Communication

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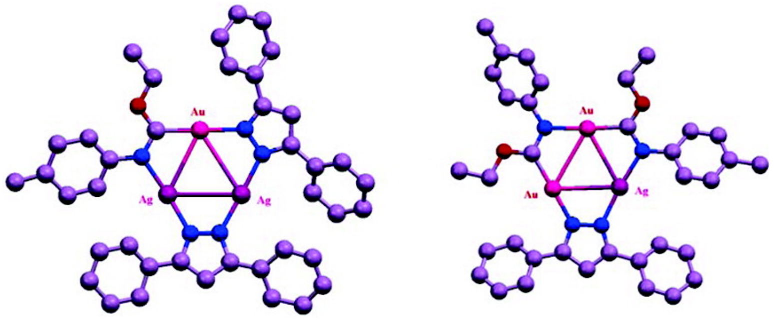

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Mixed-Metal Triangular Trinuclear Complexes: Dimers of Gold−Silver Mixed-Metal Complexes from Gold(I) Carbeniates and Silver(I) 3,5-Diphenylpyrazolates

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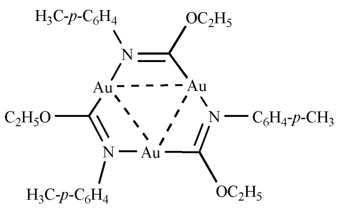
Pioneering works of Pignolet[1] and others[2−4] have described gold containing carbonyl or phosphine clusters with small-to-modest ratios of Au to other active metals. Some of these mixed-metal species have been reported to have catalytic activity. However, organic solvent soluble, stoichiometric, mixed-metal compounds containing gold are relatively rare. Molecular species containing 1:1[5] Au:Ag and 6:1[6] Au:Ag have been reported from our laboratory. This paper describes a successful approach to the synthesis of organic solvent soluble mixed-metal gold−silver compounds with 2:1 and 1:2 Au:Ag ratios.

Heterobimetallic molecular species can produce unique optical, catalytic,[7] and electronic properties. For example, gold−silver clusters have been synthesized and found to be highly efficient optical materials[8,9] which possess enhanced Non-Linear Optical activity (NLO) over that of the pure silver and gold complexes. A recent review describes some of the other interesting properties of gold nanoparticles.[10] Recently, nanoparticles of gold on oxide surfaces,[11] formed by calcination of organic solvent soluble, multinuclear gold compounds, have been found to be excellent room temperature oxidants for CO. Mixed-metal gold−silver nanoparticles of well-defined Au:Ag ratios appear to offer some interesting new opportunities.

Balch[12] and ourselves[13] reported the interaction of trinuclear gold carbeniates and benzylimidazolates with π-organic acids. The trinuclear Au(I) compound, **1**, interacts with acidic cations, such as Ag(I) and Tl(I), to form chains in which the acidic metal cation interacts with the trinuclear Au(I) compounds in a [BBA] repeat pattern (A/B is acid/base).[6] This pattern is also observed when the neutral, acidic trinuclear Hg(II) complex, $[Hg_3(C_6F_4)_3]$, or the organic electron acceptor TCNQ interacts with these trinuclear bases. Some organic acids, such as C_6F_6, $C_{10}F_8$, and C_6F_5Br, produce a stacked BABA pattern.[13] It also has been demonstrated that the AB units retain some integrity in organic solvents.[6c]



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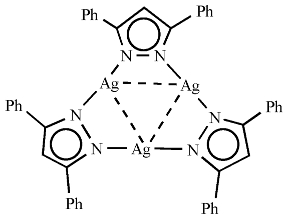

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In continuing studies of the interactions of π-acids with trinuclear gold bases, the gold(I) carbeniate, **1**, was reacted with the silver(I) 3,5-diphenylpyrazolate, **2** (see graphic above). *The crystalline products were not the expected acid−base adducts but mixed-metal gold−silver complexes.* The lability of the Au−N bond of the gold(I) carbeniate apparently allows the nine-membered ring to open and then close again after capturing one or two silver pyrazolate units, depending upon the ratio of the component trinuclear starting materials. Thus, the mixed-metal products, $\mathrm{Au(carb)Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2}$, **3**, and $\mathrm{Au_2(carb)_2Ag(\mu\text{-}3,5\text{-}Ph_2pz)}$, **4**, are produced (Figures 1 and 2). The compounds were analyzed using powder diffraction and compared with the pattern generated from the single crystal data.

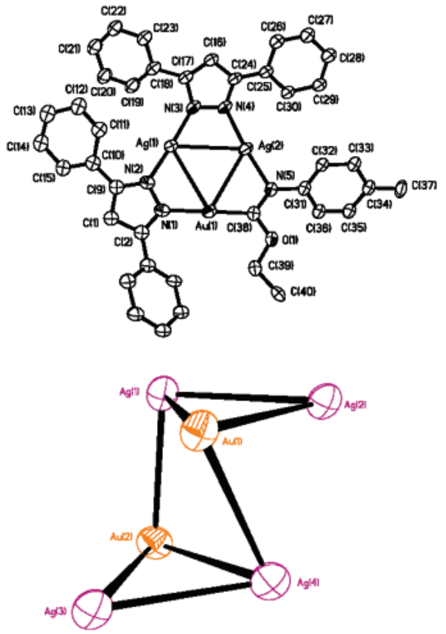

Figure 1. (Top) Thermal ellipsoid representation (50%) of a trinuclear unit in **3**. (Bottom) Dimer of trinuclear **3**. Selected bond lengths (Å) and angles (deg): Au(1)···Ag(2) 3.264(2), Au(1)···Ag(4) 3.309(2), Au(1)···Ag(1) 3.405(2), Au(2)···Ag(1) 3.082(2), Au(2)···Ag(4) 3.2156(2), Ag(1)···Ag(2) 3.289(2); Au(1)···Ag(2)···Ag(1) 62.66(4).

Compounds **3** and **4** were synthesized by the reaction of **1** and **2** in CH_2Cl_2 in stoichiometric ratios of 1:2 and 2:1, respectively (Supporting Information). The crystals were grown by slow evaporation from CH_2Cl_2 solution over a few days. Hairlike crystals of **3** and **4** were isolated with no evidence from the powder patterns of mixtures being formed. Each compound crystallizes with one independent dimer under triclinic $P\bar{1}$ ($Z = 2$) and orthorhombic $Pca2_1$ ($Z = 4$) symmetry, respectively (Supporting Information). The white powders of **3** and **4** show a strong green luminescence under UV excitation at room temperature and a yellow luminescence at 77 K, a *luminescence thermochromism*, as reported for $\mathrm{[Ag(TRbz)_2][BF_4]}$, where TRbz = $\mathrm{(\mu\text{-}N^3,C^2\text{-}bzimAu)_3}$.[6] The new

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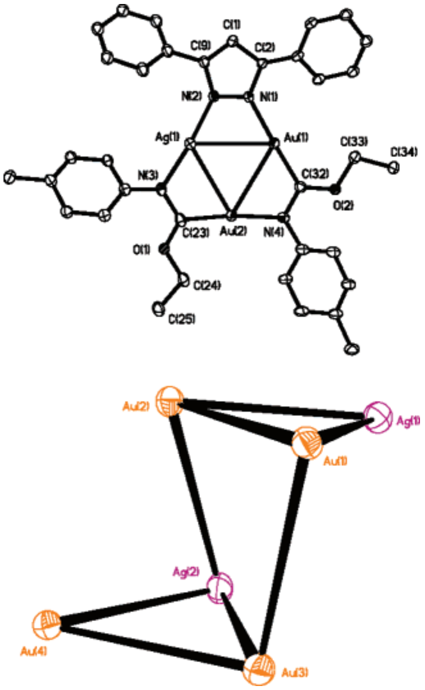

Figure 2. (Top) Thermal ellipsoid representation (50%) of one of the trinuclear units in **4**. (Bottom) Dimer of trinuclear **4**. Selected bond lengths (Å) and angles (deg): Au(1)⋯Au(2) 3.275(2), Au(1)⋯Ag(1) 3.280(2), Au(2)⋯Ag(1) 3.243(2), Au(1)⋯Au(3) 3.335(1); Au(2)⋯Ag(1)⋯Au(1) 60.26(3).

compounds are soluble in most organic solvents in which they are stable (by ^{1}H NMR and emission), and they are stable at room temperature in the solid state.

The structure of **3** is a dimer of the trinuclear units with two intermolecular interactions between gold and silver of Au⋯Ag 3.309(2) and 3.082(2) Å (Figure 1). The structure of **4** (Figure 2) shows one intermolecular Au⋯Au interaction of 3.335(1) Å between the trinuclear units. A long interaction of 3.426 Å exists for Ag(2)⋯Au(2). The Au⋯Au distances in the starting trinuclear gold(I) carbeniates **1** are 3.224, 3.288, and 3.299 Å. Dimer **1** contains two Au⋯Au interactions of 3.225 Å between the trinuclear units.[14] The structure of the dimer of the trinuclear silver pyrazolate, **2**, shows only one Ag⋯Ag interaction, ∼3.0 Å between these units with intratriangular Ag⋯Ag distances of ∼3.3−3.5 Å.[15]

The metallocycles of **3** and **4** are irregular and puckered similar to **1** and **2**. The puckering is greater in **3** than in **4**. The mean deviation of the atoms from a plane for one of the trinuclear units in **3** is 0.47 and 0.34 Å in **4**. The two complexes show independent units in their packing pattern similar to that of the starting materials. The structural chemistry of gold−silver complexes has been reviewed recently.[16]

In summary, this communication describes two new organic solvent soluble mixed-metal gold−silver complexes which have been obtained by mixing the gold(I) carbeniate, **1**, and the silver(I) pyrazolate, **2**, in specific stoichiometric ratios, exploiting what appears to be the relative lability of the gold−nitrogen bonds.[17] The properties of these new mixed-metal complexes and their potential as mixed-metal catalyst precursors are being investigated.

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Supporting Information Available: X-ray crystallographic files for **3** and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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