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# Gold(I) Compounds without Significant Aurophilic Intermolecular Interactions: Synthesis, Structure, and Electronic Properties of $Ph_3PAuC(O)NHMe$ and $Au_3(PhCH_2N{=}COMe)_3$: Comparative Monomeric and Trimeric Analogues of the Solvoluminescent Trimer, $Au_3(MeN{=}COMe)_3$

**Alan L. Balch,* Marilyn M. Olmstead, and Jess C. Vickery**

Department of Chemistry, University of California, Davis, California 95616

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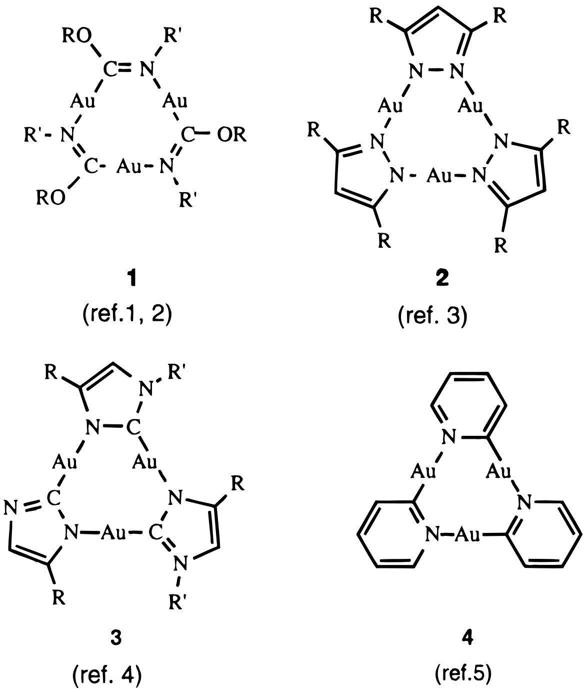
The preparations of $Ph_3PAuC(O)NHMe$ and $Au_3(PhCH_2N{=}COMe)_3$ are reported. In solution $Ph_3PAuC(O)NHMe$ is unstable and readily deposits metallic gold. Colorless needles of the monomeric complex, $Ph_3PAuC(O)NHMe$, crystallize in the monoclinic space group $P2_1/c$, with $a = 8.993(2)$ Å, $b = 22.583(5)$ Å, $c = 8.932(2)$ Å, $\beta = 98.22(2)°$, at 123 K with $Z = 4$. Refinement of 2609 reflections and 114 parameters yielded $R = 0.0455$. A hydrogen-bonded intermolecular network links molecular units through N−H···O hydrogen bonds. No aurophilic interactions are present in this solid. The crystal structure of the cyclic trinuclear organogold compound, $Au_3(PhCH_2N{=}COMe)_3$, reveals that the complex does not associate into a trigonal prismatic array via intermolecular interactions of gold(I) centers as is seen in the triangular complex, $Au_3(MeN{=}COMe)_3$. Rather, the complex packs in a stair-step fashion with eight discrete molecules in the asymmetric unit. Additionally, the solvent-stimulated emission (solvoluminescence) associated with $Au_3(MeN{=}COMe)_3$ is not observed for this complex. Colorless needles of $Au_3(PhCH_2N{=}COMe)_3$ crystallize in the monoclinic space group $P2_1$, with $a = 17.311(6)$ Å, $b = 34.761(10)$ Å, $c = 18.052(6)$ Å, $\beta = 94.73(2)°$, at 133 K with $Z = 16$. Refinement of 16 250 reflections and 985 parameters yielded $R = 0.0735$.

## Introduction

A number of triangular trigold(I) complexes, $Au_3L_3$, exist with linear, two-coordinated gold centers connected by bridging ligands to form nearly strain-free, nine-membered rings.[1−5] Representative examples are shown in Scheme 1. While molecules of this type have been known for over 20 years, it is only recently that some remarkable chemical reactivities and physical properties of these molecules have been recognized.

In terms of chemical reactivity, complexes of types **1**−**3** undergo oxidative addition of halogens ($X_2$) to form a series of mixed-valence Au(I)/Au(III) complexes of the types $Au^{I}_2Au^{III}X_2L_3$ and $Au^{I}Au^{III}_2X_4L_3$ as well as, in some cases, the $Au^{III}$ trimer, $Au^{III}_3X_6L_3$. For example, for compound **1** (R, R′ = Me), the three complexes $Au^{I}_2Au^{III}I_2L_3$, $Au^{I}Au^{III}_2I_4L_3$, and $Au^{III}_3I_6L_3$ have been characterized crystallographically,[6,7] but with complexes of type **2** only the $Au^{I}_2Au^{III}$ complex has been observed.[8,9] Treatment of the trimer **3** (R = H, R′ = benzyl) with silver$^{I}$ tetrafluoroborate results not in oxidation but in the formation of a sandwich compound in which two trimers surround a silver ion with Ag−Au distances ranging from 2.731(2) to 2.922(2) Å.[10]

**Scheme 1**



**1** (ref.1, 2)
**2** (ref. 3)
**3** (ref. 4)
**4** (ref.5)

Pyrazolate complexes of the type **2** form columnar mesophases at room temperature.[11,12] The properties of these liquid-

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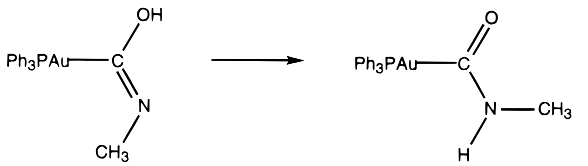
crystalline phases show a marked dependence on the identity of the peripheral substituents on the pyrazolate rings. Aurophilic interactions are believed to be important in ordering these phases.

Recently this laboratory reported that the colorless, crystalline gold trimer **1** (R, R′ = Me) displays a novel phenomenon, solvoluminescence.[13,14] After irradiation with near-UV light, crystals of **1** (R, R′ = Me) show a long-lived photoluminescence that is readily detected by the human eye for tens of seconds after cessation of irradiation. Addition of dichloromethane or chloroform to these previously irradiated crystals produces a bright burst of light. Since the intensity of this emission is greatest for those liquids that are good solvents for the gold complex, the phenomenon has been termed solvoluminescence. The solid state structure of **1** (R, R′ = Me) is crucial to the occurrence of solvoluminescence since the emission has been shown to correlate with the emission characteristics of the solid rather than those of the molecule in solution.

Here we report on synthetic studies that were designed to produce new complexes with the cyclic framework that is characteristic of **1**. Our goals were to determine how common is the columnar, prismatic stacking that is seen in **1** (R, R′ = Me) in the solid state and to prepare analogues capable of additional supramolecular organization through hydrogen bonding.

## Results and Discussion

**Synthetic Studies.** In order to prepare a version of **1** with *R* = OH that might be capable of hydrogen bonding, the reaction used to form **1** (R, R′ = Me) was modified so that it could be conducted in water. Addition of methyl isocyanide to a suspension of $Ph_3PAuCl$ in an aqueous potassium hydroxide solution resulted in the initial dissolution of the gold(I) phosphine complex and the eventual precipitation of a new colorless solid, $Ph_3PAuC(O)NHMe$. The product is relatively unstable, and recrystallization was successful only when performed at low temperature. At room temperature, solutions of $Ph_3PAuC(O)NHMe$ readily deposit a film of metallic gold. The infrared spectrum of the solid complex shows bands at 1478 and 1433 $cm^{-1}$ that are assigned to the C−N and C−O stretches and a band at 3058 $cm^{-1}$ that is due to the N−H stretch. The low energy of this feature is consistent with the presence of hydrogen bonding of the N−H group, which is consistent with the X-ray diffraction data. The formation of $Ph_3PAuC(O)NHMe$ rather than a cyclic complex of type **1** probably results from the facile tautomerization of the initially formed carbene complex into the final product as seen in eq 1.



(1)

In order to examine the effects of modification of the substituent R′ on the structure of the trimers, the synthesis of **1** was attempted using several different isocyanides. Colorless, trimeric $Au_3(PhCH_2N{=}COMe)_3$ was produced by the addition of benzyl isocyanide to a suspension of $Ph_3PAuCl$ in a methanol solution of potassium hydroxide. The reaction proceeded with the initial dissolution of the gold(I) phosphine starting material followed by the eventual precipitation of the colorless product. The process resembles that initially developed for the preparation of $Au_3(MeN{=}COMe)_3$. $Au_3(PhCH_2N{=}COMe)_3$ is soluble in dichloromethane and chloroform but insoluble in methanol and diethyl ether. The complex is considerably more stable thermally and photochemically than $Ph_3PAuC(O)NHMe$. The $^1H$ NMR spectrum of the trimer in chloroform-*d* solution shows a singlet resonance at 3.38 ppm due to the methylene protons, a singlet at 4.22 ppm due to the methoxy protons, and an unresolved multiplet at 7.27 ppm due to the phenyl protons. The infrared spectrum of the complex shows no bands in the region where an isocyanide group would absorb but a strong feature at 1535 $cm^{-1}$ for the C=N stretch of the newly created bridging ligand.

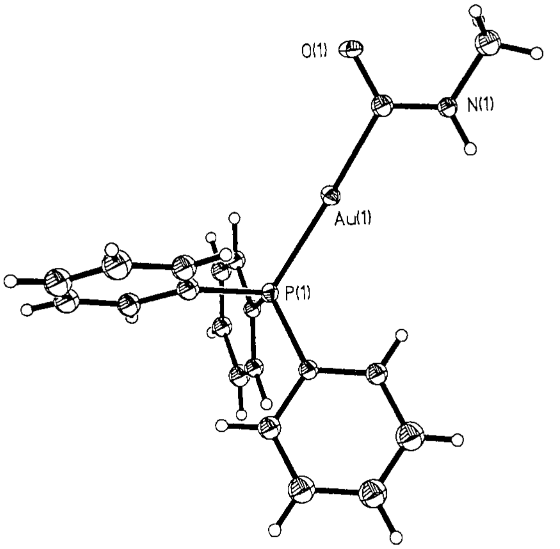


**Figure 1.** Perspective view of $Ph_3PAuC(O)NHMe$ with 50% thermal contours for all non-hydrogen atoms. The hydrogen atoms are shown as open circles; the remaining unlabeled atoms are carbon atoms.

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for $Ph_3PAuC(O)NHMe$

| | | | |
|---|---|---|---|
| Bond Lengths(Å) | | | |
| Au(1)−C(2) | 2.056(13) | O(1)−C(2) | 1.29(2) |
| Au(1)−P(1) | 2.306(3) | N(1)−C(2) | 1.31(2) |
| P(1)−C(9) | 1.804(12) | N(1)−C(1) | 1.48(2) |
| P(1)−C(3) | 1.815(13) | N(1)−H(1) | 0.945(3) |
| P(1)−C(15) | 1.823(12) | N(1)···O(1)′ | 2.905(3) |
| Bond Angles(deg) | | | |
| C(2)−Au(1)−P(1) | 177.7(4) | C(9)−P(1)−Au(1) | 112.3(4) |
| O(1)−C(2)−Au(1) | 120.5(9) | C(3)−P(1)−Au(1) | 112.7(4) |
| N(1)−C(2)−Au(1) | 118.8(9) | C(15)−P(1)−Au(1) | 115.6(4) |
| C(2)−N(1)−C(1) | 120.7(11) | C(9)−P(1)−C(3) | 104.9(6) |
| O(1)−C(2)−N(1) | 120.7(12) | C(9)−P(1)−C(15) | 106.2(6) |
| N(1)−H(1)−O(1)′ | 166.3(2) | C(3)−P(1)−C(15) | 104.2(6) |

Efforts to prepare other complexes of type **1** through the reaction of $Ph_3PAuCl$ in methanolic potassium hydroxide with *tert*-butyl isocyanide and cyclohexyl isocyanide were unsuccessful. Ill-defined white solids were obtained in ca. 5% yield, but these precipitates defied attempts at purification and crystallization.

**Structural Characterization by X-ray Diffraction. A. $Ph_3PAuC(O)NHMe$.** Figure 1 shows a drawing of the entire molecule, which has no crystallographically imposed symmetry. Selected interatomic distances and angles for this complex are given in Table 1. The structure consists of a normal triphenylphosphine ligand and a nearly planar AuC(O)NHMe moiety

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with linear coordination at the gold(I) center. The C−O and C−N distances within $Ph_3PAuC(O)NHMe$ are 1.29(2) and 1.31 (2) Å, respectively. The ligand distribution about gold in this complex is consistent with typical two-coordination found for many gold(I) centers. The gold−carbon bond length is 2.056(13) Å, a value which is consistent with the assignment of carbene-like character to the carbon atom in question. Typical bond lengths of $sp^3$-hybridized C to Au fall within the range 2.1−2.3 Å as is seen for $Ph_3PAuMe$ with a bond length of 2.124(28) Å. For an $sp^2$-hybridized C−Au bond one would expect shortening due to the change in hybridization by about 0.03 Å, giving a C−Au bond length in the range 2.07−2.10 Å. Comparatively, even shorter bond lengths have been observed for the imidazolylgold(I) complex, $ClAu(CN(CH_2Ph)CH{=}CHNCOOCH_2Me)$, in which the carbene−gold bond length is 1.972(8) Å,[15] and the liquid-crystalline gold(I)−(alkoxy)(amino)carbene complex, $ClAu(C(OC_2H_5)(NHC_6H_4CO_2C_6H_4\text{-}OC_2H_5))$, which has a Au−C bond length of 1.985(7) Å.[16] The Au−P bond length in $Ph_3PAuC(O)NHMe$, 2.306(3) Å, is consistent with typical phosphorus−gold(I) bond lengths which fall in the range 2.2−2.4 Å.[17]

The solid state structure of $Ph_3PAuC(O)NHMe$ does not show signs of aurophilic interactions. The shortest intermolecular Au···Au distance is 6.033 Å, which is beyond the normally accepted contact limit of 3.6 Å for significant aurophilic interactions. However, $Ph_3PAuC(O)NHMe$ displays a hydrogen-bonding network that involves the ligand NH group as the donor and the ligand C=O group of another complex as the acceptor. A portion of this extended hydrogen-bonding network is illustrated in Figure 2. The N−H(1)···O(1′) distance in $Ph_3PAuC(O)NHMe$ is 1.978(3) Å, the N···O separation is 2.905(3) Å, and the N−H···O bond angle is 166.3(2)°. The N−H···O interaction in $Ph_3PAuC(O)NHMe$ is quite similar to those observed in related organometallic gold(I) complexes.[18] In $[Au(NH{=}C(Me)_2)_2{}^+](CF_3SO_3{}^-)$, there is a hydrogen-bonded chain that involves alternating anions and cations that are linked through N−H···O groups.[19] The corresponding N···O distances fall in the range 2.89−2.91 Å, and the N−H···O bond angles occur in the range 158−167°. Unlike the case of $Ph_3PAuC(O)NHMe$ where the complexes are connected only through hydrogen bonding, the salt $[Au(NH{=}C(Me)_2)_2{}^+](CF_3SO_3{}^-)$, also contains an extended, linear chain of gold(I) centers with Au···Au separations of ca. 3.17 Å. In the carbene complex $[(HNC_5H_4)_2Au^+]Cl\cdot 2H_2O$ the two N−H groups are hydrogen bonded to either a water molecule or a chloride ion.[20] With hydrogen bonding to the water molecule, the N···O separation is 2.83 Å. The are no short Au···Au contacts in this salt.

**B. $Au_3(PhCH_2N{=}COMe)_3$.** Figure 3 shows a drawing of one of the eight independent molecules in the asymmetric unit. The other seven molecules of have similar structures with a planar $Au_3L_3$ core and the benzylic portions jutting out from the core. Each of the molecules lacks any crystallographically imposed symmetry. Table 2 presents a set of average bonding parameters as well as the ranges of these for this trimer. The overall geometry is, as expected, similar to that seen for $Au_3(MeN{=}COMe)_3$. Thus, the average intramolecular $Au^I\cdots Au^I$ separation in $Au_3(PhCH_2N{=}COMe)_3$ is 3.316 Å, while it is 3.308 Å in $Au_3(MeN{=}COMe)_3$. The average C−Au−N angle within $Au_3(PhCH_2N{=}COMe)_3$ is 176°, the average C−Au bond length is 1.97 Å, and the average Au−N bond length is 2.04 Å.

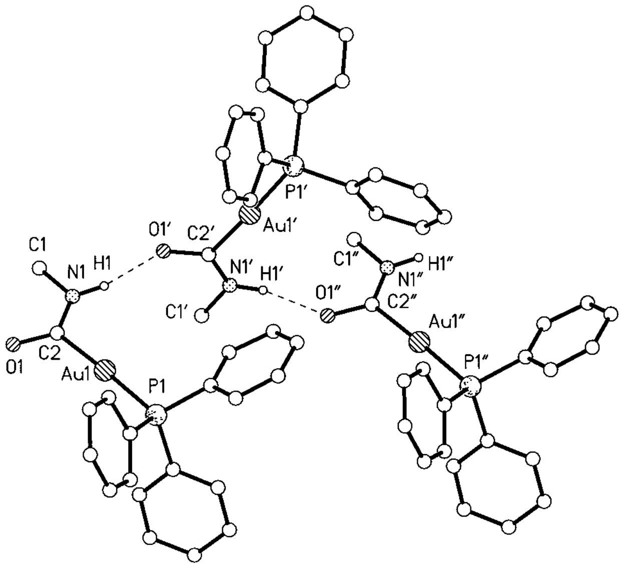

**Figure 2.** View of the packing of three molecules of $Ph_3PAuC(O)NHMe$ which shows the hydrogen bonding between them.

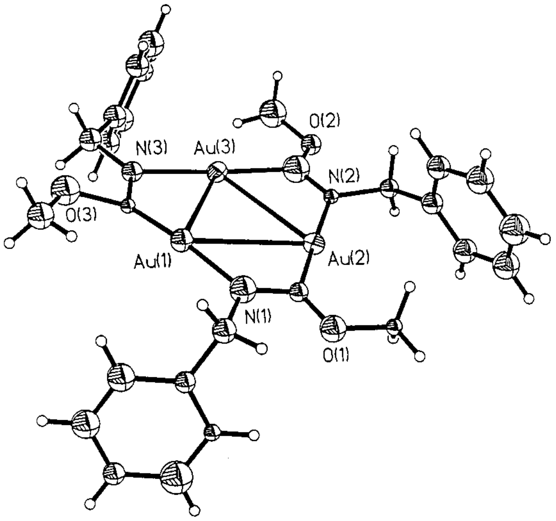

**Figure 3.** Perspective view of one molecule of $Au_3(PhCH_2N{=}COMe)_3$ with 50% thermal contours for all non-hydrogen atoms. The hydrogen atoms are shown as open circles; the remaining unlabeled atoms are carbon atoms. The seven other molecules in the asymmetric unit have similar but not identical structures.

**Table 2.** Selected Interatomic Distances and Angles in $Au_3(PhCH_2N{=}COMe)_3$

| | av | range |
|---|---|---|
| | Bond Lengths (Å) | |
| Au···Au | 3.32(3) | 3.248(3)−3.363(3) |
| Au−C | 1.97(7) | 1.78(4)−2.07(5) |
| Au−N | 2.04(4) | 1.98(5)−2.16(4) |
| | Bond Angles (deg) | |
| Au···Au···Au | 60.0(9) | 58.26(6)−61.61(7) |
| C−Au−N | 176(2) | 172(2)−179(2) |

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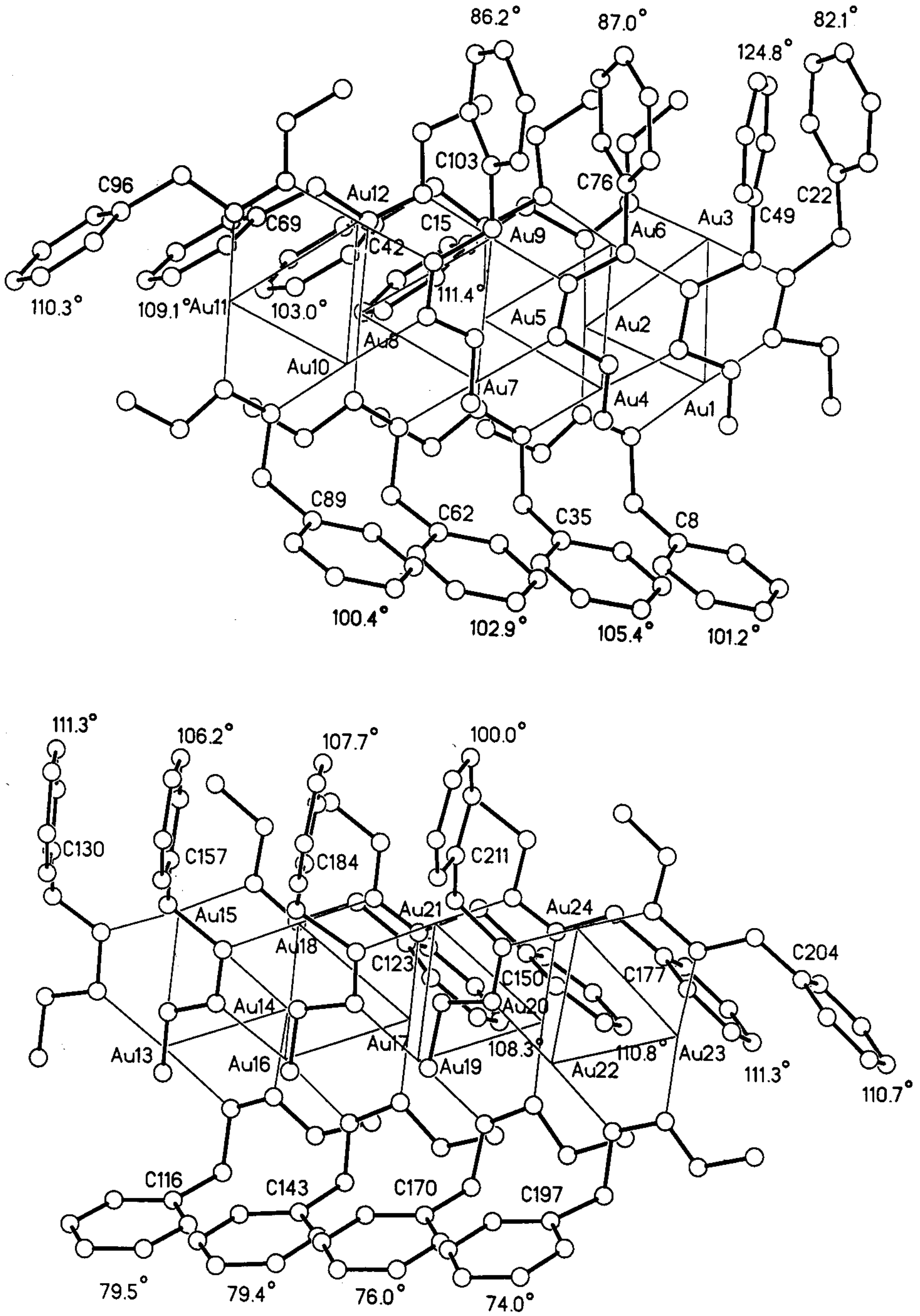

**Figure 4.** View of the molecular packing in $Au_3(PhCH_2N{=}COMe)_3$. The orientations of the phenyl rings of the benzyl groups are shown by giving the dihedral angles between these rings and those of the adjacent $Au_3$ plane.

There are no short aurophilic contacts between the $Au_3(PhCH_2N{=}COMe)_3$ molecules in the solid state, and the columnar structure observed for $Au_3(MeN{=}COMe)_3$ is not present in $Au_3(PhCH_2N{=}COMe)_3$. Figures 4 and 5 show aspects of the packing of the eight independent molecules within this solid. As seen in Figure 5, the closest contact between gold atoms of different molecules is 3.662 Å. Substituents on the periphery of molecules of type **1** appear to affect the extent of aurophilic interactions between these triangular complexes. With the smallest substituents, methyl groups, **1** (R, R′ = Me) adopts the prismatic columnar structure. In **1** with *R* = ethyl and R′ = *p*-tolyl the complex assumes a solid state structure in which pairs of triangular complexes meet in face-to-face fashion through two close (3.244(1) Å) contacts.[21] In $Au_3(PhCH_2N{=}COMe)_3$ there are no close Au···Au contacts at all.

A remarkable feature of this solid is the existence of eight independent copies of the same molecule in the asymmetric unit. As seen in Figure 5, the eight different $Au_3$ triangles are spaced differently with the closest Au···Au contacts between adjacent triangles ranging from 3.662 to 4.100 Å. The essential differences within the individual molecules in the asymmetric unit (beyond the slight differences in Au···Au and metal−ligand bond distances) are the positions of the benzyl groups and the nearby methyl groups. There is a slight twisting of the orientations of these benzyl groups which differentiate one molecule from another. This variation in benzyl group orientation is shown in Figure 5.

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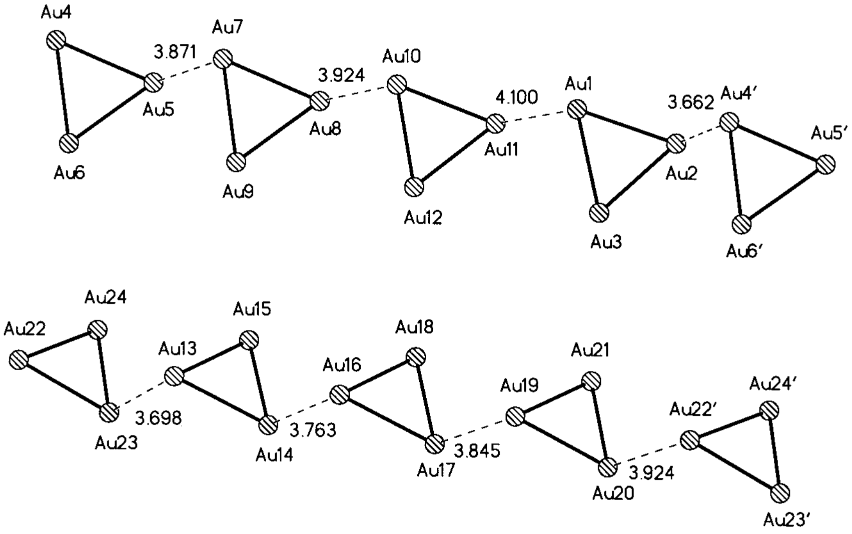

**Figure 5.** View of the molecular packing that emphasizes the interactions between the triangular units in $Au_3(PhCH_2N{=}COMe)_3$ . Only the positions of the gold atoms are shown.

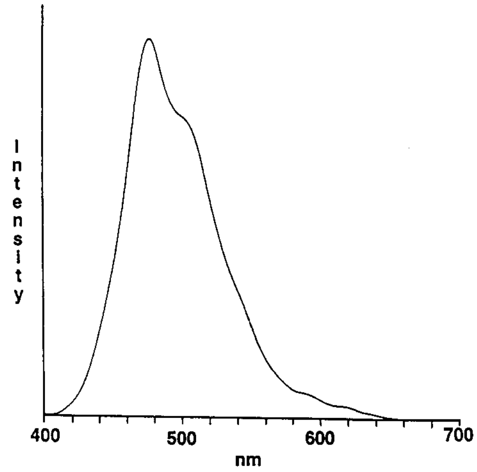

**Figure 6.** Emission spectrum of solid $Ph_3PAuC(O)NHMe$ with excitation at 310 nm.

The existence of multiple discrete molecules appearing within the asymmetric unit of a crystal is not a phenomenon unique to this material, nor is eight the largest number of discrete molecules known within an asymmetric unit. Structures are reported in the Cambridge Structural Database with 12,[22,23] 15,[24] 16,[25,26] and even 32[27] molecular units within the asymmetric unit of the crystal.

**Excitation and Emission Spectra.** Both $Ph_3PAuC(O)NHMe$ and $Au_3(PhCH_2N{=}COMe)_3$ are luminescent at room temperature as solids, but neither shows the solvoluminescence that is observed for $Au_3(MeN{=}COMe)_3$. The room temperature emission spectrum of solid $Ph_3PAuC(O)NHMe$ is shown in Figure 6. The excitation wavelength for the emission spectrum was 310 nm. The wavelength of maximum emission for this complex is centered over a broad region between 475 and 510 nm and is not a function of the excitation wavelength provided that the source wavelength is not above approximately 350 nm. Above this excitation threshold, the complex is essentially nonemissive. The excitation spectrum for this complex shows a broad maximum at 310 nm with a shoulder at 260 nm. A number of two-coordinate gold(I) complexes with aromatic phosphine ligands have been found to be luminescent, and analysis of the luminescence has shown it to arise from phenyl-localized states.[28−30]

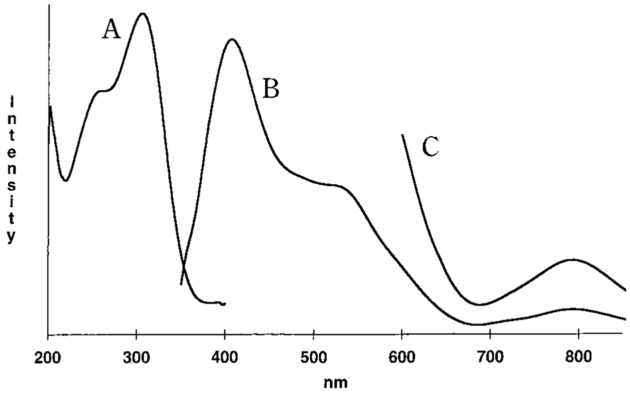

**Figure 7.** (A) Excitation spectrum for solid $Au_3(PhCH_2N{=}COMe)_3$ with emission monitored at 525 nm. (B, C) Emission spectrum of solid $Au_3(PhCH_2N{=}COMe)_3$ with excitation at 255 nm.

The solid state excitation and emission spectra for $Au_3(PhCH_2N{=}COMe)_3$ are shown in Figure 7. The excitation spectrum shows a maximum at 306 nm with a shoulder at 255 nm. The emission spectrum displays at least three prominent features. The emission maximum at 404 nm is followed by a shoulder at 525 nm, and there is a third, low-energy feature centered at 793 nm. This last feature is enhanced in trace C, where the excitation slit widths were widened. The complexity of this emission spectrum is not unexpected given the complexity of the molecular solid with eight different copies of the molecule in the asymmetric unit. The solution-phase emission spectrum of $Au_3(PhCH_2N{=}COMe)_3$ in chloroform exhibits two

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closely spaced features at 482 and 508 nm that roughly correlate with the two features which appear as shoulders in the solid state emission spectrum. The absorption spectrum in chloroform solution reveals absorption maxima at 290 and 264 nm with molar absorptivities of $2.5 \times 10^3$ and $7.7 \times 10^3$ $M^{-1}$ $cm^{-1}$, respectively. These features are similar to those seen in the absorption spectrum of **1** in chloroform solution and are likely to be due to metal-to-ligand charge transfer.[14]

## Experimental Section

**Preparation of Compounds.** All solvents were dried and distilled prior to use. Benzyl isocyanide was purchased from Aldrich Chemicals and used without further purification. Methyl isocyanide was purchased from Karl Industries. $Ph_3PAuCl$ was also synthesized via the standard route from tetrachloroauric acid in ethanol.[31]

**A. $Ph_3PAuC(O)NHMe$.** A 1.41 g (2.85 mmol) portion of $Ph_3PAuCl$ was added to a solution of 0.165 g (2.95 mmol) of potassium hydroxide in 48 mL of water to yield an opaque suspension. Methyl isocyanide, 0.20 mL (3.0 mmol), was added dropwise to the white suspension. The suspension quickly dissolved, and within 30 s a new colorless, highly crystalline material precipitated. Over the course of a few minutes this material began to degrade and formed a film of metallic gold on the surface of the container. The crystalline material was collected by filtration, dissolved in a minimum of dichloromethane, and recrystallized by the addition of excess diethyl ether. The resultant solid was washed three times with 30 mL portions of diethyl ether and dried under vacuum in the dark (yield: 1.26 g, 86%). Single crystals of X-ray diffraction quality were grown from dilute dichloromethane/diethyl ether solution at low temperature in a dry ice/acetone bath (~195 K). The infrared spectrum shows a C−N stretch at 1478 $cm^{-1}$ and a C−O stretch at 1433 $cm^{-1}$.

**B. $Au_3(PhCH_2N{=}COMe)_3$.** A 1.39 g (2.81 mmol) portion of $Ph_3PAuCl$ was suspended in 20 mL of methanol. A solution of 0.16 g (2.8 mmol) of potassium hydroxide dissolved in 15 mL of methanol was added to this mixture. Subsequently, 0.40 mL (3.4 mmol) of benzyl isocyanide was added dropwise to this suspension over the course of 5 min. Upon completion of this addition, the suspension dissolved to give an off-white solution, which persisted for approximately 30 min. Subsequently a white precipitate formed. This white, crystalline product was collected by filtration, washed with methanol and diethyl ether, and then dried under vacuum (yield: 0.6973 g, 72%). Room temperature $^1H$ NMR in chloroform-*d* yielded an unresolved multiplet at 7.27 ppm and singlet resonances at 4.22 and 3.38 ppm for the aromatic, methoxy, and methylene protons of the complex. X-ray quality crystals were grown by the slow diffusion of a methanol antisolvent into a solution of $Au_3(PhCH_2N{=}COMe)_3$ in chloroform at room temperature.

**Physical Measurements.** $^1H$ NMR spectra were recorded for chloroform-*d* solutions on a General Electric QE-300 NMR spectrometer operating at 300 MHz with an external tetramethylsilane standard and the high-field positive convention for chemical shifts. Infrared spectra were recorded as pressed KBr pellets or mineral oil mulls on a Matteson Galaxie Series FTIR 3000 spectrometer. Electronic absorption spectra were recorded using a Hewlett-Packard 8450A diode array spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrophotometer.

**X-ray Crystallography. A. Data Collection. 1. $Ph_3PAuC(O)NHMe$.** A colorless needle was mounted on a glass fiber with silicon grease and placed in the cold stream of the Siemens P4/RA copper rotating anode diffractometer equipped with a nickel monochromator and a Siemens LT-2 low-temperature device operating at 133(2) K. Unit cell parameters were determined by least-squares refinement of 50 reflections with $30° < 2\theta < 40°$. The axial lengths and monoclinic crystal system were verified by examination of axial photographs. Check reflections (2, every 198 reflections) showed only random fluctuations (<2%) in intensity throughout the data collection. The data were corrected for absorption, Lorentz, and polarization effects. Crystal data are found in Table 3.

**Table 3.** Crystal Structure Data

| | $Ph_3PAuC(O)NHMe$ | $Au_3(PhCH_2N{=}COMe)_3$ |
|---|---|---|
| formula | $C_{20}H_{19}Au_1N_1O_1P_1$ | $C_{27}H_{30}Au_3N_3O_3$ |
| fw | 517.30 | 1035.44 |
| space group | $P2_1/c$, monoclinic | $P2_1$, monoclinic |
| *a*, (Å) | 8.993(2) | 17.311(6) |
| *b*, (Å) | 22.583(5) | 34.761(10) |
| *c*, (Å) | 8.932(2) | 18.052(6) |
| α, (deg) | 90 | 90 |
| *β*, (deg) | 98.22(2) | 94.73(2) |
| *γ*, (deg) | 90 | 90 |
| *V* (Å$^3$) | 1795.4(7) | 10 826(6) |
| *T* (K) | 123(2) | 133(2) |
| *Z* | 4 | 16 |
| $d_{calc}$ (Mg/m$^3$) | 1.914 | 2.541 |
| radiation (Å) | $\lambda$(Cu Kα) = 1.541 78 | $\lambda$(Mo Kα) = 0.710 73 |
| $\mu$, (mm$^{-1}$) | 16.3 | 16.3 |
| R1[a] | 0.0455 | 0.0735 |
| wR2[b] | 0.0755 | 0.1775 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, observed data ($>4\sigma I_o$). [b] $wR2 = [\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]]^{1/2}$, all data.

**2. $Au_3(PhCH_2N{=}COMe)_3$.** A colorless needle was mounted on a glass fiber with silicon grease and placed into the 123(2) K nitrogen stream of a Siemens R3m/v diffractometer that was equipped with graphite-monochromated Mo Kα radiation and a modified Enraf-Nonius low-temperature device. Unit cell parameters were determined by least-squares refinement of 50 reflections with $4.7° < 2\theta < 37°$. The axial lengths and monoclinic crystal system were verified by examination of axial photographs. Check reflections (2, every 198 reflections) showed only random fluctuations (<2%) in intensity throughout the data collection. The data were corrected for absorption, Lorentz, and polarization effects. Crystal data are found in Table 3.

**B. Solution and Structure Refinement. 1. $Ph_3PAuC(O)NHMe$.** Calculations were performed using SHELXTL V.5.03 software. Tables of neutral atom scattering factors and absorption coefficients are from a standard source.[32] The positions of all atoms were located via direct methods. The gold, phosphorus, oxygen, and nitrogen atoms were refined with anisotropic thermal parameters, while the remaining atoms were refined isotropically. Hydrogen atoms were placed on all carbon atoms where chemically justified, with the exception of H(1), which was located on the Fourier difference map. A riding model was used to calculate the hydrogen atom positions with the C−H vectors fixed at 0.96 Å and the thermal parameters set at 1.2 times that of the bound carbon atom. An empirical absorption correction was applied.[33] The largest remaining peak in the electron difference map was 0.96 Å from Au(1) and was 1.15 e/Å$^3$.

**2. $Au_3(PhCH_2N{=}COMe)_3$.** Refinement was carried out using block diagonal least squares with individual trimers in each block. The absolute structure was determined by estimation of the absolute structure parameter, *x*, in the final structure factor calculation.[34] The value obtained was −0.01(3), which indicates that the correct choice was made. Only the gold atoms were assigned anisotropic thermal ellipsoids. The C−C bond distances within the benzyl group were fixed at 1.39 Å. An empirical absorption correction was applied.[32] The largest remaining peak in the electron difference map was 1.34 Å from Au(20) and was 2.81 e/Å$^3$.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for $Ph_3PAuC(O)NHMe$ and $Au_3(PhCH_2N{=}COMe)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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