Synthesis of a New Pentanuclear Gold Cluster by Metal Evaporation. Preparation and *X*-Ray Structure Determination of [Tris{bis(diphenylphosphino)methane}][bis(diphenylphosphino)methanido]pentagold Dinitrate

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Summary The evaporation of metallic gold into an ethanolic solution of bis(diphenylphosphino)methane (dppmH) and NH_4NO_3 results in the formation of $[Au_5(dppmH)_3(dppm)](NO_3)_2$ with (dppm) = $[Ph_2PCHPPh_2]^-$; *X*-ray structure analysis reveals the presence of an Au–C bond.

METAL atom synthesis has proved to be a useful technique for the preparation of gold clusters containing eleven and nine gold atoms.[1,2] We now report the preparation of a new cluster containing five gold atoms by the evaporation of metallic gold into an ethanolic solution of bis(diphenylphosphino)methane (dppmH) and NH_4NO_3. Different mol ratios were used, all of which resulted in the formation of $[Au_5(dppmH)_3(dppm)]^{2+}$ (Figure 1). The red reaction mixture was evaporated to dryness and subsequently passed over a celite 505 column to remove any metallic gold. Red crystals were isolated by crystallization from methylene chloride–diethyl ether.

The analytical data for these crystals were consistent with the formula $[Au_5(dppmH)_3(dppm)](NO_3)_2$, the molecular structure of which was determined by *X*-ray analysis. *Crystal data:* $Au_5C_{100}H_{87}N_2O_6P_8$, monoclinic, space group $P2_1$; unit cell $a = 15{\cdot}796(3)$, $b = 23{\cdot}19(2)$, $c = 15{\cdot}280(4)$ Å, $\beta = 118{\cdot}47(2)^\circ$, $U = 4920{\cdot}3$ Å^3, $Z = 2$, $D_c = 1{\cdot}786$ g cm^{-3}. The *X*-ray data were measured on a Nonius CAD-4 diffractometer, (θ—2θ) scan, with monochromated Mo-$K\alpha$ radiation. During the measurements the crystal was kept in a sealed capillary. When exposed to *X*-ray radiation the crystal decomposed and the intensities of the control reflections reduced to *ca.* 40%, at which point the measurements were terminated. The control reflections

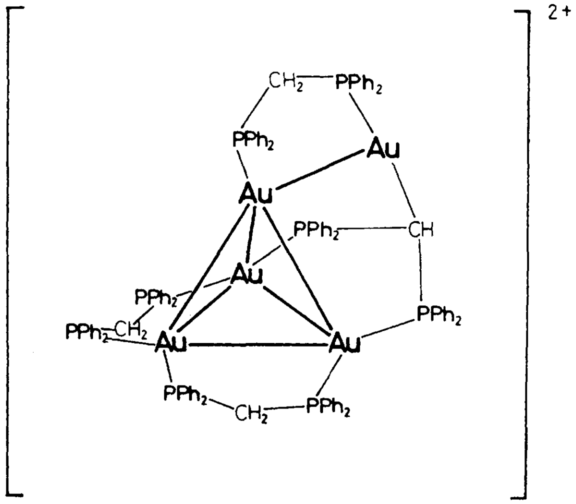

FIGURE 1. Line drawing of the $[Au_5(dppmH)_3(dppm)]^{2+}$-cluster; dppmH = $Ph_2PCH_2PPh_2$, dppm = $[Ph_2PCHPPh_2]^-$.

showed large local variations in intensity caused by positional changes of the crystal during the measurements. A total of 3412 symmetry independent reflections were measured, of which 3082 had an intensity of $I > 3\sigma$ (σ based on counting statistics).

The positions of the five gold atoms were obtained from a Patterson interpretation. In applying the DIRDIF[3] procedure we found eight P atoms and no more Au atoms. All carbon atoms and two NO_3 groups were found by successive least-squares and difference-Fourier techniques. At the present stage of the refinement the R-value is 0·07.†

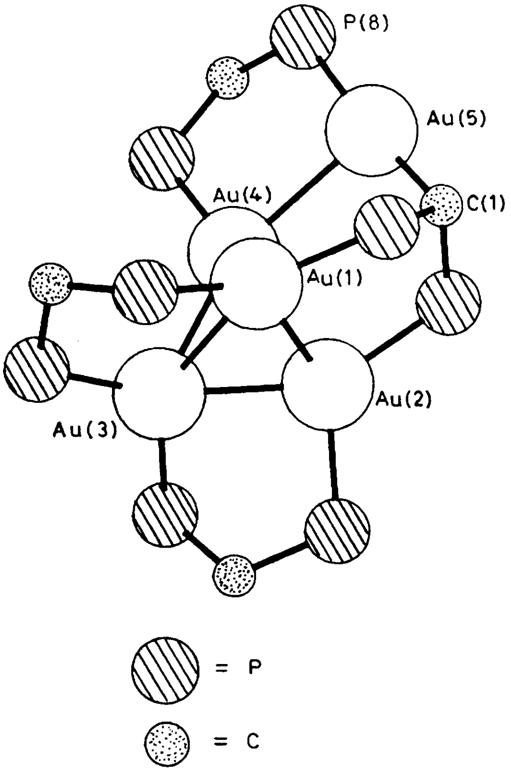

FIGURE 2. Structure of the $[Au_5(dppmH)_3(dppm)]^{2+}$ cluster. The methylidyne carbon is denoted C(1); the phenyl groups have been omitted for clarity.

The result of the crystal structure determination is shown in Figure 2. The Au skeleton can be described as a tetrahedron of four Au atoms with the fifth Au atom being attached to Au(4). A diphosphine group bridges these two Au atoms. The remaining Au atoms [Au(1), Au(2), and Au(3)] are bridged by one dppm and two dppmH ligands. The methylene bridge [C(1)] of the dppm ligand has lost a hydrogen atom and is bonded to the fifth Au atom. In this way Au(5) becomes almost linearly co-ordinated between C(1) and P(8) [$\angle$C(1)–Au(5)–P(8) = 174°]. The description of this compound as a tetranuclear cluster, incorporating a linear Au^I-entity, could be appropriate and its structural resemblance to $Au_2(Ph_2PCHPPh_2)(H_2CPEt_2CH_2)$ is interesting.[4] The nitrate ions are situated in between the phenyl rings, away from the gold atoms.

The Au–Au distances (2·70—3·01 Å) and Au–P distances (2·28—2·42 Å) are normal for gold–phosphine clusters.[5–7] The Au–C bond [Au(5)–C(1) 2·08(13) Å] lies within the range normally found in organogold compounds. The presence of the Au–C bond is consistent with C(1) being bound tetrahedrally as indicated by the bond angles. The observed diamagnetism of the dipositive cluster supports the proposed deprotonation of the methylene carbon atom bonded to gold.

The presence of the Au–C bond in this new gold cluster is not its only remarkable feature. The co-ordination of two phosphorus atoms to one gold atom [for Au(1), Au(2), and Au(3)] is also new for gold–phosphine clusters, since normally one phosphorus atom is bonded to one gold atom. Full physical data, including ^{31}P n.m.r. and Mössbauer spectra will be reported later.

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† The atomic co-ordinates for this work are available on request from the Director of 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] F. A. Vollenbroek, P. C. P. Bouten, J. M. Trooster, J. P. van den Berg, and J. J. Bour, *Inorg. Chem.*, 1978, **17**, 1345.
[2] F. A. Vollenbroek, Ph.D. Thesis, University of Nijmegen, 1979.
[3] T. E. M. van den Hark, P. Prick, and P. T. Beurskens, *Acta Cryst.*, 1976, **A32**, 816.
[4] H. Schmidbaur and J. R. Mandl, *Angew. Chem.*, 1977, **89**, 679.
[5] L. Malatesta, *Gold Bulletin*, 1975, **8**, 48.
[6] M. Manassero, L. Naldini, and M. Sansoni, *J.C.S. Chem. Comm.*, 1979, 385.
[7] F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik, and P. T. Beurskens, *J.C.S. Chem. Comm.*, 1979, 387.