial disorder of the structure resulting from the approximate tetrahedral symmetry of the $AuPt_3(PCy_3)_4$ moiety. Least-squares refinement of the remaining atoms (Pt and Au anisotropic) has led to a current R of 0.085*. The PF_6^- anions are disordered about a position of two-fold symmetry and a centre of symmetry in the unit cell. Larger and better quality crystals have now been obtained and a data set with Mo-K_α radiation is being collected.

The structure illustrated in Fig. 1 for the $[Pt_3Au(CO)_3(PCy_3)_4]^+$ cation II has confirmed the symmetrical tetrahedral structure suggested by the spectroscopic evidence. The cation has a total of 54 valence electrons which makes it isoelectronic and isostructural with the tetrahedral $[Au_4I_2(PPh_3)_4]$ cluster [10], but it has two electrons fewer than the tetrahedral $[Pt_4H_8(PPr^i_2Ph)_4]$ cluster [11]. The platinum—platinum bond lengths in II are significantly shorter (average 2.696(9) Å) than the platinum—gold bonds (average 2.758(5) Å), but longer than those reported for the parent triangulo cluster (viz. 2.655(2) Å) [12]. The carbonyl ligands remain essentially coplanar with the platinum triangle, but the phosphine ligands make an average angle of 17° to this plane and point towards the centroid of the tetrahedron, thereby minimising interligand repulsions and maximising the metal—metal bonding.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.