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Preliminary communication

Platinum–silver clusters: synthesis and crystal structure of $[Pt_3Ag(\mu\text{-}CO)_3(PPh_3)_5]ClO_4 \cdot 2H_2O$

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Abstract

Reaction of $[NBu_4]_2[Pt_{12}(CO)_{24}]$ with $[Ag(PPh_3)_4]ClO_4$ and PPh_3 leads to two isolable platinum–silver clusters; the title complex was characterised by single crystal X-ray diffraction. The Pt_3Ag core is tetrahedral; one Pt atom is seven-coordinate, the other two are six-coordinate.

We recently reported the synthesis, X-ray structure determination and catalytic activity of a platinum-iridium cluster [1]. The platinum carbonyl complex $[NBu_4]_2[Pt_{12}(CO)_{24}]$ (I) was found to be a useful precursor. Here we report that the reaction of I with $[Ag(PPh_3)_4]ClO_4$ (II) and PPh_3 leads to two platinum-silver clusters. The cluster $[Pt_3Ag(\mu\text{-}CO)_3(PPh_3)_5]ClO_4 \cdot 2H_2O$ (III) has been characterised by single crystal X-ray diffraction. We believe this is the first structural characterisation of a platinum-silver cluster, although a few compounds containing platinum–silver bonds are known [2]. There are indeed few clusters of silver with any transition metal [3].

The addition of increasing amounts of solid II to a solution of I in tetrahydrofuran leads to $[NBu_4]_2[Pt_{18}(CO)_{36}]$ (V), a species formulated as $[NBu_4][Pt_6Ag(PPh_3)_4(CO)_8]$ (IV), and III, respectively. V was characterised by comparison of its spectra with those of an authentic sample [4] and III and IV were identified from complete elemental analysis and infrared and ^1H NMR spectra [5 *]. The formation of metallic silver, the isolation of the known cluster $[Pt_3(CO)_3(PPh_3)_4]$ (VI) [6], and the improved yields of III and IV with added PPh_3 suggest that the reaction

* Asterisk indicates a note in the list of references.

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pathway is as shown in equations 1–3. Indeed, optimum yields of V, IV and III are obtained when the stoichiometries shown in eq. 1–3 are used.

$$3(I) + 2(II) \rightarrow 2(V) + 2Ag + 2Bu_4N^+ClO_4^- + 8PPh_3 \quad (1)$$

$$3(I) + 4(II) + 24PPh_3 \rightarrow 2(IV) + 2Ag + 4Bu_4N^+ClO_4^- + 8(VI) + 32CO \quad (2)$$

$$3(I) + 8(II) + 18PPh_3 \rightarrow 2(III) + 6Ag + 6Bu_4N^+ClO_4^- + 10(VI) + 36CO \quad (3)$$

The nature of III was unambiguously confirmed by a single crystal X-ray diffraction study (see Fig. 1). As expected from its characteristic electron count (56), the Pt_3Ag core is tetrahedral [7]. Comparison with the 54-electron platinum-gold cluster $[Pt_3Au(CO)_3(Pcy_3)_4]ClO_4$ (VII) [8], which also contains a tetrahedral core, reveals the following differences. Unlike VII, where all the Pt atoms are six-coordinate and equivalent, III contains a unique seven-cooordinate platinum atom, Pt(1). The average Pt–Pt bond lengths are identical in the two clusters (2.696 Å), but the Pt–Ag bonds are appreciably longer than the Pt–Au bonds (av. 2.827, 2.758 Å respectively). The Pt–Ag bond lengths differ considerably (2.741–2.915 Å), in accordance with theoretical predictions [7]. The Pt–Ag bond lengths in the literature [2] lie in the range 2.772–2.815 Å with the exception of one very short bond, 2.637 Å.

Compound IV has a characteristic electron count of 96, the expected value for an edge-sharing seven-vertex polyhedron. Attemps to grow a single crystal of IV are in progress.

X-Ray structure determination of III

Crystal data. $C_{93}H_{79}AgClO_9P_5Pt_3$, $M_r = 2222.1$. Monoclinic, $P2_1/n$, a 14.021(4), b 25.553(7), c 24.265(7) Å, β 90.86(3)°, U 8693 Å^3, Z 4, D_x 1.70 g cm^{-3}, $F(000)$ 4320, λ(Mo-K_α) 0.71069 Å, μ 5.3 mm^{-1}. 13343 profile-fitted reflections [9] measured on Stoe-Siemens four-circle diffractometer, $2\theta_{max}$ 50°. 8778 unique reflec-

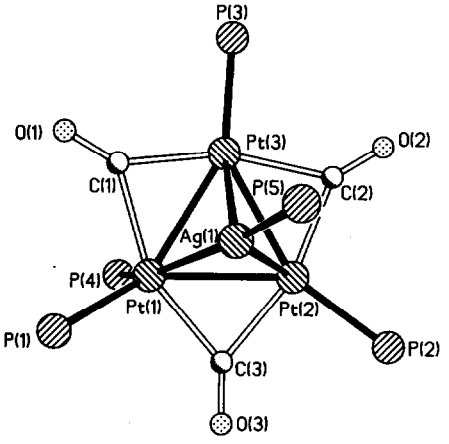

Fig. 1. The $Pt_3Ag(CO)_3P_5$ core of compound III in the crystal. Selected bond lengths (Å): Pt(1)–Pt(2) 2.712(1), Pt(1)–Pt(3) 2.701(1), Pt(2)–Pt(3) 2.674(1), Pt(1)–Ag(1) 2.741(1), Pt(2)–Ag(1) 2.823(1), Pt(3)–Ag(1) 2.915(1), Pt(1)–P(1) 2.329(3), Pt(1)–P(4) 2.393(4), Pt(2)–P(2) 2.274(4), Pt(3)–P(3) 2.266(3), Ag(1)–P(5) 2.392(4).

tions with $|F| > 4\sigma(F)$ used for all calculations (program system SHELX). Crystal size $0.7 \times 0.2 \times 0.15$ mm (red needle, elongated along [103]). Absorption correction based on azimuthal scans (transmissions 0.70–0.87). Heavy-atom method, refinement on F to R 0.061, R_w 0.053 for 347 parameters (Pt, Ag, P, carbonyl O anisotropic; phenyl rings as rigid groups with C–C 1.395, C–H 0.96 Å, all angles 120°; perchlorate disordered over two positions with one common O; two water O consistent with NMR spectrum; weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\ F^2$). Further crystallographic details (atom coordinates, complete bond lengths and angles, structure factors and temperature factors) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, F.R.G. Please quote reference number CSD 52356 and the full literature citation.

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5 Micro crystals of III and IV, bright red and deep-brown, respectively, were obtained by recrystallization from a mixture of dichloromethane, methanol and diethyl ether after purification by passing the complexes through a short silica gel column with dichloromethane/methanol (50/50) as eluant (III; Found: C, 50.1; H, 3.4. $C_{93}H_{79}O_9P_5ClAgPt_3$ calcd.: C, 50.2; H, 3.5%; IV: Found: C, 41.2; H, 3.5; N, 0.5. $C_{96}H_{96}NO_8P_4Pt_6Ag$ calcd.: C, 41.3; H, 3.4; N, 0.5%). Heavy atom ratios were determined by EDAX analysis and were consistent with the formulations. IR data III, 1825 (s), and 1840 (s) cm^{-1}; IV, 2040 (s), 2020 (s), 1970 (w), 1950 (m), 1830 (vs), 1800 (vs) cm^{-1} in CH_2Cl_2. Proton NMR for both in CD_3COCD_3 7.3 (b) ppm; for IV additional signals at 0.9 (b) and 1.2 (b) ppm.

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