

Luminescent Heteronuclear Au^IAg^I₈ Complexes of {1,2,3-C₆(C₆H₄R-4)₃}³⁻ (R = H, CH₃, Bu) by Cyclotrimerization of Arylacetylides

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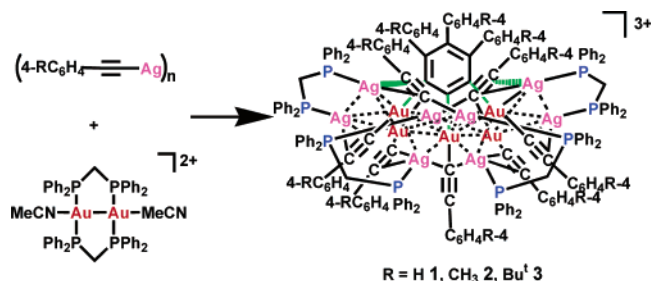
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Recent interest in group 11 metal alkynyl complexes has primarily focused on their manifold emissive properties.^{1–4} Aiming at attaining photoluminescent Au^I–Ag^I heterometallic alkynyl complexes,⁵ one feasible approach is to incorporate polymeric silver arylacetylide (AgC≡CC₆H₄R-4)_n with binuclear Au^I components [Au₂(μ-dppm)₂(MeCN)₂]²⁺ (dppm = bis(diphenylphosphino)methane).⁶ Remarkably, the reaction allows isolation of Au^I–Ag^I heterometallic complexes [Au₅Ag₈(μ-dppm)₄{1,2,3-C₆(C₆H₄R-4)₃}- (C≡CC₆H₄R-4)₇]³⁺ (R = H **1**, CH₃ **2**, Bu **3**) with unprecedented trianion μ₅-{1,2,3-C₆(C₆H₄R-4)₃}³⁻ derived from cyclotrimerization of arylacetylide C≡CC₆H₄R-4.

As shown in Scheme 1, complexes **1–3** were prepared by reaction of [Au₂(μ-dppm)₂(MeCN)₂]²⁺ with three equivalent (AgC≡CC₆H₄R-4)_n in dichloromethane with exclusion of light to give green solutions. Layering diethyl ether onto the acetonitrile solutions without exclusion of light gave the products as red crystals in 17–54% yields (based on Ag). It is noteworthy that reaction of [Ag₂(μ-dppm)₂(MeCN)₂]²⁺ with (AuC≡CC₆H₄R-4)_n also affords complexes **1–3** in lower yields.

Scheme 1



The structure of compound **1**(PF₆)₃ was determined by X-ray crystallography. It contains five Au^I and eight Ag^I centers linked together by bridging dppm, phenylacetylide C≡CC₆H₅, and trianion {1,2,3-C₆(C₆H₅)₃}³⁻ as depicted in Figure 1. The Au^I–Au^I and Ag^I–Ag^I distances are 3.1490(7) and 3.1674(18) Å, respectively, implicating that intramolecular Au^I–Au^I and Ag^I–Ag^I interactions are operative.⁷ Extensive ranges of Au–Ag (2.7434(14)–3.1490(15) Å) contacts are present in the Au₅Ag₈ cluster core.⁷ Of the seven phenylacetylides C≡CC₆H₅, three adopt μ₃-η¹(σ) and four exhibit μ-η¹(σ), η²(π) bonding modes. The μ₃-η¹-C≡CC₆H₅ is bound to one Au^I and two Ag^I centers, whereas the μ-η¹, η²-C≡CC₆H₅ is bonded to Au^I and Ag^I centers via η¹(σ-bonding) and η²(π-bonding) coordination, respectively. The bond lengths of Au–C_{acetylide} and Ag–C_{acetylide} are in the range 2.023–2.035 and 2.318–2.576 Å, respectively. The trianion {1,2,3-C₆(C₆H₅)₃}³⁻ displays an unusual μ₅-bonding fashion bound to three Au^I and two Ag^I centers as shown in Figure 2. While the three Au–C_{aryl} (2.011 and 2.084 Å) bonds are almost coplanar with the trianionic phenyl ring, the two Ag–C_{aryl} (2.672 Å) bonds are oriented in an anti conformation (Figure

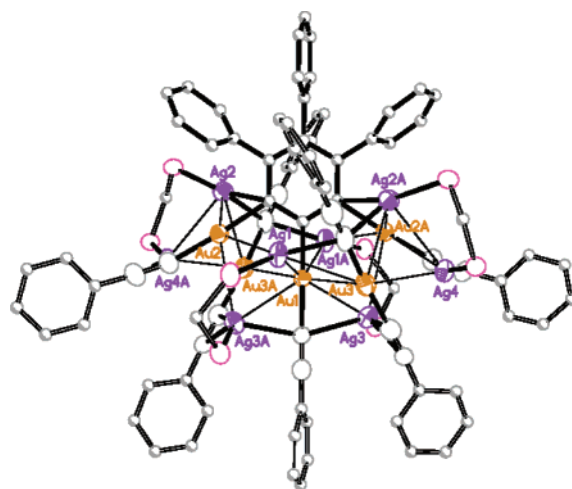


Figure 1. View of complex **1** with atom labeling scheme (30% thermal ellipsoids). Phenyl rings on the phosphorus atoms are omitted for clarity.

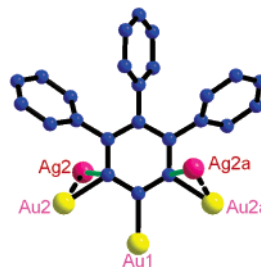
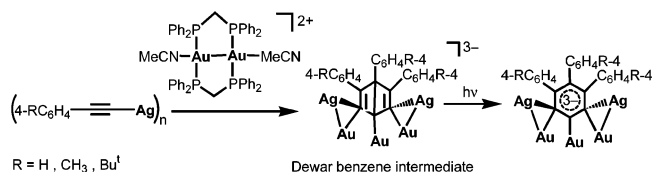


Figure 2. View of μ₅-{1,2,3-C₆(C₆H₅)₃}³⁻ coordination, showing an anti-orientation of the two Ag–C_{aryl} bonds.

2) and the atoms Ag^I2 and Ag^I2a are located up and down this phenyl ring 2.393 Å, respectively. It has been established that trianionic aryl derivatives usually adopt 1,3,5-C donors bound to metal ions.^{8,9} Thus, the μ₅-coordination of trianion {1,2,3-C₆(C₆H₅)₃}³⁻ bound to Au₃Ag₂ centers by 4,5,6-C donors (Figure 2) is unprecedented. The four dppm link eight Ag^I centers to form four binuclear Ag₂–(μ-dppm) units. The five Au^I centers are all in a linear σ (η¹) coordination (C–Au–C = 173.2–180.0°), adopting acetylide and aryl C donors. Depending on the chromophores, the Ag^I centers, however, afford different geometries built by acetylide and/or aryl C and diphosphine P donors. The centers Ag^I1 and Ag^I1a, Ag^I2 and Ag^I2a, Ag^I3 and Ag^I3a, and Ag^I4 and Ag^I4a afford distorted V-shaped, T-shaped, triangle-planar, and linear geometries, respectively.

The ES-MS show [M–(SbF₆)₃]³⁺ as the principal peaks for **1**(SbF₆)₃–**3**(SbF₆)₃ (Figures S1–S3, Supporting Information). Typical ν(C≡C) stretching frequencies occur at ca. 2050 cm⁻¹ in the IR spectra of **1**(SbF₆)₃–**3**(SbF₆)₃.⁶ The ³¹P NMR spectra in CD₃-CN reveal characteristic Ag–P and P–P couplings with J_{Ag–P} and

Scheme 2



J_{P-P} in the ranges 450–720 and 35–45 Hz, respectively (Figures S4–S6, Supporting Information). Four sets of multiplet signals with equal intensity are observed, coinciding with the presence of four inequivalent P donors in the solid structures.

The UV–vis spectra of compounds **1**(SbF₆)₃–**3**(SbF₆)₃ are characterized by high-energy absorptions at 230–290 nm and low-energy bands at ca. 365 and 440 nm, respectively. With the excitation $\lambda_{\text{ex}} > 350$ nm, compounds **1**(SbF₆)₃–**3**(SbF₆)₃ emit intense red luminescence ($\lambda_{\text{em}} = 630$ –680 nm). By comparison of the emission spectra of compounds **1**(SbF₆)₃–**3**(SbF₆)₃ (Table S3, Supporting Information), it is observed that introducing an electron-donating substitute such as methyl (**2**) and *tert*-butyl (**3**) to phenylacetylide results in a slight blue shift of the emission band. The emissive origin is therefore tentatively assigned as an admixture of MLCT (Au₅Ag₈ → C≡CC₆H₄R-4) transition and a metal cluster-centered excited-state modified by metal–metal interactions.^{1b,6b,7b}

It has been demonstrated that cyclotrimerization of substituted alkynes catalyzed by transition-metal complexes usually gives 1,3,5- and/or 1,2,4-trisubstituted benzene derivatives in high selectivity.¹⁰ To our knowledge, isolation of 1,2,3-trisubstituted counterparts by this approach, however, has been attained in few cases.^{11–13} It has been revealed that thermal cyclotrimerization of *tert*-butylfluoroacetylene ((CH₃)₃CC≡CF)¹² and perchlorophenylacetylene (C₆Cl₅C≡CCl)¹³ can afford 1,2,3-tri-*tert*-butyltrifluorobenzene and perchloro-1,2,3-triphenyl-benzene, respectively. A reaction mechanism involved in generation of intermediates such as cyclobutadiene and Dewar benzene derivatives was proposed on the basis of a series of experimental and theoretical evidences.^{11–13}

ES-MS (Figure S7, Supporting Information) of the green intermediate is similar to that of compound **1**(SbF₆)₃ with high abundance ratio of molecular ion peaks [M-(SbF₆)₃]³⁺. It is likely that the green substances formed by reaction of [Au₂(μ -dppm)₂(MeCN)₂]²⁺ with (AgC≡CC₆H₄R-4)_n afford Dewar benzene intermediates (Scheme 2), which convert gradually into the red compounds **1**(SbF₆)₃–**3**(SbF₆)₃ when put aside without exclusion of light. With the excitation $\lambda_{\text{ex}} > 350$ nm, the green intermediate of compound **1**(SbF₆)₃ affords strong yellow-green luminescence at ca. 560 nm (Figure S8, Supporting Information) in acetonitrile. Upon formation of compound (SbF₆)₃**1**, a red shift (ca. 70–120 nm) in the emission wavelength relative to the green Dewar benzene intermediate is likely ascribed to the modification of metal–metal contacts involved.^{7b,14}

In summary, the present study describes preparation and characterization of the unusual Au₅Ag₈ complexes by highly selective cyclotrimerization of metalated 1-yne to afford the {1,2,3-C₆-(C₆H₄R-4)₃}³⁻ trianion with an unprecedented μ_5 -bonding mode. Further work is underway to attain crystallographic characterization of the green intermediates.

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Supporting Information Available: Detailed experimental procedures including preparation and characterization of compounds **1**(SbF₆)₃–**3**(SbF₆)₃; the positive ES-MS of compounds **1**(SbF₆)₃ (Figure S1), **2**(SbF₆)₃ (Figure S2), and **3**(SbF₆)₃ (Figure S3); the ³¹P NMR spectra of compounds **1**(SbF₆)₃ (Figure S4), **2**(SbF₆)₃ (Figure S5), and **3**(SbF₆)₃ (Figure S6); the ES-MS of the green intermediate of **1**(SbF₆)₃ (Figure S7); the absorption and emission spectra of **1**(SbF₆)₃ and its green intermediate (Figure S8); the X-ray crystallographic file in CIF format for the structure determination of compound **1**(PF₆)₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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