# ORGANOMETALLICS

### Luminescent Homo- and Heteropolynuclear Gold Complexes Stabilized by a Unique Acetylide Fragment

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Supporting Information

**ABSTRACT:** In this paper we describe the reactivity of the gold acetylide derivatives  $[Au(C \equiv CR)(PPh_3)]$  (R = Ph, 2-py). Reactions of these complexes with fragments of the type  $[M(PPh_3)_2]^+$  (M = Au, Ag, Cu) afford a series of novel discrete molecules stabilized not only by interactions with the triple bond but also by the formation of strong metal–gold interactions. The crystal structures of the gold–gold and gold–silver species confirm their similar behavior, while X-ray diffraction establishes a different arrangement for the copper complex with pyridine acetylide as a consequence of the coordination of this metal center to the nitrogen atom of pyridine and to the carbons of the alkyne. The luminescent properties of the complexes were also studied.



#### INTRODUCTION

Part of the fascination of gold(I) chemistry is due to the frequent formation of intramolecular gold—gold interactions (aurophilicity)<sup>1</sup> and the tendency to adopt linear coordination.<sup>2</sup> For gold(I) alkynyl complexes, the combined linear geometries together with the stiffness of the alkynyl groups make these derivatives suitable as building blocks for polymers<sup>3</sup> or can provide materials that show unusual nonlinear optical or photoemission properties involved in the design of sensors or devices.<sup>4</sup> Thus, the photophysical properties of gold have been profusely studied in the past few years because of their versatility and the development of related technological applications.<sup>5</sup>

The reactivity of alkynes toward transition metals has been the subject of many studies, because of the versatility in the bonding properties of the acetylide group.<sup>6</sup> In the case of gold, the most studied reactivity has related to bis(acetylide) gold substrates or dimeric species formed by gold acetylide fragments and diphosphine ligands. The great majority of these compounds are polymeric species in which gold is  $\pi$ -coordinated at least through two alkyne fragments, providing very symmetrical structures that show limited solubility in organic solvents.<sup>7</sup> Mononuclear systems are less common, and examples of discrete molecules are scarce.<sup>8</sup> There is also considerable interest in the isolation of coinage metal acetylide complexes consisting of discrete molecules, because they are key compounds in many transformations involving alkynes: cycloadditions,

alkyne coupling processes, heteroatom—hydrogen bond additions, hydrogenations,  $C_{sp}$ —H bond functionalizations, etc.<sup>9</sup> Furthermore, gold is an excellent catalyst: for example, in the hydrochlorination of acetylene to give vinyl chloride, a very important industrial process. This type of complex could therefore be suitable for the study of alkyne—metal bonds and provide relevant information about reaction mechanisms.

Moreover, one of the main goals in modern chemistry is the understanding of the relation between the properties of matter and the specific structure, and new potent instrumental methods are a useful tool for this. However, it was not easy to find reports where synthesis, reactivity, crystal structures, and luminescent properties had been related in a thorough study.

In order to study the reactivity of neutral gold acetylide derivatives, we tested the reactions of the compounds [Au(C=CR)-(PPh<sub>3</sub>)] (R = Ph, 2-py) with the cationic species of group 11 metals [M(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. The substrates thus obtained showed not only novel structural properties but also interesting luminescent behavior. Whereas the gold and silver structures are very similar,

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#### Scheme 1<sup>*a*</sup>



<sup>a</sup> Legend: (i) [Au(acac)(PPh<sub>3</sub>)]; (ii) [Au(PPh<sub>3</sub>)<sub>2</sub>]OTf; (iii) [Ag(PPh<sub>3</sub>)<sub>2</sub>]-OTf; (iv) [Cu(O<sub>2</sub>NO)(PPh<sub>3</sub>)<sub>2</sub>].

copper showed notable differences as a consequence of the participation of the pyridyl group in the coordination sphere of the metal.

Here we report new examples of homo- and heterometallic gold acetylide compounds where the  $\pi$ -bonded metal is stabilized by a unique metal—alkyne interaction and strong metallophilic interactions. Furthermore, we have been able to determine their crystal structures by X-ray diffraction in order to understand better their luminescent behavior.

#### RESULTS

The neutral derivative  $[Au(C \equiv CPh)(PPh_3)]$  (1) was prepared from phenylacetylene and  $[Au(acac)PPh_3]$  in equimolar amounts (Scheme 1), making use of the excellent properties as deprotonating/aurating agent of the latter,<sup>10</sup> rather than the other preparative methods previously reported.<sup>11</sup>

In order to study the reactivity of this unsaturated bond toward cationic species of group 11 metals, we decided to test the reactions of 1 with the species  $[M(PPh_3)_2]X$  (M = Au (2), Ag (3), Cu (4); X = OTf (trifluoromethylsulfonate; 2, 3), NO<sub>3</sub> (4)), which lead to the formation of the respective dinuclear derivatives  $[AuM(C \equiv CPh)(PPh_3)_3]X$  (Scheme 1). Complexes 2–4 are obtained as stable white solids, soluble in most common solvents but insoluble in diethyl ether and hexane. Their analytical and spectroscopic data are in accordance with the proposed stoichiometries.

Their IR spectra show bands assignable to triflate (2, 3) or nitrate (4) at  $\nu$  1264 (vs, br) and 1147 cm<sup>-1</sup> (m, br) (2) and at 1264 (vs, br) and 1146 cm<sup>-1</sup> (m, br) (3) or at 1071 (w), 998 (m), and 691 cm<sup>-1</sup> (vs) (4). Additionally, it is noteworthy that the absorption arising from the C=C group  $\sigma$ -bonded to gold at  $\nu$  2113 cm<sup>-1</sup> (w) in the starting material (1) does not appear in these three derivatives. That seems to indicate that the triple bond has been modified by the interaction with the newly incorporated second metal center.

The  ${}^{31}P{}^{1}H$  NMR spectra of the complexes show broad signals at room temperature. We therefore decided to register the NMR measurements at low temperature. Thus, signals were split

Scheme 2<sup>*a*</sup>



<sup>*a*</sup> Legend: (i) [Au(acac)(PPh<sub>3</sub>)]; (ii) [Au(PPh<sub>3</sub>)<sub>2</sub>]OTf; (iii) [Ag(PPh<sub>3</sub>)<sub>2</sub>]-OTf; (iv) [Cu(O<sub>2</sub>NO)(PPh<sub>3</sub>)<sub>2</sub>].

into two, arising from the two types of phosphorus atoms that are assigned to PPh<sub>3</sub> bonded to the gold center  $\sigma$ -coordinated to the alkyne (PPh<sub>3</sub>AuC $\equiv$ C) at  $\delta$  41.0 (2), 39.9 (3), and 42.0 ppm (4) and another broad signal arising from the fragments  $M(PPh_3)_2$ . The latter appear as singlets for complexes **2** and **4** ( $\delta$  43.4 and -2.3 ppm, respectively) but in the case of the gold-silver derivative the signal is split into two doublets because of the coupling of the phosphorus with the magnetically active <sup>107</sup>Ag and <sup>109</sup>Ag isotopes of the silver center ( $\delta$  8.8 ppm (3)). The <sup>19</sup>F NMR spectra of 2 and 3 show the resonance from the fluorine atoms of the triflate anion ( $\delta$  -78.0 (2), -77.9 ppm (3)). Their <sup>1</sup>H NMR spectra only show resonances attributed to aromatic protons from the triphenylphosphine ligands or from the aryl moiety of the acetylide group. None of the molecular peaks are detected in the mass spectra; however, several peaks corresponding to various fragments are observed (see the Experimental Section). Most representative peaks are those arising from the loss of a PPh<sub>3</sub> ligand  $[AuM(C \equiv CPh)(PPh_3)_2]^+$  at m/z 1019 (17%, **2**), 931 (8%, **3**), and 885 (10%, **4**). Crystals of complexes **2** and 3 suitable for X-ray diffraction analyses were grown by slow diffusion of hexane into a dichloromethane solution of the complex (see Crystal Structure Analyses).

With these examples we can conclude that gold, silver, and copper present a similar behavior with the alkyne triple bond.

In order to study the effect of the presence of other groups with donor properties in the same gold fragment, we decided to study similar reactions toward a pyridine derivative. Thus, by a similar methodology used for the compound 1, we prepared  $[Au(C \equiv Cpy)PPh_3]$  (5) by reaction of 2-pyridylacetylene and [Au(acac)PPh<sub>3</sub>] in dichloromethane. The reaction of this product with [Au(PPh<sub>3</sub>)<sub>2</sub>]OTf or [Ag(PPh<sub>3</sub>)<sub>2</sub>]OTf leads to the formation of  $[AuM(C \equiv Cpy)(PPh_3)_3]OTf$  (M = Au (6), Ag (7)) (see Scheme 2). These compounds are obtained as air- and moisture-stable white solids at room temperature and they are soluble in chlorinated solvents but insoluble in hexane. Their IR spectra show the characteristic bands of the trifluoromethylsulfonate anion. Again the alkyne absorption does not appear in the IR spectra of the new compounds, due to the participation of this electron density in the bonds to the second metallic center. Their <sup>31</sup>P{<sup>1</sup>H} NMR spectra show two resonances corresponding to the two different types of PPh<sub>3</sub> groups present in the molecules.

In order to increase the resolution of the spectra, the temperature of measurement was lowered to 223 K. While for the homonuclear derivative two signals in an approximate ratio 2:1 appear at 44.4  $(Au(PPh_3)_2)$  and 41.5 ppm (Au-P terminal), the spectrum of the mixed gold-silver derivative shows a broad signal related to the phosphorus atom coordinated to gold (40.0 ppm) and two doublets at higher field as a consequence of the Ag-P coupling (8.8 ppm). Their <sup>19</sup>F NMR spectra show the presence of triflate, and only phenyl or pyridyl protons are observed in the <sup>1</sup>H NMR spectra of 6 and 7. In the mass spectrum (MALDI) of 6 the molecular peak is detected at m/z1282 (2%). For the silver compound, several peaks corresponding to various fragments are observed (see the Experimental Section). Layering a chloroform solution of complex 7 with hexane afforded crystals of this derivative which were suitable for X-ray diffraction studies (see Crystal Structure Analyses).

The tendency of copper to coordinate to nitrogen donor ligands is well-known.<sup>12</sup> Thus, in order to compare the relative reactivities of gold, silver, and copper we tested the reaction between compound 5 and  $[Cu(O_2NO)(PPh_3)_2]$  in a 1:1 molar ratio. In this case the final color of the solution reaction is yellow, in contrast to the gold-gold and gold-silver solutions, which are colorless. Thus, compound 8, which matches the formula  $[AuCu(C \equiv Cpy)(PPh_3)_2](NO_3)$ , is obtained as a yellow solid, stable to air and moisture and soluble in chlorinated solvents and acetone, but insoluble in hexane. In this case a major attraction between copper and nitrogen donor ligands causes the interchange of PPh<sub>3</sub> by a Cu-pyridine interaction (Scheme 2). Unlike the case for the IR spectra registered for the Au-Au and Au-Ag compounds, an analysis of the IR spectra of the gold-copper compound shows the stretching band  $C \equiv C$  at 2112 cm<sup>-1</sup>, revealing a different behavior of copper from the heavier metals in the group. The broad signals found in the  ${}^{31}P{}^{1}H{}$  NMR spectrum of 8 in CDCl<sub>3</sub> at 223 K are assigned to the phosphorus atom coordinated to gold at  $\delta$  40.9 ppm and at high field to the fragment Cu–PPh<sub>3</sub> ( $\delta$  –0.4 ppm). Its <sup>1</sup>H NMR spectrum only displays the resonances arising from phenyl or pyridine groups. The molecular cation was not detected in its mass spectrum; however, several revealing fragments were found, such as the peaks due to  $[AuCu(C \equiv Cpy)(PPh_3)_2]^+$   $(m/z \ 886,$ 25%) or  $[Au_2Cu(C \equiv Cpy)_2(PPh_3)_2]^+$  (*m*/*z* 1185, 5%).

Layering a chloroform solution of complex 8 with hexane afforded crystals of the copper compound that were suitable for X-ray diffraction studies (see Crystal Structure Analyses).

Crystal Structure Analyses. The crystal structures of the mixed gold-gold and gold-silver derivatives 2, 3, and 7 have been determined by X-ray diffraction (Figures 1-3). Selected bond lengths and angles are collected in Table 2. The molecules of these complexes have a similar array of atoms, as can be seen in Figures 1–3 with the metal of one  $[Au(PPh_3)_2]^+$  (2) or [Ag- $(PPh_3)_2$ <sup>+</sup> fragment (3, 7) bonded to both the acetylene gold atom and one carbon  $(C_{\alpha})$  atom of the acetylene group (distances to the  $C_{\beta}$  atom are appreciably longer). The short intramolecular goldgold (2.9165(5) Å in 2) and gold-silver distances (2.8600(2) Å in 3 and 2.9643(2) Å in 7) indicate normal  $d^{10}-d^{10}$  interactions between the metals. Complexes 2 and 7 are isostructural, with closely similar unit cells in the orthorhombic space group Pna21 (experimental data shown in Table 1); complex 3 crystallizes in the triclinic system, space group  $P\overline{1}$ . The angles  $P-Au-C_{\alpha}$  (from  $176.69(8)^{\circ}$  to  $178.3(2)^{\circ}$ ) are only slightly distorted from linearity by the coordination of the  $[M(PPh_3)_2]^+$  fragment to the gold(I) acetylene complex.



Figure 1. Structure of the cation of complex 2. Hydrogen atoms have been omitted for clarity.



Figure 2. Structure of the cation of complex 3. Hydrogen atoms have been omitted for clarity.

The C=C bond distances found in the complexes (range from 1.186(8) Å in 2 to 1.217(2) Å in 7) are normal for a carbon– carbon triple bond and show no significant differences from C=C bond distances present in the corresponding starting materials  $[Au(C=CPh)(PPh_3)]^{13}$  (1) (1.16(2), 1.18(2) Å; two molecules connected through a weak Au···Au interaction) or  $[Au(C=Cpy)-(PPh_3)]^{14}$  (5) (1.21(1) Å × 2; two independent molecules in each asymmetric unit without an intermolecular metal–metal bond). In addition, the Au–C<sub> $\alpha$ </sub> bond distances of the phenylacetylene gold(I) group (ranging from 1.997(3) Å in 7 to 2.032(6) Å in 2) are similar to those exhibited by the corresponding starting materials  $[Au(C=CPh)(PPh_3)]$  (1.97(2), 2.02(2) Å) and  $[Au(C=Cpy)(PPh_3)]$  (1.95(1), 1.97(1) Å).

The acetylene ligand in each compound can be seen as an asymmetric bridge between the two metals, with one of the  $M-C_{\alpha}$  distances being much shorter than the other (the asymmetric  $\mu$ - $\eta^1:\eta^1$  mode is probably forced by the metallophilic interaction). The longer distances, which correspond to the metal of the  $[M(PPh_3)_2]^+$  fragment, are 2.602(5) Å in 2 (Au- $C_{\alpha}$  bond), 2.463(3) Å in 3, and

2.482(3) Å in 7 (Ag– $C_{\alpha}$  bond); the last two compare well with the Ag– $C_{\alpha}$  distances observed in the complex  $[Ag\{(AuPTo_3)_2\{\mu-Ar(C\equiv C)_2\}\}_2]ClO_4 \cdot 2CHCl_3$  (To =  $C_6H_4$ Me-4, Ar =  $C_6Me_4$ )<sup>15</sup> in which one silver atom is bonded to four AuC=C fragments in a similar asymmetric mode. Furthermore, the distances  $M \cdot \cdot \cdot C_{\beta}$  are notably longer and range from 2.817 Å in 7 to 3.133 Å in **2**.

The crystal structure of complex 8 has also been established by X-ray diffraction, and the molecule is shown in Figure 4. Selected bond lengths and angles are collected in Table 2. The compound is a dimer with two  $Ph_3P-Au-C \equiv Cpy$  units bridging two



Figure 3. Structure of the cation of complex 7. Hydrogen atoms have been omitted for clarity.

copper atoms. Each copper atom is bonded symmetrically to the acetylene group in a  $\eta^2$  fashion, with Cu–C distances ranging from 2.027(7) to 2.108(8) Å. These are similar to those found in the complex  $[Cu_4(\mu - \eta^1: \eta^2 - C \equiv C)(\mu - dppm)_4](BF_4)_2$  (2.12(1) and 2.13(1) Å).<sup>16</sup> The coordination of the metal to the acetylene moiety produces only a minimal lengthening of the carboncarbon bond distance, which goes from 1.21(1) Å in the starting material<sup>14</sup> to 1.222(11) or 1.231(11) Å in the gold-copper derivative. In contrast to the other complexes described in this paper, there are no short Au···Cu contacts: the distances are 3.480 and 3.540 Å, which are too long to involve any bonding interaction. The nature of the copper bond to the gold acetylene compounds is different from that shown by the silver and gold atoms. The copper centers are four-coordinated to one phosphine ligand, to both carbon atoms of the acetylene, and to the nitrogen atom of the pyridine group; the geometry is far from an ideal tetrahedron, with dihedral angles between the planes N(2)Cu(1)P(3) and C(1)Cu(1)C(2) of 17.2° and N(1)Cu-(2)P(4) and C(41)Cu(2)C(42) of  $0.2^{\circ}$ , and thus can be better described as trigonal, with the midpoint of the carbon-carbon triple bond as one ligand. Also, the copper atoms lie only 0.195 and 0.002 Å out of the plane formed by their four donor atoms. The gold centers are linearly coordinated, and the bond lengths and angles are normal.

**Optical Properties.** The absorption data of complexes 2-8 are summarized in Table 3.

The electronic absorption spectra of 2-4 in dichloromethane at 298 K show very intense bands at 233–240 nm ( $\varepsilon = 13560$ , 17 109, 13 804 mol<sup>-1</sup> L cm<sup>-1</sup>, respectively) and a shoulder at 270 nm with tails extending to ca. 320 nm (see Figure 5). The assignation of the absorptions is made by comparison with those

	2	$3 \cdot 2 CH_2 Cl_2$	7	8.5CHCl <sub>3</sub>
formula	C62H50Au2F2O2P3S	C65H54AgAuF3O3P3SCl4	C62H40AgAuF2NO2P2S	Co1H72Au2Cl15Cu2N4O6P4
Mr	1430.93	1511.69	1342.83	2495.18
habit/color	prism/colorless	prism/colorless	Tablet/colorless	needle/colorless
cryst size (mm)	$0.42 \times 0.23 \times 0.11$	$0.25 \times 0.12 \times 0.12$	0.35  imes 0.35  imes 0.10	0.20 imes 0.07 imes 0.06
cryst syst	orthorhombic	triclinic	orthorhombic	triclinic
space group	$Pna2_1$	$P\overline{1}$	$Pna2_1$	$P\overline{1}$
cell constants				
a (Å)	20.097(4)	11.3194(3)	19.8613(3)	14.822(3)
b (Å)	17.631(4)	14.9455(3)	17.5402(3)	15.542(3)
c (Å)	15.462(3)	18.3582(5)	15.5700(3)	22.752(5)
$\alpha$ (deg)		94.351(1)		88.03(3)
$\beta$ (deg)		94.243(1)		86.85(3)
$\gamma$ (deg)		93.381(1)		66.90(3)
Ζ	4	2	4	2
$D_{\rm exptl}  ({ m Mg}  { m m}^{-3})$	1.735	1.629	1.644	1.722
$\mu (\mathrm{mm}^{-1})$	5.532	3.035	3.247	4.011
F(000)	2792	1500	2664	2452
T (°C)	-173	-173	-173	-173
$2\theta_{\max}$ (deg)	51	55	59	51
no. of rflns				
measd	77 283	54 081	236 891	71 486
indep	10 149	14 051	15 010	17 848
transmissions	0.2047, 0.5813	0.5783-0.5136	0.59915-1.00000	0.5009-0.7948
R <sub>int</sub>	0.0268	0.0480	0.0562	0.062
no. of params	677	730	677	1154
no. of restraints	19	0	651	211
$R_{\rm w}(F^2, {\rm all \ rflns})$	0.0875	0.0580	0.0577	0.157
$R(I > 2\sigma(I))$	0.0318	0.0261	0.0262	0.060
S	1.036	1.035	0.995	1.025
Flack param	0.224(7)		0.585(3)	
max $\Delta  ho$ (e Å <sup>-3</sup> )	1.893	1.728	3.139	4.65

Table 1. X-ray Data for Complexes 2, 3, 7, and 8

## Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2, 3, 7, and 8

Complex 2							
$\begin{array}{l} Au(1)-C(1) \\ Au(1)-P(1) \\ Au(1)-Au(2) \\ Au(2)-P(2) \end{array}$	2.032(6) 2.2838(17) 2.9165(5) 2.281(2)	Au $(2)-P(3)$ Au $(2)-C(1)$ C $(1)-C(2)$	2.303(2) 2.602(5) 1.186(8)				
$\begin{array}{l} C(1)-Au(1)-P(1)\\ C(1)-Au(1)-Au(2)\\ P(1)-Au(1)-Au(2)\\ P(2)-Au(2)-P(3)\\ P(2)-Au(2)-C(1) \end{array}$	178.2(2) 60.33(15) 121.34(5) 147.92(7) 111.0(2)	$\begin{array}{l} P(3)-Au(2)-C(1)\\ P(2)-Au(2)-Au(1)\\ P(3)-Au(2)-Au(1)\\ C(1)-Au(2)-Au(1) \end{array}$	100.3(2) 105.93(6) 101.57(6) 42.75(13)				
	Com	plex 3					
Au-C(8) Au-P(1) Au-Ag Ag-P(3)	2.019(3) 2.2780(7) 2.8600(2) 2.4344(7)	Ag-P(2) Ag-C(8) C(7)-C(8)	2.4408(7) 2.463(3) 1.203(4)				
C(8)-Au-P(1) P(3)-Ag-P(2) P(3)-Ag-C(8) P(2)-Ag-C(8)	176.69(8) 131.67(2) 114.10(6) 111.43(7)	P(3)-Ag-Au P(2)-Ag-Au C(8)-Ag-Au	114.194(17) 109.459(17) 43.78(6)				
	Com	plex 7					
Au-C(1) Au-P(1) Au-Ag Ag-P(2)	1.997(3) 2.2780(7) 2.9643(2) 2.4075(13)	Ag-P(3) Ag-C(1) Ag-C(2) C(1)-C(2)	2.4171(13) 2.482(3) 2.817(2) 1.217(4)				
$\begin{array}{c} C(1)-Au-P(1)\\ C(1)-Au-Ag\\ P(1)-Au-Ag\\ P(2)-Ag-P(3)\\ P(2)-Ag-C(1)\\ P(3)-Ag-C(1)\\ P(2)-Ag-C(2) \end{array}$	178.3(2) 56.05(8) 123.87(2) 140.19(3) 113.66(17) 106.14(18) 110.60(13)	$\begin{array}{l} P(3)-Ag-C(2)\\ C(1)-Ag-C(2)\\ P(2)-Ag-Au\\ P(3)-Ag-Au\\ C(1)-Ag-Au\\ C(2)-Ag-Au\\ \end{array}$	105.48(13) 25.57(8) 105.78(3) 103.10(3) 41.86(6) 67.39(5)				
	Com	plex 8					
$\begin{array}{l} Au(1)-C(1)\\ Au(1)-P(1)\\ C(1)-C(2)\\ C(1)-Cu(1)\\ C(2)-Cu(1)\\ N(1)-Cu(2)\\ C(41)-C(42)\\ C(41)-Au(2) \end{array}$	2.002(8) 2.272(2) 1.222(11) 2.108(8) 2.068(8) 1.984(7) 1.231(11) 2.011(8)	$\begin{array}{c} C(41)-Cu(2)\\ C(42)-Cu(2)\\ C(43)-N(2)\\ N(2)-Cu(1)\\ Au(2)-P(2)\\ Cu(1)-P(3)\\ Cu(2)-P(4) \end{array}$	2.065(8) 2.027(7) 1.361(10) 2.027(6) 2.281(2) 2.251(2) 2.255(2)				
$\begin{array}{c} C(1)-Au(1)-P(1)\\ Au(1)-C(1)-Cu(1)\\ Au(2)-C(41)-Cu(2)\\ C(41)-Au(2)-P(2)\\ N(2)-Cu(1)-C(2)\\ N(2)-Cu(1)-C(1)\\ C(2)-Cu(1)-C(1)\\ N(2)-Cu(1)-P(3) \end{array}$	$\begin{array}{c} 172.6(2) \\ 115.7(4) \\ 2) 121.6(4) \\ 175.6(2) \\ 104.5(3) \\ 136.7(3) \\ 34.0(3) \\ 107.1(2) \end{array}$	$\begin{array}{c} C(2)-Cu(1)-P(3)\\ C(1)-Cu(1)-P(3)\\ N(1)-Cu(2)-C(42)\\ N(1)-Cu(2)-C(41)\\ C(42)-Cu(2)-C(41)\\ N(1)-Cu(2)-P(4)\\ C(42)-Cu(2)-P(4)\\ C(41)-Cu(2)-P(4)\\ \end{array}$	146.5(2) 112.5(2) 104.4(3) 139.4(3) 35.0(3) 106.29(19) 149.3(2) 114.3(2)				

of the precursor complex [Au( $C \equiv CPh$ )(PPh<sub>3</sub>)]. This complex shows absorption bands in the range 268–276 nm characteristic of triphenylphosphine, probably in the phenyl groups of the phosphine ligands (IL  $\pi\pi^*$  transitions), since similar absorption bands are also observed in [AuClPPh<sub>3</sub>].<sup>17</sup> In addition, the bands assigned to  $\pi \rightarrow \pi^*(C \equiv C)$  are reported at 317–335 nm, as in the precursor complex [Au( $C \equiv CPh$ )(PPh<sub>3</sub>)].<sup>18</sup> Therefore, the broad band that appears in the range 270–320 nm in the complexes would involve both types of transitions.

In the case of the precursor complex  $[Au(C \equiv CPy)(PPh_3)]$  (5) a broad and poorly structured band with two maxima at



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Figure 4. Structure of the cation of complex 8. Hydrogen atoms have been omitted for clarity.

Table 3. UV–Visible	e Data for Complexe	s 2-8 in Dichlor-
omethane (5 $ imes$ 10 $^{-5}$	M)	

compd	$\lambda_{\max} (nm) \left[ \epsilon (dm^3 mol^{-1} cm^{-1}) \right]$
2	233 [13 560], 270 [6107], 280 [4993]
3	240 [17 109], 270 [16 300]
4	230 [13 804], 270 [9620]
5	220 [12 595], 275 [24 185]
6	230 [13 867], 290 [3604]
7	230 [15 004]
8	230 [20 234], 350 [1217]



Figure 5. Electronic absorption spectrum of 4 in dichloromethane solution at 298 K.

220 nm ( $\varepsilon = 12595 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) and 275 nm ( $\varepsilon = 24185 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) with a tail extending to ca. 325 nm appears. The position of the first maximum can be assigned to a transition located in the pyridine ring, probably between  $\pi\pi^*$  orbitals. This assignation is in accordance with the data obtained from gold(I) pyridine complexes, which show absorptions at similar energies.<sup>19</sup> As before, the maximum at lower energy could contain the

Tab	le 4.	Photop	hysical	Data	for	Comp	lexes	2 - 8	in	Solution
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	soln at room temp <sup>a</sup>		glass soln <sup>b</sup>		
compd	excitation $\lambda_{\rm max}/{\rm nm}$	emission $\lambda_{\rm max}/{ m nm}~( au/\mu s)$	excitation $\lambda_{\rm max}/{\rm nm}$	emission $\lambda_{ m max}/ m nm$	
2	305	419 (11)	285	485	
3	315	430, 455 <sup>c</sup> (9)	305	465	
4	295, 330, 375	408, 432, 458 <sup>c</sup> (10)	330	445, 485 <sup>c</sup>	
5	308, 360	450 (10)	285	460	
6	307, 370	460 (10)	300	470	
7	313, 360	460 (10)	300	470	
8	355, 372, 392	406, 432, 459 <sup>c</sup> (9)	288, 355	516	
<sup><i>a</i></sup> In diclorometha	ne at 298 K. <sup><i>b</i></sup> In CH <sub>2</sub> Cl <sub>2</sub> /MeOl	H/EtOH (1/2/8). <sup>c</sup> Vibronic-structured	l emission band.		

Table 5. Photophysical	Data for	Complexes	2 - 8	in the	Solid	State
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	solid at re	oom temp (298 K)	solid at low temp (77 K)			
compd	excitation $\lambda_{max}/nm$	emission $\lambda_{ m max}/ m nm$ $( au/\mu s)$	excitation $\lambda_{\rm max}/{\rm nm}$	emission $\lambda_{\rm max}/{\rm nm}$		
2	280, 360	490 (26)	280, 350	465		
3	345	482 (41)	345	427, 467, 510 <sup><i>a</i></sup>		
4	321, 366	$475^{a}$ (13)	323	426, 448, 457, 469, 481, 493, 506 <sup>a</sup>		
5	313	420, 447, 460 <sup><i>a</i></sup> (5)	274	418, 437, 449, 461, 483, 496, 510 <sup>a</sup>		
6	280, 350	488 (20)	275, 360	475		
7	275, 320	480 (32)	275	470		
8	360	542 (13)	340	600		
<sup><i>a</i></sup> Broad and par	tially structured emission ba	nd.				

transitions characteristic of triphenylphosphine and the alkynyl ligands. In the case of the polynuclear complexes **6**–**8**, all of them show almost identical spectra with maxima at 230 nm and a shoulder at 290 nm that is more evident in the case of complex **6**. Very interestingly, in all the described polynuclear complexes, the expected red shift of the absorptions of the alkynyl ligands, as a consequence of the lowering of the  $\pi^*$  orbital by the  $\pi$  coordination of this ligand to the metal centers, is not apparent. This result perhaps is indicative of a weaker coordination of these metals to the alkynyl unit in solution, or even their complete dissociation, although it is also possible that the expected shift is masked by the broadness of the absorptions from the triphenyl-phosphine ligands.

The emission data of 2-8 are summarized in Tables 4 and 5. These Au–Au-, Au–Ag-, or Au–Cu-containing complexes show intense room- and low-temperature luminescence in both the solid state and solution with lifetimes in the microsecond range (see the spectra of 3 in Figure 6, as an example). These values together with the relatively large Stokes shifts are suggestive of triplet excited-state characters.

In the solid-state spectra of complexes 2-4 at room temperature a slight shift to lower energies in the sequence Cu > Ag > Au is observed. Also, an incipient vibrational structure begins to appear. This is evident in the spectra at 77 K, especially in the case of the gold—copper complex (see Figure 7). At room temperature this complex shows a broad band in the solid-state spectra centered at approximately 475 nm. The differences in energies between the copper derivative and the gold and silver dinuclear complexes can be related to the participation of the heterometal centers in the excited states responsible for the emissions. In contrast, at low temperature, the spacing between maxima in



Figure 6. Normalized excitation and emission spectra of 3 in dichloromethane solution at 298 K.

the solution spectrum of the gold–copper derivative of ca. 1400 cm<sup>-1</sup> is in line with the C=C stretching frequencies of the phenyl rings, indicative of the involvement of the Ph rings in the excited-state origin. In the rest of the complexes the resolution of the spectra does not permit confirmation of this fact.

As has been reported, heterometallic complexes containing platinum and silver or copper with phenylacetylide moieties show emissions substantially dependent on the ease of MMLCT  $(d_{\sigma}^*Pt_2 \rightarrow p_{\sigma}(Pt_2)\pi^*(C \equiv CR))$  transitions. Thus, the presence of the heterometals produces a reduction of electron density at platinum as a result of an increase of the  $\pi$ -accepting ability of the



Figure 7. Solid-state emission spectrum of 4 at 77 K.

PhC≡C groups upon  $\pi$  donation to Ag or Cu, resulting in a narrowing of the HOMO–LUMO gap and, hence, a lower emission energy.<sup>20</sup> In addition, in related [R<sub>3</sub>PAuC≡CC-(CH<sub>3</sub>)=CH<sub>2</sub>] complexes, the  $\pi$  coordination of Cu<sup>+</sup> or Ag<sup>+</sup> ions produces a lowering of the  $\pi^*(C≡CR)$  orbital, giving rise to lower energy emissions. Between them, the slightly higher emission of the silver as compared to that of the copper derivative has been ascribed to the weaker Lewis acidity of Ag(I).<sup>21</sup>

Similarly, in the case of  $[Au(C \equiv CPh)(PPh_3)]$  the emission origin is derived from an admixture of metal perturbed  ${}^3[\pi \rightarrow \pi^*(C \equiv C)]$  IL and  ${}^3[\sigma(Au-P) \rightarrow \pi^*(C \equiv C)]$  MLCT states.<sup>17,22</sup> Therefore, the coordination of the heterometals would produce effects in the emission spectra similar to those described if the excited states responsible for the emissions were formed in those transitions. We propose that in complexes 2–4 the transitions that are the origin of the luminescence are an admixture of  ${}^3\text{IL}(\pi\pi^*)$  states, mostly located in the phenyl rings of the triphenylphosphine ligands, slightly perturbed by the metals, although a contribution of the  $\pi^*(C \equiv C)$  orbitals cannot be excluded.

Similarly, in the case of complexes 5-8 with the ligand  $-C \equiv$ CPy, they all display luminescence in the solid state at room or at low temperature and in fluid solution (see Tables 4 and 5), but with some differences with respect to those previously described. First, the energies for the precursor gold complex [Au(C=CPy)]-(PPh<sub>3</sub>)] (5) and the polynuclear gold and silver derivatives in solution are virtually the same, indicating similar excited states responsible for the emissions, and therefore, we can propose that the donation of electron density from the acetylide moieties to the metals through their coordination does not affect the orbitals that contribute to the excited states. In the case of the tetranuclear gold-copper complex a vibronic structure is observed in the fluid solution at room temperature with bands at 406, 432, and 459 nm, similar to those in the gold-copper complex 4 noted previously. This coincidence rules out the possibility that the excited states in solution are influenced by the substituent of the acetylide (pyridyl or phenyl) and, hence, by their donor capabilities, by the number of metal-metal interactions, or by the number of phosphines bonded to the copper centers; in contrast, this coincidence seems to confirm the involvement of the Ph groups in the excited-state origin.

In the solid-state spectra, the emissions of the dinuclear gold and silver complexes are also similar to those in the previous phenylacetylide derivatives **2** and **3**, and therefore, we propose a



Figure 8. Normalized solid-state emission spectra of 4 and 8 at 298 K.

similar assignment. Interestingly, the gold–copper complex 8 shows a band shifted to red (542 nm) with respect to that found in the dinuclear complex 4 (475 nm) (see Figure 8). Previous studies of heteropolynuclear gold–copper complexes carried out by our group established that, on irradiation with UV light, the copper center together with the electron-rich gold atom can act as a source of electron density and the aromatic nitrogen donor ligand as a receptor of it, forming an MMLCT (metal–metal to ligand charge transfer) excited state.<sup>23</sup> In this case, the emission energies in the solid state or in glassy solution at low temperature differ considerably in energy from those of the other complexes in the same media, suggesting that the excited states responsible for the emissions are different. Therefore, for this low-energy emission we propose that the excited state arises from an admixture of IL and M(Cu)L(pyridine) CT transitions.

#### CONCLUSIONS

The incorporation of coinage metal fragments into neutral gold acetylide starting materials is favored by the high  $\pi$ -electron density of the alkyne and the formation of strong metal—gold interactions that stabilize the structures of discrete cationic bimetallic complexes.

This coordination mode is confirmed by the crystallographic data, which reveal that the metal of the cationic moiety is situated at asymmetrically short distances to both carbons of the alkyne and to the gold atom from the starting acetylide substrate. This proximity is observed in both examples of gold—gold and gold—silver complexes. However, the crystal structure obtained for the complex of copper and pyridine acetylide reveals a very different disposition. This metal coordinates symmetrically to both carbon atoms of the alkyne group and also to the pyridine nitrogen. The lack of proximity of copper to the gold atom indicates that this interaction is not necessary for the stabilization of the structure.

The compounds described in this paper show intense roomand low-temperature luminescence. After the optical behavior is analyzed, the origin of the luminescence in most of the states studied is assigned to an  ${}^{3}\text{IL}(\pi\pi^{*})$  located in the phenyl rings of the phosphine ligand where the metal is weakly involved, although a contribution from the acetylene ligand cannot be excluded. In the case of the copper complexes, solution excited states do not seem to be influenced by the acetylene substituent or the structure of the compound, whereas in the solid state the assignment of the origin is clearly different, being proposed as an admixture of IL and MLCT for the dinuclear compound.

#### EXPERIMENTAL SECTION

Instrumentation. Solution <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded using a Bruker ARX 400 spectrometer and a Bruker Avance II 300 spectrometer. The chemical shifts ( $\delta$ , ppm) were referenced to residual solvent resonances and external 85% H<sub>3</sub>PO<sub>4</sub> in the <sup>1</sup>H and  $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$  spectra, respectively. Mass spectra were recorded both with a ESI-TOF MicrotofQ instrument in MeOH and with a MALDI-TOF Microflex instrument with a N2 laser (337 nm, 3.68 eV) ionization source, with DITRANOL matrix. Infrared spectra were recorded in the range 4000-250 cm<sup>-1</sup> on a Perkin-Elmer Spectrum 100 FTIR spectrometer. C, H, N, and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. UV/vis spectra were recorded with an Evolution 600 spectrophotometer (dichloromethane 5  $\times$  10<sup>-5</sup> M solutions). Steady-state photoluminescence spectra were recorded with a Jobin-Yvon Horiba Fluorolog FL-3 spectrometer using band pathways of 3 nm for both excitation and emission. Phosphorescence lifetimes were recorded with a Fluoromax phosphorimeter accessory containing a UV xenon flash tube at a flash rate between 0.05 and 25 Hz. The lifetime data were fit using the Jobin-Yvon software package<sup>24</sup> and the Origin 5.0 program.25

**Starting Materials.** The starting materials  $[Au(acac)(PPh_3)]$ ,<sup>26</sup>  $[M(PPh_3)_2]OTf (M = Au, Ag)$ ,<sup>27,28</sup> and  $[Cu(O_2NO)(PPh_3)_2]^{29}$  were prepared analogously to published procedures. All other reagents were commercially available.

**Solvent and Reagent Pretreatment.** Solvents were purchased from commercial sources; dichloromethane and THF were distilled prior to use. Reactions involving copper(I) starting materials were carried out under an atmosphere of purified argon. For reactions involving silver(I), the flasks were covered with aluminum foil to protect from light.

Synthesis of  $[Au(C \equiv CPh)(PPh_3)]$  (1). HC  $\equiv$  CPh (0.022 mL, 0.2 mmol) was added to a solution of  $[Au(acac)PPh_3]$  (0.112 g, 0.2 mmol) in dichloromethane (10 mL). The mixture was stirred for 2.5 h; then the volume was reduced to 2 mL and hexane was added to precipitate the product as a white powder (86 mg). Yield: 77%.

**Synthesis of** [Au<sub>2</sub>(C≡CPh)(PPh<sub>3</sub>)<sub>3</sub>]**OTf** (2). To a solution of [Au(C≡CPh)PPh<sub>3</sub>] (1; 112 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added [Au(PPh<sub>3</sub>)<sub>2</sub>]OTf (175 mg, 0.2 mmol). The mixture was stirred for 1.5 h and concentrated under vacuum to ca. 2 mL. The addition of Et<sub>2</sub>O caused the precipitation of the compound **2** as a white solid (214 mg). Yield: 75%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -50 °C):  $\delta$  43.4 (s, 2P, Au(PPh<sub>3</sub>)<sub>2</sub>), 41.0 (s, AuPPh<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  -78.0 (s, CF<sub>3</sub>SO<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  7.70–7.20 (m, 50 H, Ph). IR (solid):  $\nu$  1264 (vs, br), 1147 cm<sup>-1</sup> (m, br, CF<sub>3</sub>SO<sub>3</sub>). MS (MALDI<sup>+</sup>/ DIT): *m*/*z* (%) 721 (100) [Au(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>], 1019 (17) [*M*<sup>+</sup> – PPh<sub>3</sub>]. Anal. Calcd for C<sub>63</sub>H<sub>50</sub>Au<sub>2</sub>F<sub>3</sub>O<sub>3</sub>P<sub>3</sub>S: C, 52.88; H, 3.52; S, 2.24. Found: C, 52.95; H, 3.54; S, 2.74.

**Synthesis of [AuAg(C≡CPh)(PPh<sub>3</sub>)<sub>3</sub>]OTf (3).** To an acetone solution (20 mL) of [Au(C≡CPh)PPh<sub>3</sub>] (1; 112 mg, 0.2 mmol) was added [Ag(PPh<sub>3</sub>)<sub>2</sub>]OTf (156 mg, 0.2 mmol). After 1 h of stirring, the reaction mixture was concentrated under vacuum and Et<sub>2</sub>O was added to give a white precipitate (174 mg). Yield: 65%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  40.8 (m, AuPPh<sub>3</sub>), 10.9 (m, 2P, Ag(PPh<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -50 °C):  $\delta$  39.9 (s, AuPPh<sub>3</sub>), 8.8 (2d, *J*(<sup>107</sup>Ag,P) = 424 Hz, *J*(<sup>109</sup>Ag,P) = 482 Hz, 2P; Ag(PPh<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  −77.9 (s, 3F, CF<sub>3</sub>SO<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.57−7.09 (m, 50 H, Ph). IR (solid):  $\nu$  1264 (vs, br, CF<sub>3</sub>SO<sub>3</sub>), 1146 cm<sup>-1</sup> (m, br, CF<sub>3</sub>SO<sub>3</sub>). MS (MALDI<sup>+</sup>/DIT): *m/z* (%) 631 (8) [Ag(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>], 669 (7) [*M*<sup>+</sup> − 2PPh<sub>3</sub>], 931 (8) [*M*<sup>+</sup> − PPh<sub>3</sub>]. Anal. Calcd for C<sub>63</sub>H<sub>50</sub>AgAuF<sub>3</sub>O<sub>3</sub>P<sub>3</sub>S: C, 56.39; H, 3.76; S, 2.39. Found: C, 56.46; H, 3.88; S, 2.41.

Synthesis of [AuCu(C≡CPh)(PPh<sub>3</sub>)<sub>3</sub>]NO<sub>3</sub> (4). [Cu(O<sub>2</sub>NO)-(PPh<sub>3</sub>)<sub>2</sub>] (130 mg, 0.2 mmol) was added to a THF (20 mL) solution of [Au(C≡CPh)PPh<sub>3</sub>] (1; 112 mg, 0.2 mmol). The resulting solution was stirred under a nitrogen atmosphere for 1.5 h and concentrated under vacuum to ca. 2 mL. The white solid was obtained after Et<sub>2</sub>O addition (130 mg). Yield: 54%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  0.0 (m, 3P, PPh<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (HDA, -80 °C):  $\delta$  42.0 (s, AuPPh<sub>3</sub>), -2.3 (s, 2P, Cu(PPh<sub>3</sub>)<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  7.47−7.10 (m, 50 H, Ph). IR (solid):  $\nu$  1071 (w, NO<sub>3</sub>), 998 (m, NO<sub>3</sub>), 691 cm<sup>-1</sup> (vs, NO<sub>3</sub>). MS (ESI<sup>+</sup>): *m/z* (%) 587 (100) [Cu(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>], 885 (10) [*M*<sup>+</sup> − PPh<sub>3</sub>]. Anal. Calcd for C<sub>62</sub>H<sub>50</sub>AuCuNO<sub>3</sub>P<sub>3</sub>: C, 61.52; H, 4.16; N, 1.16. Found: C, 61.57; H, 4.41; N, 1.36.

Synthesis of  $[Au(C=Cpy)(PPh_3)]$  (5). A mixture of HC=CPy (0.022 mL, 0.2 mmol) and  $[Au(acac)PPh_3]$  (0.112 g, 0.2 mmol) in dichloromethane (10 mL) was stirred for 2.5 h. Then the volume of the solution was reduced to 2 mL and hexane was added to give 5 as a white precipitate (84 mg). Yield: 75%.

**Synthesis of**  $[Au_2(C=CPy)(PPh_3)_3]OTf$  (6). To a solution of [Au(C=Cpy)PPh\_3] (5; 112 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added [Au(PPh\_3)<sub>2</sub>]OTf (175 mg, 0.2 mmol). The mixture was stirred for 1.5 h at room temperature and concentrated to 2 mL. The addition of Et<sub>2</sub>O caused the precipitation of 6 as a white solid (166 mg). Yield: 58%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -50 °C):  $\delta$  44.4 (*s*, 2P, Au(PPh\_3)<sub>2</sub>), 41.5 (*s*, AuPPh\_3). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  -78.0 (*s*, CF<sub>3</sub>SO<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  -78.0 (*s*, CF<sub>3</sub>SO<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  8.43 (ddd, <sup>3</sup>J(H<sub>a</sub>,H<sub>b</sub>) = 4.9 Hz, <sup>4</sup>J(H<sub>a</sub>,H<sub>c</sub>) = 1.7 Hz, <sup>5</sup>J(H<sub>a</sub>,H<sub>d</sub>) = 0.9 Hz, H<sub>a</sub>), 7.60-7.35 (m, 46 H, Ph + H<sub>d</sub>), 7.32 (d"t", <sup>3</sup>J(H<sub>c</sub>,H<sub>b</sub>) = 7.7 Hz), 7.03 (ddd, <sup>3</sup>J(H<sub>b</sub>,H<sub>c</sub>) = 7.7 Hz, <sup>4</sup>J(H<sub>b</sub>,H<sub>a</sub>) = 4.9 Hz, <sup>5</sup>J(H<sub>b</sub>,H<sub>d</sub>) = 1.2 Hz, H<sub>b</sub>). IR (solid):  $\nu$  2110 (vw, C=C), 1263 (vs, br, CF<sub>3</sub>SO<sub>3</sub>), 1149 cm<sup>-1</sup> (m, br, CF<sub>3</sub>SO<sub>3</sub>). MS (MALDI<sup>+</sup>/DIT): *m/z* (%) 721 (100) [Au(PPh\_3)<sub>2</sub><sup>+</sup>], 1020 (14) [*M*<sup>+</sup> – PPh\_3], 1282 (2) [*M*<sup>+</sup>]. Anal. Calcd for C<sub>62</sub>H<sub>49</sub>Au<sub>2</sub>F<sub>3</sub>NO<sub>3</sub>P<sub>3</sub>S: C, 52.00; H, 3.45; N, 0.98; S, 2.24. Found: C, 51.98; H, 3.52; N, 0.94; S, 2.33.

**Synthesis of [AuAg(C≡CPy)(PPh<sub>3</sub>)<sub>3</sub>]OTf (7).** [Ag(PPh<sub>3</sub>)<sub>2</sub>]-OTf (156 mg, 0.2 mmol) was added to an acetone (20 mL) solution of [Au(C≡CPy)PPh<sub>3</sub>] (112 mg, 0.2 mmol). After 1 h of stirring, the reaction mixture was concentrated under vacuum and Et<sub>2</sub>O was added to give a white precipitate (210 mg). Yield: 78%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  41.0 (m, AuPPh<sub>3</sub>), 12.3 (m, 2P, Ag(PPh<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (HDA, -80 °C):  $\delta$  40.0 (s, AuPPh<sub>3</sub>), 8.8 (2d, *J*(<sup>107</sup>Ag,P) = 411 Hz, *J*(<sup>109</sup>Ag,P) = 475 Hz, 2P; Ag(PPh<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  -77.9 (s, 3F, CF<sub>3</sub>SO<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  8.19 (d, <sup>3</sup>*J*(H<sub>4</sub>,H<sub>b</sub>) = 4.4 Hz, H<sub>a</sub>), 7.57 (m, H<sub>b</sub>), 7.41−7.10 (m, 47 H, Ph + H<sub>c</sub> + H<sub>d</sub>). IR (solid):  $\nu$  1258 (vs, br, CF<sub>3</sub>SO<sub>3</sub>), 1148 cm<sup>-1</sup> (m, br, CF<sub>3</sub>SO<sub>3</sub>); MS (MALDI<sup>+</sup>/DIT): *m/z* (%) 721 (100) [Au(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>], 822 (55) [*M*<sup>+</sup> − AgPPh<sub>3</sub>]. Anal. Calcd for C<sub>62</sub>H<sub>49</sub>AgAuF<sub>3</sub>NO<sub>3</sub>P<sub>3</sub>S: C, 55.45; H, 3.68; N, 1.04; S, 2.39. Found: C, 55.40; H, 3.74; N, 1.01; S, 2.56.

**Synthesis of**  $[Au_2Cu_2(C≡CPy)_2(PPh_3)_4](NO_3)_2$  (8). Solid  $[Cu(O_2NO)(PPh_3)_2]$  (130 mg, 0.2 mmol) was added to a  $CH_2Cl_2$  (20 mL) solution of  $[Au(C≡CPy)PPh_3]$  (112 mg, 0.2 mmol). The solution, which turned yellow immediately, was stirred under nitrogen for 3 h and concentrated under vacuum to ca. 2 mL. A yellow solid was obtained after hexane addition (136 mg). Yield: 71%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -50 °C):  $\delta$  40.9 (m, Au(PPh\_3)), -0.4 (m, CuPPh\_3). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.45 (m, 2H<sub>4</sub>), 7.51 (m, 2H<sub>c</sub>), 7.40–7.15 (m, 62 H, 12 Ph +2H<sub>d</sub>), 7.05 (m, 2H<sub>b</sub>). IR (solid):  $\nu$  2112 (w, C≡C), 1071 (w, NO<sub>3</sub>), 997 (m, NO<sub>3</sub>), 690 cm<sup>-1</sup> (s, NO<sub>3</sub>). MS (MALDI<sup>+</sup>/DIT): m/z (%) 587 (87) [Cu(PPh\_3)\_2<sup>+</sup>], 721 (100) [Au(PPh\_3)\_2<sup>+</sup>], 886 (25) [(M/2)<sup>+</sup>], 1185 (5) [Au<sub>2</sub>Cu(C≡Cpy)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>]. Anal. Calcd for C<sub>86</sub>H<sub>68</sub>Au<sub>2</sub>Cu<sub>2</sub>. N<sub>4</sub>O<sub>6</sub>P<sub>4</sub>: C, 54.41; H, 3.61; N, 2.95. Found: C, 54.78; H, 3.52; N, 2.94.

**Crystallography.** Data were registered on an Oxford Diffraction Xcalibur (2, 7, and 8) or a Bruker AXS BV Kappa CCD diffractometer (3). The crystals were mounted in inert oil on a glass fiber and transferred to the cold gas stream of the corresponding diffractometer. Data were collected using monochromated Mo K $\alpha$  radiation

 $(\lambda = 0.71073)$  in the  $\omega$ -scan mode. Absorption corrections based on multiple scans were applied. The structures were solved by direct methods and refined on  $F^2$  using the program SHELXL-97.<sup>30</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further crystal data are given in Table 1.

#### ASSOCIATED CONTENT

**Supporting Information.** CIF files giving crystallographic data for 2, 3, 7, and 8. This material is available free of charge via the Internet at http://pubs.acs.org. The files CCDC 792104, 792105, 792107, and 792108 also contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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#### DEDICATION

Dedicated to the memory of Prof. F. Gordon A. Stone.

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