Preparation, Identification, and *X*-Ray Structure of a Novel Pentanuclear Gold–Copper Cluster Complex

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The reaction of $[NBu^n_4][PhC_2AuC_2Ph]$ with a mixture of $[AuC_2Ph]_n$ and $[CuC_2Ph]_n$ yields mainly the pentanuclear cluster $[NBu^n_4][Au_3Cu_2(C_2Ph)_6]$.

It has been reported recently that $[(PPh_3)_2N][PhC_2AuC_2Ph]$ depolymerises both gold phenylacetylide and silver *p*-tolylacetylide, but not copper *p*-tolylacetylide, to give dinuclear complexes believed to contain metal–metal bonds.[1] We report here the isolation, characterization, and *X*-ray structural determination of a novel pentanuclear cluster $[NBu^n_4][Au_3$-

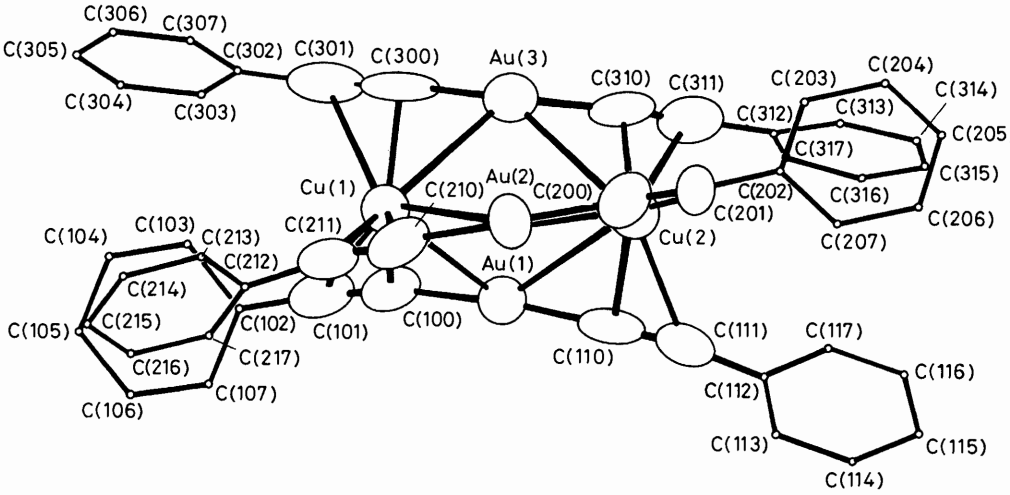

Figure 1. The molecular structure of the anion of $[NBu^n_4][Au_3Cu_2(C_2Ph)_6]$. Hydrogen atoms have been omitted for clarity.

$Cu_2(C_2Ph)_6]$ from the reaction of $[NBu^n{}_4][PhC_2AuC_2Ph]$ and a mixture of $[AuC_2Ph]_n$ and $[CuC_2Ph]_n$. Thus the addition of gold phenylacetylide to a mixture in tetrahydrofuran of $[NBu^n{}_4][PhC_2AuC_2Ph]$ and $[CuC_2Ph]_n$, in equimolar ratio, resulted in a change of colour from yellow to yellow-green. Normal work-up after 1.5 h, and crystallization from CH_2Cl_2–hexane, afforded mainly yellow-green crystals of the cluster $[NBu^n{}_4][Au_3Cu_2(C_2Ph)_6]$ in *ca.* 55% yield. The molecular formula of this complex was deduced from elemental analyses, ^1H n.m.r. spectroscopy, and vapour-phase molecular weight determination [found M (acetone) = 968; calculated M = 1566].

Single crystal *X*-ray structural studies† revealed a trigonal bipyramidal arrangement of metal atoms; two copper atoms in apical positions and three gold atoms that form an equilateral triangle (Figure 1). The main feature of the structure is that each gold atom is σ-bonded to two acetylide groups in almost linear co-ordination and each copper atom is asymmetrically π-bonded to three alkyne groups in a manner similar to the bonding of copper atoms, each to two alkyne groups, in the cluster $[Ir_2Cu_4(C_2Ph)_8(PPh_3)_2]$.[2] The i.r. spectrum showed a single band at *ca.* 2075 cm^{-1} assigned to ν(C≡C). This frequency is lower by *ca.* 25—30 cm^{-1} than the corresponding ν(C≡C) band of the anion $[PhC_2AuC_2Ph]^-$.[3,4] *X*-Ray structural studies of the chain polymers $[\{AuAg(C_6F_5)_2(SC_4H_8)\}_n]$ and $[\{AuAg(C_6F_5)_2(C_6H_6)\}_n]$ which have gold–silver bonds, indicated that the geometry of the two pentafluorophenyl groups is almost linear.[5]

There is no bonding interaction between the gold atoms, Au · · · Au 3.44—3.53 Å. However, Au–Cu distances lie in the range 2.783—3.016(3) Å, averaging 2.896(3) Å. This value is comparable to Ir–Cu average distances (2.871 Å) in the cluster $[Ir_2Cu_4(C_2Ph)_8(PPh_3)_2]$. Each copper atom asymmetrically π-bonds to three C_2Ph groups, Cu–C 2.08—2.15 Å for C bonded to Au and Cu–C 2.35—2.65(3) Å for C bonded to a phenyl group.

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† *Crystal data:* $[C_{16}H_{36}N]^+[C_{48}H_{30}Cu_2Au_3]^-$, M = 1566, triclinic, space group $P\bar{1}$, a = 18.1469(15), b = 18.8652(15), c = 19.0368(15) Å, α = 72.726(2), β = 103.170(2), γ = 107.988(2)°, U = 5831.7 $Å^3$, Z = 4, D_c = 1.75 g cm^{-3}, μ(Mo-K_α) = 82.3 cm^{-1}, R = 0.058, R_W = 0.066, error of fit = 1.863. Data were collected at 295 K by the θ—2θ scan technique with Mo-K_α radiation (graphite monochromator) to 2θ = 54° on a modified Picker automated diffractometer. A total of 25565 unique reflections were measured; 8045 for which $I > 3\sigma(I)$ were used in determination of the structure. Data were corrected for Lorentz and polarization effects and for absorption (maximum and minimum transmission 0.7291 and 0.3899, applied to F). The structure was solved by direct methods (MULTAN 78). All 140 non-hydrogen atoms were located. The two crystallographically unrelated molecules are essentially identical. In all, 587 parameters were refined, with anisotropic thermal parameters for Au, Cu, and non-phenyl C of the anion and isotropic thermal parameters for the remaining non-hydrogen atoms. The twelve phenyl groups were constrained to be rigid Ph groups, C–C = 1.395, C–H = 1.0 Å, angles 120°. No attempt was made to locate hydrogen atoms of the cation. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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