Reactions of Gold–Phosphine Cluster Compounds. Preparation and *X*-Ray Structure Determination of Octakis(triphenylphosphine)-octa-gold Bis(hexafluorophosphate)

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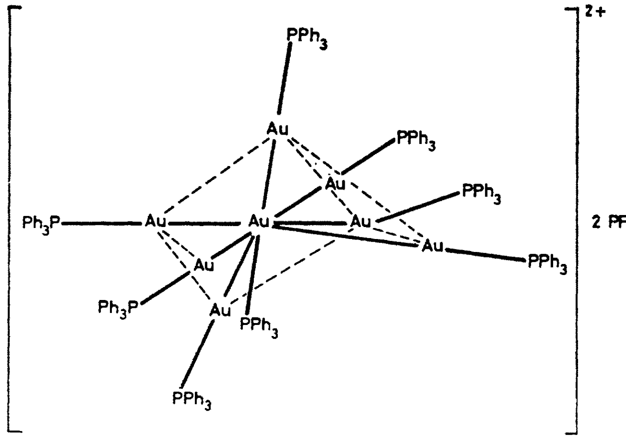
Summary $[Au_9L_8]^{3+}$ (L = PPh_3) reacts with L to form $[Au_8L_8]^{2+}$ and $[AuL_2]^+$; preliminary *X*-ray structural results are reported for $[Au_8L_8][PF_6]_2.2CH_2Cl_2$ (**1**).

Previously we have reported Mössbauer and ^{31}P n.m.r. investigations on cluster compounds containing eleven[1] and nine[2] gold atoms. In the latter communication preliminary results of the reactivity of $[Au_9L_8]^{3+}$ (L = PPh_3) towards phosphines and halides were mentioned. At that time we concluded that $[Au_9L_8]^{3+}$ reacts with L to give $[Au_9L_{10}]^{3+}$. Further investigations, however, revealed that the reaction product is not $[Au_9L_{10}]^{3+}$ but surprisingly contains a novel type of gold cluster with the formula $[Au_8L_8]^{2+}$, together with AuL_2^+.

The ^{31}P n.m.r. spectrum of a mixture of 1 equiv. of $[Au_9L_8]^{3+}$ and 2 equiv. of L in CD_2Cl_2 shows, apart from one singlet at −53·0 p.p.m. due to $[Au_8L_8]^{2+}$, a singlet at −42·6 p.p.m. relative to trimethyl phosphate. As the singlet at −42·6 p.p.m. is also obtained when 1 equiv. of $AuLNO_3$ and 1 equiv. of L react in CD_2Cl_2 to give AuL_2^+, it can be concluded that AuL_2^+ is formed according to the reaction $[Au_9L_8]^{3+} + 2L \rightarrow [Au_8L_8]^{2+} + AuL_2^+$.

Red crystals of $[Au_8L_8][PF_6]_2.2CH_2Cl_2$ can be isolated when toluene is allowed to diffuse slowly into a methylene chloride solution of $[Au_9L_8][PF_6]_3$ and excess of L. After drying *in vacuo* the analytical data for these crystals were consistent with the formula $Au_8[PPh_3]_8[PF_6]_2.CH_2Cl_2$. The Mössbauer spectrum of $[Au_8L_8]^{2+}$ shows one quadrupole pair and one singlet with the same parameters as reported earlier for the $[Au_8L_8]^{2+}$ and AuL_2^+ mixture.[2] That no separate doublet of AuL_2^+ can be observed in the spectrum of the mixture may be due to the small quantity of AuL_2^+ which is present (only 1/9 of the gold atoms). The molecular structure of $[Au_8L_8][PF_6]_2.2CH_2Cl_2$ (**1**) was elucidated by *X*-ray structure analysis.



(**1**)

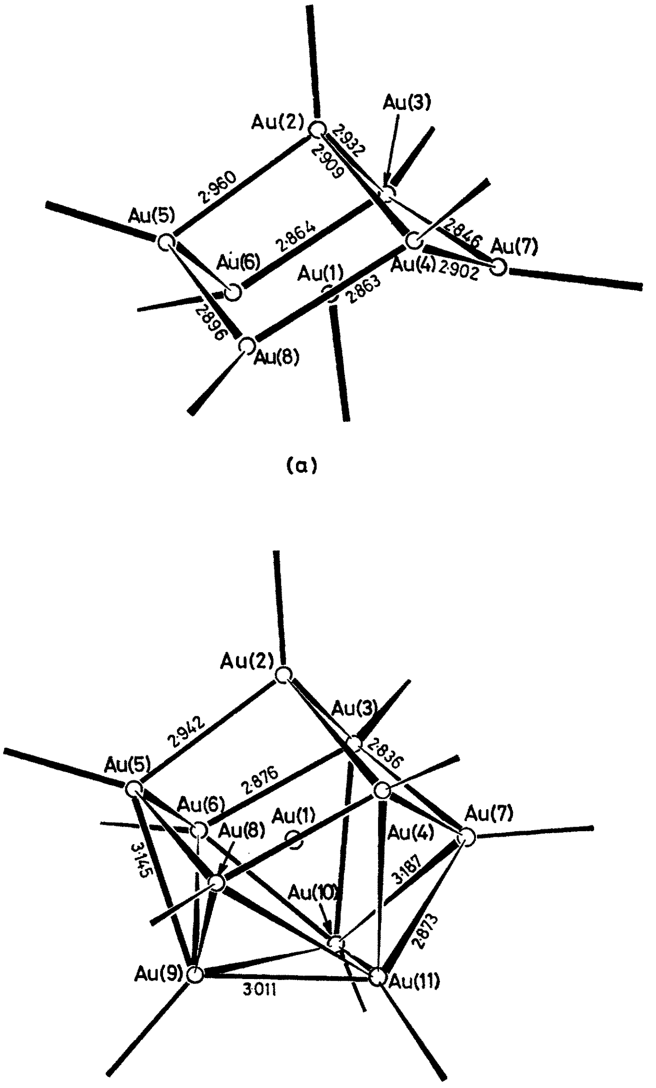


Figure. Structures of gold clusters in (a) $Au_8(PPh_3)_8(PF_6)_2\cdot 2CH_2Cl_2$ and (b) $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$ (ref. 4). Distances between central [Au(1)] and peripheral atoms are: (a) Au(2) 2·635; Au(3) 2·699; Au(4) 2·709; Au(5) 2·682; Au(6) 2·721; Au(7) 2·707; and Au(8) 2·723; (all ±0·008); (b) Au(2) 2·600; Au(3), Au(4), Au(5), 2·680; Au(6), Au(7), Au(8) 2·718; Au(9), Au(10), Au(11) 2·671. Distances are in Å.

Crystal data: triclinic, space group $P\bar{1}$, $a = 17{\cdot}445(3)$, $b = 29{\cdot}410(5)$, $c = 17{\cdot}625(3)$ Å, $\alpha = 79{\cdot}42(2)$, $\beta = 120{\cdot}93(1)$, $\gamma = 95{\cdot}04(2)°$, $U = 7624$ Å^3; $D_m = 1{\cdot}83(8)$, $D_c = 1{\cdot}80$ 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. During the measurements the crystals were kept in the mother liquor in a sealed capillary as removal of the solvent causes cracking of the crystals and loss of one solvent molecule. Under exposure to X-ray radiation the crystals decomposed. A freshly prepared crystal was mounted after two or three days when the intensities of the control reflections had been reduced to *ca.* 80%. To obtain the complete set of intensity data four crystals were used for the measurements with overlapping ranges in order to calculate the relative scaling factors. The control reflections showed variations in intensity of up to 15% caused by positional changes of the crystals during the measurements. The relative scaling factors based upon 757 doubly measured reflections could be obtained with an accuracy of 10%.†

A total of 12,294 symmetry-independent reflections were measured, of which 9139 had an intensity of $I > 3\sigma$ (σ based on counting statistics). The positions of three gold atoms were obtained from a Patterson interpretation; the positions of the remaining five gold atoms were found by the DIRDIF procedure.[3] Fourier methods revealed the positions of most of the other non-hydrogen atoms. Block diagonal least-squares refinement with restrained phenyl-rings gave an R value of 0·10. A difference Fourier showed the presence of two PF_6 ions and of two CH_2Cl_2 molecules. One of the CH_2Cl_2 molecules was very poorly resolved.

The geometry of the Au_8 skeleton (see Figure a) can be described as being derived from that of the Au_{11} cluster[4] (see Figure b) by removal of the three gold atoms of the basal triangle. The $Au_8L_8{}^{2+}$ cluster then can be thought as the result of the co-ordination of a phosphine to each of the remaining eight gold atoms including the now exposed, formerly central, gold atom Au(1). The distances of this atom to the other gold atoms remain short *i.e.*, 2·635(8)—2·723(8) Å. Therefore we shall still call this atom the central gold atom.

The distances between peripheral gold atoms in the $Au_8L_8{}^{2+}$ cluster are in the range 2·826(8)—2·960(8) Å and are also very close to those in the Au_{11} cluster.[4] Both clusters do not depart very much from C_{3v} symmetry. The Au(central)–Au(peripheral)–P angles are: Au(2) 180°; Au(3) 176; Au(4) 176; Au(5) 179; Au(6) 167; Au(7) 164; and Au(8) 165 (all ± 1°); Au(2)–Au(1)–P = 176(1). The peripheral Au–P distances are in the range 2·29—2·33 Å and the central Au–P distance is 2·42 Å (all ± 0·03).

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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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