

Trinuclear Gold(I) Pyrazolate Complexes Exhibiting Hexagonal Columnar Mesophases with Only Three Side Chains¹

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Reaction of long-chain alkyl-substituted pyrazoles with AuCl(SMe₂) yields trinuclear gold(I) pyrazolate complexes, two of which exhibit monotropic mesophases. Optical microscopy and/or X-ray diffraction studies show that these compounds form hexagonal columnar mesophases. They are only the third examples of discotic mesogens possessing only three aliphatic side chains. The X-ray crystal structure of one compound reveals that two molecules form a "dimer" mainly through intermolecular Au–Au interactions. The "dimers" are stacked in a tilted fashion to form columns along the *b* axis in the crystal phase, which are presumably rearranged to the hexagonal columnar structure in the mesophase.

Introduction

Metallomesogens, liquid crystals containing metal ions, have attracted much attention in expectation of unique properties due to metals in addition to the intrinsic liquid crystalline properties of organic compounds. A large number of metallomesogens containing various metal ions have been prepared and their optical, magnetic, and electronic properties have been reported.² Although multinuclear metal complexes often give rise to important physical properties such as ferromagnetic coupling and mixed oxidation states,³ few liquid crystals containing multiple metal centers have been investigated.⁴ We therefore decided to explore novel liquid crystalline materials containing multinuclear metal cores. Among several potential candidates for multinuclear metallomesogens, tri(μ -pyrazolato-*N,N*)trigold-

(I)⁵ was chosen for study because of its easy synthesis, high thermal stability, and, above of all, unique structure. We thought that its large trigonal planar geometry may lead to a discotic mesophase if suitable substituents are introduced on the pyrazole rings. Indeed, when we introduced an octyl group at the 4 position of the pyrazole ligand, the resulting tri(μ -pyrazolato-*N,N*)trigold(I) complex exhibited a hexagonal columnar mesophase. Encouraged by this observation, we synthesized a series of analogous compounds and investigated their mesogenic properties. While our work was near completion, however, similar trinuclear gold pyrazolate complexes exhibiting hexagonal columnar mesophases were reported.⁶ Our compounds are not only different from the reported gold complexes but also quite unique because our compounds have *only three aliphatic side chains*. There are only two other examples of discotic mesogens that possess only three aliphatic side chains.⁷ We were also able to determine an X-ray crystal structure of one of the mesogenic compounds. Herein we present the details of our own work: syntheses, mesogenic properties, and X-ray crystal structures of the mesogenic trinuclear gold pyrazolate complexes.

Results and Discussion

Synthesis. The synthesis of the tri(μ -pyrazolato-*N,N*)trigold(I) complexes **1–5** is shown in Scheme 1.

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Scheme 1

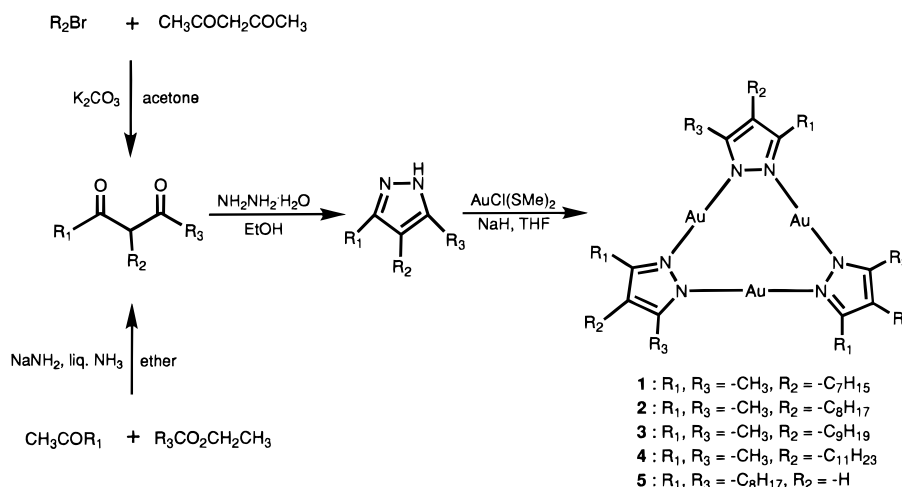


Table 1. Phase Behavior of 1–5

no.	phase transition behavior ^a	
	heating	cooling
1	K 71 (4.6) K' 116 (10.3) I	I 112 (2.9) D 99 (7.6) K
2	K 56 (1.5) K' 112 (25.7) I	I 85 (2.9) D 61 (22.0) K
3	K 82 (21.6) K' 90 (2.1) I	I 39 (17.8) K
4	K 87 (5.9) I	I 14 (17.5) K
5	K 58 (6.1) K' 80 (32.4) I	I 52 (36.9) K

^aThe transition temperatures (°C) and enthalpies (J/g, in parentheses) were determined by DSC (scan rate 10 °C/min). K, K', crystalline phase; D, discotic phase; I, isotropic phase.

The pyrazoles with long alkyl substituents at their 4 position or 3 and 5 positions were prepared according to literature procedures with minor modifications.⁸ The substituted pyrazoles react with $AuCl(SMe)_2$ to produce the tri(μ -pyrazolato-*N,N*)trigold(I) complexes **1–5** in ~75% yield. All the compounds were characterized by ¹H NMR, mass, and IR spectroscopy and elemental analysis. These compounds are different from the ones reported recently by Oro and Serrano⁶ in that their compounds have substituted phenyl groups at 3 and 5 positions of the pyrazole rings.

Mesogenic Properties. The thermal behavior of the trinuclear gold complexes is listed in Table 1. Complexes **1** and **2**, which have a heptyl group and an octyl group, respectively, at 4 position of each pyrazole ring, show monotropic mesophases. Upon cooling, for example, **1** exhibits a transition from an isotropic phase to a mesophase at 112 °C and transition from the mesophase to a crystalline phase at 99 °C (the transition temperatures were measured by DSC). Longer alkyl substituents of **2** make the transition temperatures for **2** lower than those for **1** and results in a mesophase between 61 and 85 °C for **2**. They are only the third examples of discotic mesogens that possess only three aliphatic side chains.⁷ This mesogenic behavior appears to be related to formation of a weak "dimer" due to Au–Au interactions, which will be discussed later. However, neither **3** and **4**, the congeners with even longer alkyl chains, nor **5**, having octyl groups on the 3 and 5 positions of the pyrazole, exhibit a mesophase. Upon cooling they change directly from isotropic phases to



Figure 1. Texture of **2** under a polarizing microscope at 82 °C obtained after cooling from the isotropic phase to the given temperature.

crystalline phases.⁹ It is not well understood at this time why **2** and **3** show dramatically different mesogenic behavior although the only structural difference between **2** and **3** is one additional CH_2 unit in each alkyl chain in **3**.

Examination by polarizing optical microscopy confirms that **1** and **2** form a monotropic mesophase on cooling. In the mesophases **1** and **2** exhibit a spiral and a leaflike texture, respectively, which are both characteristic of hexagonal columnar phases. Figure 1 shows the photomicrograph of **2**, taken at 82 °C on cooling from the isotropic liquid. The mesogenic behavior of these complexes is reproducible during several heating and cooling cycles.

To obtain information on the structure of **2** in the mesophase, X-ray diffraction analysis was carried out at 80 °C. The X-ray photograph (Figure 2) taken with a flat plate camera unambiguously demonstrates the hexagonal columnar structure of **2**. The X-ray diffraction pattern (Figure 3) of **2** is also consistent with the hexagonal columnar arrangement of the complexes in the mesophase. The first three reflections in the low-

(9) A reviewer suggested that we study the thermal behavior of these complexes under different controlled cooling rates. Even when the cooling rate was switched to 0.2 °C min⁻¹, however, the same phase behavior was observed, except that the transition temperatures were shifted to higher temperatures by ~20 °C in all complexes.

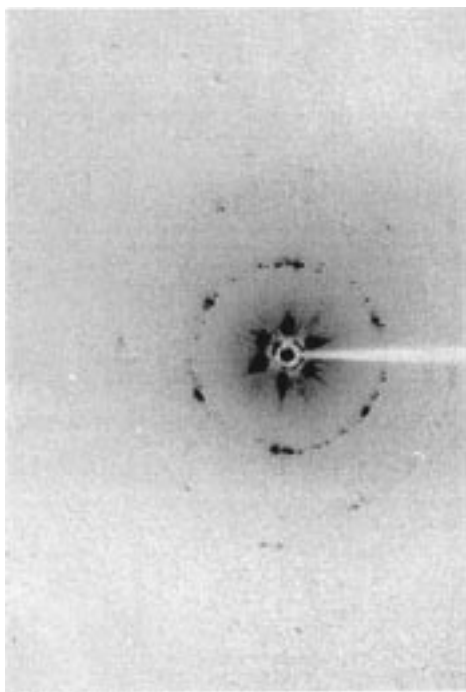


Figure 2. X-ray photograph of **2** taken with a flat-plate camera at 80 °C.

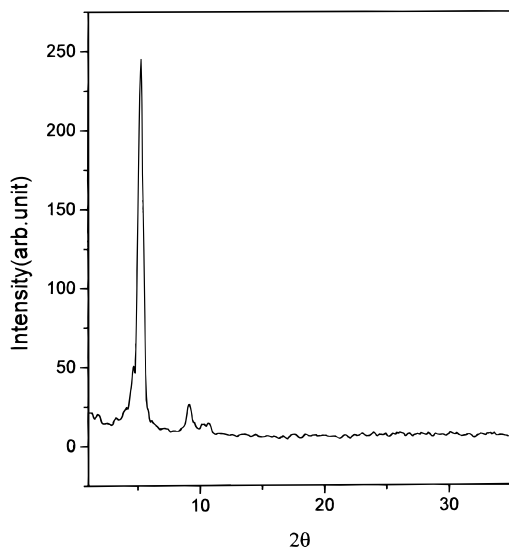


Figure 3. X-ray diffraction pattern of **2** taken at 80 °C.

angle region with the d -spacing ratio of 1:1/ $\sqrt{3}$:1/2 can be assigned to (10), (11), and (20) reflections of a two-dimensional hexagonal array with a lattice constant $a = 19.5$ Å. In Figure 3, however, no broad halo in the high angle region, corresponding to the liquidlike arrangement of alkyl tails, is evident, presumably because the low-angle scattering from the hexagonal arrangement of the gold complex is predominant.

Crystal Structure of 2. The X-ray crystal structure of **2** was determined at room temperature in order to compare its structures in the mesophase and the crystal phase. Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The crystal structure of **2** consists of the discrete trimeric molecules depicted in Figure 4. Selected bond distances and angles are given in Table 2. As expected, the core structure of **2** is essentially the same as that of $[\text{Au}(\mu\text{-}3,5\text{-Ph}_2\text{pz})]_3$.^{5c} Three pyrazolate rings and three Au atoms form a large equilateral

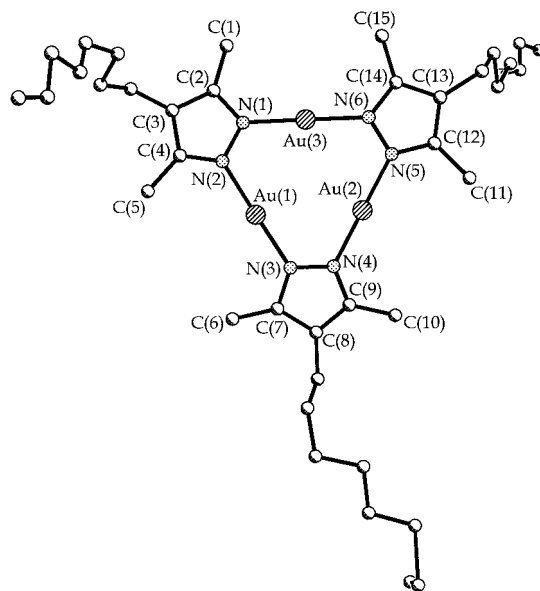


Figure 4. Molecular structure of **2** in the crystal phase. Octyl side chains are disordered; only one preferred conformation for each side chain is displayed.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**^a

Au(1)···Au(2)	3.354(1)	Au(1)–N(2)	1.98(1)
Au(1)···Au(3)	3.356(1)	Au(1)–N(3)	1.99(1)
Au(2)···Au(3)	3.335(1)	Au(2)–N(5)	1.97(1)
Au(2)···Au(3')	3.255(2)	Au(2)–N(4)	1.99(2)
Au(3)···Au(2')	3.255(2)	Au(3)–N(1)	1.98(2)
		Au(3)–N(6)	1.97(1)
Au(2)···Au(1)···Au(3)	59.61(3)	N(2)–Au(1)–N(3)	178.5(6)
Au(3)···Au(2)···Au(1)	60.22(3)	N(5)–Au(2)–N(4)	176.9(6)
Au(2)···Au(3)···Au(1)	60.17(3)	N(1)–Au(3)–N(6)	177.0(6)

^a Primed atoms are related to the corresponding unprimed atoms by the symmetry transformation $-x + 1, -y, -z + 2$.

triangular core with a side of ~ 10 Å. All the atoms on the pyrazolate rings and the Au atoms lie in a plane. The three Au atoms also form an almost perfect equilateral triangle with Au···Au separations ranging from 3.335(1) to 3.356(1) Å. The Au–N distances are not exceptional with an average Au–N distance of 1.98(2) Å. The octyl groups attached to the pyrazolate ligands are severely disordered, as often found in this type of molecule.

The most interesting feature of the structure is that the trinuclear gold complex forms a "dimer" mainly through intermolecular Au–Au contacts with a Au···Au separation of 3.255(2) Å (Figure 5). The mean distance between the planar cores of the "dimer" is 3.238(2) Å. Such weak "dimer" formation appears to be responsible for the discotic mesophase formation of **2**, which has only three aliphatic side chains. By forming a star-shaped "dimer" from two triangular monomer, it behaves like a planar disk with six side chains (Scheme 2). Recently, gold isocyanide complexes with three alkyl chains were reported to display columnar hexagonal phases at room temperature.^{7b} The authors proposed the formation of a disk by two molecules of the complex in antiparallel disposition. Similar pairing of a partial disk shape molecule to produce a disk shape has been suggested to be responsible for the formation of a stable discotic mesophase.¹⁰

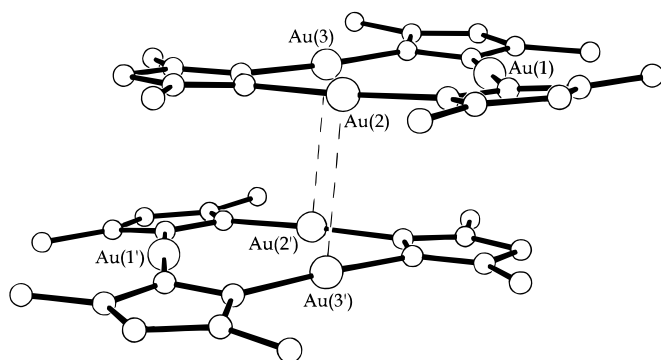


Figure 5. Intermolecular Au–Au interactions [$\text{Au}(2)\cdots\text{Au}(3) = \text{Au}(2)\cdots\text{Au}(3) = 3.255(2) \text{ \AA}$] in the crystal structure of **2**; mean interplanar distance, $3.238(3) \text{ \AA}$. Octyl groups attached to the 4 position of the pyrazole rings are omitted for clarity.

Scheme 2

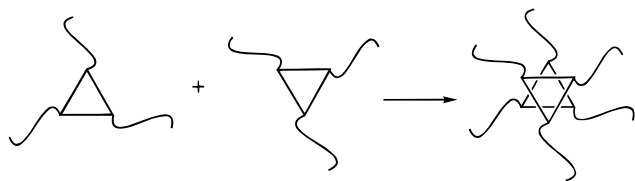


Figure 6 displays the packing diagram of **2** viewed down along the b axis. The “dimers” form a tilted columnar stack along the b axis with an average distance of 4.64 \AA . The angle between the normal of the planar core and the direction of the column is 37.6° . While two of the six alkyl chains of the “dimer” are extended in a plane parallel to the gold pyrazolate core, the rest of them are nearly perpendicular to the planar core. The former alkyl chains lie above and below the triangular gold pyrazolate cores of the neighboring “dimers”, whereas the latter alkyl chains are stacked on each other to form alkyl chain layers between stacks of the gold pyrazolate cores.

Scheme 3 compares the structures of the crystal and liquid crystalline phases. One possible scenario for the structural change associated with the phase change is that as the compound undergoes phase changes from crystal to liquid crystal, the tilted columnar stacks of the “dimer” are converted to flat columnar stacks. Consequently, the mean distance between the stacks along the a axis of the crystal increases, while those along the c axis decrease to form the hexagonal arrangement in the liquid crystal phase. Although it remains to be seen whether the weak “dimer” structure is maintained in the liquid crystalline phase, such intermolecular Au–Au interactions may play an important role in forming the hexagonal columnar structure of **2** in the mesophase.¹¹

In summary, we synthesized new trinuclear gold complexes that exhibit monotropic mesophases. The hexagonal columnar structures of the mesophases were

identified by optical microscopy and/or X-ray diffraction. They are only the third examples of discotic mesogens that possess only three aliphatic side chains. The X-ray crystal structure reveals a weak “dimer” formation through intermolecular Au–Au interactions. This “dimer” behaves as a planar disk with six side chains. Stacking of the “dimer” may lead to the hexagonal columnar structures in the mesophases. We continue to study liquid crystalline materials containing this and other multinuclear metal ion cores.

Experimental Section

Measurements. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer in CDCl_3 solution. Mass spectrometry was performed by the Nebraska Center for Mass Spectrometry. Elemental analyses were performed on a Perkin-Elmer 240B microanalyzer. The optical textures of the mesophases were studied with a Zeiss JENALAB-pol polarizing microscope equipped with a Linkam LTS 350 hot stage and a TMS 93 temperature controller. The transition temperatures and enthalpies were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter operated at a scanning rate of $10^\circ\text{C min}^{-1}$. X-ray diffraction studies were performed in the transmission mode with nickel-filtered $\text{Cu K}\alpha$ radiation supplied by a Rigaku Denki generator operating at 40 kV and 40 mA. To investigate structural changes on heating, the samples were held in an aluminum sample holder which was sealed with windows of $5 \mu\text{m}$ thick Kapton films on both sides. The samples were heated with two cartage heaters, and the temperature of the samples was monitored by a thermocouple placed close to the sample. Background scattering correction was made by subtracting the scattering from the Kapton. A flat film X-ray photograph was taken with a sample which had been spontaneously oriented within a 0.5 mm glass capillary tube.

Synthesis. All reactions were carried out using standard Schlenk techniques under an inert atmosphere of dry argon. Unless otherwise noted, all chemicals and solvents were reagent grade and used without further purification. Tetrahydrofuran (THF) was distilled from its Na/benzophenone ketyl solution. 3,5-Dimethyl-4-alkylpyrazoles (alkyl = heptyl, octyl, nonanyl, and undecanyl) and 3,5-dioctylpyrazole were prepared according to literature procedures with minor modifications.⁸ $\text{AuCl}(\text{SMe}_2)$ was also prepared according to a known method.¹²

Tris(μ -3,5-dimethyl-4-heptylpyrazolato-*N,N*)trigold(I) (1). A solution of 3,5-dimethyl-4-heptylpyrazole (0.16 g, 0.70 mmol) and sodium hydride (0.10 g, 4.17 mmol) in dry tetrahydrofuran (40 mL) was vigorously stirred for 30 min. After $\text{AuCl}(\text{SMe}_2)$ (0.18 g, 0.70 mmol) was added, the solution was stirred at room temperature for 70 h. After addition of methanol (40 mL), the solution was kept in a refrigerator overnight. Precipitate was filtered and redissolved in a small amount of THF. The solution was passed through a thin silica pad. The volume of the solution was reduced by evaporation under reduced pressure. Addition of methanol induced precipitation of the crystalline product. The product was filtered and dried in vacuo (0.20 g; 73%). ^1H NMR, δ_{H} (300 MHz, CDCl_3 , TMS): 0.88 (m, 9H), 1.26 (s, 24H), 1.39 (s, 6H), 2.12 (s, 18H), 2.31 (t, 6H). Found: C, 37.05; H, 5.88; N, 7.17. Calcd for $\text{C}_{36}\text{H}_{63}\text{N}_6\text{Au}_3$: C, 36.93; H, 5.42; N, 7.18.

Tris(μ -3,5-dimethyl-4-octylpyrazolato-*N,N*)trigold(I) (2). This compound was prepared by the same method as for **1**. The materials and quantities used are as follows: 3,5-dimethyl-4-octyl-pyrazole (0.13 g, 0.44 mmol), sodium hydride (0.11 g, 4.58 mmol), and $\text{AuCl}(\text{SMe}_2)$ (0.13 g, 0.44 mmol). Yield: 0.14 g (76%). ^1H NMR, δ_{H} (300 MHz, CDCl_3 , TMS): 0.88 (m, 9H), 1.25 (s, 30H), 1.39 (s, 6H), 2.17 (s, 18H), 2.33 (t, 6H). IR ν/cm^{-1} (KBr, disk): 2919, 1849, 1514, 1447, 1371,

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(11) In Figure 3, the sharp low-angle peaks due to the hexagonal columnar arrangement of the gold complex are so intense that the high-angle region appears to be almost featureless. It is therefore difficult to judge any possible intracolumnar ordering, such as persistence of the “dimer” structure in the mesophase, from the X-ray diffraction data.

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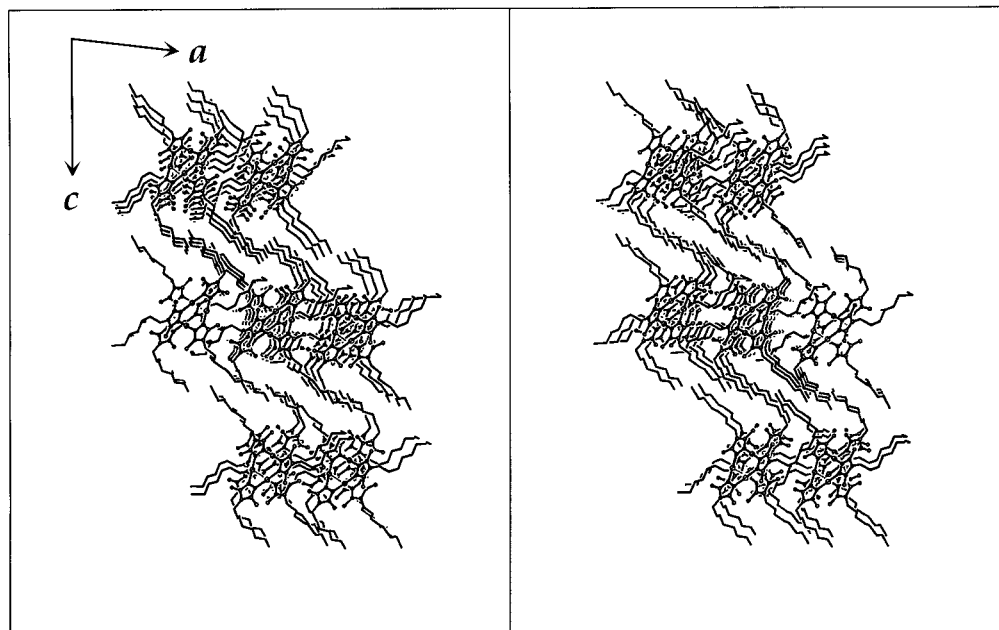
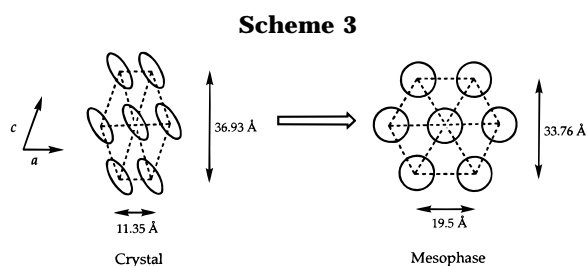


Figure 6. Stereoview of packing diagram of **2** in the crystal phase showing tilted columnar packing of the planar core along the *b* axis.



1060, 802. FAB-MS: m/z 1213.4 ($M + 1$). Found: C, 38.28; H, 5.82; N, 6.78. Calcd for $C_{39}H_{69}N_6Au_3$: C, 38.62; H, 5.73; N, 6.93.

Tris(μ -3,5-dimethyl-4-nonylpyrazolato-*N,N*)trigold(I) (3). This compound was prepared by the same method as for **1**. The materials and quantities used are as follows: 3,5-dimethyl-4-nonylpyrazole (0.21 g, 0.81 mmol), sodium hydride (0.12 g, 5.0 mmol), and $AuCl(SMe_2)$ (0.24 g, 0.81 mmol). Yield: 0.25 g (74%). 1H NMR, δ_H (300 MHz, $CDCl_3$, TMS): 0.88 (m, 9H), 1.25 (s, 36H), 1.39 (s, 6H), 2.17 (s, 18H), 2.33 (t, 6H). Found: C, 40.39; H, 6.65; N, 6.63. Calcd for $C_{42}H_{75}N_6Au_3$: C, 40.20; H, 6.02; N, 6.70.

Tris(μ -3,5-dimethyl-4-undecanylpyrazolato-*N,N*)trigold(I) (4). This compound was prepared by the same method as for **1**. The materials and quantities used are as follows: 3,5-dimethyl-4-undecanyl-pyrazole (0.23 g, 0.78 mmol), sodium hydride (0.11 g, 4.6 mmol), and $AuCl(SMe_2)$ (0.23 g, 0.78 mmol). Yield: 0.26 g (75%). 1H NMR, δ_H (300 MHz, $CDCl_3$, TMS): 0.86 (m, 9H), 1.24 (s, 48H), 1.39 (s, 6H), 2.19 (s, 18H), 2.33 (t, 6H). Found: C, 43.22; H, 7.23; N, 6.20. Calcd for $C_{48}H_{87}N_6Au_3$: C, 43.05; H, 6.55; N, 6.28.

Tris(μ -3,5-dioctylpyrazolato-*N,N*)trigold(I) (5). This compound was prepared by the same method as for **1**. The materials and quantities used are as follows: 3,5-dioctylpyrazole (0.29 g, 1.00 mmol), sodium hydride (0.054 g, 2.3 mmol), and $AuCl(SMe_2)$ (0.28 g, 0.95 mmol). Yield: 0.35 g (75%). 1H NMR, δ_H (300 MHz, $CDCl_3$, TMS): 0.87 (s, 9H), 1.18 (s, 30H), 1.83 (m, 6H), 2.67 (t, 6H), 6.13 (s, 3H). FAB-MS: m/z 1465.9 ($M + 1$). Found: C, 45.98; H, 8.04; N, 5.50. Calcd for $C_{57}H_{105}N_6Au_3 \cdot 2H_2O$: C, 45.60; H, 7.32; N, 5.60.

X-ray Crystal Structure Determination of 2. Crystals of **2** suitable for X-ray work were obtained from slow diffusion

of THF into an ethanol solution of **2**. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The intensities of three standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. The intensity data were corrected for Lorentz and polarization effects and absorption correction was also applied. The structures were solved by direct methods (SHELXS-86) and refined by full-matrix least-squares methods (SHELXL-93). All non-hydrogen atoms, except for those in octyl side chains, were refined anisotropically; carbon atoms of the octyl side chains were refined isotropically. Some of the carbon atoms were disordered; they were modeled as being disordered over two sites. The positions of hydrogen atoms of the methyl groups were idealized ($d(C-H) = 0.96 \text{ \AA}$) and included in the calculations of the structure factors as fixed contributions. No other hydrogen atoms were included. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of attached atom. Crystallographic data of **2**: $C_{36}H_{69}Au_3N_6$, fw = 1212.9, triclinic, $P\bar{1}$, $a = 11.347(2) \text{ \AA}$, $b = 11.637(2) \text{ \AA}$, $c = 18.675(4) \text{ \AA}$, $\alpha = 82.53(3)^\circ$, $\beta = 81.28(3)^\circ$, $\gamma = 66.76(3)^\circ$, $V = 2232.9(8) \text{ \AA}^3$, $Z = 2$, $d_{calc} = 1.804 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $\mu = 98.63 \text{ cm}^{-1}$, $R_1 (I > 2\sigma(I)) = 0.055$, wR_2 (all data) = 0.136 and GOF = 1.06.

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Supporting Information Available: X-ray crystallographic table and listing of atomic coordinates, thermal parameters, bond distances and angles for **2** (7 pages). Ordering information is given on any current masthead page.

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