

Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF [Au₂Pt₂(PPh₃)₄(CN-xylyl)₄](PF₆)₂: A PLATINUM–GOLD CLUSTER WITH A FLATTENED BUTTERFLY GEOMETRY

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Summary

[Au₂Pt₂(PPh₃)₄(CN-xylyl)₄](PF₆)₂ (CN-xylyl = 2,6-dimethylphenylisocyanide) has been synthesised from [Pt(C₂H₄)(PPh₃)₂] and [Au(CN-xylyl)₂]⁺ in CH₂Cl₂ and in the presence of an excess of CN-xylyl. A single crystal X-ray diffraction study has demonstrated that the metal atoms define a flattened butterfly with the gold atoms occupying the higher connectivity sites and forming a short bond of length 2.590(2) Å. The platinum–gold distances lie in the range 2.710(2)–3.026(2) Å.

Although a large number of gold–Group VIII mixed metal clusters have been characterised [1], few examples of platinum–gold compounds containing metal–metal bonds have been structurally characterised [2]. The previous communication described the characterisation of [Pt₃Au(CO)₃(PCy₃)₄](PF₆), the first example of a tetrahedral platinum–gold cluster [3]. The synthesis of this compound utilised the ability of the AuPR₃⁺ fragment to cap triangles of bonded metal atoms [4], and therefore required the prior formation of the platinum tri-angulo cluster. In this communication the synthesis of a tetranuclear platinum–gold cluster from mononuclear precursors is described.

Addition of [Au(CN-xylyl)₂](BF₄) to a solution of [Pt(C₂H₄)(PPh₃)₂] in CH₂Cl₂ led to the formation of a deep red solution. Excess CN-xylyl was added and the solution taken to dryness and extracted with EtOH. Addition of NH₄PF₆ and subsequent recrystallisation from acetone/diethyl ether led to a mixture of yellow (I) and black (II) crystals and chemical analyses suggested the formulations: [Pt₂Au(PPh₃)₂(CN-xylyl)₄](PF₆) and [Au₂Pt₂(PPh₃)₄(CN-xylyl)₄](PF₆)₂. Crystals of the latter proved suitable for a single crystal X-ray crystallographic analysis.

Crystal data. $C_{108}H_{96}Au_2F_{12}N_4P_6Pt_2$ (II), $M = 2568$, triclinic a 13.882(4), b 15.460(2), c 27.578(5) Å, α 77.99(5), β 88.95(2), and γ 67.42(5)°, U 5333 Å³, space group $P\bar{1}$, $Z = 2$, $D_c = 1.65$ g cm⁻³ $F(000)$ 2568 electrons, $\mu(Mo-K\alpha)$ 57.38 cm⁻¹. Intensity data were collected at ca. 291 K on an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo- $K\alpha$ radiation (λ 0.71069 Å). Of 5767 reflections measured in the θ range 1.5–17°, 3930 unique reflections with $I \geq 3\sigma(I)$ were used to solve (Patterson and Fourier methods) and refine (blocked matrix least-squares) the structure to a final R of 0.051*.

The structure of the $[Au_2Pt_2(PPh_3)_4(CN\text{-xylyl})_4]^{2+}$ cation II, which is illustrated in Fig. 1 has demonstrated that the metal skeletal geometry is different from the tetrahedral geometry described in the previous communication for the $[Pt_3Au(CO)_3(PCy_3)_4]^+$ cluster cation III [3]. The presence of an additional electron pair in II compared with III has resulted in the opening up of the tetrahedron and a skeletal geometry which can be described in terms of a flattened 'butterfly' [5]. In II the dihedral angle between the Pt(1)–Au(1)–Au(2) and Pt(2)–Au(1)–Au(2) planes is 168°. The platinum atoms are located at the wing-tip positions of the butterfly. Two isocyanide and one PPh₃ ligand are coordinated to each platinum atom and define a distorted T-shaped ligand environment, e.g. P(2)–Pt(1)–C(2) 94.6(8), P(2)–Pt(1)–C(3) 97.0(9) and C(2)–Pt(1)–C(3) 168(1)°. The gold atoms are coordinated only to the PPh₃ ligands.

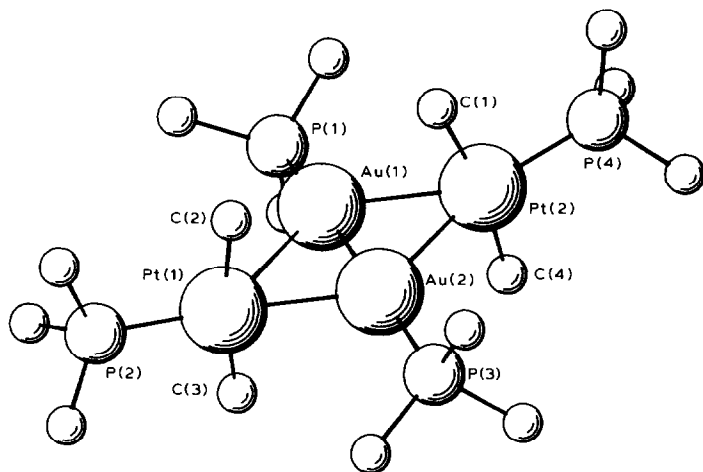
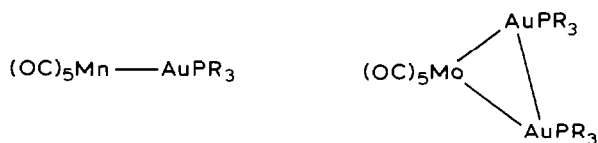


Fig. 1. Molecular structure of the $[Au_2Pt_2(PPh_3)_4(CN\text{-xylyl})_4]^{2+}$ cation. For reasons of clarity the phenyl rings have been omitted from the illustration. Important bond lengths include: Au(1)–Au(2) 2.590(2), Au(1)–Pt(1) 2.717(2), Au(1)–Pt(2) 2.711(2), Au(2)–Pt(2) 2.922(2), and Au(2)–Pt(1) 3.026(2) Å and bond angles: Pt(1)–Au(1)–Pt(2) 135.0(1), Pt(1)–Au(2)–Pt(2) 114.9(1), Au(1)–Pt(1)–Au(2) 53.3(1), Au(1)–Pt(2)–Au(2) 54.6(1), Pt(1)–Au(1)–Au(2) 69.5(1), Pt(1)–Au(2)–Au(1) 57.2(1)°, Pt(2)–Au(1)–Au(2) 66.9(1) and Pt(2)–Au(2)–Au(1) 58.3(1)°.

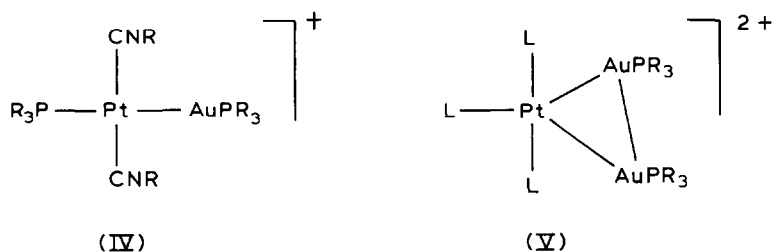
*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

The metal—metal distances in II vary over a considerable range and show a surprising asymmetry since the Au(1)—Pt distances are at least 0.20 Å shorter than the Au(2)—Pt distances, i.e. Au(1)—Pt(1) 2.717(2), Au(1)—Pt(2) 2.711(2); Au(2)—Pt(1) 3.026(2) and Au(2)—Pt(2) 2.922(2) Å. The former are comparable to the Au—Pt distances found in III, 2.750(5)—2.768(5) Å and the sum of the metallic radii (2.80 Å) [6], but the latter are at the limits of distances where metal—metal bonding is thought to be significant [7]. In contrast the Au(1)—Au(2) distance in II is one of the shortest reported for a homonuclear gold—gold bond (2.590(2) Å) [8]. A close examination of the interatomic contacts in II and the way in which the cations are packed in the unit cell suggested that steric effects were not responsible for the observed asymmetry in metal—metal bond lengths.

In previous papers we have developed the view that the AuPR₃ fragment is isolobal with H, CH₃ and metal carbonyl fragments which possess only a single frontier orbital of a₁ symmetry, e.g. Mn(CO)₅ [9,10]. Furthermore, the capability of the AuPR₃ fragment to form either localised or multicentred two-electron bonds with such fragments is illustrated by the following examples.

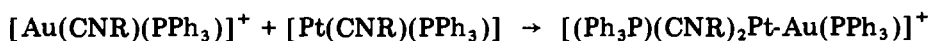
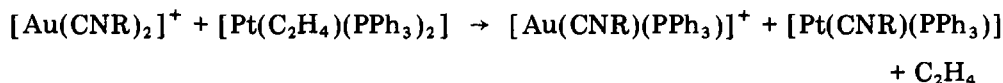


The PtL₃⁺ T-shaped fragment is isolobal with Mn(CO)₅ [10] and therefore capable of forming either localised or multicentred bonds in a similar fashion, i.e.:



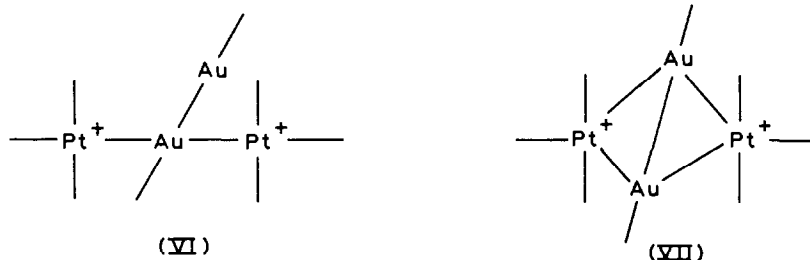
An example of the type of interaction shown in V has been recently discovered by Braunstein et al. [11].

A compound of the type shown in IV could result from [Au(CNR)₂]⁺ and [Pt(C₂H₄)(PPh₃)₂] by the following pair of ligand exchange and oxidative-addition reactions:



(IV)

The dimerisation of IV by either an oxidative-addition reaction at gold or a cyclo-addition process leads to the two alternative and extreme representations of the structure II, i.e. VI and VII. Although the observed structure of II more closely resembles that shown in VII the distortions occur along the reaction coordinate connecting VII and VI. The solid state structure thereby represents a compromise between the adoption of sp^2 hybridisation modes at both gold centres and multicentred bonding in VII or a combination of dsp^2 and sp hybridisation modes in VI.



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References

- 1 M.J. Freeman, M. Green, A.G. Orpen, I.D. Salter and F.G.A. Stone, *J. Chem. Soc. Chem. Commun.*, (1983) 1332 and ref. therein.
- 2 K.P. Hall and D.M.P. Mingos, *Prog. Inorg. Chem.*, 32 (1984) 237.
- 3 C.E. Briant, R.W.M. Wardle and D.M.P. Mingos, *J. Organomet. Chem.*, 267 (1984) C49.
- 4 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, *J. Chem. Soc. Chem. Commun.*, (1982) 314.
- 5 C.E. Briant, K.P. Hall and D.M.P. Mingos, *J. Chem. Soc. Chem. Commun.*, (1983) 843 gives an example of an iron—gold cluster which contains a flattened butterfly arrangement of gold atoms.
- 6 R.W.G. Wyckoff, *Crystal Structures*, 2nd edit., Wiley—Interscience, New York, 1963, p 10.
- 7 P.G. Jones, *Gold Bulletin*, 14 (1981) 102 and 159; 16 (1983) 114.
- 8 J.W.A. van der Velden, P.T. Beurakens, J.J. Bour, W.P. Bosman, J.H. Noordik, M. Kolenbrander and J.A.K.M. Buskes, *Inorg. Chem.*, in press have reported that $[\text{Au}_7(\text{PPh}_3)_7]^+$ has an Au—Au distance only 2.564 Å separating the axial gold atoms.
- 9 D.G. Evans and D.M.P. Mingos, *J. Organomet. Chem.*, 232 (1982) 171.
- 10 D.L. Thorn and R. Hoffmann, *J. Amer. Chem. Soc.*, 100 (1978) 2079.
- 11 P.L. Braunstein, H. Lehner, D. Matt, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem. Int. Ed.*, submitted for publication.