3818 *Organometallics* **2005,** *24,* 3818−3820

Luminescent Au_6Ag_{13} Cage Compounds of Arylacetylides, Metastable Intermediates to Au_5Ag_8 Complexes of $\{1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}^{3-}$ ($R = H, CH_3, Bu^t$)

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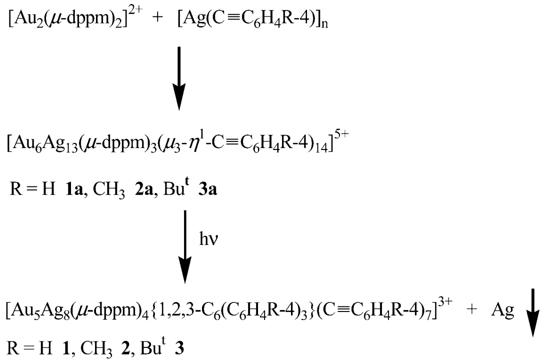
Received May 9, 2005

Summary: Crystallographic characterization of the metastable alkynyl complexes $[Au_6Ag_{13}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4R\text{-}4)_{14}]^{5+}$ *(R = H (**1a**),* CH_3 *(**2a**),* Bu^t *(**3a**)) is described. Photolysis of the green* Au_6Ag_{13} *alkynyl complexes in solutions allows isolation of the red* Au_5Ag_8 *products* $[Au_5Ag_8(\mu\text{-dppm})_4\{\mu_5\text{-}1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}(C{\equiv}CC_6H_4R\text{-}4)_7]^{3+}$ *(R = H (**1**),* CH_3 *(**2**),* Bu^t *(**3**)) together with silver precipitate. The unprecedented* $Au^I_6Ag^I_{13}$ *alkynyl cluster complexes exhibit unusual cage structures and show intense luminescence.*

Alkynyl complexes of coinage metals have attracted great attention, owing to their intriguing photoluminescence with manifold emissive origins as well as facile formation of metallicophilic interactions.[1−13] To prepare luminescent $Au^I{-}Ag^I$ heterometallic alkynyl complexes, reactions of the polymeric silver arylacetylide $(AgC{\equiv}CC_6H_4R\text{-}4)_n$ with binuclear Au^I components $[Au_2(\mu\text{-dppm})_2]^{2+}$ (dppm = bis(diphenylphosphino)methane) were investigated.[12] As shown in Scheme 1, the reactions initially afford metastable green species, which are sensitive to light and photolyzed gradually into the stable red complexes $[Au_5Ag_8(\mu\text{-dppm})_4\{\mu_5\text{-}1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}(C{\equiv}CC_6H_4R\text{-}4)_7]^{3+}$ (R = H (**1**), CH_3 (**2**), Bu^t (**3**)) by cyclotrimerization of the arylacetylide $C{\equiv}CC_6H_4R\text{-}4$ into $\{1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}^{3-}$.[12] The metastable green substances were thus assumed to be reactive intermediates with $\{1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}^{3-}$ exhibiting Dewar benzene structures.[12]

Scheme 1



Further study has been focused on accomplishing crystallographic characterization of the metastable green intermediates. Unexpectedly, they exhibit unprecedented Au_6Ag_{13} cage structures with the formula $[Au_6Ag_{13}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4R\text{-}4)_{14}]^{5+}$ (R = H (**1a**), CH_3 (**2a**), Bu^t (**3a**)), significantly different from the stable red complexes **1**−**3** with Au_5Ag_8 cluster structures.

As shown in Scheme 1, the metastable green compounds **1a**$(SbF_6)_5$−**3a**$(SbF_6)_5$, prepared by reaction of $(AgC{\equiv}CC_6H_4R\text{-}4)_n$ with $[Au_2(\mu\text{-dppm})_2](SbF_6)_2$ in dichloromethane for 2 h with exclusion of light, were isolated as green crystals in ca. 46−49% yields (based on silver content).[14] They were characterized by elemental analyses, ES-MS spectrometry, ^1H and ^{31}P NMR spectroscopy, and X-ray crystallography for **1a**$(SbF_6)_5$ and **2a**$(SbF_6)_5$.[15] The positive ion ES-MS spectra showed the molecular ion fragments $[M - (SbF_6)_5]^{5+}$ as the principal peaks.

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(14) Synthetic procedure for $[Au_6Ag_{13}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)_{14}](SbF_6)_5$ (**1a**$(SbF_6)_5$). To a dichloromethane (25 mL) solution of $[Au_2(dppm)_2](SbF_6)_2$ (132.0 mg, 0.088 mmol) was added polymeric silver phenylacetylide $(AgC{\equiv}CC_6H_5)_n$ (44.0 mg, 0.21 mmol). The suspended solution was stirred at room temperature with exclusion of light. The solution color turned gradually from pale yellow to green in 2 h. After filtration, the filtrate was concentrated under vacuum. Green crystals were isolated by layering diethyl ether onto the concentrated solution over several days when put aside with exclusion of light. Yield: 47 mg (46% based on silver content). Detailed characterization data for compounds **1a**$(SbF_6)_5$−**3a**$(SbF_6)_5$ are provided in the Supporting Information.

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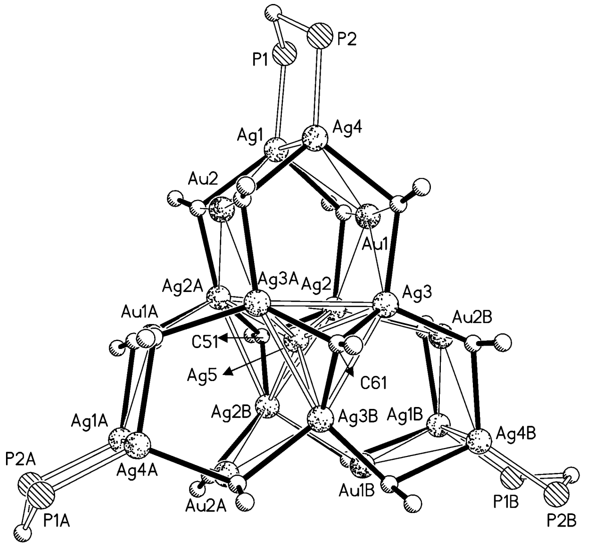

Figure 1. Views of complex **2a** with atom-labeling scheme. Phenyl rings on the phosphorus atoms and 4-methylphenyl groups of (4-methylphenyl)acetylides are omitted for clarity.

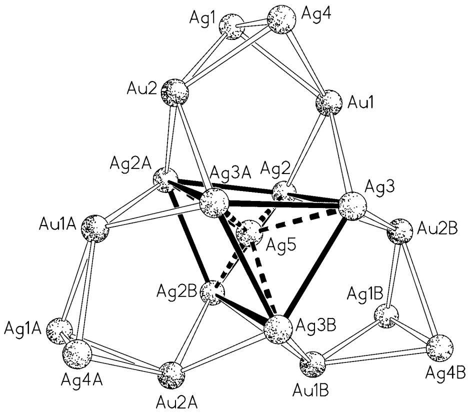

Figure 2. View of the Au_6Ag_{13} cluster core in complex **2a**.

Table 1. Photophysical Data of Compounds $\mathbf{1a(SbF_6)_5}$–$\mathbf{3a(SbF_6)_5}$

compd	medium	λ_{em}/nm ($\tau_{em}/\mu s$)^a (298 K)	Φ_{em}^{b}	λ_{em}/nm (77 K)
1a$(SbF_6)_5$	solid	525 (0.05)		536
	CH_2Cl_2	545 (0.55)	0.025	531
2a$(SbF_6)_5$	solid	545 (0.41)		562
	CH_2Cl_2	560 (5.66)	0.112	557
3a$(SbF_6)_5$	solid	523 (0.04)		540
	CH_2Cl_2	546 (0.80)	0.032	539

^{a} The excitation wavelength in the lifetime measurement is at 397 nm. ^{b} The emission quantum yields were measured at 298 K in degassed dichloromethane solution and estimated relative to $Ru(bpy)_3(PF_6)_2$ in acetonitrile (Φ_{em} = 0.062) as reference.

As depicted in Figure 1 and Figure S2 (Supporting Information), the Au_6Ag_{13} complex cation **2a** displays a cage structure that consists of 6 Au^I and 13 Ag^I centers linked together by 14 4-methylphenylacetylides and 3 dppm ligands. Thirty Ag–C bonds (highlighted by thick lines in Figure 1) make up of 3 distorted hexagonal prisms that are intersected by sharing a rim with each other. The ligand-unsupported Ag^I (Ag5) atom is situated at the center of the 3 intersected hexagonal prisms which are symmetry-related by a C_3 axis through the atoms C51Ag5C61 (Figure 1). Figure 2 depicts the spatial structure of the Au_6Ag_{13} cluster core. The middle part (highlighted by thick lines) shows a triangular-prismatic framework composed of 6 Ag^I atoms, and the ligand-unsupported Ag5 atom lies at the center of the triangular prism. As depicted in Figure 2, each Au^I atom is connected by 4 Ag^I atoms through Au^I–Ag^I contacts to afford an approximate $AuAg_4$ tetragonal pyramid with the Au^I on the pyramidal apex and 4 Ag^I atoms on the basal plane. Six of these $AuAg_4$ tetragonal pyramids are connected to one another by sharing the Ag–Ag edges. The Au^I–Ag^I and Ag^I–Ag^I distances are in the ranges of 2.94–3.22 and 2.89–3.32 Å, respectively, indicating the presence of significant metal–metal interactions.[16,17] While the Au^I centers are coordinated by two acetylide C donors in quasi-linear arrangements (C–Au–C = 168.6(8)–171.3(8)°), the Ag^I centers exhibit distorted-triangular-planar geometry composed of C_2P or C_3 donors. Of the 14 4-methylphenylacetylides in μ_3-η^1 bonding mode, 2 symmetrically cap 3 Ag^I centers, respectively, whereas the others are bound to 1 Au^I and 2 Ag^I centers in an asymmetric mode, respectively. All of the Au–C, Ag–C, and Ag–P distances are in the normal ranges[2–11] and are comparable to those found in the Au_5Ag_8 complex **1**[12] and **2** (Table S4, Supporting Information).

The absorption spectra of complexes **1a**–**3a** in dichloromethane display high-energy ligand-centered bands at ca. 250–320 nm and shoulder bands at ca. 350 nm tailing off to 500 nm, arising from metal-perturbed intraligand $\pi \rightarrow \pi^*$ (C≡C) transitions. With excitation at λ > 350 nm, complexes **1a**–**3a** show intense photoluminescence (λ_{em} = 520–570 nm) in the solid state and in solution at both 298 and 77 K. The luminescence quantum yields Φ_{em} in degassed fluid dichloromethane are in the range 0.025–0.112 (Table 1). The lifetimes on a microsecond scale at 298 K reveal a spin-forbidden triplet parentage. Typically, vibronic-structured emission bands related to the acetylides in the excited states are unobserved. Therefore, it is likely that the emission is mainly derived from triplet states of a metal-cluster-centered (d → s) character modified by metal–metal contacts.[1,8,13]

Once exposure on light, the solutions of green metastable Au_6Ag_{13} complexes **1a**–**3a** transform gradually into the red Au_5Ag_8 species **1**–**3** with precipitation of silver metal in the meanwhile (Scheme 1). It is likely that light irradiation of the green Au_6Ag_{13} compounds induces $Ag^+ \rightarrow Ag$ to occur as well as to produce free radicals necessary for formation of {μ_5-1,2,3-C_6(C_6H_4R-

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(15) Crystal data for **1a**$(SbF_6)_5\cdot H_2O$: $C_{187}H_{138}Ag_{13}Au_6F_{30}P_6OSb_5$, M_r = 6349.65, monoclinic, $P2_1/c$, a = 23.281(5) Å, b = 21.627(4) Å, c = 42.693(9) Å, β = 91.52(3)°, V = 21488(7) Å^3, Z = 4, ρ = 1.963 g cm^{-3}. Least-squares refinement based on 15 936 reflections with $I > 2\sigma(I)$ and 1415 parameters led to convergence with final R1 = 0.0892 and wR2 = 0.2638. Crystal data for **2a**$(SbF_6)_5\cdot 3H_2O$: $C_{201}H_{170}Ag_{13}Au_6F_{30}O_3P_6Sb_5$, M_r = 6582.06, rhombohedral, $R\bar{3}$, a = 25.140(4) Å, b = 25.140(4) Å, c = 59.228(12) Å, V = 32418(9) Å^3, Z = 6, ρ = 2.023 g cm^{-3}. Least-squares refinement based on 6731 reflections with $I > 2\sigma(I)$ and 461 parameters led to convergence with final R1 = 0.0975 and wR2 = 0.3007. Crystal data for **2**$(PF_6)_3$: $C_{190}H_{158}Ag_8Au_5F_{18}P_{11}$, M_r = 4971.63, monoclinic, $P2_1/n$, a = 25.9385(3) Å, b = 24.3850(4) Å, c = 33.3375(2) Å, β = 107.771(1)°, V = 20080.2(4) Å^3, Z = 4, ρ = 1.645 g cm^{-3}. Least-squares refinement based on 14 688 reflections with $I > 2\sigma(I)$ and 1901 parameters led to convergence with final R1 = 0.0921 and wR2 = 0.2080.

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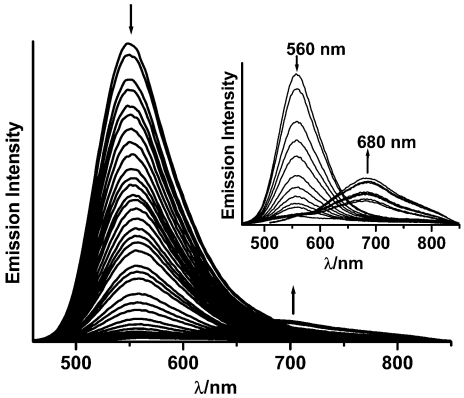

Figure 3. Emission spectra of the compound **2a**$(SbF_6)_5$ in degassed dichloromethane upon continual irradiation with a xenon lamp at 440 nm.

$4)_3\}^{3-}$ by cyclotrimerization of arylacetylide.[18] As shown in Figure 3, when the degassed dichloromethane solution of complex **2a** was irradiated continually with a xenon lamp at $\lambda = 440$ nm, the emission at 560 nm decays step by step. Moreover, a new band occurs at 680 nm and is enhanced gradually, owing to formation of the red Ag_5Ag_8 species **2**. With the green solution transforming into a red solution at room temperature, the emission at 560 nm disappears completely in 3 days, whereas the band at 680 nm enhances day by day over 1 week. Interestingly, the stable Au_5Ag_8 species **1**−**3** show much weaker photoluminescence with lower energy (ca. 70−120 nm red shift) whether in the solid state or in solution relative to that of the metastable Au_6Ag_{13} intermediates **1a**−**3a** (Figure S4, Supporting Information), probably due to the difference in their emissive origins.[12] It is noteworthy that the red Au_5Ag_8 species **1**−**3**, produced by photolysis of the dichloromethane solutions of green Au_6Ag_{13} intermediates **1a**−**3a**, were substantially identified by ES-MS and NMR spectroscopy and confirmed further by single-crystal X-ray diffraction for the red compound **2**$(PF_6)_3$ (Figure S3, Supporting Information).

In summary, the unusually photoinduced transformation of metastable Au_6Ag_{13} alkynyl intermediates into more stable Au_5Ag_8 species is described. Metastable Au_6Ag_{13} intermediates, together with their transforming Au_5Ag_8 products, were structurally characterized by X-ray crystallography. The unprecedented Au_6Ag_{13} alkynyl cluster complexes exhibit unusual cage structures and emit intense luminescence. The photoinduced formation of $\{\mu_5\text{-}1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}^{3-}$ by cyclotrimerization of metalated 1-yne is probably involved in a free radical mechanism.

Acknowledgment. This work was supported financially by the NSFC (Grant Nos. 20273074, 20490210, and 90401005), the NSF of Fujian Province (Grant Nos. E0420002 and E0310029), the fund from the Chinese Academy of Sciences, and the national basic research program (Grant No. 001CB108906) of China.

Supporting Information Available: Text, tables, and figures giving detailed experimental procedures, including the preparation and characterization of compounds **1a**$(SbF_6)_5$−**3a**$(SbF_6)_5$ and CIF files giving the X-ray crystallographic data for the structure determinations of compounds **1a**$(SbF_6)_5$, **2a**$(SbF_6)_5$, and **2**$(PF_6)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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