

Heterotopic Assemblage of Two Different Disk-Shaped Ligands through Trinuclear Silver(I) Complexation: Ligand Exchange-Driven Molecular Motion

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Abstract: The sandwich-shaped heterotopic trinuclear Ag^+ complex $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ was exclusively formed from two different tris(thiazolyl) and hexa(thiazolyl) disk-shaped ligands, **1** and **2**, with the aid of three Ag^+ ions. The variable-temperature ^1H NMR study on its complexation behavior revealed that metal–ligand exchanges between the two neighboring thiazolyl nitrogen donors of **2** take place at the three Ag^+ centers in concert. ΔH^\ddagger and ΔS^\ddagger for the exchange process were calculated to be 50.5 kJ mol^{-1} and $-26.7 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively, and its energy barrier at 298 K was estimated to be 58.5 kJ mol^{-1} . Each concerted metal–ligand exchange leads to an intramolecular 60° -rotational motion ($(P) \rightleftharpoons (M)$ conversion) between the two disk-shaped ligands.

Introduction

Self-assembly protocols with the aid of biomolecules or predesigned artificial molecules are widely used to fabricate well-defined higher-order structures with an increasing number of components.¹ For example, in biological systems, DNA duplexes are formed from two polynucleotides whose nucleobase sequences are complementary to each other,^{2a} and protein homo- or heterodimers are assembled preferentially through accurate molecular recognition between their amino acid residues at the surfaces.^{2b} As for nonnatural systems, considerable effort has been made toward the construction of multi-component systems using hydrogen-bonding,³ metal coordination,^{4,5} and aromatic interactions.⁶

Herein, we describe the quantitative heterotopic formation of a sandwich-shaped trinuclear $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex from two

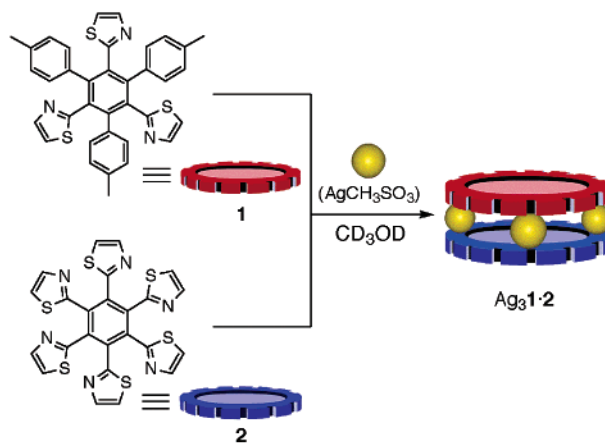


Figure 1. Schematic representation of the formation of the heterotopic sandwich-shaped $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex consisting of disk-shaped ligands, **1** and **2**, and three Ag^+ ions.

different disk-shaped ligands, a tris(thiazolyl) ligand **1** and a hexa(thiazolyl) ligand **2**, and three Ag^+ ions (Figure 1). A trinuclear $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex is exclusively formed from a mixture of **1**, **2**, and Ag^+ ions in a 1:1:3 ratio, whereas an $\text{Ag}_3\mathbf{1}_2$ complex is quantitatively obtained from **1** and Ag^+ ions in a 2:3 ratio.⁷ Introduction of **2** with an increased number of ligand rings from three to six thus alters the association pattern from “homo” to “hetero”. Moreover, variable-temperature ^1H NMR measure-

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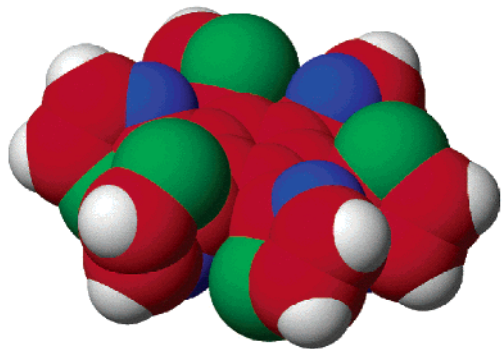
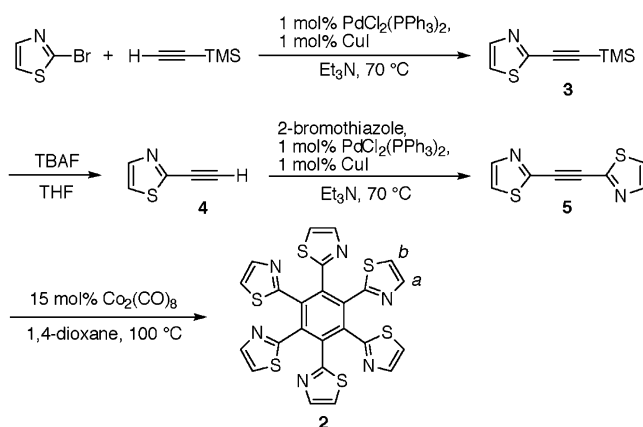


Figure 2. Crystal structure of **2**. Color labels: C (red), N (blue), S (green), and H (white).

Scheme 1. Synthesis of Hexa(thiazolyl) Ligand **2**



ments exhibited that, in $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex, the intramolecular rotational motion (i.e., $(P) \rightleftharpoons (M)$ conversion) is driven by the concerted ligand exchange in solution between the coordinatively paired ligands.

Results and Discussion

Synthesis of Disk-Shaped Ligands. The tris(thiazolyl) ligand **1** was synthesized according to our previous report.⁷ The hexa(thiazolyl) ligand **2** was prepared by trimerization of 1,2-bis(2-thiazolyl)ethyne **5** using 15 mol % of $\text{Co}_2(\text{CO})_8$ as the catalyst (Scheme 1). The alkyne **5** was prepared from 2-bromothiazole and trimethylsilyl acetylene in three steps through Sonogashira coupling and deprotection reactions. The hexamodentate ligand **2** was fully characterized by ^1H and ^{13}C NMR, electrospray ionization-time-of-flight (ESI-TOF) mass measurements, and elemental analysis. Its ^1H NMR exhibited two symmetrical signals for H^a and H^b , indicating the free rotation of each thiazolyl ring. Furthermore, single crystals of **2** were obtained by slow evaporation of CHCl_3 from a solution of **2** in CHCl_3 – CH_3OH . The X-ray diffraction of a single crystal revealed that three nitrogen atoms of every other thiazolyl rings are placed on the same side of the central benzene plane (Figure 2). Dihedral angles between the central benzene ring and three thiazolyl rings are 53.29° , 54.79° , and 84.17° .

Formation of Heterotopic Ag^+ Complex. The quantitative formation of the heterotopic $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex in solution was evidenced by ^1H NMR and ESI-TOF mass measurements. The ^1H NMR spectrum of a mixture of two ligands, **1** and **2**, and AgCH_3SO_3 in a 1:1:3 ratio in CD_3OD (Figure 3c) was quite

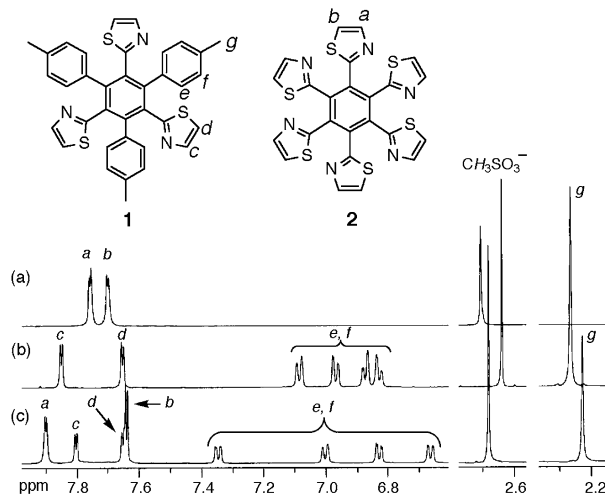


Figure 3. ^1H NMR spectra (500 MHz, CD_3OD , 293 K): (a) **2** and AgCH_3SO_3 in a 2:3 ratio, $[\mathbf{2}] = 7.2$ mM, $[\text{AgCH}_3\text{SO}_3] = 10.8$ mM; (b) $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$, $[\mathbf{1}] = 7.2$ mM, $[\text{AgCH}_3\text{SO}_3] = 10.8$ mM; (c) $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$, $[\mathbf{1}] = [\mathbf{2}] = 7.2$ mM, $[\text{AgCH}_3\text{SO}_3] = 21.6$ mM.

different from both spectra of a mixture of **2** and AgCH_3SO_3 in a 2:3 ratio (Figure 3a) and of the sandwich-shaped $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex⁷ (Figure 3b). These spectral changes suggest the quantitative formation of an Ag^+ complex comprising **1** and **2** in a 1:1 ratio through a heterotopic recognition process. In addition, the *p*-tolyl protons H^e and H^f were observed upon complexation as two inequivalent sets of signals due to the inner and outer protons in the sandwich-shaped Ag^+ complex, while the *p*-tolyl methyl protons (H^g) and the thiazolyl protons of **1** and **2** showed a symmetrical pattern as shown with free ligands **1** and **2**. The ESI-TOF mass spectrum of a mixture of **1**, **2**, and AgCH_3SO_3 in a 1:1:3 ratio showed peaks at m/z 499.3, 796.4, and 1687.4 which are assignable to $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}]^{3+}$, $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}\cdot\text{CH}_3\text{SO}_3]^{2+}$, and $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}\cdot(\text{CH}_3\text{SO}_3)_2]^{+}$, respectively (Figure 4). These results strongly suggest that the heterotopic $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex is quantitatively formed in solution.

The formation of the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex is thermodynamically favored; that is, the product does not depend on the mixing order of the components. For example, the addition of a mixture of **2** ($[\mathbf{2}] = 16.3$ mM) and AgCH_3SO_3 in a 2:3 ratio to a solution of the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex ($[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}] = 4.1$ mM) rapidly generated the heterotopic $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex only.⁸ One of the reasons for the exclusive heterotopic recognition observed here should be the relatively low stability of the entities formed from hexamodentate ligand **2** and Ag^+ ions. The ^1H NMR titration experiments using **2** and AgCH_3SO_3 showed that the signals for H^a and H^b were gradually shifted in a complicated manner to upfield and downfield, respectively, with an increasing amount of Ag^+ ions. Upon cooling the sample, prepared from **2** and AgCH_3SO_3 in a 2:3 ratio, down to 203 K, only broadening of these signals was observed. In addition, unidentified precipitates appeared when more than 6 equiv of AgCH_3SO_3 was added to a solution of **2**, suggesting the formation of some polymeric products. In the ESI-TOF mass study, the signals at m/z 755.8, 539.5, and 684.9 assignable to $[\text{Ag}_3\mathbf{2}\cdot\text{OH}\cdot\text{H}_2\text{O}]^{2+}$, $[\text{Ag}_4\mathbf{2}\cdot\text{OH}\cdot\text{H}_2\text{O}]^{3+}$, and $[\text{Ag}_2\mathbf{2}]^{2+}$, respectively, were observed

(8) No higher-order structures such as a triple decker complex, $\mathbf{1}\cdot\text{Ag}_3\cdot\mathbf{2}\cdot\text{Ag}_3\cdot\mathbf{1}$, were observed with mixtures of **1**, **2**, and AgCH_3SO_3 in various ratios. For example, the ^1H NMR spectrum of a mixture of **1**, **2**, and AgCH_3SO_3 in a 2:1:6 ratio showed the separated two sets of signals assignable to the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ and $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complexes.

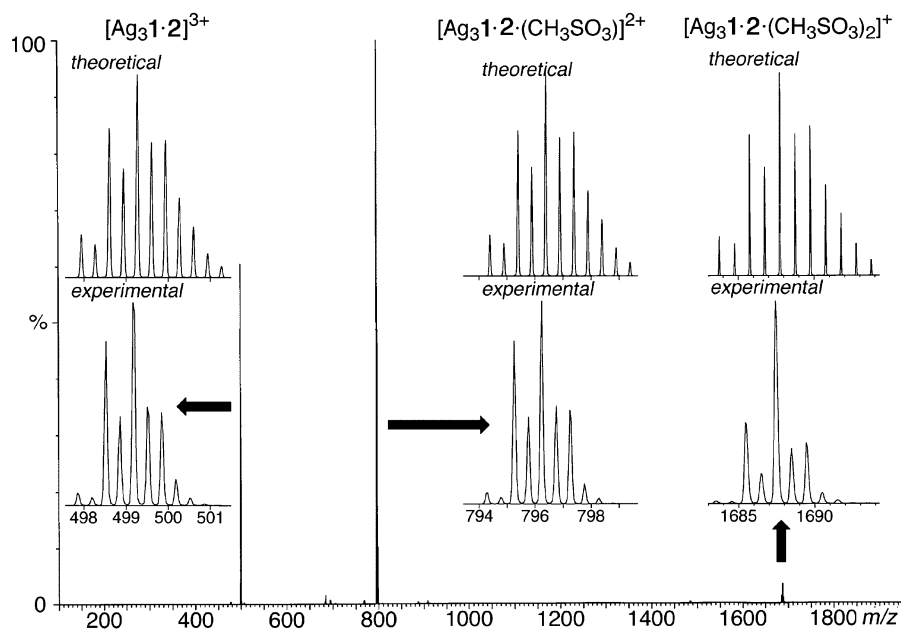


Figure 4. ESI-TOF mass spectrum of the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex.

in the presence of 1.5 equiv of AgCH_3SO_3 , whereas the former peaks changed to a single peak at m/z 539.5 for $[\text{Ag}_4\mathbf{2}_2\cdot\text{OH}\cdot\text{H}_2\text{O}]^{3+}$ with an increasing amount of Ag^+ ions within the range of $[\text{Ag}^+]:[\mathbf{2}]$ ratios from 3:2 to 6:1 (see Supporting Information, Figure S2). These results indicate that a mixture of $\mathbf{2}$ and Ag^+ ions in a 2:3 ratio does not afford any detectable, stable complex.

Variable-Temperature ^1H NMR Studies for Heterotopic Ag^+ Complex. As described above, a ^1H NMR spectrum of the heterotopic $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex showed one set of thiazolyl proton signals for H^a and H^b at 293 K (Figure 3c). There are two possible coordination structures around Ag^+ ions for $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex. One is a trigonal coordination geometry in which the neighboring two thiazolyl nitrogen atoms of $\mathbf{2}$ and one thiazolyl nitrogen atom of $\mathbf{1}$, respectively, coordinate to the Ag^+ center. The other one is a linear coordination geometry in which every other thiazolyl nitrogen atom of $\mathbf{2}$ would possibly coordinate to the Ag^+ centers and the other three nitrogen donors be uncoordinating. In this structure, metal–ligand exchanges between the two neighboring thiazolyl rings of $\mathbf{2}$ should take place at three Ag^+ ions faster than the NMR time scale. In the expectation that this metal–ligand exchange with a relative rotational motion between the two disk-shaped ligands should be temperature-dependent, we conducted variable-temperature ^1H NMR measurements of the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex. As shown in Figure 5, the dynamic behavior of the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex caused by concerted metal–ligand exchange was observed in the spectra. The ^1H NMR signals above 263 K for one set of the H^a and H^b protons of ligand $\mathbf{2}$ (Figure 5a) were separated into two sets, (H^{a1} , H^{b1}) and (H^{a2} , H^{b2}), at 203 K (Figure 5g). In contrast, the signals for ligand $\mathbf{1}$ were not divided into two sets ranging from 293 to 203 K, although the H^c and H^d signals shifted downfield and upfield, respectively, as the temperatures went down. These results overall suggest that each Ag^+ ion is linearly coordinated by two nitrogen atoms (one from $\mathbf{1}$ and the other from $\mathbf{2}$) in the ground state, where the ligand exchange between the two types of thiazolyl groups of $\mathbf{2}$, corresponding to coordinating (H^{a1} , H^{b1}) and uncoordinating (H^{a2} , H^{b2}) ones, is not fast enough to be separately observed at 203 K (Figure

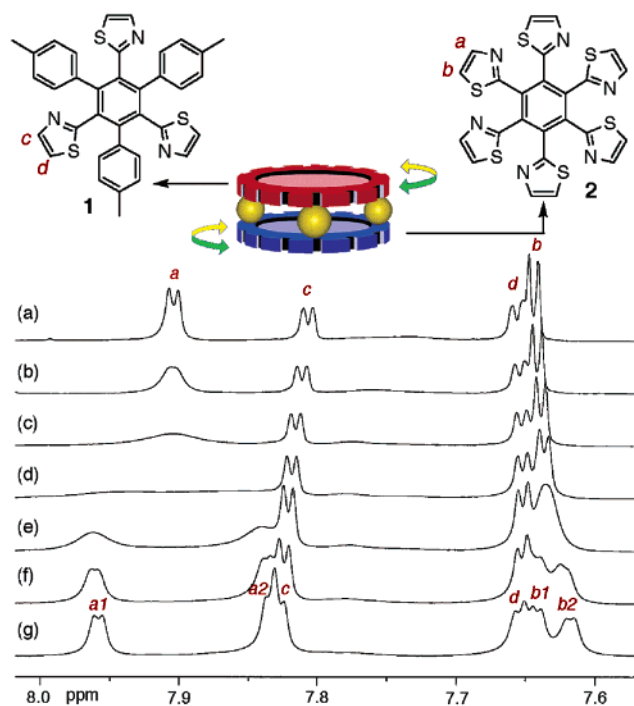


Figure 5. Variable-temperature ^1H NMR spectra of the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex (500 MHz, CD_3OD , $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}] = 7.2$ mM): (a) 263 K, (b) 253 K, (c) 243 K, (d) 233 K, (e) 223 K, (f) 213 K, and (g) 203 K.

6) but is fast enough above 253 K through $(P) \rightleftharpoons (M)$ intraconversion. The energy barrier of the $(P) \rightleftharpoons (M)$ equilibrium in the $\text{Ag}_3\mathbf{1}\cdot\mathbf{2}$ complex was evaluated by the simulation of the line shapes of the H^a and H^b signals. Based on the Eyring equation,⁹ ΔH^\ddagger and ΔS^\ddagger for the exchange process were calculated to be 50.5 kJ mol^{-1} and -26.7 $\text{J mol}^{-1} \text{K}^{-1}$, respectively, and finally the energy barrier of the exchange at 298 K (ΔG_{298}^\ddagger) was estimated to be 58.5 kJ mol^{-1} .

The metal–ligand exchange would take place by way of a plausible transition state in which three thiazolyl nitrogen atoms

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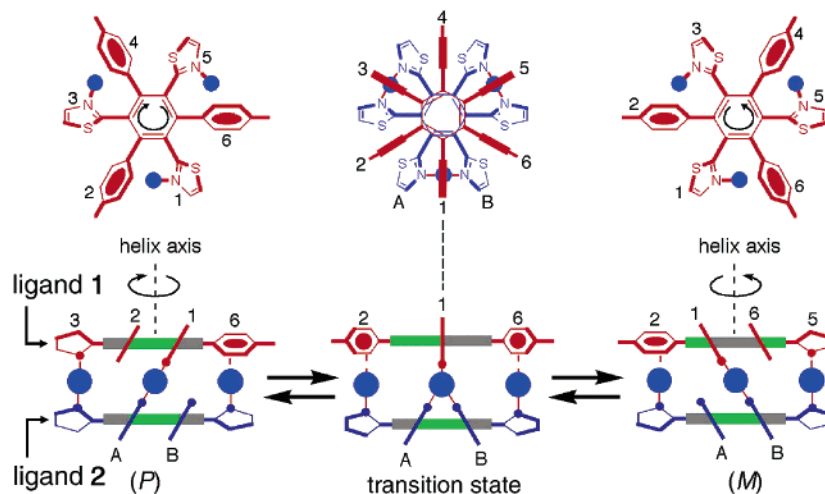


Figure 6. Plausible mechanism for the relative rotational motion mediated by intramolecular metal–ligand exchange within the $\text{Ag}_3\cdot\mathbf{1}\cdot\mathbf{2}$ complex.

(thiazolyl ring (1) from ligand **1** and (A) and (B) from ligand **2**; see Figure 6) coordinate to an Ag^+ ion with a trigonal coordination geometry. The negative value of ΔS^\ddagger should be due to the changes in the environment, i.e., solvent ordering through hydrogen bonding to the complex, association of counterions with the complex, and additional coordination of a thiazolyl nitrogen donor to the neighboring Ag^+ ion in the transition state.¹⁰ Moreover, it is worth describing that the metal–ligand exchange should give rise to the $(P) \rightleftharpoons (M)$ racemization accompanying a reversible 60° -rotational motion between the coordinatively paired ligands. In the (P) isomer, for instance, a thiazolyl ring (1) in ligand **1** and a thiazolyl ring (B) in ligand **2** coordinate to an Ag^+ ion and, after the $(P) \rightarrow (M)$ conversion, the thiazolyl ring (A) exchanged by another thiazolyl ring (B) through the 60° rotation around the helix axis leading to the (M) isomer (Figure 6).

Conclusion

In conclusion, the exclusive heterotopic assemblage was accomplished by the quantitative formation of a heterotopic $\text{Ag}_3\cdot\mathbf{1}\cdot\mathbf{2}$ complex. The reversible rotational motion between the two ligands **1** and **2** placed in parallel takes place concertedly through metal–ligand exchange at the three Ag^+ ions. Such intramolecular rotational motion between two different counterparts would be applicable to the development of novel metal-mediated molecular devices particularly for multicomponent-based molecular machinery.

Experimental Section

General. 2-Ethynylthiazole **4** was prepared according to the literature.¹⁰ All ambient and variable-temperature ^1H NMR spectra were recorded on a Bruker DRX 500 (500 MHz) spectrometer using TMS as the internal reference. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT mass spectrometer KB 201. IR spectra were recorded on a Jasco IR-Report 100. Melting points were measured on a Yanaco MP-500D.

AgCH_3SO_3 , Ag_2O (2.0 g, 8.6 mmol) was added to a solution of $\text{CH}_3\text{SO}_3\text{H}$ (1.1 mL, 17.3 mmol) in H_2O (40 mL), and the solution was

then heated at 90°C for 3 h. After cooling, the colorless solution was filtered to remove unreacted Ag_2O and then evaporated. The resulting colorless solid was washed with acetone to remove $\text{CH}_3\text{SO}_3\text{H}$ and then dried in vacuo to obtain AgCH_3SO_3 (3.18 g, 91%) as a colorless solid. ^1H NMR (500 MHz, CD_3OD) δ 2.71 (s); ^{13}C NMR (125 MHz, CD_3OD) δ 39.5.

1,2-Bis(2-thiazolyl)ethylene (5). To a solution of CuI (21 mg, 0.11 mmol, 3 mol %), $\text{PdCl}_2(\text{PPh}_3)_2$ (78 mg, 0.11 mmol, 3 mol %), and 2-bromothiazole (0.40 mL, 4.4 mmol) in Et_3N (10 mL) was added 2-ethynylthiazole **4** (0.40 g, 3.7 mmol). The mixture was degassed and heated at 70°C for 12 h under a nitrogen atmosphere. The resulting dark brown mixture was filtered, and the solvent was then removed in vacuo. Purification by silica gel chromatography was performed (*n*-hexane/ AcOEt (10:1–4:1)) to obtain the desired coupling product **5** (226 mg, 32%) as a pale yellow solid: mp 143°C ; ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 3.5$ Hz, 2H), 7.50 (d, $J = 3.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.9, 144.1, 122.1, 85.9; IR (KBr) ν 3130, 3100, 3060, 1460, 1360, 1320, 1250, 1130, 1080, 730 cm^{-1} . MS (ESI-TOF) m/z exact mass $[\text{M} + \text{Na}]^+$ 214.9697, $\text{C}_8\text{H}_4\text{N}_2\text{S}_2\text{Na}$ requires 214.9714.

Hexa(2-thiazolyl)benzene (2). $\text{Co}_2(\text{CO})_8$ (27 mg, 78 μmol , 15 mol %) and **5** (100 mg, 0.52 mmol) in 1,4-dioxane (6.0 mL) were placed in a sealed tube flask. The mixture was degassed and heated at 100°C for 10 h. The solvent was removed in vacuo. Purification by silica gel column chromatography ($\text{CHCl}_3/\text{CH}_3\text{OH}$ (50:1)) afforded the desired **2** (56 mg, 56%) as a colorless solid: mp 430°C (dec); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.67 (d, $J = 3.3$ Hz, 6H), 7.58 (d, $J = 3.3$ Hz, 6H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 161.7, 142.2, 136.8, 123.5; IR (KBr) ν 3120, 3100, 3060, 1500, 1480, 1360, 1300, 1160, 1090, 1070, 1060, 960, 770, 740 cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{N}_6\text{S}_6$: C, 49.98; H, 2.10; N, 14.57. Found: C, 49.77; H, 2.25; N, 14.40.

Formation of $\text{Ag}_3\cdot\mathbf{1}\cdot\mathbf{2}\cdot(\text{CH}_3\text{SO}_3)_3$ Complex. To a solution of AgCH_3SO_3 (1.8 mg, 8.6 μmol) and **1** (3.4 mg, 5.8 μmol) in CD_3OD (0.4 mL) was added a solution of AgCH_3SO_3 (1.8 mg, 8.6 μmol) and **2** (3.3 mg, 5.8 μmol) in CD_3OD (0.4 mL), and the mixture stood at room temperature for 5 min. Its ^1H NMR spectrum showed the quantitative formation of the $\text{Ag}_3\cdot\mathbf{1}\cdot\mathbf{2}\cdot(\text{CH}_3\text{SO}_3)_3$ complex. ^1H NMR (500 MHz, CD_3OD , 293 K) δ 7.90 (d, $J = 3.3$ Hz, 6H), 7.80 (d, $J = 3.5$ Hz, 3H), 7.66 (d, $J = 3.5$ Hz, 3H), 7.64 (d, $J = 3.3$ Hz, 6H), 7.50 (dd, $J = 1.7, 7.8$ Hz, 3H), 7.00 (d, $J = 8.0$ Hz, 3H), 6.83 (dd, $J = 1.7, 8.0$ Hz, 3H), 6.67 (d, $J = 7.8$ Hz, 3H), 2.68 (s, 9H), 2.23 (s, 9H); ^{13}C NMR (125 MHz, CD_3OD) δ 170.1, 165.2, 146.8, 144.5, 143.3, 140.6, 138.6, 135.2, 133.7, 131.9, 131.1, 130.8, 130.4, 126.6, 125.6, 39.6, 21.3; MS (ESI-TOF) (CH_3OH)

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$m/z = 499.3$ $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}]^{3+}$, 796.4 $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}\cdot(\text{CH}_3\text{SO}_3)]^{2+}$, 1687.4 $[\text{Ag}_3\mathbf{1}\cdot\mathbf{2}\cdot(\text{CH}_3\text{SO}_3)_2]^+$.

Acknowledgment. This study was supported by a Grant-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry, a Grant-in-Aid for Encouragement of Young Scientists (B) to S.H. (No. 14740361), and a Grant-in-Aid for Scientific Research on Priority Areas, “Dynamic

Complexes” to S.H. (No. 420/15036216) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: X-ray crystallographic data of **2** (CIF), Eyring plot, and ESI-TOF mass spectra of Ag^+ complexes of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA036388Q