

Journal of The Chemical Society, Chemical Communications

NUMBER 5/1981

Synthesis and X-Ray Structural Characterization of the Centred Icosahedral Gold Cluster Compound $[\text{Au}_{13}(\text{PMe}_2\text{Ph})_{10}\text{Cl}_2](\text{PF}_6)_3$; the Realization of a Theoretical Prediction

By CLIVE E. BRIANT, BRIAN R. C. THEOBALD, JAMES W. WHITE, LINDA K. BELL, and D. MICHAEL P. MINGOS*
(*Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR*)

and ALAN J. WELCH

(*Department of Chemistry, The City University, London EC1V 0HB*)

Summary The gold(I) complexes $\text{AuCl}(\text{PR}_3)$ ($\text{PR}_3 = \text{PPh}_3, \text{PMePh}_2,$ and PMe_2Ph) react with $\text{Ti}(\eta\text{-C}_7\text{H}_8)_2$ to form a variety of cationic gold cluster complexes; a single-crystal X-ray analysis of one of these, $[\text{Au}_{13}(\text{PMe}_2\text{Ph})_{10}\text{Cl}_2](\text{PF}_6)_3$, has confirmed a centred icosahedral geometry for the cluster, in agreement with an earlier theoretical prediction.

IN 1976 a general theoretical analysis of the bonding in cluster compounds of gold led to the clear prediction that it should be possible to synthesise higher nuclearity cluster cations of the type $[\text{Au}_{13}(\text{PR}_3)_{12}]^{5+}$, $[\text{Au}_{13}(\text{PR}_3)_{10}\text{X}_2]^{3+}$, and $[\text{Au}_{13}(\text{PR}_3)_8\text{X}_4]^+$ (where X = halide), in which twelve of the gold atoms would define a closed and regular icosahedral structure and the thirteenth would lie at the origin of the polyhedron.¹ This communication reports synthetic and structural studies which have confirmed this prediction.

Generally, cluster compounds of gold have been prepared either by metal vapour synthesis techniques² or sodium borohydride reductions of gold(I) triphenylphosphine complexes.³ We find that the addition of $\text{Ti}(\eta\text{-C}_7\text{H}_8)_2$ to toluene solutions of $\text{AuCl}(\text{PR}_3)$, where $\text{PR}_3 = \text{PPh}_3, \text{PPh}_2\text{Me},$ or PPhMe_2 , provides a general and high yielding route into gold cluster chemistry. For example, yields of greater than 80% based on $\text{AuCl}(\text{PPh}_3)$ have been achieved for the synthesis of $[\text{Au}_9(\text{PPh}_3)_8](\text{PF}_6)_3$.⁵ The addition of

$\text{Ti}(\eta\text{-C}_7\text{H}_8)_2$ to the gold(I) complexes leads initially to the formation of a toluene-insoluble intermediate of empirical formula $[\text{Au}_3(\text{PR}_3)_2\text{TiCl}_3]_n$,[†] which when redissolved in ethanolic solutions gives rise to a mixture of several gold cluster species, a small quantity of the mononuclear complex $\text{Au}(\text{PR}_3)_2^+$ (as established by ³¹P-¹H n.m.r. studies), and TiO_2 . The addition of large counter-anions to these alcoholic solutions results in the crystallisation of pure samples of the complexes $[\text{Au}_9(\text{PPh}_3)_8]\text{Y}_3$ ⁵ and $[\text{Au}_{11}(\text{PR}_3)_{10}]\text{Y}_3$ (where Y = PF_6 or BPh_4 and $\text{PR}_3 = \text{PPh}_2\text{Me}$ or PPhMe_2). The latter, which are red crystalline solids, have been formulated as 11-atom clusters on the basis of elemental analyses and their electronic and n.m.r. spectral properties, which bear a strong resemblance to those reported for the structurally characterised compound $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$.⁶ Single crystals of $[\text{Au}_{11}(\text{PPhMe}_2)_{10}](\text{BPh}_4)_3$ suitable for single crystal X-ray structural analysis have been obtained and work is in hand to confirm this formulation.

In the case of the PPhMe_2 complex, addition of NET_4Cl to alcoholic solutions of the $[\text{Au}_{11}(\text{PPhMe}_2)_{10}]^{3+}$ ion leads to its conversion into the higher nuclearity cluster ion $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2]^{3+}$ in high yields. Very dark red crystals of $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2](\text{PF}_6)_3$ which were suitable for X-ray crystallographic analysis were obtained by adding NH_4PF_6 to these alcoholic solutions.

[†] This compound decomposes in all solvents in which it is soluble and therefore its characterization is incomplete. X-Ray photoelectron studies of the compound in the solid state are consistent with the titanium being either in the (II) or (III) oxidation state in this compound.

Crystal data: $C_{80}H_{110}F_{18}Cl_2P_{13}Au_{13}$, $M = 4446$, triclinic, space group $P\bar{1}$, $a = 13.256(2)$, $b = 14.962(2)$, $c = 15.300(2)$ Å, $\alpha = 104.55(2)$, $\beta = 95.89(1)$, $\gamma = 92.71(3)^\circ$, $U = 2913(2)$ Å³, $Z = 1$, $D_c = 2.54$ g cm⁻³, $F(000) = 2008$ electrons, graphite monochromated radiation ($\bar{\lambda} = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 171.25$ cm⁻¹. The diffracted intensities were measured to $\theta_{\text{max}} = 22.5^\circ$ on an Enraf-Nonius CAD4 diffractometer and were corrected for absorption. 3663 reflections [$I \geq 3\sigma(I)$] were used to solve (Patterson and Fourier syntheses) the structure which has been refined (block matrix least squares) to $R = 0.0880$. ‡

The molecular structure of the $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2]^{3+}$ ion, illustrated in the Figure, establishes the theoretically predicted centred icosahedral geometry.^{1,8} This structure represents a marked contrast with the centred cubocta-

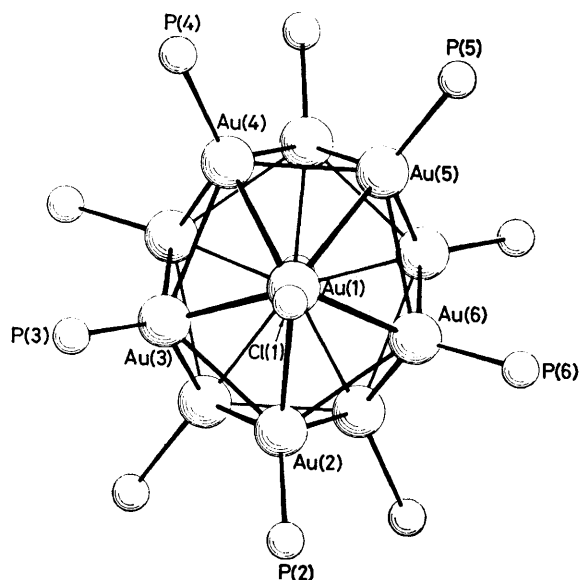


FIGURE. Molecular structure of the $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2]^{3+}$ ion. For reasons of clarity the carbon and hydrogen atoms on the phosphine ligands have been omitted.

‡ The atomic co-ordinates for this work are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1976, 1163.

² F. A. Vollenbroek, P. C. P. Bouten, J. M. Trousten, J. P. van den Berg, and J. J. Bour, *Inorg. Chem.*, 1978, **17**, 1345.

³ F. Cariati and N. Naldini, *Inorg. Chim. Acta*, 1971, **5**, 172; L. Malatesta, *Gold Bull.*, 1975, **8**, 48.

⁴ M. T. Anthony, M. L. H. Green, and D. Young, *J. Chem. Soc., Dalton Trans.*, 1975, 1419.

⁵ P. L. Bellon, F. Cariati, M. Manaserro, L. Naldini, and M. Sansoni, *Chem. Commun.*, 1971, 1423.

⁶ P. Bellon, M. Manaserro, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1972, 1481.

⁷ F. A. Vollenbroek, Ph.D. Thesis, Catholic University of Nijmegen, 1979, has synthesised the compound $\text{Au}_{13}(\text{dppm})_6(\text{NO}_3)_4$ [dppm = bis(diphenylphosphino)methane] which appears to have an icosahedral cluster unit. However, crystallographic disorder and the possibility that the unit cell contains a second unidentified cluster compound have limited the characterization of this compound.

⁸ V. G. Albano, A. Cariatti, P. Chini, G. Ciani, S. Martinego, and W. M. Anker, *J. Chem. Soc., Chem. Commun.*, 1975, 859.

⁹ K. Wade, 'Electron Deficient Compounds,' Nelson, London, 1972, describes the isomeric possibilities of the related icosahedral carboranes $\text{C}_2\text{B}_{10}\text{H}_{12}$ as *ortho*, *meta*, and *para*.

hedral geometry established for $\text{Rh}_{13}(\text{CO})_{24}\text{H}_3$.⁸ The central gold atom [Au(13)] lies on a crystallographically imposed centre of symmetry and therefore the chloride ligands are constrained to occupy *para*-vertices⁹ of the gold icosahedron [Au(1) and Au(1')]. The gold-gold distances on the periphery of the polyhedron lie in the range 2.852(3)–2.949(3) Å, and are longer than those bond lengths connecting the central gold atom to the peripheral gold atoms, which lie in the range 2.716(2)–2.789(2) Å. These bond lengths are comparable to those reported for other gold cluster compounds.^{5–7} The cluster shows significant distortions away from the idealised icosahedral geometry which arise from the different electronic and steric requirements of the chloro- and phosphine ligands. In particular the Au(13)–Au(1) bond length of 2.716(2) Å is significantly shorter than the comparable Au(13)–Au bond lengths and the Au(1) atom is displaced from the idealised five-fold axis of the icosahedral metal cluster cation resulting in a spread of bond lengths from 2.852(3)–2.949(3) between Au(1) and the adjacent pentagonal face of the icosahedron. Furthermore, Au(13)–Au–ligand bond angles show large deviations from 180° (167.4–178.0°). We attribute these distortions to the non-bonded repulsions exerted by the bulky phosphine ligands.

If crystals of $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2](\text{PF}_6)_3$ are dissolved in CD_2Cl_2 at -60°C and the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum is recorded at this temperature then only a single resonance at 36.8 p.p.m. with respect to $\text{P}(\text{OMe})_3\text{O}$ is observed. This is consistent with the presence of only the *para*-isomer. However, when the solution is allowed to warm up to room temperature additional resonances are observed at 39.0, 36.4, and 24.7 p.p.m. suggesting that at higher temperatures the *para*-isomer isomerises into the alternative *ortho*- and/or *meta*-isomers by a low energy pathway.

The S.R.C. is thanked for financial support, B. R. C. T. has held an S.R.C. C.A.S.E. Studentship with I.C.I., and Johnson Matthey Ltd. are thanked for a loan of gold metal.

(Received, 2nd December 1980; Com. 1284.)