Synthesis of a New Heteronuclear Gold–Cobalt Cluster. Preparation and *X*-Ray Structure Determination of Tetrakis(triphenylphosphine)-bis(tetracarbonylcobalt)hexagold

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Summary The reaction of $[Au_8L_7]^{2+}$ (L = PPh_3) with an excess of $Li[Co(CO)_4]$ in tetrahydrofuran results in the formation of $Au_6L_4[Co(CO)_4]_2$, the structure of which has been determined by *X*-ray crystallography.

Recently we have described[1] $[Au_8L_7]^{2+}$ (L = PPh_3), an intermediate in the formation of $[Au_8L_8]^{2+}$ [2,3] from $[Au_9L_8]^{3+}$. Preliminary *X*-ray results indicated it to be structurally related to $[Au_9L_8]^{3+}$ which lacks a gold–phosphine entity originally bonded to the central gold atom. As the central gold is exposed it should be reactive towards Lewis bases. We therefore explored its reaction with $LiCo(CO)_4$. The $[Au_8L_7][NO_3]_2$ needed for this work was prepared by the reaction of $[Au_8L_8]^{2+}$ with the phosphine scavenger $[RhCl(C_8H_{14})_2]_2$ in a 4 : 1 ratio. When $[Au_8L_7]^{2+}$ and $Li[Co(CO)_4]$ were mixed in a molar ratio of 1 : 2 in tetrahydrofuran (THF) at room temperature a red-brown colour developed in 30 min. This solution was filtered and the product precipitated by addition of n-hexane and recrystallized from toluene. A small amount of air-stable dark red-brown crystals, suitable for an *X*-ray structure determination, was obtained by the diffusion of a toluene solution into n-hexane. *X*-Ray analysis revealed the molecular structure of the first heteronuclear gold–cobalt cluster, $Au_6(PPh_3)_4[Co(CO)_4]_2$ (Figure 1).

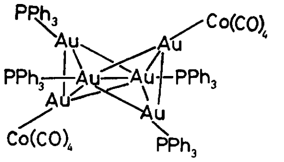

Figure 1. Line drawing of the $Au_6(PPh_3)_4[Co(CO)_4]_2$ cluster.

Crystal data: triclinic, space group $P\bar{1}$, a = 13·672(6), b = 13·524(4), c = 14·160(5) Å, α = 119·72(2), β = 118·83(3), γ = 71·32(2)°, U = 1980·6 Å^3, D_m = 1·47 g/cm^3, Z = 2. The *X*-ray data were measured on a Nonius CAD-4 diffractometer (θ—2θ) scan, with monochromated Mo-K_α radiation. A total of 2723 symmetry-independent reflections were measured, of which 1240 had $I > 3\sigma(I)$ [$\sigma(I)$ based on counting statistics]. The positions of three gold atoms were obtained from a Patterson map; the positions of the phosphorus and cobalt atoms were found by the DIRDIF[4] procedure. Difference Fourier maps revealed the positions of most of the carbon and oxygen atoms. The result of the crystal structure determination is shown in Figure 2, and shows a centrosymmetric molecule. The Au skeleton can be described as two tetrahedrons with one common edge. Four gold atoms (1, 1′, 2, 2′) are bonded to phosphine ligands, while the two apical gold atoms are co-ordinated to tetracarbonylcobalt. The $Co(CO)_4$ entity has the same trigonal bipyramidal co-ordination as was found in $PPh_3AuCo(CO)_4$.[5] The distances Au(1)–Au(1′) (2·66 Å) and Au(2)–Au(3) (2·62 Å) are significantly shorter than the other Au–Au distances (2·77—2·81 Å). The Au–P distances (2·28—2·37 Å) are normal for gold–phosphine clusters.[2,3,6] The Au–Co distances (2·46 Å) are about the same as found in the mononuclear $PPh_3AuCo(CO)_4$.[5] All metal–ligand vectors are

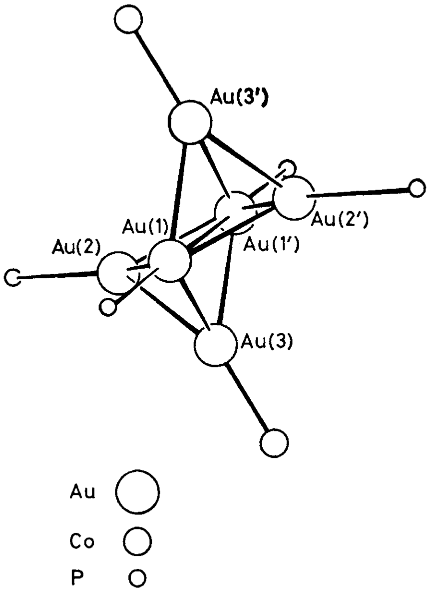

Figure 2. Structure of the $Au_6(PPh_3)_4[Co(CO)_4]_2$ cluster; the phenyl groups have been omitted for clarity.

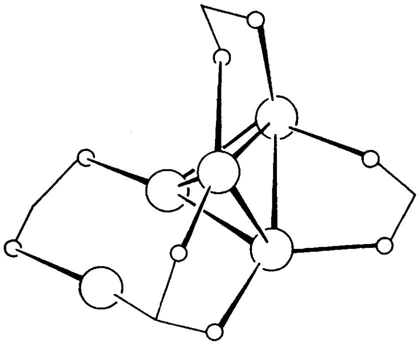

Figure 3. Structure of the $[Au_5(PPh_2-CH_2-PPh_2)_3(PPh_2-CH-PPh_2)]^{2+}$ cluster (ref. 8). The phenyl groups have been omitted for clarity.

approximately directed towards the tetrahedron centres, with the exception of the almost linear P–Au(1)–Au(1′)–P moiety [∠P–Au(1)–Au(1′) = 178·6°].†

The gold skeleton in this heteronuclear gold–cobalt cluster deviates from the squeezed octahedron in $Au_6[(p\text{-}tolyl)_3P]_6[BPh_4]_2$.[7] A tetrahedral skeleton has so far only been reported for $[Au_5(PPh_2\text{–}CH_2\text{–}PPh_2)_3(PPh_2\text{–}CH\text{–}PPh_2)]^{2+}$ which was described as a tetrahedral cluster, incorporating a mononuclear Au^I entity[8] (Figure 3).

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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.

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