

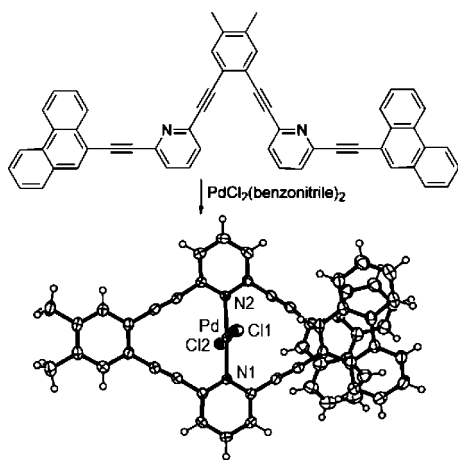
## Cation-Induced $\pi$ -Stacking

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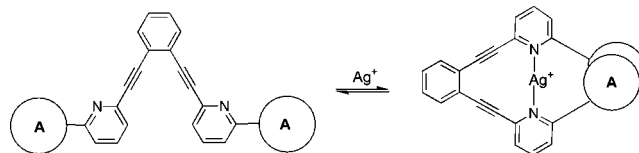
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The design and synthesis of a new dipyridyl ligand with appended phenanthryl moieties is described. On addition of increments of silver(I) trifluoromethanesulfonate to a solution of the ligand, the phenanthryl protons shift upfield in the <sup>1</sup>H NMR spectrum, suggesting that the phenanthrenes  $\pi$ -stack on coordination of silver(I). In accord with this, the oxidation potential decreased from 1.74 to 1.55 V on complexation of silver(I). The  $\pi$ -stacking was confirmed with the single-crystal X-ray structure of a palladium(II) coordination complex.

The cofacial  $\pi$ -stacking of aromatic compounds is a fundamental noncovalent interaction that has long been recognized as a central feature in nature. On a synthetic level, the cofacial  $\pi$ -stacking of aromatic systems is increasingly utilized in

## SCHEME 1. Proposed Cation-Induced Folding of the Dipyridyl Ligand



materials science,<sup>1</sup> synthesis,<sup>2</sup> molecular recognition,<sup>3</sup> and supramolecular chemistry.<sup>4</sup> Many of these applications take advantage of charge-transfer interactions between electron donor–acceptor matched aromatics,<sup>5</sup> while others rely on secondary intermolecular interactions such as hydrogen bonding.

In contrast, the spontaneous cofacial  $\pi$ -stacking of similar aromatics in solution is much less common. Indeed, there is considerable evidence that edge-to-face aromatic interactions dominate with small aromatic rings devoid of polar substituents.<sup>6</sup> This is also the case for polycyclic aromatics where analysis of the crystal structures of a series of polycyclic aromatic hydrocarbons led to the conclusion that a herringbone structure is found if the aromatic has a relatively large amount of hydrogen atoms.<sup>7</sup> Careful analysis of the crystal structures of 24 planar aromatic hydrocarbons, however, identified a clear tendency for larger aromatic hydrocarbons to  $\pi$ -stack with intermolecular distances significantly less than the sum of the van der Waals radii.<sup>8</sup> Recently, Rathore studied the cofacial stacking of a family of oligomeric fluorenones that favor  $\pi$ -stacking in solution despite the fact that they have conformational freedom.<sup>9</sup> There, however, remain few systems in which similar aromatic rings  $\pi$ -stack in a cofacial fashion in solution. We have been intrigued by the possibility of using metal cation coordination to induce  $\pi$ -stacking. To this end, we reasoned that we should be able to modify the pincer-like dipyridyl ligand, 1,2-bis(2'-pyridylethynyl)benzene, such that pendant aromatic rings would  $\pi$ -stack when a metal cation was bound by the dipyridyl moiety. We had previously demonstrated that 1,2-bis(2'-pyridylethynyl)benzene formed planar coordination complexes with silver(I) cation as well as with palladium(II) cations.<sup>10,11</sup> We reasoned that the attachment of planar moieties (A in Scheme 1) at the 6'-position of each of the two pyridine moieties would result in  $\pi$ -stacking following coordination of a metal cation.

We chose 9-ethynylphenanthrene as the appendage since molecular modeling studies suggested that the phenanthryl

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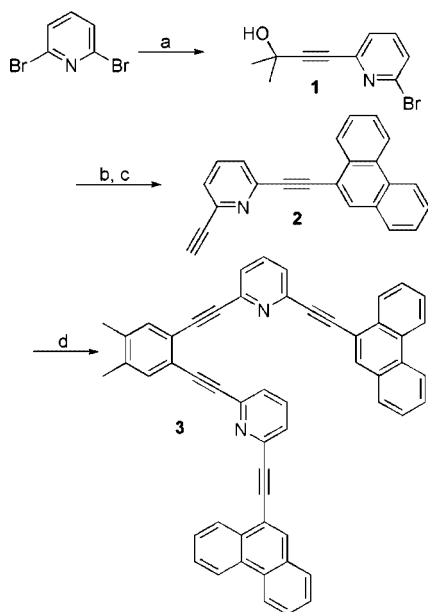
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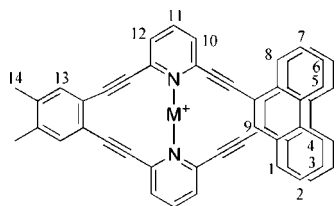
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SCHEME 2. Synthesis of Dipyridyl Ligand 3<sup>a</sup>

<sup>a</sup> Conditions: (a) 2-methyl-3-butyn-2-ol, (PPh<sub>3</sub>)PdCl<sub>2</sub>, CuI, NEt<sub>3</sub>, reflux; (b) CuI, (PPh<sub>3</sub>)PdCl<sub>2</sub>, 9-ethynylphenanthrene, CH<sub>2</sub>Cl<sub>2</sub>/piperidine; (c) NaH, toluene, reflux; (d) 0.5 equiv of 1,2-diiodo-3,4-dimethylbenzene, (PPh<sub>3</sub>)PdCl<sub>2</sub>, CuI, CH<sub>2</sub>Cl<sub>2</sub>, piperidine.

## SCHEME 3. Labeled Metal-Bound Folded Conformation



groups would  $\pi$ -stack. We then synthesized molecule **3** as shown in Scheme 2. 2,6-Dibromopyridine was coupled with 3-methyl-1-butyn-3-ol to form **1**.<sup>12</sup> The resultant asymmetric pyridine **1** was coupled with 9-ethynylphenanthrene followed by deprotection with sodium hydride in refluxing toluene to form ethynylpyridine **2**. Finally, coupling of **2** with 0.5 equiv of 4,5-diiodo-1,2-dimethylbenzene yielded the desired dipyridine **3** in modest yield.

We expected that, in the absence of metal cations, the predominant conformation of the dipyridine **3** would be a planar open form similar to that shown in Scheme 1 or 2. In contrast, we expected that, in the presence of metal cations such as silver(I) or palladium(II), the ligand would fold as shown in Scheme 3 to form a complex with overlapping phenanthrene rings. Accordingly, we studied the NMR spectral behavior of **3** in dimethylsulfoxide-*d*<sub>6</sub> on addition of silver(I) trifluoromethanesulfonate. Clearly, the silver complexed ligand has three distinct types of aromatic hydrogen atoms, those on the pyridine rings complexed to the silver(I) cation, those on the phenanthrene rings which are expected to be  $\pi$ -stacked, and those on the benzene ring remote to the silver(I) cation (see Scheme 3).

The series of spectra obtained on sequential addition of the silver salt are shown in Figure 1. Noteworthy in this series of spectra is the consistent upfield shift of the signals labeled a, b,

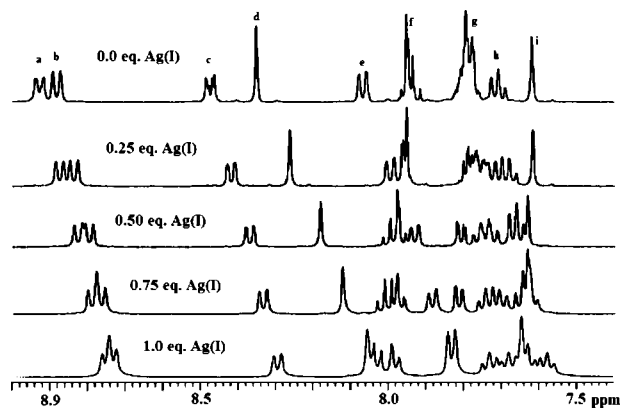


FIGURE 1. Addition of silver(I) trifluoromethanesulfonate to a DMSO-*d*<sub>6</sub> solution of dipyridine **3**.

c, d, and e. These peaks correspond to hydrogens on the phenanthrene nucleus, and the upfield shift is the result of the shielding of the aromatic nuclei following cation-induced  $\pi$ -stacking of the phenanthrene rings. Singlet d is assigned to H-9 (see Scheme 3), peaks a and b correspond to the two bay-region protons H-4 and H-5, and peaks c and e correspond to protons H-8 and H-1. Similar upfield shifts were observed in the detailed spectroscopic studies of *syn*-[2.2]phenanthrenophanes of Nishimura et al.<sup>13</sup>

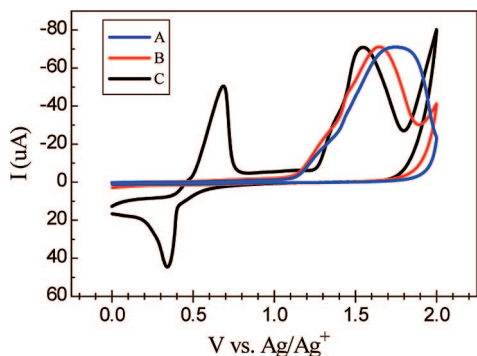
In contrast, portions of the multiplets labeled f, g, and h corresponding to H's 10–12 (Scheme 3) shift downfield slightly. As expected, the singlet labeled i, corresponding to proton H-13, does not shift significantly.

The absorption bands of the ligand in methanol,  $\lambda = 258, 332, 350$  (sh), were shifted to  $\lambda = 254, 360$  nm on addition of silver(I) triflate. The emission spectrum of the ligand alone was essentially independent of excitation wavelength over the range of 254 to 375 nm with a strong emission band centered at 374 nm and a weak band at 743 nm. On exposure to silver(I) triflate, the emission with excitation at  $\lambda = 390$  or 416 nm resulted in two emission bands: a weak band at 393 nm (fwhm = 6.6 nm) and a strong, broad featureless band at 456 nm (fwhm = 69 nm), reminiscent of the fluorescence spectrum recorded by Nishimura et al. in his studies with the *syn*-[2.2]phenanthrenophanes.

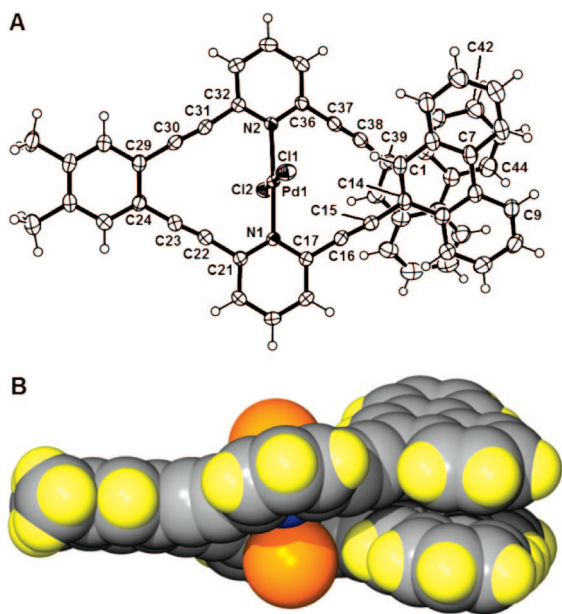
We sought further confirmation of the  $\pi$ -stacking of the phenanthryl rings in solution by monitoring the changes in oxidation potential of the ligand on complexation of silver(I). In this regard, Rathore's elegant publication had earlier demonstrated the 300 mV reduction in oxidation potential on  $\pi$ -stacking of linked fluorenes.<sup>9</sup> Accordingly, oxidation potentials were determined for the ligand **3** alone, the ligand with 1 equiv of silver triflate, and the ligand with an excess of silver triflate. All potentials were referenced to Ag/Ag<sup>+</sup>. For the ligand alone, the oxidation potential was  $E_{\text{ox}} = 1.74$  V. On addition of 1 equiv of silver triflate to the analyte,  $E_{\text{ox}}$  was indeed lowered to 1.64 V, confirming the  $\pi$ -stacking. There was no evidence of a redox couple for the silver triflate, suggesting it was largely complexed with the ligand. When an excess amount of silver triflate was added,  $E_{\text{ox}}$  lowered further to 1.55 V for the complexed ligand and the asymmetrical oxidation–reduction

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**FIGURE 2.** Cyclic voltammograms of 3.0 mM ligand in dichloromethane and 0.100 M TBAHFP with (A) no silver triflate, (B) 1 equiv of silver triflate, or (C) excess silver triflate.



**FIGURE 3.** (A) Ortep III plot of the coordination complex **4** formed between ligand **3** and palladium(II) dichloride. Thermal ellipsoids drawn at the 50% level. The dichloromethane of solvation is omitted for clarity. (B) Space-filling model of complex **4**.

wave appeared for silver triflate with  $E_{1/2} = 0.59$  V, indicating the presence of uncomplexed silver triflate (Figure 2).

To further confirm the  $\pi$ -stacking within the complex, we attempted to crystallize coordination complexes containing either silver(I) or palladium(II) cation. We were successful in obtaining single crystals of the complex **4** formed between **3** and palladium(II) dichloride suitable for X-ray crystallographic analysis. The structure of the complex **4** is shown in Figure 3.<sup>14</sup>

The palladium–nitrogen bond distances of 2.039 and 2.041 Å are only slightly longer than the bond distances of 2.022 and 2.025 Å reported in the X-ray structure of the parent bis(pyridine) PdCl<sub>2</sub> complex.<sup>15</sup> The geometry about the Pd center is

(14) X-ray data were collected on a Bruker SMART CCD area detector. The crystal structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$ . Crystal data for **6**: Mr = 971.04, monoclinic, space group  $P2_1/n$ ,  $a = 13.0636(7)$  Å,  $b = 16.6814(9)$  Å,  $c = 20.7723(11)$  Å,  $\beta = 106.7990(10)^\circ$ ,  $V = 4333.5(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $F_{\text{calcd}} = 1.120$  g cm<sup>-3</sup>,  $l = 0.71075$  Å,  $T = 173(2)$  K, 26 642 reflections collected, 9548 independent reflections, GOF on  $F^2 = 1.022$ ,  $R1 = 0.0893$ ,  $wR2 = 0.1275$ ; data deposited with the Cambridge Data Base, CCDC 612388.

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square planar with a N(1)–Pd(1)–N(2) bond angle of 177.00(12)°, a Cl(1)–Pd(1)–Cl(2) bond angle of 176.79(4)°, and N–Pd–Cl bond angles of 87.85(9), 89.04(9), 90.96(9), and 92.30(9)° for N(2)–Pd(1)–Cl(1), N(1)–Pd(1)–Cl(2), N(1)–Pd(1)–Cl(1), and N(2)–Pd(1)–Cl(2), respectively (see Figure 3A). The four alkynes are slightly bent from linearity to accommodate the folding of the molecule with bond angles ranging from 171.0° for angle C(30)–C(31)–C(32) and 172.0° for C(15)–C(16)–C(17) to 175.2° for C(22)–C(23)–C(24). The interplanar distance between the two phenanthrene moieties ranges from about 3.4 to 3.7 Å with a distance of 3.356 Å between C(14) and C(39), a distance of 3.517 Å between C(7) and C(42), a distance of 3.569 Å between C(1) and C(39), and a distance of 3.702 Å between C(9) and C(44).

In summary, we have used a combination of NMR, electrochemical, and X-ray studies to demonstrate the principle of cation-induced  $\pi$ -stacking. It is interesting to note that a related molecular hinge was published in this journal following submission of our paper.<sup>16</sup> Our future work will explore ligands that incorporate the principle of cation-induced  $\pi$ -stacking for the selective sensing of transition metal cations, especially silver(I).

## Experimental Section

**4-(6-Bromopyridin-2-yl)-2-methylbut-3-yn-2-ol.** **1** was prepared in similar method to that reported by Pennington et al.<sup>13</sup> **1** was obtained as an off-white solid (16.01 g, 63%): mp 76–78 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.63 (s, 6H), 2.48 (s, 1H), 7.37 (dd,  $J = 1.2, 8.0$  Hz, 1H), 7.42 (dd,  $J = 1.2, 8.0$  Hz, 1H), 7.50 (t,  $J = 8.0$  Hz, 1H); <sup>13</sup>C NMR  $\delta$  31.3, 65.7, 80.7, 95.5, 126.2, 127.8, 138.5, 141.9, 143.7. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>BrNO: C, 50.02; H, 4.20; N, 5.83. Found: C, 50.47; H, 4.07; N, 5.62.

**Synthesis of 2-Ethynyl-6-(phenanthren-9-ylethynyl)pyridine, 2.** 9-Ethynylphenanthrene (3.98 g, 19.7 mmol), **1** (4.80 g, 20 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (256 mg), CuI (52 mg), and PPh<sub>3</sub> (205 mg) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Piperidine (5 mL) was added and nitrogen bubbled through the mixture for 5 min. The reaction mixture was sealed and stirred at room temperature for 3 days. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and saturated NaCl, and the organic layer dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude solid was chromatographed on SiO<sub>2</sub> with hexane/EtOAc solvent to yield the acetone-protected compound (5.98 g, 84%) as an off-white solid: mp 130–135 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.67 (s, 6H), 2.78 (br s, 1H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.56 (t,  $J = 8.0$  Hz, 1H), 7.60–7.70 (m, 5H), 7.84 (d,  $J = 8.0$  Hz, 1H), 8.14 (s, 1H), 8.53–8.55 (m, 1H), 8.63 (d,  $J = 8.0$  Hz, 1H), 8.65–8.68 (m, 1H); <sup>13</sup>C NMR  $\delta$  31.4, 65.7, 81.5, 88.4, 92.7, 94.7, 118.7, 122.9, 123.0, 126.5, 126.8, 127.3, 127.4, 127.5, 128.2, 129.0, 130.3, 130.8, 131.1, 131.2, 133.5, 136.7, 143.7, 144.0. Anal. Calcd for C<sub>26</sub>H<sub>19</sub>NO·(H<sub>2</sub>O)<sub>0.67</sub>: C, 83.61; H, 5.49; N, 3.75. Found: C, 83.51; H, 5.19; N, 3.59. The acetone-protected compound (5.98 g, 16.59 mmol) was added to toluene (200 mL) and heated to reflux with an azeotrope condenser attached. The first 20 mL of distillate was discarded, and then NaH (700 mg) was added to the solution and refluxing continued for 10 min. Water was added to quench the solution, and the toluene evaporated. The crude solid was chromatographed on SiO<sub>2</sub> with hexane/EtOAc solvent to yield **2** (1.91 g) as an off-white solid: mp 162–165 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.21 (s, 1H), 7.47 (dd,  $J = 7.6, 0.8$  Hz, 1H), 7.59–7.74 (m, 5H), 7.88 (d,  $J = 7.6$  Hz, 1H), 8.18 (s, 1H), 8.55–8.58 (m, 1H), 8.67 (d,  $J = 7.6$  Hz, 1H), 8.69–8.71 (m, 1H); <sup>13</sup>C NMR  $\delta$  (CDCl<sub>3</sub>) 77.9, 82.6, 88.4, 92.7, 118.7, 122.9, 123.0, 126.8, 127.3, 127.3, 127.4, 127.5, 128.2, 129.1, 130.3, 130.9, 131.1, 131.3, 133.5, 136.8,

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143.1, 144.2. Anal. Calcd for  $C_{23}H_{13}N$ : C, 91.06; H, 4.32; N, 4.62. Found: C, 90.83; H, 4.23; N, 4.67.

**Synthesis of 4,5-Dimethyl-1,2-bis(2'-(6'-phenanthryl-9'-ethynyl)pyridylethynyl)benzene, 3.** 4,5-Diiodo-*o*-xylene (668 mg, 1.87 mmol), **2** (1.28 g, 3.75 mmol),  $PdCl_2(PPh_3)_2$  (276 mg), CuI (56 mg), and  $PPh_3$  (245 mg) were dissolved in  $CH_2Cl_2$  (20 mL). Piperidine (3 mL) was added, nitrogen bubbled through the mixture for 5 min, and the resultant solution was stirred at 40 °C for 24 h. The solution was filtered and the solid washed with a mixture of hexane and  $CH_2Cl_2$  (45:5 mL). The solid was then stirred with an aqueous  $Na_2CO_3$  solution for 1 h and filtered to yield **3** as a cream colored powder (358 mg, 28%): mp 227–230 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.27 (s, 6H), 7.46 (s, 2H), 7.47 (d,  $J = 8.4$  Hz, 2H), 7.59 (t,  $J = 6.8$  Hz, 2H), 7.605–7.71 (m, 6H), 7.87 (t,  $J = 7.4$  Hz, 2H), 8.14 (s, 2H), 8.56 (dd,  $J = 1.6, 7.6$  Hz, 2H), 8.68 (d,  $J = 8.0$  Hz, 2H), 8.71 (dd,  $J = 1.6, 8.0$  Hz, 2H);  $^{13}C$  NMR  $\delta$  19.8, 87.7, 88.8, 92.2, 93.0, 118.6, 122.6, 122.8, 123.0, 126.4, 127.1, 127.1, 127.2, 127.3, 127.9, 128.8, 130.0, 130.6, 130.9, 131.0, 133.1, 133.2, 136.7, 138.3, 143.6, 144.2. Anal. Calcd for  $C_{54}H_{32}N_2 \cdot (H_2O)_{0.4}$ : C, 90.58; H, 4.62; N, 3.91. Found: C, 90.65; H, 4.49; N, 4.01.

**Synthesis of Palladium Complex, 4.** A solution of  $PdCl_2(CH_3CN)_2$  (5.1 mg, 0.014 mmol) in  $CH_3CN$  (2 mL) was carefully layered over a solution of the dipyriddy ligand **3** (10 mg, 0.014 mmol) in  $CH_2Cl_2$  (2 mL). After 2 days, small block-like crystals began to form. A single crystal of dimensions  $0.50 \times 0.15 \times 0.10$  was selected for X-ray analysis. The crystals were insoluble in common deuterated organic solvents.

**Electrochemistry.** Cyclic voltammetry (CV) was performed on a CH Instruments 702A electrochemical analyzer. The CV cell was a  $25 \times 40$  mm glass cell fitted with a Teflon cap to hold electrodes and a gas line which blanketed the cell with argon. A  $0.0314$  cm<sup>2</sup> Pt disk embedded in Teflon served as the working electrode. A

platinum wire was used as the reference electrode. The  $Ag/Ag^+$  reference electrode was constructed from a glass casing and contained a silver wire in a 0.1 M solution of  $AgNO_3$  in  $CH_3CN$ . It was sealed with a glass frit. The CV measurements were carried out in a solution of 0.1 M supporting electrolyte ( $Bu_4PF_6$ ) with  $3.0 \times 10^{-3}$  M ligand concentration in dry  $CH_2Cl_2$  blanketed by argon. All the cyclic voltammograms were recorded at the sweep rate of  $50$  mV  $s^{-1}$ . The oxidation potentials ( $E_{ox}$ ) were referenced to  $Ag/Ag^+$  which was calibrated with  $3.0 \times 10^{-3}$  M ferrocene ( $E_{1/2} = 0.19$  V vs  $Ag/Ag^+$ ). Oxidation potentials were determined for the ligand alone, the ligand with 1 equiv of silver triflate, and the ligand with an excess of silver triflate. All are referenced to  $Ag/Ag^+$ . For the ligand alone, the oxidation potential ( $E_{ox}$ ) was 1.74 V. When 1 equiv of silver triflate was added to the analyte,  $E_{ox}$  was lowered to 1.64 V with no evidence of a redox couple for the silver triflate, suggesting it was complexed with the ligand. When an excess amount of silver triflate was added,  $E_{ox}$  lowered further to 1.55 V for the complexed ligand but an obvious quasi-reversible oxidation–reduction wave appeared for silver triflate with  $E_{1/2} = 0.59$  V, indicating the presence of uncomplexed silver triflate.

**Acknowledgment.** This research was supported by the National Science Foundation, Grant 0415711, and the Graduate College at Missouri State University.

**Supporting Information Available:** Copies of  $^1H$  and  $^{13}C$  NMR spectra for compounds **1–3** and intermediate compounds as well as X-ray structural data for complex **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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