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Synthesis and Characterization of Square-Planar Tetranuclear Silver and Gold Clusters Supported by a Pyrazole-Linked Bis(N-heterocyclic carbene) Ligand

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The N-heterocyclic carbene (NHC) precursor 3,5-bis((*N*-methylimidazoliumyl)methyl)pyrazole bis(hexafluorophosphate) ($H_3L(PF_6)_2$) reacted with Ag_2O to afford the silver complex $[Ag_4L_2](PF_6)_2\cdot 0.5Et_2O$ (**5**). Reaction of **5** with $Au(Et_2S)Cl$ forms the corresponding Au(I) complex, $[Au_4L_2](PF_6)_2$ (**6**). These complexes were characterized by ^1H NMR, ^{13}C NMR, UV−vis, luminescence spectroscopy, elemental analysis, mass spectrometry, and X-ray crystallography. The two isostructural complexes contain tetrametallic cores which are nearly square planar. Each L behaving as anionic tetradentate ligand links four different metal atoms, and each metal atom is coordinated by a carbenic carbon and a pyrazolate nitrogen atom. Both complexes and the ligand precursor are intensely luminescent in the solid state.

Introduction

The organometallic and coordination chemistry of N-heterocyclic carbenes (NHCs) has become a well-established area of research.[1] Numerous NHC complexes have been reported, and many of them have been successfully used as catalysts in various reactions over the past decade.[2] In recent years, the research interests of metal−NHCs has spread toward many other fields such as material science[3] and medicinal chemistry.[4] Heteroditopic NHC ligands incorporating donating heteroatoms such as the functionalized NHCs bearing various functional groups such as pyridyl,[5] phosphinyl,[6] pyrazolyl,[7] thioether,[8] RO−,[9] imino,[10] etc. have been reported.

Our interests lie in the design and synthesis of transition-metal complexes with metal−metal interactions, which have potentially useful chemical and physical properties such as catalytic behavior and magnetic, optical, and electronic properties.[11] Taking into account the strong σ-donating abilities of NHCs, the pyrazole-linked bis(NHC) ligand as a potentially anionic tetradentate linker would be expected to be a suitable candidate to connect transition metals into organometallic aggregates. In addition, pyrazole and its derivatives are good dinucleating ligands to form bimetallic complexes and allow two metals bonded together with short metal−metal contacts.[12] As a continuation of our studies on the bonding and optical properties of closed-shell heterometallic interactions,[11d,e] herein

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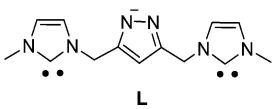
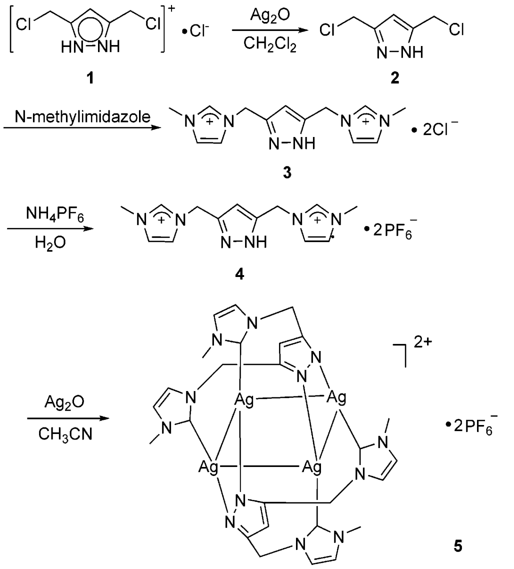
Chart 1. Illustration of the Tetradentate CNNC Ligand



Scheme 1. Synthesis of Imidazolium Salts and Complex 5



we report the synthesis and characterization of novel tetranuclear Ag and Au clusters supported by a pyrazole-linked bis(N-heterocyclic carbene) ligand (Chart 1).

Results and Discussion

Synthesis and NMR Spectra. The direct reaction of 3,5-bis(chloromethyl)pyrazole hydrochloride (**1**) with an excess of *N*-methylimidazolium did not afford the expected imidazolium salt. Free 3,5-bis(chloromethyl)pyrazole (**2**) could not be obtained by neutralization of **1** by bases such as Na_2CO_3, $NaHCO_3$, KOH, NaOH, and Et_3N, probably due to intermolecular polymerization. Compound **2** was produced in high yield by treatment of **1** with Ag_2O. Although it is not economical, this method is efficient. The imidazolium salt **3** was prepared by the nucleophilic substitution of 3,5-bis(chloromethyl)pyrazole with *N*-methylimidazole, shown in Scheme 1. The imidazolium chloride was isolated as a pale yellow hygroscopic solid. Subsequent addition of NH_4PF_6 to the aqueous solution of **3** afforded **4** as a white solid. These compounds were characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy.

Treatment of **4** with Ag_2O in CH_3CN afforded the silver–NHC complex $[Ag_4L_2](PF_6)_2{\cdot}0.5Et_2O$ (**5**). The formulation was determined by elemental analysis and further confirmed by the NMR observations. The reaction is independent of the imidazolium/Ag_2O ratio. Variation of the ratio from 1:0.5 to 1:1.5 gave the same silver compound, and no other silver species were detected by ^1H NMR spectroscopy. The absence of acidic NH and CH proton resonances in its ^1H NMR spectrum illustrates that the ligand is coordinated to silver in a monoanionic bis(NHC) form. Notably, two singlets at 178.1 and 175.8 ppm in the ^{13}C NMR spectrum are seen, which are assigned to NHC carbene carbon resonances. Other ^{13}C resonance signals are consistent with its formulation. It seems that the NHC rings bonded to Ag(1) and Ag(2) are magnetically inequivalent (see Figure 1), probably because anionic pyrazolate is not fully electron-delocalized. Their small chemical shift difference of 23 Hz may not arise from Ag–C coupling. The carbenic ^{13}C resonances of the silver–NHC complexes cover a wide range from 213.7 to 163.2 ppm,[1a] depending on the structural motifs and the ancillary ligands. The Ag–C coupling constants for Ag–NHC complexes are normally in the range of 180–270 Hz. The sole exception was found for a silver–NHC cluster which gave coupling constants of 220 and 47 Hz, assigned to σ- and π-bonding interactions, respectively.[13a] The majority of Ag–NHC complexes exhibit no resolved coupling due to the dynamic behavior in solution and the poor relaxation of the carbenic carbon. The silver complex **5** as an N-heterocyclic carbene reagent was reacted with $Au(SEt_2)Cl$ to yield the corresponding $[Au_4L_2](PF_2)_2$ (**6**) in ca. 50% yield. Attempts to prepare a AgAu mixed cluster by changing the ratio of **5** and $Au(SEt_2)Cl$ failed, and workup only afforded **6** and unreacted **5**. The ^{13}C NMR spectrum exhibited a singlet at 164.9 ppm. The carbenic carbon resonances ranging from 166 to 195 ppm for Au–NHC complexes having C–Au–X (X = halide) and C–Au–C motifs have been observed.[4a]

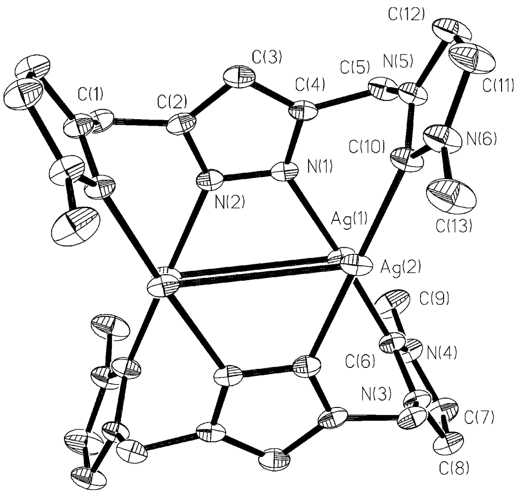


Figure 1. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Ag(1)–Ag(2) = 3.208(2), Ag(1)–Ag(2)#1 = 3.295(2), Ag(1)–C(6) = 2.072(6), Ag(1)–N(1) = 2.093(5), Ag(2)–C(10) = 2.054(7), Ag(2)–N(2)#1 = 2.083(5); C(6)–Ag(1)–N(1) = 176.7(2), C(10)–Ag(2)–N(2)#1 = 179.6(2), Ag(1)–Ag(2)–Ag(1)#1 = 91.90(4), Ag(2)–Ag(1)–Ag(2)#1 = 88.10(4). Symmetry transformations used to generate equivalent atoms: (#1) $-x + 2$, $-y + 1$, $-z + 1$; (#2) $-x + 2$, $-y + 2$, $-z$.

These silver and gold complexes are quite stable toward air and moisture, and ^1H NMR spectra show no changes after standing for 5 months. In the ES-MS spectrum of **5** in acetonitrile, the most intense peak was observed at *m*/*z* 1086.8, corresponding to $[Ag_4L_2(PF_6)]^+$ (calcd *m*/*z* 1087.0), whereas the peak at *m*/*z* 960.9 could be assigned to $[Ag_4L_2(H_2O)]^+$ (calcd *m*/*z* 960.1). Interestingly, the peaks at *m*/*z* 471.1, 659.0, and 768.4 were also observed and ascribed to $[Ag_2L]^+$ (calcd *m*/*z* 471.0), $[Ag_2L(PF_6)(CH_3CN)]^+$ (calcd *m*/*z* 657.1), and $[Ag_2L_2(CH_3CN)]^+$ (calcd *m*/*z* 767.4), respectively. Similarly, the electrospray mass spectrum of **6** in acetonitrile gave a peak at *m*/*z* 1443.1 assigned to $[Au_4L_2(PF_6)]^+$ (calcd *m*/*z* 1443.4). The results presented above suggest that the tetranuclear cores are maintained in the gas phase and in solution.

The details of the molecular structure of **5** in the solid state were established by an X-ray diffraction study. The molecular

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structure of **5** is depicted in Figure 1. The asymmetric unit is composed of half of the molecule with two independent silver atoms and one 3,5-bis((*N*-methylimidazolidiumyl)methyl)-pyrazolate. The compound has an orthogonal planar core in which four silver atoms are held together by two ligands. Both L ligands link four different silver atoms by using two pyrazolate nitrogen and two NHC carbon atoms acting as monoanionic tetradentate ligands. All silver atoms are coordinated by a NHC and a pyrazolate nitrogen atom in a nearly linear coordination geometry with C−Ag−C angles of 176.7(2) and 179.6(2)°. The silver−carbene distances of Ag(1)−C(6) and Ag(2)−C(10) are 2.072(6) and 2.054(7) Å, respectively, consistent with the known values of other silver−NHC complexes. The four silver atoms form a rectangular ring because of argentophilic attraction and the functionality of the pyrazolate-linked NHC ligands with relatively long Ag−Ag contacts of 3.208(2) and 3.295(2) Å, slightly shorter than the sum of van der Waals radii (3.4 Å). These four atoms are coplanar, as evidenced by the sum of each two adjacent Ag−Ag−Ag angles being equal to 180°. The dihedral angles between pyrazolate rings and NHC rings across each silver atom range from 84 to 89°, illustrating that the same metals are nearly perpendicular.

Although a large number of Ag−NHC complexes have been structurally characterized, only a few trinuclear[13] and tetranuclear[14] silver clusters stabilized by NHCs were reported by Youngs' and Catalano's groups, respectively. For all these clusters the silver atoms are all bonded to two NHCs with an average Ag−C bond distance of 2.259(9) Å. The silver−carbene bond distances of the silver clusters seem to be longer than for other Ag−NHC complexes.[1a] However, the Ag−C bond distances of **5** are considerably shorter than those of the previously reported silver clusters[13,14] but are consistent with the majority of those in Ag−NHC complexes. The bond parameters also compare with those of Ag−NHC complexes supported by bidentate pyrazole/NHC ligands without apparent Ag−Ag interactions.[7b] Furthermore, the Ag−N distances of **5** are 2.083(5) and 2.093(5) Å, which are significantly shorter than typical Ag−N bonds.[7b,15] In contrast to the shorter Ag−C bonds of **5**, the Ag−Ag distances are remarkably longer than those of the tetranuclear clusters (2.768(1)−2.971(1) Å) and trinuclear clusters (2.725(1)−2.851(1) Å) found in the literature.

So far, most of the structurally characterized silver NHC complexes can be classified into categories of C_2−Ag, C−Ag−X_n (X = halides, n = 1−3), and C−Ag−Ag, respectively.[1a] The C−Ag−Y (Y = coordinating anions other than halides) type complexes are relatively rare; only a few mono(N-heterocyclic carbene) complexes have been reported with silver linearly bound to a carbene moiety and aryloxyl anion.[16] Ag−NHC complexes containing an anionic nitrogen ligand have not been reported.

As shown in Figure 2, complex **6** is isostructural with **5**. The compound also consists of a square gold ring. The gold−carbene distances for Au(1)−C(1) and Au(2)−C(9) are 1.985(18) and 1.988(16) Å, respectively, which is comparable with other known Au^{I}−NHC linkages. The four gold atoms display a linear geometry with the C−Au−N angles of 177.2(6) and 178.7(6)°. The metal···metal distances are 3.292(1) and 3.276(1) Å, which are very close to the Ag−Ag contacts in complex **5**. The two independent Au−Au−Au angles are 88.99(3) and 91.01(3)°, which are close to 90°, and their sum is equal to 180°, illustrating that the four-membered gold ring is planar. The closest intermolecular Au−Au separation is 5.452 Å, excluding any bonding interactions.

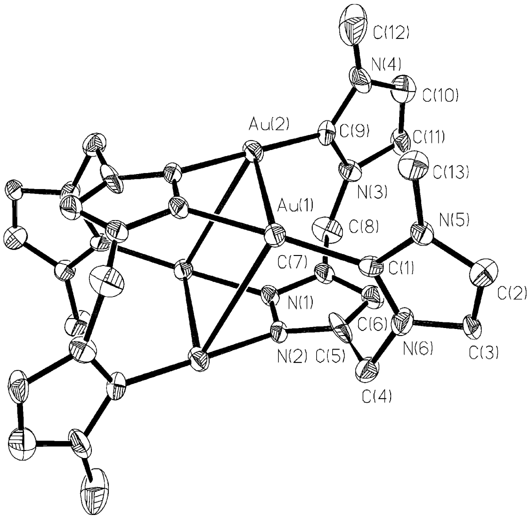

Figure 2. Molecular structure of **6**. Selected bond distances and angles: Au(1)−Au(2) = 3.276(1), Au(1)−Au(2)#1 = 3.292(1), Au(1)−C(1) = 1.985(18), Au(1)−N(1)#1 = 2.039(13), Au(2)−C(9) = 1.988(16), Au(2)−N(2)#1 = 2.035(14); C(1)−Au(1)−N(1)#1 = 177.2(6), C(9)−Au(2)−N(2)#1 = 178.7(6), Au(2)−Au(1)−Au(2)#1 = 88.99(3), Au(1)−Au(2)−Au(1)#1 = 91.01(3). Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1$, $-y$, $-z + 2$.

Gold tends to form multinuclear clusters due to aurophilic attractions,[17] and a large number of Au(I) complexes containing short Au−Au bonds have been investigated extensively with phosphine[18] and thiolates.[19] Several Au(I) complexes with NHCs have been recently studied,[20] and some of them show strong Au−Au interactions. However, to our knowledge, Au clusters stabilized by N-heterocyclic carbenes have not been reported

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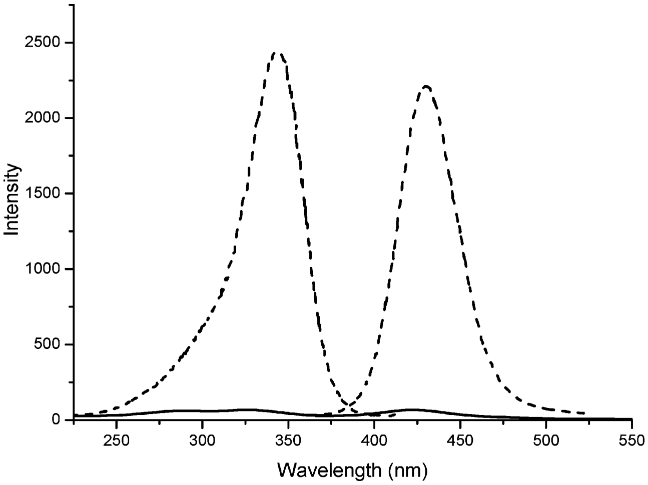

Figure 3. Solid-state emission (right) and excitation (left) spectra of **5** (solid line) and **6** (dashed line).

Table 1. Summary of X-ray Crystallographic Data for Complexes 5 and 6

	5	**6**
formula	$C_{28}H_{35}Ag_4F_{12}N_{12}O_{0.5}P_2$	$C_{26}H_{30}Au_4F_{12}N_{12}P_2$
fw	1269.60	1588.43
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.535(7)	8.526(2)
b/Å	11.568(10)	11.475(2)
c/Å	13.079(11)	13.172(3)
α/deg	66.041(11)	65.11(3)
β/deg	71.700(12)	71.51(3)
γ/deg	86.735(12)	86.56(3)
V/Å^3	1116.6(16)	1104.6(4)
Z	1	1
D/g cm^{-3}	1.887	2.388
cryst size/mm	0.52 × 0.46 × 0.32	0.10 × 0.08 × 0.04
no. of rflns collected	5843	7748
no. of inded rflns, R_{int}	3889, 0.0265	3779, 0.0466
goodness of fit on F^2	1.071	1.045
R1, wR2 ($I > 2\sigma(I)$)	0.0402, 0.1060	0.0723, 0.1834
R1, wR2 (all data)	0.0607, 0.1210	0.0896, 0.1932

so far;[21] thus, complex **6** represents the first example of a multinuclear gold compound supported by a functionalized NHC ligand.

Electronic Spectra and Solid-State Emission. The electronic absorption spectrum of **5** shows a notable absorption band centered at 225 nm and a shoulder band at 255 nm in acetonitrile, whereas the electronic absorption spectrum of **6** shows absorption bands at 225 and 260 nm in acetonitrile. The low-wavelength bands are comparable to the $\pi-\pi$ band absorption at 212 nm for the carbene precursor **4**.

The ligand precursor **4** and its silver and gold clusters are emissive in their solid states. In the emission spectrum of **4**, a single broad band at 424 nm was observed when excited at 322 nm. The tetranuclear Au complex **6** shows a broad emission band centered at 431 nm upon excitation at 344 nm, while the tetranuclear Ag complex **5** emits at slightly higher energy at 425 nm upon excitation at 330 nm. The emission spectra are shown in Figure 3. The similarity between the complexes and the ligand precursor illustrates that the emission should originate from the intraligand processes rather than metal-centered processes.

In summary, we have described the synthesis and characterization of silver and gold clusters stabilized by the pyrazole-linked bis(NHC) ligand. New structural motifs of Ag and Au clusters containing linear C−M−N moieties were obtained. Complexes **5** and **6** are luminescent in their solid state. The ligand precursor is easily prepared, and its coordinating abilities may be tuned by varying the N substituents; thus, it would be useful in the preparation of metal aggregates with novel structural motifs and physical properties.

Experimental Section

Starting materials were obtained from commercial suppliers and used without further purification or drying. 3,5-Bis(chloromethyl)-pyrazole hydrochloride salt[22] and $Au(SEt_2)Cl$[23] were synthesized according to the reported methods. ^1H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance (400 MHz) spectrometer, Elemental analyses were performed on a Flash EA1112 instrument. UV−vis spectra were obtained using a Hewlett-Packard 8453 diode array spectrometer. The photoluminescence study was carried out on powdered samples in the solid state at room temperature using a Hitachi 850 spectrometer. Mass spectral data were acquired using a Waters Micromass ZQ mass spectometer (+ mode, ESI source).

3,5-Bis(chloromethyl)pyrazole (2). Ag_2O (5.8 g, 25 mmol) was added to a suspension of **1** (10.1 g, 50 mmol) in CH_2Cl_2 (150 mL), and the mixture was stirred for 2 days with exclusion of light at room temperature. After filtration and removal of the solvent, a pale yellow solid was obtained. The product was recrystallized from acetone and isolated as a colorless crystalline solid. Yield: 7.7 g (46.6 mmol, 93.2%). ^1H NMR (400 MHz, $CDCl_3$): δ 14.09 (s, 1H), 6.49 (s, 1H), 4.68 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 105.8, 35.6. Anal. Calcd for $C_5H_6Cl_2N_2$: C, 36.39; H, 3.66; N, 16. 98. Found: C, 36.38; H, 3.66; N, 17.00.

3,5-Bis((*N*-methylimidazoliumyl)methyl)pyrazole Dichloride (3). A mixture of 3,5-bis(chloromethyl)pyrazole (3.3 g, 20 mmol) and *N*-methylimidazole (16.4 g, 200 mmol) was stirred at room temperature for 36 h. Et_2O (100 mL) was dropped into the solution with vigorous stirring. The resulting precipitate was washed with acetone and Et_2O. The compound was obtained as a pale yellow hygroscopic solid. Yield: 6.0 g, 91.1%. ^1H NMR (400 MHz, D_2O): δ 8.72 (s, 4H), 7.41 (s, 2H), 7.39 (s, 2H), 6.53 (s, 1H), 5.41 (s, 4H), 3.82 (s, 6H). ^{13}C NMR (100 MHz, D_2O): δ 136.2, 123.9, 123.8, 122.1, 106.1, 44.4, 35.8.

3,5-Bis((*N*-methylimidazoliumyl)methyl)pyrazole Bis(hexafluorophosphate) (4). A solution of **3** (3.3 g, 10 mmol) in water (10 mL) was dropped into a saturated NH_4PF_6 aqueous solution (30 mL) with stirring. The resulting precipitate was filtered and washed with H_2O, ethanol, and Et_2O. Compound **4** was obtained as a white solid. Yield: 3.7 g, 67.2%. Anal. Calcd for $C_{13}H_{18}F_{12}N_6P_2$: C, 28.48; H, 3.31; N, 15.33. Found: C, 28.59; H, 3.29; N, 15.44. ^1H NMR (400 MHz, DMSO-d_6): 13.23 (s, 1H), 9.14 (s, 1H), 9.10 (s, 1H), 7.71 (s, 2H), 7.68 (s, 2H), 6.44 (s, 1H), 5.48 (s, 2H), 5.39 (s, 2H), 3.85 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.2, 123.9, 123.8, 122.1, 106.1, 45.9, 42.9, 35.9, 35.8.

$[Ag_4(L_2)](PF_6)_2\cdot 0.5Et_2O$ (5). Ag_2O (20 mmol, 464 mg) was added to a solution of **4** (0.56 mg, 10 mmol) in CH_3CN (30 mL), and the mixture was refluxed for 8 h with exclusion of light. After filtration through a plug of Celite, the solvent was removed in vacuo and washed with H_2O, CH_3OH, and Et_2O. Complex **5** was obtained as a white powder. Yield: 3.68 g, 67.2%. Crystals suitable for X-ray single-crystal diffraction were grown by slow diffusion of Et_2O into the CH_3CN solution. Anal. Calcd for $C_{28}H_{35}Ag_4F_{12}N_{12}O_{0.5}P_2$: C, 26.50; H, 2.78; N, 13.24. Found: C, 26.45; H, 2.74; N, 13.32. ^1H NMR (400 MHz, DMSO-d_6): 7.63 (s, 2H), 7.43 (s, 2H), 6.25

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(s, 1H), 5.41 (d, ${}^2J = 15.6$ Hz, 2H), 5.26 (s, ${}^2J = 15.6$ Hz, 2H), 3.79 (s, 6H, CH_3). ${}^{13}C$ NMR (100 MHz, DMSO-d_6): δ 178.2, 175.8, 151.5, 124.2, 122.2, 103.3, 48.5, 39.3.

$[Au_4L_2](PF_2)_2$ (6). A mixture of $Au(SEt_2)Cl$ (129 mg, 0.4 mmol) and complex **5** (126 mg, 0.1 mmol,) in CH_3CN (10 mL) was stirred for 15 h with exclusion of light at room temperature. The resulting mixture was filtered through a plug of Celite. Et_2O was added to the clear solution, and complex **6** was collected as a colorless powder. Crystals suitable for X-ray single-crystal diffraction were grown by slow diffusion of Et_2O into the solution of the complex in CH_3CN. Anal. Calcd for $C_{26}H_{30}Au_4F_{12}N_{12}P_2$: C, 19.61; H, 2.15; N, 10.56. Found: C, 19.76; H, 2.18; N, 10.48. ${}^1H$ NMR (400 MHz, DMSO-d_6): 7.70 (s, 2H), 7.52 (s, 2H), 6.67 (s, 1H), 5.41 (s, 4H), 3.79 (s, 6H). ${}^{13}C$ NMR (100 MHz, DMSO-d_6): δ 164.9, 151.0, 124.5, 122.2, 105.4, 47.2.

X-ray Diffraction Analysis. Single-crystal X-ray diffraction data for the complexes were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å) by using an $\omega-2\theta$ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software.[24] All structures were solved by direct methods and refined against F^2 by full-matrix least-squares techniques.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. The oxygen and carbon atoms of the diethyl ether molecule are disordered over two positions, which were modeled successfully at 50% occupancy for each atom. Disordered solvent could not be modeled successfully and was removed from the reflection data of **6** with SQUEEZE[26] (solvent accessible void volume 185.00 Å^3). Details of the X-ray experiments and crystal data are summarized in Table 1.

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Supporting Information Available: Structural parameters for **5** and **6** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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