Inorganica Chimica Acta, 45 (1980) L151–L152
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A New Type of Gold Cluster Compound. The Syntheses and X-Ray Structure Analysis of Pentakis(tricyclohexylphosphino)tris(thiocyanato)enneagold, $[Au_9\{P(C_6H_{11})_3\}_5(SCN)_3]$, and Bis{tri(cyclohexyl)phosphinato}gold(I) Hexafluorophosphate, $[Au\{P(C_6H_{11})_3\}_2][PF_6]$

MERVYN K. COOPER, GARY R. DENNIS

School of Chemistry, The University of Sydney, Sydney, N.S.W. 2006, Australia

KIM HENRICK and MARY McPARTLIN

Department of Chemistry, The Polytechnic of North London, London N7 8DB, U.K.

Received May 16, 1980

Although the first high nuclearity cluster compounds of any transition metal to be characterised were the neutral gold species $[Au_{11}L_7X_3]$ {L = $P(aryl)_3$ and X^- = I^-, SCN^- and CN^-} [1], which have metal geometries based on centred arachno-icosahedra, the chemistry of gold cluster compounds has developed very slowly in comparison to that of the polynuclear carbonyls obtained with other metals. In the eleven years since the undecagold clusters were first discovered only five new cluster species have been obtained all of which have been cationic *viz.* $[Au_9L_8]^{3+}$ {L = PPh_3 or $P(p\text{-tolyl})_3$} [2], $[Au_8(PPh_3)_8]^{2+}$ [3], $[Au_6\{P(p\text{-tolyl})_3\}_6]^{2+}$ [4] and $[Au_5(dppmH)dppm]^{2+}$ { dppmH = bis(diphenylphosphino)methane} [5].

The first neutral enneagold cluster compound has been isolated and it has been shown by X-ray analysis to have the structure illustrated in Fig. 1. The two previously reported [2] cationic Au_9 species have metal geometries of D_{2h} symmetry that may be derived directly from a centred icosahedron of metal atoms by removal of four vertices as shown in Fig. 2a. In contrast the new neutral Au_9 cluster has a metal arrangement of virtual C_s symmetry only. Its derivation from a centred icosahedron is less direct because in addition to removal of four vertices the subsequent breaking of a peripheral Au–Au bond is required (Fig. 2b). Therefore $[Au_9\{P(C_6H_{11})_3\}_5(SCN)_3]$ (I) is the first example of a new type of gold cluster compound.

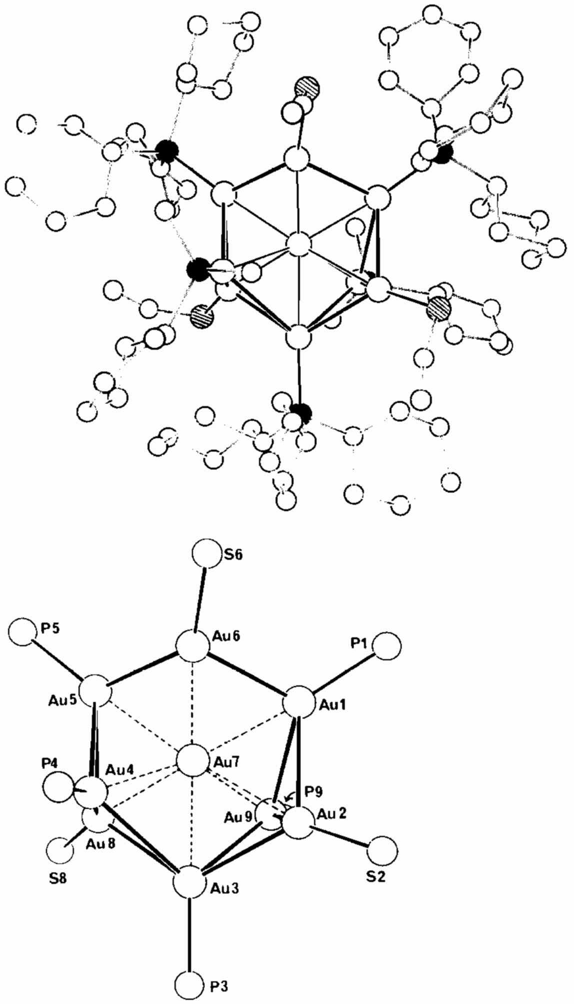

Fig 1. (a) The structure of $[Au_9\{P(C_6H_{11})_3\}_5(SCN)_3]$ (I). Four of the cyclohexyl rings have been partially omitted for clarity and for these only the carbon attached to the P atom is shown. (b) The $Au_9P_5S_3$ core of the cluster. Gold–gold bond distances (A) are: (1)–(2) 2.825(5); (1)–(6) 2.809(5); (1)–(7) 2.656(5); (1)–(9) 3.053(5); (2)–(3) 2.811(5); (2)–(7) 2.771(5); (2)–(9) 2.691(5); (3)–(4) 3.168(5); (3)–(7) 2.703(5); (3)–(8) 2.811(6); (3)–(9) 2.978(5); (4)–(5) 2.939(6); (4)–(7) 2.703(5); (4)–(8) 2.683(5); (5)–(6) 2.799(5); (5)–(7) 2.671(5); (5)–(8) 2.885(5); (6)–(7) 2.684(5); (7)–(8) 2.756(5); (7)–(9) 2.709(4). Au–P bond lengths are 2.26–2.29(2) and Au–S bond lengths 2.35–2.43(2) A. Ligand–gold–(central gold) angles X(n)–Au(n)–Au(7) are for X(n) = P(1) 174(1), S(2) 155(1), P(3) 173(1), P(4) 135(1), P(5) 169(1), S(6) 164(1), S(8) 144(1), P(9) 136(1)°.

Reduction of tri(cyclohexyl)phosphinogold(I) thiocyanate with sodium borohydride gave a product which on fractional crystallisation from n-heptane/CH_2Cl_2 yielded a microcrystalline material from which some larger red crystals were selected (dec. 129 °C; ν(CN) 2100 cm^{-1}; ^{31}P NMR (85% H_3PO_4) δ 72.98 ppm.) and were fully characterised by X-ray analysis as $[Au_9\{P(C_6H_{11})_3\}_5(SCN)_3]$ (I). The elusiveness of gold cluster compounds is illustrated by a recent report [6] of this reaction yielding, *via* thin layer chromatography, yellow crystals of $[Au\{P(C_6H_{11})_3\}_2]^+$ (II) as the thiocyanate salt and unidentified red crystals. The measured density of the red crys-

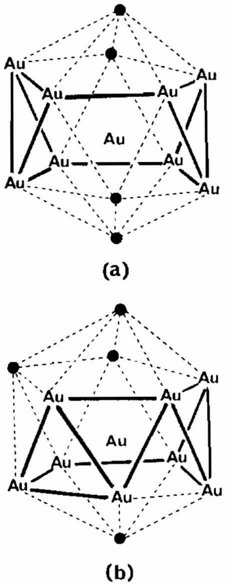

Fig. 2. The derivation of the two types of enneagold clusters from a centred icosahedron: (a) The cationic clusters (D_{2h}); (b) The neutral cluster (C_s). There is a distortion from the idealised icosahedral sites which corresponds to the breaking of an Au–Au bond.

tals was 1.99 g cm^{-3} and is sufficiently close to the calculated density of 1.94 g cm^{-3} for (I) to be a very strong indication that they also were the neutral enneagold cluster (I).

Interestingly the mononuclear cation (II) is the only gold containing species so far characterised from reactions of sodium borohydride with tri(cyclohexyl)phopshinogold(I) salt of non-coordinating anions which might have been expected to yield one of the established cationic types of gold cluster compound. In the hexafluorophosphate salt the cation (II) has the nearly linear structure shown in Fig. 3. The tri(cyclohexyl)phosphine ligands have an approximately eclipsed conformation similar to that found in the thiocyanate and in contrast to the staggered conformation of the methyldiphenylphosphine ligands in the hexafluorophosphate salt of the [Au(PMePh$_2$)]$^+$ cation [7].

Crystal Data. $C_{93}H_{165}Au_9N_3P_9S_3$ (I), monoclinic, *I2/c*, *a* = 44.488(3), *b* = 22.089(2), *c* = 23.407(2) Å, β = 91.35(3)°, *V* = 22995.5 Å^3, *Z* = 8, D_c = 1.935 g cm^{-3}. Solution and refinement were based on 3333 unique reflections, $I/\sigma(I) > 2.5$, measured with a Philips PW100 four-circle diffractometer using

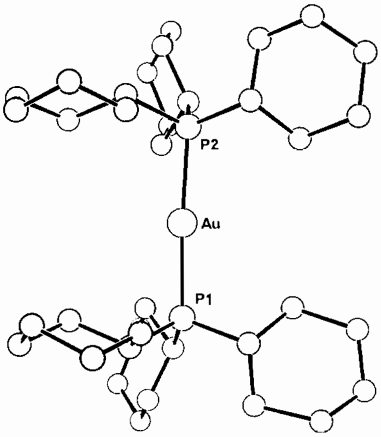

Fig. 3. The structure of the [Au{P(C$_6$H$_{11}$)$_3$}$_2$]$^+$ cation in the [PF$_6$]$^-$ salt. The principal bond lengths (Å) and angles (°) are Au–P(1) 2.325(6), Au–P(2) 2.324(6) Å P–C 1.842 - 1.877(21) and P(1)–Au–P(2) 178.0(2), Au–P–C 107.6–114.1(7).

graphite crystal monochromated Mo-K$_\alpha$ radiation. Refinement of the atomic parameters (Au atoms anisotropic) has given an *R* value of 0.092.

$C_{38}H_{66}AuF_6P_3$ (hexafluorophosphate of II), orthorhombic, *Pbca*, *a* = 19.347(2), *b* = 26.805(3), *c* = 15.530(2) Å, *V* = 8053.8 Å^3, *Z* = 8, D_c = 1.529 g cm^{-3}. Solution and refinement were based on 4049 unique reflections, $I/\sigma(I) > 3.0$ (Mo-K$_\alpha$). Refinement of the atomic parameters (Au, P atoms anisotropic) has given an *R* value of 0.054.

References

1 M. McPartlin, R. Mason and L. Malatesta, *Chem. Comm.*, 334 (1969); V. G. Albano, P. L. Bellon, M. Manassero and M. Sansoni, *Chem. Comm.*, 1210 (1970).
2 P. L. Bellon, F. Cariati, M. Manassero, L. Naldini and M. Sansoni, *Chem. Comm.*, 1423 (1971); F. Cariati and L. Naldini, *J. Chem. Soc. Dalton*, 2286 (1972).
3 M. Manassero, L. Naldini and M. Sansoni, *J. Chem. Soc. Chem. Comm.*, 385 (1979); F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik and P. T. Beurskens, *J. Chem. Soc. Chem. Comm.*, 387 (1979).
4 P. Bellon, M. Manassero, L. Naldini and M. Sansoni, *J. Chem. Soc. Chem. Comm.*, 1035 (1972).
5 J. W. A. van der Velden, J. J. Bour, F. A. Vollenbroek, P. T. Beurskens and J. M. M. Smits, *J. Chem. Soc. Chem. Comm.*, 1162 (1979).
6 J. A. Muir, M. M. Muir and E. Lorca, *Acta Cryst., B36*, 931 (1980).
7 J. J. Guy, P. G. Jones and G. M. Sheldrick, *Acta Cryst., B32*, 1937 (1976).