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Inorganic Chemistry Article

Gold(I) and Silver(I) Mixed-Metal Trinuclear Complexes: Dimeric Products from the Reaction of Gold(I) Carbeniates or Benzylimidazolates with Silver(I) 3,5-Diphenylpyrazolate[†]

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Trinuclear mixed-metal gold–silver compounds are obtained by the reaction of gold(I) carbeniate [Au(μ-C(OEt)$=$NC$_6$H$_4$-*p*-CH$_3$)]$_3$, TR(carb), or gold(I) imidazolate [Au-μ-C,N-1-benzyl-2-imidazolate]$_3$, TR(bzim), with silver(I) pyrazolate [Ag(μ-3,5-Ph$_2$pz)]$_3$. The crystalline products are mixed-ligand, mixed-metal dimeric products [Au(carb)Ag$_2$(μ-3,5-Ph$_2$pz)$_2$], [Au$_2$(carb)$_2$Ag(μ-3,5-Ph$_2$pz)]·CH$_2$Cl$_2$, [Au(bzim)$_2$Ag$_2$(μ-3,5-Ph$_2$pz)], and [Au$_2$(bzim)$_2$Ag(μ-3,5-Ph$_2$pz)]. They have been characterized by elemental analysis and ^{1}H NMR and mass spectrometry. The X-ray structure of [Au(carb)Ag$_2$(μ-3,5-Ph$_2$pz)$_2$] shows it to be a dimer with two Ag···Au contacts between the trinuclear units of 3.083(2) and 3.310(2) Å and with average intramolecular Ag···Ag and Au···Ag distances of ~3.3 and 3.2 Å, respectively. The structure of [Au$_2$(carb)$_2$Ag(μ-3,5-Ph$_2$pz)]·CH$_2$Cl$_2$ is a dimer with one intermolecular Au···Au attraction of 3.3354(10) Å and a short Ag···Au distance of ~3.42 Å and intramolecular Ag···Au and Au···Au contacts of ~3.2 and ~3.3 Å, respectively. Packing diagrams of both complexes show that the dimeric units are independent, similar to their parent molecules. The dimers of trinuclear [Au(carb)Ag$_2$(μ-3,5-Ph$_2$pz)$_2$] and [Au$_2$(carb)$_2$Ag(μ-3,5-Ph$_2$pz)]·CH$_2$Cl$_2$ crystallize in the triclinic space group $P\bar{1}$ ($Z = 2$), $a = 9.688(3)$ Å, $b = 15.542(4)$ Å, $c = 23.689(6)$ Å, $\alpha = 82.560(5)°$, $\beta = 87.887(6)°$, $\gamma = 78.060(5)°$, and the orthorhombic space group *Pca*2$_1$ ($Z = 4$), $a = 29.644(4)$ Å, $b = 7.4582(10)$ Å, $c = 30.473(4)$ Å, respectively. The structure of [Au(bzim)Ag$_2$(μ-3,5-Ph$_2$pz)$_2$] is a dimer with two metallophilic Ag···Au interactions of 3.14 Å. The complex crystallizes in the monoclinic space group *C*2/*c* ($Z = 4$), $a = 26.368(5)$ Å, $b = 15.672(3)$ Å, $c = 17.010(3)$ Å, $\beta = 102.206(3)°$.

Introduction

Attention has been given to the syntheses and properties of bimetallic clusters because of their unique catalytic,[1] optical, and electronic properties.[2] Small gold−silver clusters (nanomaterials) have been found to be highly effective in catalysis and medicine.[3] The silver−gold clusters proved to be more effective catalysts than the pure metals because of their increased activity, resistance to poisoning, and selectivity.[4] Recently, molecular materials with gold and silver nanoclusters and nanowires have been synthesized. These

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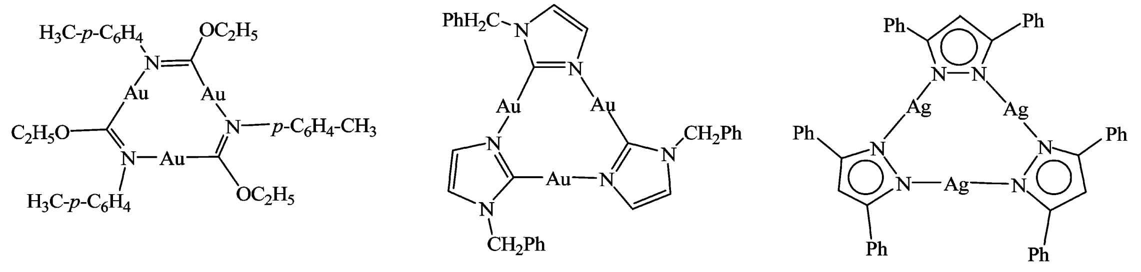
Chart 1. Trinuclear Carbeniate, TR(carb) (**1**), Benzylimidazolate, TR(bzim) (**2**), and Pyrazolate (**3**), Starting Materials



1 **2** **3**

materials are considered to be good candidates for electronic nanodevices and biosensors.[5]

Current understanding of the chemistry of neutral trinuclear cyclic gold complexes[6] includes the synthesis and structure of complexes that contain ancillary ligands, $[Au(C,N)]_3$ or $[Au(N,N)]_3$, where $[Au(C,N)]_3$ is a carbeniate, TR(carb), such as **1**, or a benzylimidazolate, TR(bzim), such as **2**, and $[Au(N,N)]_3$ is a pyrazolate, like the $[Ag(N,N)]_3$ shown as **3**, Chart 1.[7−10] The structure of $\{[Au\{\mu\text{-}C(OMe){=}N(CH_3)\}]_3\}_n$ was reported first as an infinite trigonal column with extensive intermolecular Au···Au interactions, not known to exist in other related structures.[11] The material now is known to show several crystalline oligomeric polymorphs. Balch reported that the columnar $\{[Au\{\mu\text{-}C(OMe){=}N(CH_3)\}]_3\}_n$ also displays a novel phenomenon he has described as solvoluminescence.[11a] Crystals of this material show a long-lived photoluminescence that is readily detected by the human eye for tens of seconds after cessation of irradiation. Addition of a drop of dichloromethane or chloroform to previously irradiated crystals produces a bright burst of light. This phenomenon does not occur with the other polymorphs of this gold(I) carbeniate.[11b,c]

We have shown that trinuclear gold(I) compounds such as **1** and **2** interact with Lewis acid salts such as silver(I) and thallium(I) to form chains in which the cation interacts with the trinuclear gold(I) compounds in a $[(Au_3Au_3MAu_3Au_3)M]_n$ ($M = Tl^+$ or Ag^+, Au_3 = TR(carb) or TR(bzim)) pattern.[12] Treatment of the TR(carb) or TR(bzim) with $AgBF_4$ or $TlPF_6$ results in the formation of yellow crystals of these sandwich compounds in which the trinuclear units surround the silver or thallium ion with M···Au distances ranging from 2.7 to 3.0 Å.

The reaction of trinuclear gold(I) compounds TR(carb) or TR(bzim) with trinuclear Hg(II) complex $[Hg(C_6F_4)]_3$ forms a repeat pattern of $[Au_3Hg_3Au_3Hg_3]$ (Au_3 = TR(carb) or TR(bzim), $Hg_3 = [Hg(C_6F_4)]_3$), with Hg···Au distances of ∼3.2 Å.[13] The trinuclear gold(I) units are isolated from each other with no intermolecular Au···Au interactions. A similar arrangement has been found in π acid A, π base B compounds, isolated with C_6F_6 and $C_{10}F_8$[14] intercalated between trinuclear carbeniate or benzylimidazolate units. With the organic π-acid TCNQ, an AB_2AB_2 pattern of acid−base interaction is observed. With nitrofluorenones, Balch also observed both patterns, i.e., ABAB and AB_2AB_2.[8d] Unpublished DFT calculations from our laboratory suggest that the π basicity of $[TR(carb)]_2$ is about 50% greater than for the [TR(carb)] alone.

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Various bimetallic gold−silver clusters have been synthesized during the past decade.[15−23] Au_nAg_m, Au_nPt_m, and even $Au_nAg_mPt_o$ carbonyl clusters[21] have been prepared and characterized crystallographically. Fackler et al.[22] reported the bridged mixed-metal $[AuAg(mtp)_2]$ (mtp = diphenylmethylenethiophosphinate) several years ago. Unbridged, base-free gold−silver polymeric chains such as $[\{AgAu(C_6F_5)_2(THT\ \text{or benzene})\}_n]$,[19] $[\{Au_3(\mu\text{-bzim-}N^3,C^2)_3\}_2Ag]$,[12] $[Ag_2Au_2(CH_2PPh_3)_4(ClO_4)_4]$,[20] and the base-stabilized complex[23] $[AgAu_4(CH_2SiMe_3)_4(\mu\text{-dppm})_2][CF_3SO_3]$ are known. A Au−Ag complex that is three-coordinate at each metal center, $[AuAg(dpim)_3]^{2+}$ (dpim = 2-(diphenylphosphino)-1-methylimidazole), has been reported by Catalano.[21c]

In this paper, we describe the synthesis of mixed-metal trinuclear gold−silver complexes by the direct reaction of gold(I) carbeniate (**1**) and gold(I) benzylimidazolate (**2**) with the silver(I) pyrazolate complex (**3**). The complexes $[Au(carb)Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2]$ (**4**), $[Au_2(carb)_2Ag(\mu\text{-}3,5\text{-}Ph_2pz)]\cdot CH_2Cl_2$ (**5**), and $[Au(bzim)Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2]$ (**6**) have been characterized by X-ray crystallography. A communication describing these mixed-metal complexes has appeared.[24]

Experimental Section

General. Unless otherwise noted, all reactions and manipulations were carried out under an inert atmosphere with a positive nitrogen gas flow, using standard Schlenk techniques. Dichloromethane was distilled over P_4O_{10}. Chemicals were purchased from Aldrich Chemical Co. and used as received. The mass spectrometer used in all the analyses involving APCI, atmospheric pressure chemical ionization, was the Hewlett-Packard 1100 MSD; the software employed was that included in the Work-Station HP package. The experimental conditions are as follows: organic phase flow, 300 μL/min; drying gas flow (N_2), 10 L/min; nebulization pressure, 30 psig; temperature of the drying gas, 350 °C; capillary potential, 4000 V. The value for the fragmentor was fixed to 30 and the acquisition of the data was performed by scanning in ranges from 100 to 1500 and 1400 to 3000 amu. Attempts to obtain good spectra using electrospray techniques were not as successful. Elemental analyses were carried out with a Carlo Erba 1106 elemental microanalyzer. ^1H NMR spectra were performed in CD_3CN solution on Varian VXR-300 spectrometers. Referencing is relative to TMS (^1H). Emission spectra were recorded on a SLM AMINCO model 8100 spectrofluorometer equipped with a xenon lamp. Spectra were corrected for instrumental response. Solid-state low-temperature measurements were made using a cryogenic sample holder of local design. Powder samples were attached to the holder with a mixture of copper powder, cryogen oil (used for mounting crystals for X-ray structures), and collodion (an ether- and alcohol-soluble transparent nitrocellulose). The glue was scanned for a baseline subtraction. Liquid nitrogen was used to obtain the 77 K measurements.

Synthesis of $[Au(carb)Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2]$ (4). An 80 mg (0.40 mmol) sample of **3** is dissolved in 5 mL of dichloromethane. A 44 mg (0.20 mmol) sample of **1** is added to the solution of **3**, and the mixture is stirred for 1 h at room temperature. The colorless solution forms a white precipitate after layering the sample with hexanes or ether. Yield: 106 mg, 86%. X-ray quality crystals are grown by very slow evaporation from dichloromethane over a few weeks. Layering the solution with ether or hexanes gives thin crystals of a lower crystallographic quality. Mp: 207−210 °C. Anal. Calcd for $C_{80}H_{68}N_{10}Ag_4Au_2O_2$: C, 47.41; H, 3.38; N, 6.91. Found: C, 46.72; H, 3.39; N, 6.72. APCI-MS (m/z, positive field): 1046.9, 301.1, 221.1; (m/z, negative field) 1047.8, 1080.9, 863.7. ^1H NMR ($CDCl_3$, 293 K): δ 1.05 (m, 3H), 2.3 (s, 3H), 4.13 (m, 2H), 6.8 (s, 1H), 6.95 (s, 1H), 7.0−7.4 (m, 17 H), 7.6−7.83 (m, 7H).

Synthesis of $[Au_2(carb)_2Ag(\mu\text{-}3,5\text{-}Ph_2pz)]\cdot CH_2Cl_2$ (5). We used a procedure similar to that used for **4** but with a 2:1 stoichiometry of **1**:**3**. X-ray quality crystals are grown by slow evaporation from a dichloromethane solution. Yield: 122 mg, 83%. Mp: 120−122 °C and changed to brown at 140 °C. Anal. Calcd for $C_{71}H_{72}N_8Ag_2Au_4O_4Cl_2$: C, 39.19; H, 3.34; N, 5.15. Found: C, 39.26; H, 3.52; N, 5.16. APCI-MS (m/z, positive field): 1298.1, 1164.0, 1119.1, 1078.1, 1046.9, 1001.0, 221.1; (m/z, negative field) 1168.8, 1111.9, 1080.9, 1034.9, 865.8. ^1H NMR ($CDCl_3$, 293 K): δ 1.15 (m, 6H), 2.32 (s, 6H), 4.24 (m, 4H), 6.82−7.2 (m, 8H), 7.26−7.41 (m, 7H), 7.78−7.95 (m, 4H).

Synthesis of $[Au(bzim)Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2]$ (6). Following a procedure analogous to the synthesis of **4**, we obtained compound **6** in 51% yield. Mp: 248−250 °C. Anal. Calcd for $C_{80}H_{62}N_{12}Ag_4Au_2$: C, 47.64; H, 3.1; N, 8.33. Found: C, 46.56; H, 3.07; N, 7.97.^1H NMR ($CDCl_3$, 293 K): δ 4.94 (s, 1.5H), 5.16 (s, 0.5H), 6.0−8.0 (m, 29H).

Synthesis of $[Au_2(bzim)_2Ag(\mu\text{-}3,5\text{-}Ph_2pz)]$ (7). Following a procedure analogous to the synthesis of **5**, we obtained compound **7** in 32% yield. Mp: 163−166 °C. Anal. Calcd for $C_{70}H_{58}N_{12}Ag_2Au_4$: C, 40.6; H, 2.82; N, 8.12. Found: C, 40.36; H, 2.87; N, 7.89.^1H NMR ($CDCl_3$, 293 K): δ 5.08 (s, 1.5H), 5.16 (s, 0.5H), 5.21 (s, 1.5H), 5.39 (s, 0.5H), 6.78−7.5 (m, 21H), 7.9−8.0 (m, 4H).

Data Collection. Data for **4**−**6** were collected using a Siemens (Bruker) SMART CCD (charge-coupled device)-based diffractometer equipped with an LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using ω scans of 0.3E per frame for 60 s, such that a hemisphere was collected. A total of 1271 frames were collected, with a final resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART

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Table 1. Crystal Data, Data Collection, and Structure Refinement for **4**−**6**

	4	**5**	**6**
empirical formula	$C_{80}H_{68}Ag_4Au_2N_{10}O_2$	$C_{71}H_{72}Ag_2Au_4Cl_2N_8O_4$	$C_{80}H_{62}Ag_4Au_2N_{12}$
fw	2026.87	2175.89	2016.84
T (K)	110(2)	110(2)	110(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	Triclinic	Orthorhombic	Monoclinic
space group	$P\bar{1}$	Pca21	$C2/c$
a (Å)	9.688(3)	29.644(4)	26.368(5)
b (Å)	15.542(4)	7.4582(10)	15.672(3)
c (Å)	23.689(6)	30.473(4)	17.010(3)
α (deg)	82.560(5)		
β (deg)	87.887(6)		102.206(3)
γ (deg)	78.060(5)		
V (Å^3)	3460.4(16)	6737.3(16)	6870(2)
Z	2	4	4
D_{calcd} (mg/m^3)	1.944	2.145	1.950
abs coeff (mm^{-1})	5.390	9.382	5.428
GOF on F^2	0.764	1.019	1.082
R1, wR2 [$I > 2\sigma(I)$]	0.0721, 0.1249	0.0597, 0.1332	0.0433, 0.0781

Table 2. Selected Bond Distances and Angles of Complex **4**

	Bond Distances (Å)		
Au(1)−C(38)	1.960(18)	Au(2)···Ag(4)	3.2136(19)
Au(1)−N(1)	2.011(17)	Ag(1)−N(2)	2.003(15)
Au(1)···Ag(2)	3.2663(19)	Ag(1)···Ag(2)	3.285(2)
Au(1)···Ag(4)	3.311(2)	Ag(2)−N(4)	2.099(17)
Au(2)···Ag(1)	3.082(2)	Ag(3)···Ag(4)	3.283(2)
	Bond Angles (deg)		
N(4)−Ag(2)−N(5)	174.9(6)	Au(1)···Ag(2)···Ag(1)	62.62(4)
C(38)−Au(1)−N(1)	176.2(7)	Ag(2)···Au(1)···Ag(4)	65.96(5)
C(78)−Au(2)−N(9)	176.9(7)	N(2)−Ag(1)−N(3)	171.8(6)
N(7)−Ag(3)−N(8)	172.9(7)	Au(2)···Ag(4)···Ag(3)	63.41(5)
N(6)−Ag(4)−N(10)	164.5(6)	N(5)−C(38)−Au(1)	121.4(13)

software and refined using SAINT on all observed reflections.[25] Data reduction was performed using the SAINT software, which corrects for Lp and decay.[26] Absorption corrections were applied using SADABS, supplied by George Sheldrick.[27] The structures are solved by the direct method using the SHELXS-97 program and refined by the least-squares method on F^2, SHELXL-97, incorporated in SHELXTL-PC V 5.03.[28,29]

The structures of **4**−**6** were solved in the triclinic, orthorhombic, and monoclinic space groups $P\bar{1}$, $Pca21$, and $C2/c$, respectively, by analysis of systematic absences. The Flack parameter for **5** is 0.000(9). All non-hydrogen atoms are refined anisotropically. Hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystallographic details are given in Table 1, and bond distances and angles are listed in Tables 2−4.

Table 3. Selected Bond Distances and Angles of Complex **5**

	Bond Distances (Å)		
Au(1)···Au(2)	3.2746(11)	Au(1)···Ag(1)	3.2803(16)
Au(1)···Au(3)	3.3354(10)	Au(2)···Ag(1)	3.2427(16)
Au(3)···Ag(2)	3.2169(17)	Au(3)···Au(4)	3.3411(11)
Au(4)···Ag(2)	3.2456(17)	Au(1)−C(32)	1.982(18)
Au(1)−N(1)	2.065(15)	Ag(2)−N(8)	2.057(15)
	Bond Angles (deg)		
C(32)−Au(1)−N(1)	177.5(6)	Au(2)···Au(1)···Ag(1)	59.30(3)
Ag(1)···Au(2)···Au(1)	60.44(3)	N(2)−Ag(1)−N(3)	173.7(6)
Au(2)···Ag(1)···Au(1)	60.26(3)	Ag(2)···Au(3)···Au(1)	93.98(3)

Table 4. Selected Bond Distances and Angles of Complex **6**

	Bond Distances (Å)		
Ag(1)···Ag(2)	3.3516(8)	Au(1)···Ag(1A)	3.1423(8)
Ag(1)−N(3)	2.085(5)	Au(1)−C(31)	1.995 (6)
Au(1)−N(1)	2.060(5)		
	Bond Angles (deg)		
C(31)−Au(1)-N(1)	174.7(2)	N(2)−Ag(1)−N(3)	170.27(19)
Ag(2)−N(4)−N(3)	116.8(3)		

Results and Discussion

Synthesis. On the basis of the fact that π-acids interact with trinuclear gold(I) pi-bases TR(carb) and TR(bzim), we reacted trinuclear 3,5-diphenylpyrazolate silver(I) complex **3** with each of them. Mixing **1** or **2** with **3** in CH_2Cl_2 in stoichiometric ratios of 1:2 and 2:1 produced complexes **4**−**7**. A colorless solution forms from the mixing of **1** or **2** with **3**, whereas a yellow suspension forms when a solution of Ag[PF_6] reacts with **1**. Reactions occur rapidly, and evaporation of a drop from the reaction mixture on a filter paper within a few minutes of mixing produces a spot that gives a strong green or orange luminescence under a hand-held UV lamp. Crystals were grown by slow evaporation from a CH_2Cl_2 solution over a few weeks. The crystalline products were not the expected acid−base adducts but rearranged dimeric, trinuclear products. Thus [Ag(μ-3,5-Ph$_2$pz)]$_3$ behaves differently from the π-acid complex [Hg(C_6F_4)]$_3$ reported by Gabbai.[30] It is suspected that the lability of the M−N bond (M = Au, Ag) in these complexes results in the subsequent cleavage of the cyclic complexes to produce the product statistically expected from the stoichiometry of materials used. Thus the mixed metal products [Au(carb)Ag$_2$(μ-3,5-Ph$_2$pz)$_2$] (**4**), [Au$_2$(carb)$_2$Ag(μ-3,5-Ph$_2$pz)]·CH_2Cl_2 (**5**), [Au(bzim)Ag$_2$(μ-3,5-Ph$_2$pz)$_2$] (**6**), and [Au$_2$(bzim)$_2$Ag(μ-3,5-Ph$_2$pz)] (**7**) crystallize from the medium.

The products also were analyzed using X-ray powder diffraction, and the patterns were compared with the patterns generated from the single-crystal data. The compounds are stable in the solid state at room temperature. The IR spectra do not show major changes from the starting materials in the range 4000−600 cm^{-1}. The complexes are very soluble in most organic solvents, which make them very good candidates for catalytic studies. Preliminary catalysis results show that these complexes form nanoclusters on a TiO_2 surface upon reduction and calcination.[31] Resulting mixed-metal clusters have been found to be active to room-temperature CO oxidation in air. Most of the molecular gold−silver complexes reported to date contains metal centers coordinated to phosphorus and sulfur-donor ligands. These ancillary ligands are often poisonous to catalysis, making their applications limited.

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(25) *SMART Software for the CCD Detector System*, version 4.043; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(26) *SAINT Software for the CCD Detector System*, version 4.035; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(27) Blessing, R. H. SADABS Program for Absorption Corrections Using Siemens CCD Based on the Method of Robert Blessing. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(28) Scheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structure;* University of Göttingen: Göttingen, Germany, 1997.

(29) *SHELXTL 5.03 (PC version), Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(30) Haneline, M. R.; Gabbai, F. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 5471.

(31) Chusuei, C. C.; Lai, X.; Davis, K. A.; Bowers, E. K.; Fackler, J. P.; Goodman, D. W. *Langmuir* **2001,** *17,* 4113.

The stability of compounds **4** and **5** in solution is also highlighted by APCI mass spectrometry. The parent ions have been observed for both compounds as adducts with solvents, protons, and chloride ions, both as positive and negative ions. The metallocyclic rings are incompletely rearranged in methylene chloride/acetonitrile solutions, which yield evidence for the starting compounds. Also, traces of the dimer of trimers are detected in the range 1500−3000 amu. The ^{1}H NMR spectra demonstrate the stability of the heterometallocyclic rings, although the NMR patterns are more complex than expected from the individual trinuclear species. The ethoxy group of the carbeniate ligand in complex **4** should exhibit a quartet and a triplet, and the methylene group of the benzylimidazolate ligand in **6** should be a singlet. What is observed is the superimposition of two quartets and two triplets of different intensity for the ethoxy of **4** and two singlets of different intensities for the methylene group of **6**. In complexes **5** and **7**, the two carbeniate or benzylimidazolate ligands are not magnetically equivalent. The spectra for the ethoxy groups are a superimposition of at least three quartets and three triplets of different intensities resulting in resolved but crowded multiplets (assigned as multiplets in the Experimental Section). For **7**, four singlets of different intensities are observed for the methylene groups ($CH_2{-}Ph$). By comparing these data and ruling out the presence of starting materials, we can attribute the complexity of the signals (in addition to the nonequivalences) to the presence of dimeric structures in solution, as described in a previous NMR study on analogous substrates.[12c]

Gold(I) carbeniate−silver(I) pyrazolate complexes **4** and **5** give a green luminescence under a UV lamp, whereas gold(I) benzylimidazolate−silver(I) pyrazolate complexes **6** and **7** show an orange luminescence under UV lamp excitation at room temperature. The emission spectra of **6** and **7** in the solid state at 77 K show a strong emission centered at ∼460 nm with vibronic structure. It is an emission typical of ligand-based excited-state spectra of Au(I) pyrazolates and benzylimidazolates with a large Stokes' shift. The excitation centers around 275 nm. The vibronic separations are suggestive of C═N and N═N stretching modes. The emission spectra of these four complexes will be reported and discussed in a future paper.

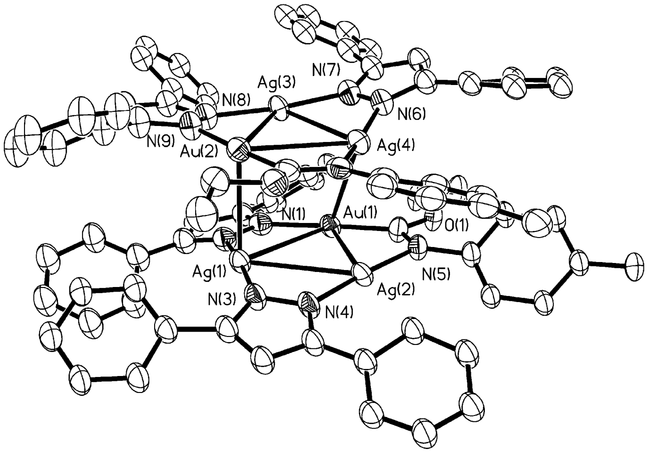

Figure 1. ORTEP diagram of $[Au(carb)Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2]_2$, **4**.

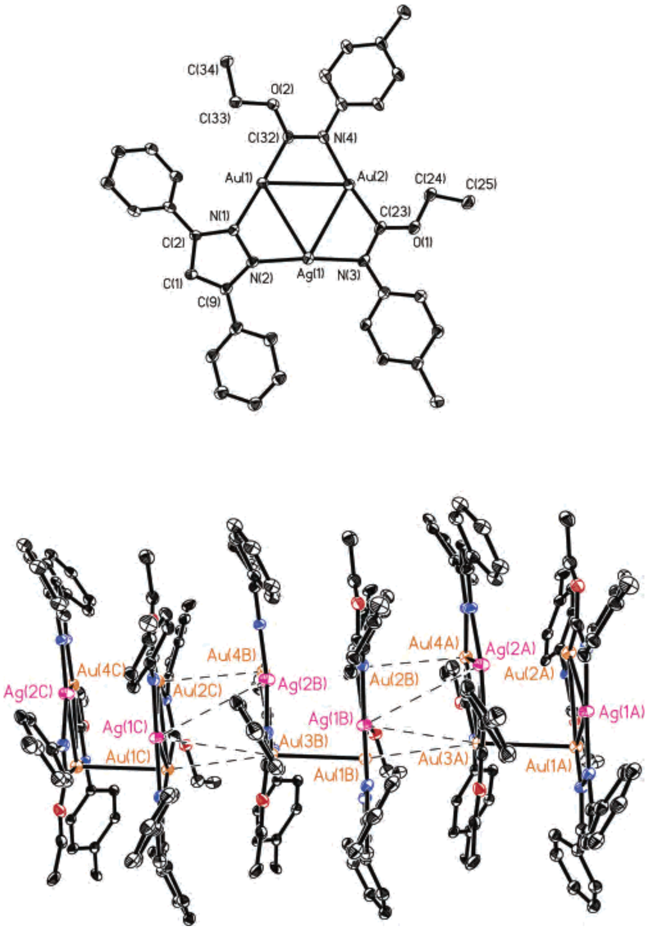

Figure 2. Top: ORTEP diagram of an asymmetric unit of $[Au_2(carb)_2Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_2$, **5**. Bottom: Packing diagram.

Molecular Structures. X-ray Structure of 4. The structure of $[Au_2(carb)_2Ag_4(\mu\text{-}3,5\text{-}Ph_2pz)_4]$ (**4**; Figure 1) is not unlike that reported for the dimer of **3**, $[Ag_3(\mu\text{-}3,5\text{-}Ph_2pz)_3]_2$,[32] but it crystallizes with a different space group and a different dimeric arrangement. The hairlike crystals of **4** belong to the triclinic space group $P\bar{1}$ ($Z = 2$), whereas $[Ag_3(\mu\text{-}3,5\text{-}Ph_2pz)_3]_2$ crystallizes in the monoclinic space group *C2/c*. The two trinuclear moieties of the dimer of **3** are rotated anti to each other, but this arrangement is less apparent in **4**. The shortest Ag···Ag interactions within the metallocycle rings of the dimer of **3** are ca. 3.4 Å, whereas between the trinuclear units. the Ag···Ag distance is 2.9712(14) Å. The Au···Ag distances between trinuclear units in **4** are 3.311(2) and 3.082(2) Å (Table 2). There are no short Au···Au or Ag···Ag interactions. The metallocycles in **4** are irregular and puckered, similar to those in the dimer of **3,** with a mean deviation of 0.469 Å of the trinuclear units from a plane. The packing diagrams of the dimer of **3** and **4** show structurally independent dimeric units.

X-ray Structure of 5. The hairlike crystals of **5** crystallize in the orthorhombic space group $Pca2_1$. The structure of **5** (Figure 2) shows one intermolecular interaction between the trinuclear gold units, with a Au···Au distance of 3.33 Å. This is slightly longer than the Au···Au distances, 3.224−

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(32) Mohamed, A. A.; Perez, L. M.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2005**, *358*, 1657−1662.

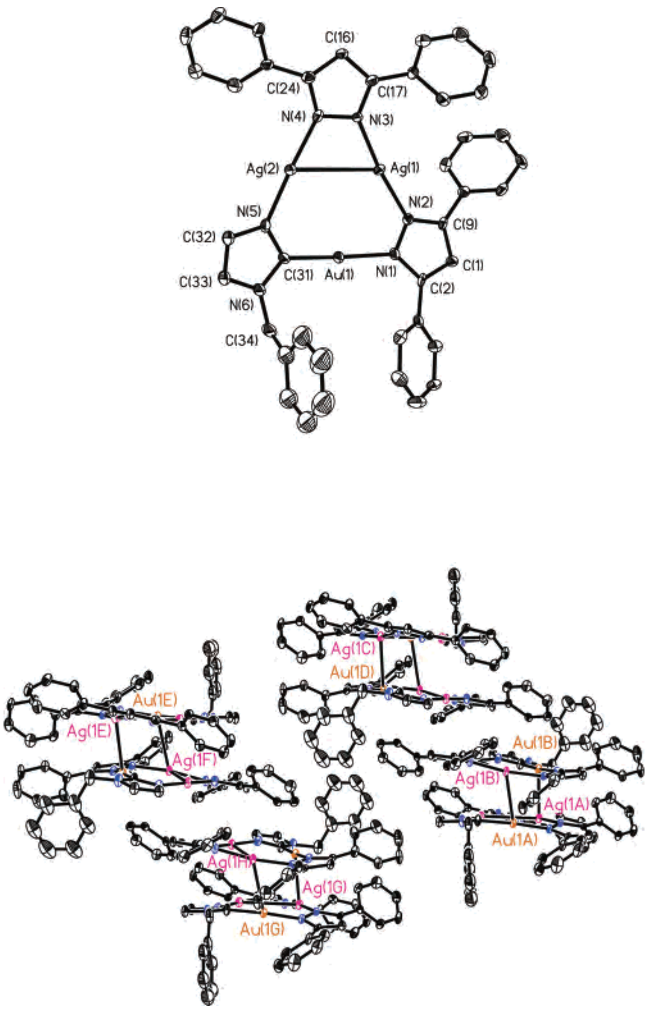


Figure 3. Top: ORTEP diagram of an asymmetric unit of [Au(TRbz)-$Ag_2(\mu\text{-}3,5\text{-}Ph_2pz)_2]_2$, **6**. Bottom: Packing diagram.

3.299 Å, in the irregular and puckered nine-membered ring[6] of the dimer of **1.** The Au···Ag distances in **5** are 3.22−3.28 Å (Table 3). The average distance of the two closest Au atoms between the trinuclear units of each dimer is 3.2 Å.

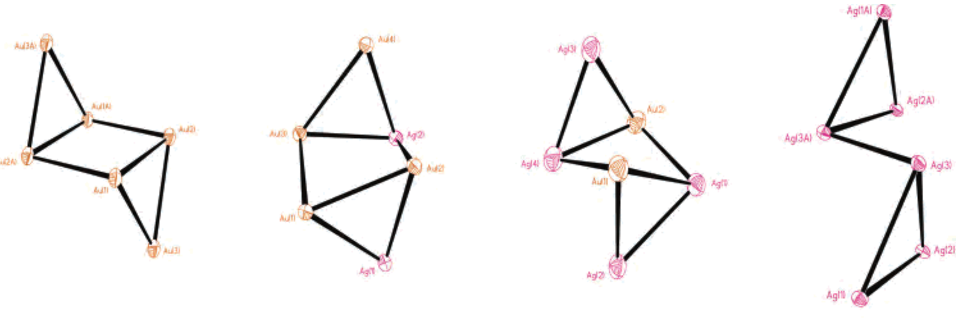
The metallocycles in **5** are irregular and puckered, similar to those in the dimer of **1,** but with a puckering smaller than that in **4**. The deviation from the mean plane of one of the trinuclear units is 0.342 Å. A packing diagram (Figure 2) shows a Au···Au interaction, 3.857 Å, between the dimer units similar to the distance observed[6] in **1**, 3.824 Å. The N−M−N angle in **5** is 173.7°, with a lesser deviation from linearity at the N−Au−C angle, 177.5°.

X-ray Structure of 6. The inter-trinuclear Au···Ag interaction in **6** is 3.1423(8) Å. The two benzyl groups are perpendicular to the planes of the trinuclear units and hinder further interactions between them, Figure 3. The intermolecular distances in **6**, Au···Ag = 3.53 and 3.38 Å and Ag···Ag = 3.35 Å, are longer than those in the dimer of **4**.

A few additional structural comparisons between the homonuclear gold and silver complexes and the mixed gold and silver complexes are of interest. In the dimer of the trinuclear silver(I) 3,5-diphenylpyrazolate (**3**) the six silver atoms are arranged as two triangles connected by only one short interaction, Chart 2. This drastically changes when a gold atom is introduced into the trinuclear unit as in **4**. An irregular square is formed by two Ag and two Au atoms with M−M distances in the range 3.08−3.40 Å. The other two silver atoms are above and below the plane of the square. A metallophilicity is observed in **4** in which each of the two gold atoms interact with three silver atoms. In **5**, three Au and one Ag form a nearly regular square with distances ranging from 3.21 to 3.42 Å. The homonuclear, trinuclear Au compounds generally form dimers with nearly perfect squares, Au−Au ca. 3.2 Å, as seen in the structure of the dimer of **1**.

The Ag−Au distance in the trinuclear $[\{Au\text{-}\mu\text{-mesityl})AsPh_3\}_2Ag]ClO_4$ is 2.7758(8) Å,[15g] which is shorter than all Au−Ag distances in **3**−**5**. In the bridged Ag−Au complex $\{Ag(\mu\text{-dppm})_2\{Au(mesityl)\}_2]ClO_4$, the distances are 2.944(2) and 2.946(2) Å.[15h] The structure of the complex $[Au_2Ag_2(C_6F_5)_4(OCMe_2)_2]_n$ forms infinite chains by repetition of the Au_2Ag_2 core through short Au···Au contacts of 3.1674(11) Å.[15j] The silver atoms in the main unit are bonded to two gold atoms with Au−Ag distances of 2.7903(9) and 2.7829(9) Å. The two silver centers make a close contact of 3.1810(13) Å. The Au−Ag separations in the dinuclear complexes are 2.8635(15) Å in the three-coordinate $[AuAg(dpim)_3]^{2+}$ (dpim = 2-(diphenylphosphino)-1-methylimidazole),[21c] 2.9124(13) Å in $AgAu(MTP)_2$ (MTP = diphenylmethylenethiophosphinate),[22] and 2.820(1) Å in $[AuAg(dppy)_2(ClO_4)_2]$ (dppy = 2-(diphenylphosphino)pyridine).[33] Laguna and Pyykkö studied theoretically the interactions in the unsupported $[Ag(pyridine)_3][Au(C_6F_5)_2]$pyridine gold−

Chart 2 Intermetallic Arrangements of the Metal Atoms in the Dimers of **1**, **3**, **4**, and **5**



Au_6, the dimer of **1** Ag_2Au_4, **5** Ag_4Au_2, **4** Ag_6, the dimer of **3** silver chains.[15i] Here, the Ag···Au bonding is largely formed by electrostatic attraction and dispersion-type correlation effects. The Ag···Au interactions when the naked Ag(I) is sandwiched between **1** or **2** are 2.73−2.92 Å.[12]

A series of vertex-sharing polyicosahedral phosphine Au−Ag halide clusters have been reported by Teo.[16] The general synthesis of these "clusters of clusters" involves the reduction of a mixture of PPh_3AuX and PPh_3AgX with $NaBH_4$. The metal−metal distances in the tri-icosahedral structure of cluster $[(PPh_3)_{12}Au_{12}Ag_{13}Cl_6]^{m+}$ follow the trend of Au−Au < Au−Ag < Ag−Ag.[16a]

The sum of the covalent radii of metallic gold and silver is 2.89 Å. In the complexes reported here, the shortest unbridged Ag−Au distance is 3.08 Å, and the shortest bridged Ag−Au distance is 3.21 Å, in agreement with the reported values of many other Ag−Au complexes.

Conclusions

As a result of the lability of Au−N and Ag−N bonds and the stability of Au−C bonds, mixed-metal gold−silver dimers of planar, trinuclear complexes are readily formed by mixing gold(I) carbeniates or gold(I) benzylimidazolates with silver(I) pyrazolate in stoichiometric ratios. The complexes retain the ligands associated with the metal atoms of the starting materials. The clusters produced are similar in their crystalline structure to the starting materials. Ligand-bridged metal−metal distances display longer M−M distances than in the unbridged complexes. In the compounds studied, the nonbridged intermolecular M−M distances follow the order: Ag−Ag < Au−Ag < Au−Au, whereas the intrametallocycle M−M distances with bridging-ligand bonding follow the order Au−Au < Au−Ag < Ag−Ag. The synthesis of these mixed gold−silver compounds represents a new approach to cluster mixed-metal synthesis with potential use in mixed-metal catalysis.

Acknowledgment. The Robert A. Welch Foundation of Houston, Texas, and the University of Camerino, Italy, are acknowledged for financial support.

Supporting Information Available: X-ray crystallographic files for **4**−**6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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