

Preliminary communication

A NEW CLASS OF CLUSTER COMPLEXES BETWEEN GROUP IB METAL ARYLACETYLIDES. PREPARATION AND X-RAY STRUCTURE OF A NOVEL TETRANUCLEAR GOLD-SILVER CLUSTER

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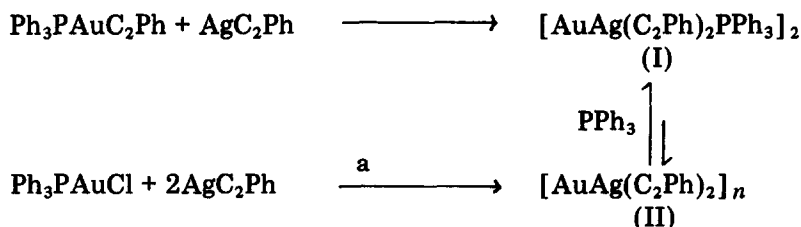
Summary

The cluster $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph})_4(\text{PPh}_3)_2]$ has been prepared by the reaction of $\text{Ph}_3\text{PAuC}_2\text{Ph}$ with $[\text{AgC}_2\text{Ph}]_n$ and by that of Ph_3P with the polymer $[\text{AuAg}(\text{C}_2\text{Ph})_2]_n$. The structure of the new cluster involves a linear arrangement of two phenylacetylide groups about each gold atom, with each silver atom asymmetrically π -bonded to two triple bonds and one phosphine ligand.

It has been shown recently that the reaction between $[\text{NBu}_4^+][\text{PhC}_2\text{AuC}_2\text{Ph}]^-$ and a mixture of gold phenylacetylide and copper phenylacetylide affords mainly the anionic cluster $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$ [1]. We report here the preparation and X-ray structural characterization of a novel tetranuclear complex which is a representative of another class of clusters between Group IB metal arylacetylides. Thus when silver phenylacetylide (1 mol equiv.) was added to a solution of $\text{Ph}_3\text{PAuC}_2\text{Ph}$ in dichloromethane at room temperature, it dissolved in 2–3 min to give a pale yellow solution. Addition of pentane produced colorless crystals of the cluster $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph})_4(\text{PPh}_3)_2]$ (I) in high yield, contaminated with a small quantity of the yellow polymer $[\text{AuAg}(\text{C}_2\text{Ph})_2]_n$ (II). (Recrystallization of complex I gives more of complex II.) However, when the reaction was carried out in the presence of Ph_3P only the colorless cluster was formed.

Complex I can also be prepared by treating a suspension in toluene of complex II (which was prepared recently in very high yield from Ph_3PAuCl and

AgC_2Ph ($\frac{1}{2}$ mol equiv.) at room temperature with an excess of PPh_3 [2] (Scheme 1).



SCHEME 1. A reaction product of route a is $[\text{Ph}_3\text{PAgCl}]_4$.

Such reactions, in which Ph_3P in $\text{Ph}_3\text{PAuC}_2\text{Ph}$ or both ligands in Ph_3PAuCl are exchanged for acetylide ligands are striking. Previous work showed that ethynylation of some gold complexes by the anionic copper(I) complex $[\text{PhC}_2\text{CuC}_2\text{Ph}]^-$ involves the transfer of only one acetylide group from the copper reagent [3].

Crystal data: $[\text{C}_{68}\text{H}_{50}\text{Ag}_2\text{Au}_2\text{P}_2]$, $M = 1539$, monoclinic, space group $P2_1/n$, a 11.5317(12), b 28.8083(26), c 22.3132(31) Å β 93.263(4) $^\circ$, U 5614.6 Å 3 , $Z = 4$, D_c 1.82 g cm $^{-3}$, $\mu(\text{Mo-K}\alpha)$ 59.8 cm $^{-1}$, $R = 0.046$, $R_w = 0.054$, error of fit = 1.46. Data were collected at 295 K by the $\theta-2\theta$ scan technique with Mo- $K\alpha$ radiation (graphite monochromator) to 2θ 50 $^\circ$ on a modified Picker automated diffractometer. A total of 9874 unique reflections were measured and 4748 for which $I > 3\sigma(I)$ were used in the structure determination. Data were corrected for Lorentz and polarization effects and for absorption (maximum and minimum transmission 0.7875 and 0.5431, applied to F). The structure was solved by direct methods (MULTAN 80). In all, 247 parameters were refined, with anisotropic thermal parameters for Au, Ag, P, and non-phenyl C of the anion and isotropic thermal parameters for the remaining non-hydrogen atoms. The ten phenyl groups were constrained to be rigid C_6H_5 groups, C—C 1.395, C—H 1.0 Å, angles 120 $^\circ$.

The structure of complex I involves a nearly square planar arrangement of metal atoms. There is no bonding interaction between gold atoms, Au...Au 4.013 Å, or between silver atoms, Ag...Ag 4.343 Å. The gold—silver distances range from 2.894 to 3.028 Å, indicating appreciable metal—metal bonding [4].

As shown in Fig. 1 each gold atom is σ -bonded to two acetylide groups in almost linear coordination. Gold—carbon bonds range from 1.98 to 2.00(2) Å and C—Au—C are 175.0 and 177.6(6) $^\circ$. Each silver is bonded to triphenylphosphine and is asymmetrically π -bonded to two alkyne groups in a manner similar to the bonding of the silver atoms, each to three alkyne groups, in the zwitterionic complex $[\text{RhAg}_2(\text{C}_2\text{C}_6\text{F}_5)_5(\text{PPh}_3)_3]$, which does not have metal—metal bonding [5]. Silver—carbon distances range from 2.27 to 2.55(1) Å

* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

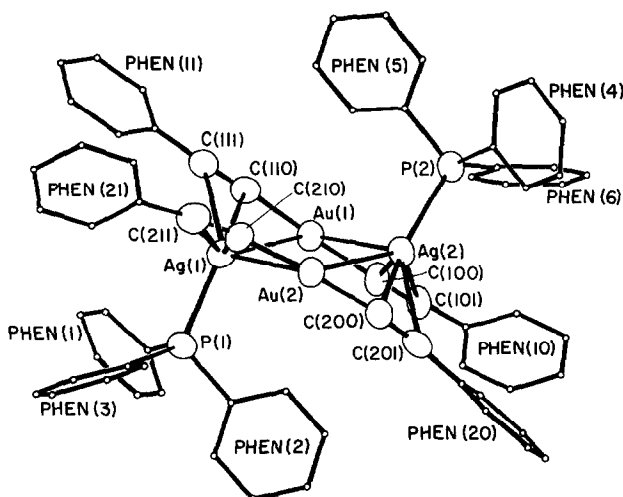


Fig. 1. The molecular structure of $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph})_4(\text{PPh}_3)_2]$. Hydrogen atoms have been omitted for clarity. Thermal parameters for phenyl groups are not indicated. Principal bond parameters are $\text{Ag}(1)-\text{Au}(1)$ 2.989(1), $\text{Ag}(1)-\text{Au}(2)$ 2.894(1), $\text{Ag}(2)-\text{Au}(1)$ 2.913(1), $\text{Ag}(2)-\text{Au}(2)$ 3.028(1), $\text{C}(100)-\text{Au}(1)$ 1.991(15), $\text{C}(110)-\text{Au}(1)$ 1.981(16), $\text{C}(200)-\text{Au}(2)$ 2.002(16), $\text{C}(210)-\text{Au}(2)$ 1.983(16), $\text{C}(100)-\text{C}(101)$ 1.231(18), $\text{C}(110)-\text{C}(111)$ 1.212(18), $\text{C}(200)-\text{C}(201)$ 1.203(17), $\text{C}(210)-\text{C}(211)$ 1.236(18) Å; $\text{Au}(1)-\text{Ag}(2)-\text{Au}(2)$ 84.91(3), $\text{Ag}(2)-\text{Au}(1)-\text{Ag}(1)$ 94.77(3), $\text{Ag}(1)-\text{Au}(2)-\text{Ag}(2)$ 94.34(3), $\text{Au}(2)-\text{Ag}(1)-\text{Au}(1)$ 85.98(3)°.

(for carbon bonded to Au) and from 2.67–3.10(3) Å (for carbon bonded to a phenyl group).

The IR spectrum showed a single band at ca. 2075 cm^{-1} assigned to $\nu(\text{C}\equiv\text{C})$. The frequency is similar to that observed for $\nu(\text{C}\equiv\text{C})$ in the anionic cluster $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$, and is lower by ca. 25–30 cm^{-1} than that of the corresponding bond of the anion $[\text{PhC}_2\text{AuC}_2\text{Ph}]^-$ [3, 6].

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