

A New Type of Luminescent Alkynyl Au₄Cu₂ Cluster†

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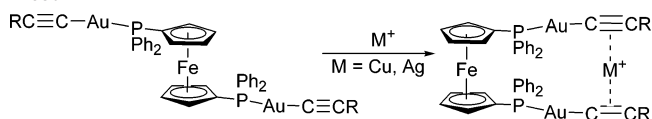
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Changes in the optical properties of an alkynylgold(I) complex upon reaction with Cu(I) are associated with a complicated structural change to form an unusual Au₄Cu₂ cluster with metallophilic interactions as well as π -alkyne coordination.

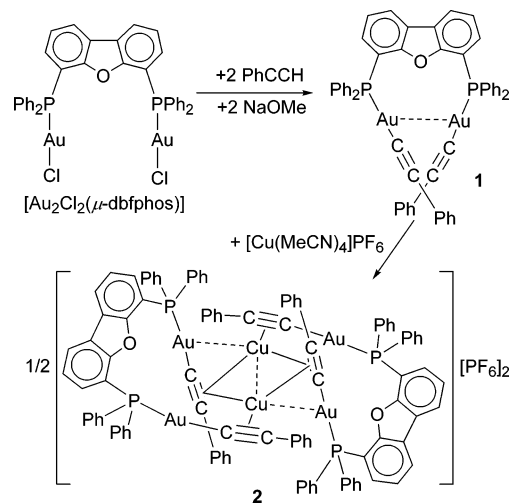
Extensive research on Au(I)⋯Au(I) (aurophilic) interactions has been stimulated by the interesting photophysical properties they confer on Au(I) complexes. The possibility of switching “on” and “off” the emission of Au(I) compounds by favoring or restricting aurophilicity can be exploited in the development of molecular sensors or optical devices. For example, Yam et al.¹ have undertaken pioneering work on the use of dinuclear Au(I) complexes containing crown ether fragments or alkynyl ligands (Scheme 1) that are capable of trapping an additional metal ion and concomitantly alter the emission of the compounds. However, the structures of the final products in these “switches” are unknown, and it is therefore difficult to establish to what extent variable Au⋯Au distances are actually responsible for the observed changes in the emission. To get a better insight into this type of “switch”, we have prepared a digold(I) alkynyl complex containing the rigid diphosphine 4,6-bis(diphenylphosphino)-dibenzofuran (dbfphos), in contrast to the more flexible phosphines of the previous examples, and studied its reactivity toward Cu(I). The crystal structures and optical behavior of both the precursor and final compounds are described. As expected, the optical properties are perturbed in the presence of Cu(I), but instead of π -alkynyl coordination of a single Cu(I) ion, a dimeric species with an unprecedented Au₄Cu₂ core, partly held through Au(I)⋯Cu(I) and Cu(I)⋯Cu(I) interactions, is found in the solid state.

Complex [Au₂{(C≡C(C₆H₅))₂(μ -dbfphos)}] (**1**) was readily obtained by the reaction of [Au₂Cl₂(μ -dbfphos)]² with

Scheme 1. Example of a Digold Compound Proposed as a Cation Probe^{1c}



Scheme 2. Synthesis of Complexes **1** and **2**



PhC≡CH in the presence of a base (Scheme 2). Its structure (Figure 1) exhibits a very weak intramolecular Au⋯Au contact of 3.401(1) Å.³ The gold alkynyl fragments are almost perpendicular to each other, and the geometries around the metal atoms are slightly distorted from linearity, with P1–Au1–C13 and P2–Au2–C33 angles of 166.4(2)° and 171.1(2)°, respectively.

Addition of [Cu(MeCN)₄][PF₆] to a solution of **1** resulted in an immediate color change from off-white to orange as complex **2** formed. It crystallized as the dimer [(μ -dbfphos)-

† Dedicated to Dr. José-Antonio Abad on the occasion of his retirement.
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(3) Crystal data for C₅₂H₃₆Au₂OP₂ (**1**): *M* = 1132.68, orthorhombic, space group *P*2₁2₁2₁, *a* = 11.5165(1) Å, *b* = 18.0618(2) Å, *c* = 19.6211(2) Å, *U* = 4081.36(7) Å³, *T* = 150 K, *Z* = 4, μ = 7.299 mm⁻¹, *R*_{int} = 0.0871. A total of 72 223 reflections were measured for the angle range 2.95 < 2 θ < 27.43°, and 9294 independent reflections were used in the refinement. The final residuals were wR2 = 0.0757 and R1 = 0.0310 [*I* > 2 σ (*I*)].

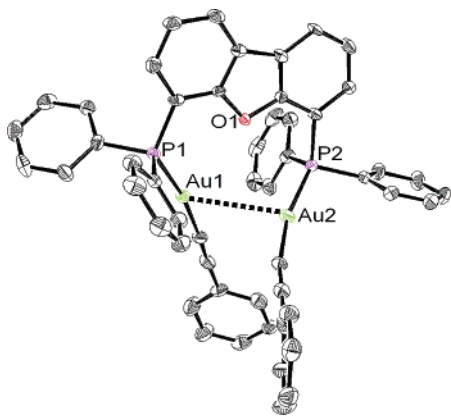


Figure 1. Crystal structure of **1** (H atoms omitted for clarity).⁴

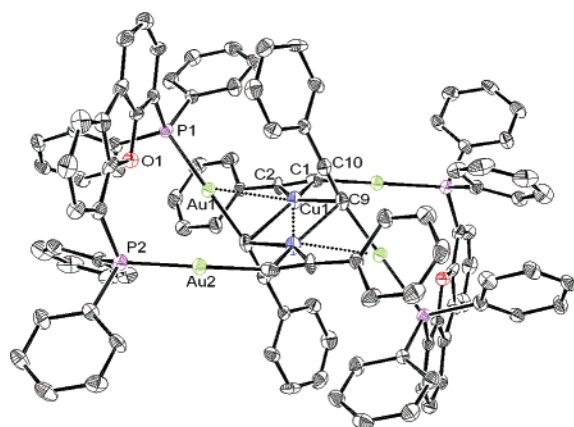


Figure 2. Crystal structure of the cation in **2** (H atoms omitted for clarity).⁴

$\text{Au}_2\{\eta^2\text{-C}\equiv\text{C}(\text{C}_6\text{H}_5)\}_2\text{Cu}_2[\text{PF}_6]_2\cdot 2\text{Cl}_2\text{CH}_2$ (Scheme 2 and Figure 2). Its room-temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR show broad peaks, indicating a dynamic process in solution. Thus, in addition to the $[\text{PF}_6]^-$ septuplet at -143 ppm, the room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** contains a broad signal at ca. 24 ppm, which becomes sharper at 213 K. In the crystal structure of **2** (Figure 2), the two P atoms of each diphosphine are inequivalent. If complex **2** adopts the same structure in solution as it does in the crystal, the P centers must be in fast exchange, even at low temperature, to give rise to only one singlet. In this case, the broadness of the room-temperature signal would have to be due to a different dynamic process (e.g., different species in exchange). After several hours, additional species are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. A full investigation of these solution processes is currently underway and will be included in a full-length paper following this Communication.

The solid-state IR spectrum of **2** shows the $\nu(\text{C}\equiv\text{C})$ stretching at 2031 cm^{-1} , shifted to lower frequency in relation to that of **1** (2116 cm^{-1}), as expected from the weakening of the $\text{C}\equiv\text{C}$ bond upon π coordination.^{1c}

The crystal structure of **2** (Figure 2) contains a dimeric cation of C_2 symmetry with four Au(I) and two Cu(I) atoms.⁵ There are also two PF_6^- anions and two molecules of $\text{CH}_2\text{-Cl}_2$ per dication. Instead of a weak $\text{Au}\cdots\text{Au}$ interaction (as

in **1**), there are two $\text{Cu}\cdots\text{Au}$ contacts of $2.8524(16)\text{ \AA}$ ($\text{Cu1}\cdots\text{Au1}$). This distance is shorter than the sum of the Au and Cu van der Waals radii (3.06 \AA) and lies within the range found in other Au(I)/Cu(I) complexes ($2.6\text{--}3.0\text{ \AA}$).^{6–8} The distance between Cu1 and Au2 [$3.2847(16)\text{ \AA}$] is significantly longer, but it could still contribute to the overall stability of the cluster. In addition, a $\text{Cu}\cdots\text{Cu}$ contact of $2.898(3)\text{ \AA}$, slightly above the sum of the van der Waals radii of two Cu atoms (2.8 \AA), is found. Although other mixed-metal alkynyl clusters have been reported,⁶ including the pentanuclear Au_3Cu_2 alkyne derivative $[\text{N}^n\text{Bu}_4][\text{Au}_3\text{-Cu}_2(\text{C}_2\text{Ph})_6]$ [$\text{Au}\cdots\text{Cu}$, $2.783\text{--}3.016(3)\text{ \AA}$],^{6a} the nuclearity of **2** is unique. Moreover, in contrast with the abundance of crystallographic evidence on $\text{Au(I)}\cdots\text{Au(I)}$ and, to a much lesser extent, $\text{Au(I)}\cdots\text{Ag(I)}$ contacts, data on $\text{Au(I)}\cdots\text{Cu(I)}$ interactions are still very rare.⁹

The Cu atoms in **2** can be considered as pentacoordinated, each interacting with the other Cu, one Au atom, and three alkynyl groups. One alkyne ($\text{C9}\equiv\text{C10}$) of each $[\mu\text{-dbfphos-Au}_2\{\eta^2\text{-C}\equiv\text{C}(\text{C}_6\text{H}_5)\}_2]$ fragment bridges between the two Cu atoms, whereas the other ($\text{C1}\equiv\text{C2}$) coordinates only to one Cu. The Cu–alkyne bonds with $\text{C9}\equiv\text{C10}$ are highly asymmetric, with the Cu1-C10 distance [$2.420(12)\text{ \AA}$] being significantly longer than that of Cu1-C9 [$2.182(12)\text{ \AA}$]. In each case, the Cu–C distance for the C bonded to Au ($2.016\text{--}2.200\text{ \AA}$) is shorter than that for the C attached to the phenyl group. Analogous asymmetric Cu–alkyne π bonding has been found in $[\text{N}^n\text{Bu}][\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]$.^{6a} The Au–C, Au–P, and $\text{C}\equiv\text{C}$ distances are not affected by Cu(I) π coordination because they are similar in both **1** and **2**. The coordination around each Au atom in **2** is distorted from linearity with angles of $171.2(4)^\circ$ (P1-Au1-C9) and

- (5) Crystal data for $\text{C}_{106}\text{H}_{76}\text{Au}_4\text{Cl}_4\text{Cu}_2\text{F}_{12}\text{O}_2\text{P}_6$ (**2**): $M = 2852.23$, monoclinic, space group $P2(1)/c$, $a = 14.0349(10)\text{ \AA}$, $b = 18.0306(14)\text{ \AA}$, $c = 19.9673(15)\text{ \AA}$, $\alpha = 90^\circ$, $\beta = 107.5050(10)^\circ$, $\gamma = 90^\circ$, $V = 4818.9(6)\text{ \AA}^3$, $Z = 2$, $\mu = 6.785\text{ mm}^{-1}$, $R_{\text{int}} = 0.0942$. A total of 41 379 reflections were measured for the angle range $1.52 < 2\theta < 28.34^\circ$, and 11 259 independent reflections were used in the refinement. The final parameters were $wR2 = 0.1374$ and $R1 = 0.0657$ [$I > 2\sigma(I)$].
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- (9) A recent search in the Cambridge Data Base resulted in ca. 800 and ca. 50 hits for complexes with $\text{Au}\cdots\text{Au}$ and $\text{Au}\cdots\text{Ag}$ contacts, respectively, whereas only 16 complexes with $\text{Au(I)}\cdots\text{Cu(I)}$ contacts were found (see refs 6–8). Most of these are trimetallic clusters of the type $\text{Au}_n\text{Cu}_m\text{M}_l$ ($M = \text{Fe, Pt, Ru, or Re}$ and $n + m + l = 4\text{--}12$; see ref 8).

(4) ORTEP representations have been done using ORTEP-3 for Windows (Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565). Ellipsoids are drawn at 40% (Figure 1) or 30% (Figure 2) probability.

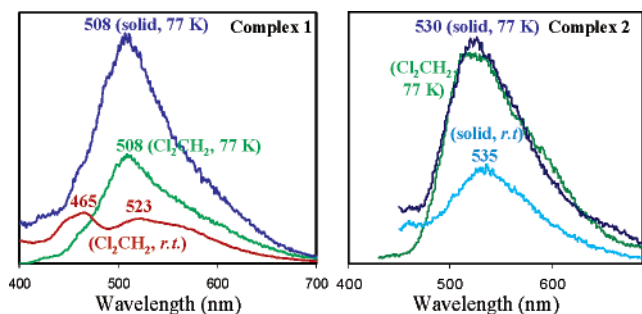


Figure 3. Emission spectra (intensity in arbitrary units) of **1** ($\lambda_{\text{exc}} = 320$ nm) and **2** ($\lambda_{\text{exc}} = 350\text{--}395$ nm).

176.9(4) $^\circ$ (P2–Au2–C1). The larger distortion in the former corresponds to the P–Au–C strand supporting the Au \cdots Cu interaction. The Au1–C9 \equiv C10 and Au2–C1 \equiv C2 angles are 162.6(11) $^\circ$ and 164.5(12) $^\circ$, respectively. The torsion angle between the two Au–alkynyl axes of each diphosphine is of ca. 41 $^\circ$.

The UV–vis spectrum of **1** in dichloromethane contains a broad, intense high-energy (HE) absorption between 230 and 300 nm with local maxima at 265 and 284 nm ($\epsilon = 70\,695$ and $72\,794$ dm 3 mol $^{-1}$ cm $^{-1}$, respectively). In addition, there is a low-energy (LE) shoulder at ca. 307 nm ($\epsilon = 20\,832$ dm 3 mol $^{-1}$ cm $^{-1}$) with a tail extending to ca. 330 nm. The absorption spectrum of **2** in dichloromethane also has a HE broad band at 250–320 nm and a LE tail reaching to longer wavelengths (ca. 350 nm) than that of **1**. The broad HE absorptions are likely to originate from intraligand (IL) $\pi \rightarrow \pi^*$ (C \equiv CAr) transitions of the alkynyls (i.e., the free alkynes also have intense bands at 250–300 nm). However, π^* orbitals associated with the aromatic groups of the phosphine can also be involved in such transitions because the electronic absorption spectra of both the free dbfphos and [Au $_2$ Cl $_2$ (μ -dbfphos)] also have broad bands in the same region.² The LE shoulders/tails may arise from $\sigma \rightarrow \pi^*$ absorptions involving the promotion of an electron from the σ (Au–P) bond orbital to an empty antibonding orbital of π origin (C \equiv CPh or phosphine), but they could also correspond to metal- or cluster-centered transitions. In addition, the lowest-energy absorption in **2** (330–350 nm) could also be associated with the Cu– π -(alkynyl) core (i.e., the π^* (C \equiv C) orbital decreases in energy upon coordination to Cu).

Luminescence was observed for both compounds in solution and in the solid state at 77 K. Room-temperature emission was measured for **1** in solution and for **2** in the solid state (Figure 3). The emission of **2** was recorded at various wavelengths, between 320 and 395 nm, and no significant changes were observed (see the Supporting Information). Compound **1** did not exhibit significant emission in the solid state at room temperature, whereas complex **2** showed room-temperature solution emission, but the spectra were not reproducible, presumably because of the formation of different species with time (as observed by NMR, see above). A full account of the solution behavior of this and analogous compounds will be included in a full-length paper.

The solid-state spectra of both compounds consist of broad bands, with that of **2** (ca. 530 nm) red-shifted relative to the emission of **1** (508 nm). The lifetime of **1** measured in the solid state at 77 K ($\lambda_{\text{exc}} = 325$ nm) is 41.6 μ s, and it is consistent with an excited state of triplet parentage. The emission of other phosphinylalkynylgold complexes has previously been assigned to σ (Au–P) \rightarrow π^* (C \equiv CPh) and/or σ (Au–P) \rightarrow π^* (aryl–phosphine).¹⁰ In the present case, a σ (Au–P) \rightarrow π^* (C \equiv CPh) origin, where the π^* orbital of the acetylide decreases in energy when coordinated to Cu(I), is a plausible assignment. However, some metal character in the excited states of both **1** and **2** should also be considered. The excitation spectrum of **1** shows a maximum at ca. 320 nm, whereas that of **2** appears featureless and consists of broad continuous excitations extending to ca. 420 nm. These features correspond with the LE shoulders observed in the absorption spectra of **1** and **2** and support Au- and cluster-centered origins for their respective emissions. Although relatively long metallophilic contacts are found in **1** (3.401 \AA) and **2** [e.g., Cu1 \cdots Au2, 3.2847(16) \AA], shortening of the metal \cdots metal distances in the excited state has been shown to be responsible for intense luminescence in multimetallic complexes.¹¹

The excitation and emission of **1** in dichloromethane at 77 K are similar to those of the solid, whereas at room temperature, an additional band is observed at 465 nm. This could be related to IL [$\pi \rightarrow \pi^*$ (C \equiv CPh and/or phosphine)] transitions. In glassy dichloromethane, the emission of **2** is similar to that of the solid when measured immediately upon dissolution, indicating that the same structure remains in these conditions.

In conclusion, whereas the coordination of Cu(I) to Au–alkyne moieties significantly perturbs the optical properties of the parent compound, the resulting product has a complex solid-state structure involving weak Cu \cdots Cu/Au interactions and π -alkyne coordination. Analogous processes described before¹ may also involve complicated structural changes.

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Supporting Information Available: Experimental section; absorption, excitation, and emission spectra; lifetime of the solid-state emission of **1**; and CIF files for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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