Novel Phenanthroline-Containing Trinuclear Double-Stranded Helicates: Self-Recognition between Helicates with Phenanthroline and Bipyridine Binding Sites

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The ligands 6,6′-bis[(2-methyl-1,10-phenanthrolin-9-yl)methylenoxymethylenyl] 2,2′-bipyridine (**1**)- and 2,9-bis[(2-methyl-1,10-phenanthrolin-9-yl)methylenoxymethylenyl] -1,10-phenanthroline (**2**) were prepared and shown to self-assemble into double-stranded $[(\mathbf{L})_2Cu_3]^{3+}$-type helicates upon reaction with Cu^+. Although the reaction of **1** with $AgCF_3SO_3$ afforded the double-stranded helicate $[(\mathbf{1})_2Ag_3]^{3+}$, reaction of **2** with this salt yielded a mixture of several complexes, all of apparently double-strand nature, based on their diffusion coefficients. Addition of a large excess of $AgCF_3SO_3$ afforded $[(\mathbf{2})_2Ag_3]^{3+}$ as the sole product. In addition, it was found that the reaction of Cu^+ with mixtures of **1** and 6″,6‴-bis[(6-methyl-2,2′-bipyridin-6′-yl)methylenoxymethylenyl]-2″,2‴-bipyridine (**4**) or of **2** with 2,9-bis[(6-methyl-2,2-bipyridin-6′-yl)methylenoxymethylenyl]-1,10-phenanthroline (**3**) afforded mixtures of homoleptic and heteroleptic helicates. Helicate distribution seems to follow statistical expectations. Mixing of the double-stranded copper helicates of **2** and **3** in DMSO-d_6 afforded, after 2 weeks, a statistical mixture of the homoleptic and heteroleptic helicates, i.e., $[(\mathbf{2})_2Cu_3]^{3+}$, $[(\mathbf{3})_2Cu_3]^{3+}$, and $[(\mathbf{2/3})Cu_3]^{3+}$. However, a statistical mixture was obtained within minutes from the double-stranded silver helicates of **2** and **3** in CD_3CN. We conclude therefore that even **2** and **3**, which contain three phenanthroline and three bipyridine binding sites, are not "sufficiently instructed" to avoid the formation of a heteroleptic helicate in the course of their self-assembly process.

Introduction

Self-assembly is an important mechanism by which nature creates large, functional supramolecular systems from relatively simple building units.[1] In recent years, self-assembly has been used for the preparation of synthetic supramolecular systems through noncovalent interactions.[2,3] Some of these supramolecular systems were shown to function as molecular sensors and molecular switches.[3,4] Lately, metallosupramolecular systems have attracted considerable attention and such systems of different size, shape, and architecture have been prepared and characterized.[3c,e,5−7]

Helicates prepared by self-assembly of organic ligands and metal cations have been the subject of many studies.[8−10] Double- and triple-stranded helicates were prepared from bidentate ligands and tetrahedral or octhahedral cations, respectively. Lanthanide triple-stranded helicates were also prepared with tridentate ligands.[11] These helicates are promising candidates for the preparation of molecular probes.[4c,d,11] Most recently, water-soluble helicates of this nature were reported.[11c]

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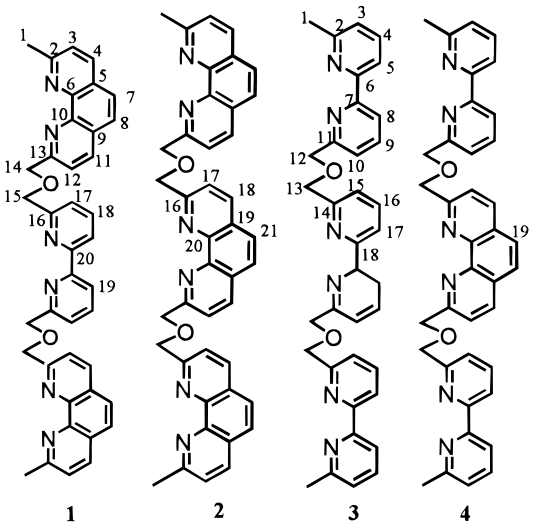
Scheme 1



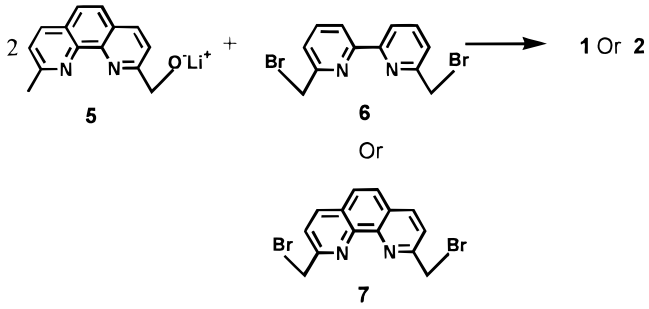
1 **2** **3** **4**

Homoleptic helicates have been studied much more extensively than heteroleptic helicates.[12] In addition, it was reported that mixtures of ligands with different numbers of bipyridine binding sites afford only homoleptic helicates.[13a] On the basis of this study, it was suggested that the self-assembly of copper helicates occurs with a high degree of self-recognition. However, more recently it was demonstrated that organic ligands having three bipyridine binding sites with different bridges afford both homoleptic and heteroleptic helicates.[13b] To further examine the notion of self-recognition in the self-assembly process of helicates, we prepared the new ligands **1** and **2** as well as ligands **3**[8a] and **4**[14] (Scheme 1). We first prepared and characterized the new homoleptic double-stranded helicates of **1** and **2**, and then we studied the helicate distributions obtained from the reaction of Cu^+ with mixtures of ligands **1**−**4** (Scheme 1). Our conclusion is that even ligands **2** and **3**, composed of three phananthroline and bipyridine binding sites, respectively, are not "sufficiently instructed" to preclude the formation of their heteroleptic helicate upon reaction with Cu^+.

Results and Discussion

Ligands Synthesis. Ligands **1** and **2** (Scheme 1) were prepared by reacting 2 equiv of the lithium or the sodium salts of 2-(hydroxymethyl)-9-methyl-1,10-phenanthroline (**5**) with 1 equiv of 6,6′-bis(bromomethyl)-2,2′-bipyridine (**6**) or 2,9-bis(bromomethyl)-1,10-phenanthroline (**7**), respectively, in dry THF (Scheme 2).

Scheme 2



5 **6** **7**

Ligands **3** and **4** were prepared according to Lehn et al.[8a] and Greenwald et al.,[14] respectively. Compound **5** was prepared from 2,9-dimethyl-1,10-phenanthroline (**7**)- by selective mono-N-oxidation, acetylation of **8**, and deprotection of the acetyl group by NaOH, as shown in Scheme 3.[15] Dibromide **6** was prepared from 2,2-bipyridine (**10**) by dimethylation with methyllithium in dry THF[16a] followed by bromination with *N*-bromosuccinimide (NBS) in CCl_4. Dibromide **14** was prepared from 2,9-dimethyl-1,10-phenanthroline (**7**) by oxidation of the methyl groups with SeO_2,[16b] reduction of the obtained dialdehyde (**12**) to the respective dialcohol (**13**), and finally bromination of **13** with 47% HBr (Scheme 3).

Synthesis and Characterization of the New Homoleptic Double-Stranded Helicates of 1 and 2. Figures 1 and 2 show the ^{1}H NMR spectra of **1**, **2**, and their respective copper and silver complexes. From these figures it is clear that the reaction of 2 equiv of **1** or **2** with 3 equiv of tetrakis(acetonitrile)copper(I) hexafluorophosphate $[Cu(CH_3CN)_4PF_6]$[17] afforded the expected homoleptic double-stranded helicates $[(\mathbf{1})_2Cu_3]^{3+}$ and $[(\mathbf{2})_2Cu_3]^{3+}$, respectively. The copper helicates were the only products of these reactions (Figures 1B and 2B). The reaction of 2 equiv of **1** with 3 equiv of silver trifluoromethylsulfonate ($AgCF_3SO_3$) afforded $[(\mathbf{1})_2Ag_3]^{3+}$ (Figure 1C). However, under the same conditions **2** unexpectedly afforded a mixture of complexes. In DMSO-d_6 solution, the ^{1}H NMR spectrum of **2** upon addition of Ag^+ was broad and gave no information on the nature of the formed complex. In a CD_3CN solution, however, the ^{1}H NMR spectrum consisted of sharp lines and was tentatively assigned to a mixture of complexes of a double-stranded nature (Figure 2C). Addition of a large excess of $AgCF_3SO_3$ to the CD_3CN solution of **2** afforded much simpler ^{1}H and ^{13}C NMR spectra which are in line with that expected for $[(\mathbf{2})_2Ag_3]^{3+}$ (Figure 2D). Figures 1 and 2 show the dramatic changes observed in the ^{1}H NMR spectra of the ligands upon helicate formation. Complete assignment of the ^{1}H NMR spectra of **1**, **2**, and their respective copper and silver complexes was achieved by long-range COSY (LR-COSY).[18] In these ^{1}H 2D NMR

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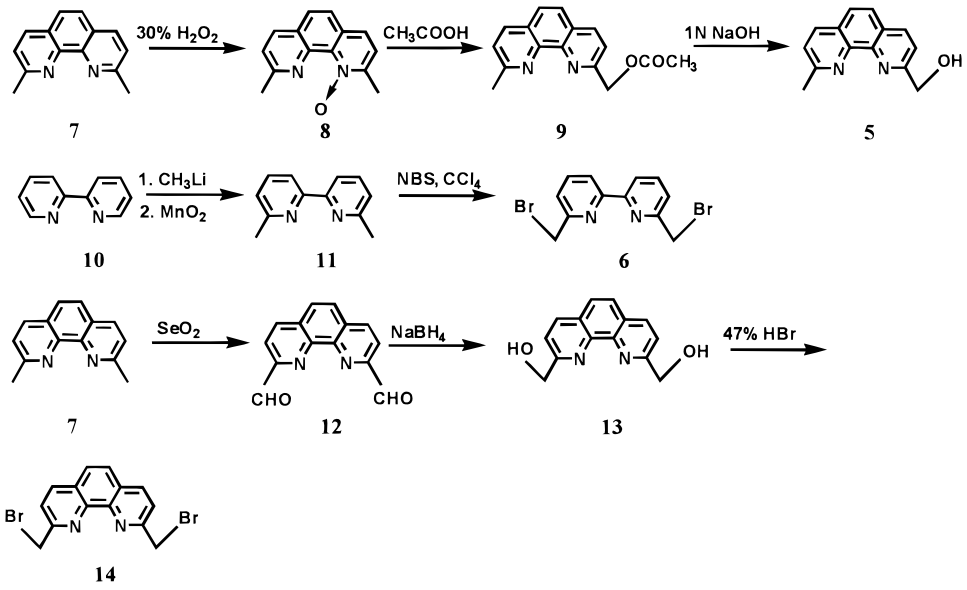
Scheme 3



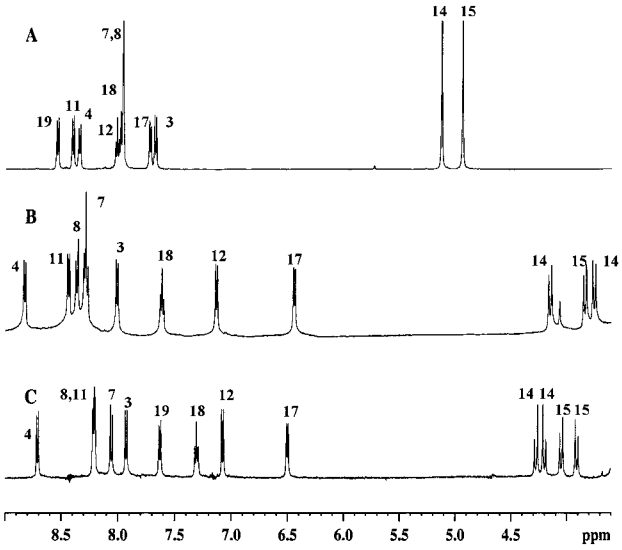


Figure 1. ^{1}H NMR spectra (500 MHz) at 25 °C of (A) **1**, (B) $[(\mathbf{1})_2Cu_3]^{3+}$, and (C) $[(\mathbf{1})_2Ag_3]^{3+}$ in DMSO-d_6. Only the aromatic and methylene bridge regions are shown.

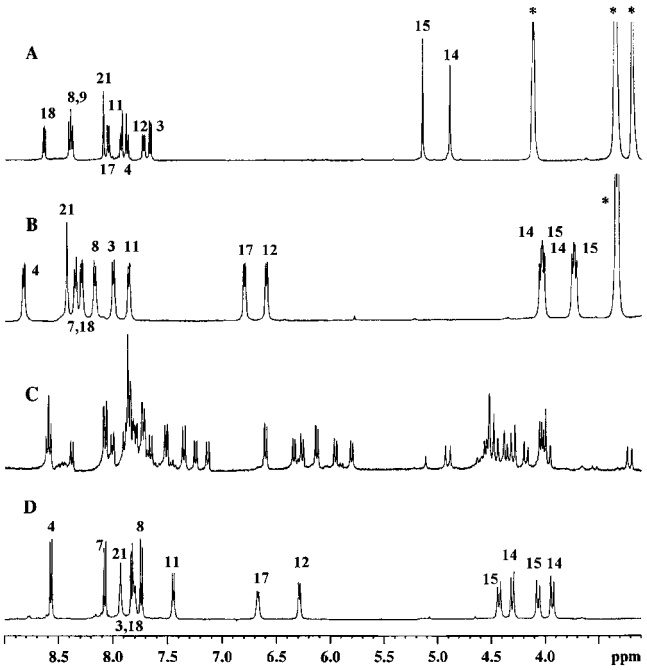


Figure 2. ^{1}H NMR spectra (500 MHz) at 25 °C of (A) **2** in DMSO-d_6, (B) $[(\mathbf{2})_2Cu_3]^{3+}$ in DMSO-d_6, (C) the silver complexes of **2** in CD_3CN, and (D) same as (C) after the addition of excess of Ag^+, i.e., $[(\mathbf{2})_2Ag_3]^{3+}$. Only the aromatic and methylene bridge regions are shown. The signalsmarked with an asterisk indicate the peaks of residual water and methanol.

spectra the cross-peaks between the methyl and the methylene protons of the bridges and their neighboring aromatic protons were identified, allowing unequivocal assignment of all the protons of the ligands and complexes. As an example, the LR-COSY ^{1}H NMR spectrum of $[(\mathbf{2})_2Cu_3]^{3+}$ is shown in Figure 3. The signals of the protonated carbons in the ^{13}C NMR spectra were assigned by an HMQC experiment.[18b] The spectral parameters of ligands **1**, **2**, and their copper and silver helicates are summarized in the Experimental Section.

The formation of double-stranded copper helicates of **1** and **2** was corroborated by fast atomic bombardment mass spectrometry (FAB-MS). Well-defined peaks at *m*/*z* of 1737.0 and 1785.3 with the relative intensities of 20% and 25%, respectively, were observed for the copper complexes of **1** and **2**. These peaks correspond to $[(\mathbf{1})_2Cu_3(PF_6)_2]^+$ and $[(\mathbf{2})_2Cu_3(PF_6)_2]^+$, respectively. The FAB-MS of the silver complexes of **1** and **2** were much less informative, and no peaks which correspond to the $[(\mathbf{L})_2Ag_3(CF_3SO_3)_2]^+$-type ion could be observed. In fact, no peaks that could corroborate the double-strand nature of the silver helicates were detected by FAB-MS.[19,20] This is to be expected as it is well known that 2,2′-bipyridine and 1,10-phenanthroline complexes of Ag^+ are significantly less stable than the respective Cu^+ complexes.[19,20]

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(20) Electrospray mass spectrometry (ES-MS) was recently shown to be the more suitable technique for obtaining molecular peaks of relatively weak metallosupramolecular complexes. However, this technique is not currently available to us. For a discussion on the different MS techniques used for helicate characterization, see ref 10b, pp 2047−2050, and the references therein.

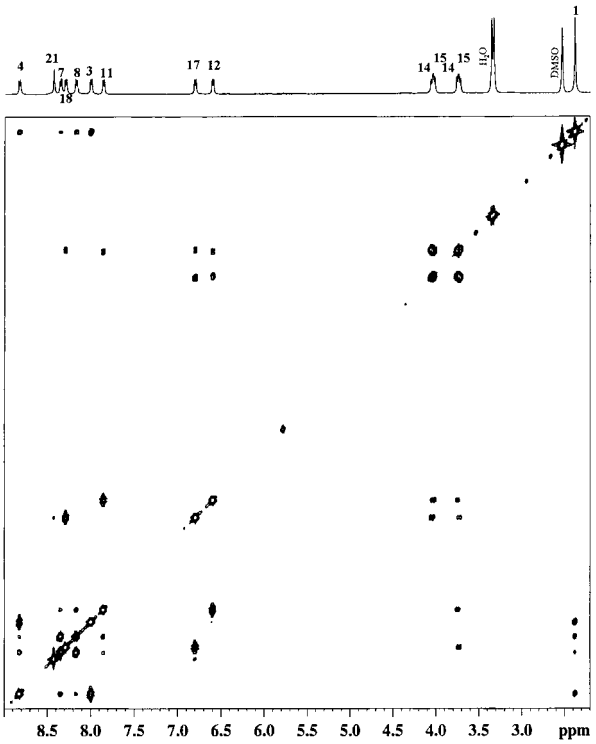

Figure 3. A 500 MHz, ^{1}H 2D long-range COSY NMR spectrum of $[(\mathbf{2})_2Cu_3]^{3+}$ in DMSO-d_6.

The ^{1}H NMR spectrum of the reaction mixture obtained by reacting 2 equiv of **2** with 3 equiv of Ag^+ in CD_3CN indicates that three different silver complexes are formed (Figure 2C). The similarity of the ^{1}H NMR spectra of these species seems to suggest that all three complexes are double-stranded. However, the MS results failed to corroborate this conclusion. To further confirm that the three complexes were of double-stranded nature, we performed NMR diffusion experiments as described previously.[14] One of the dominant factors affecting the diffusion coefficients of organic species in organic solvents is their molecular weight. As single- and double-stranded complexes differ considerably in their molecular weight, we have measured the diffusion coefficients of **1** and of the silver complexes of **2** in CD_3CN, using the pulsed gradient spin echo (PGSE) technique.[21] We could not measure the diffusion coefficient of **2** in CD_3CN due to its low solubility in this solvent. These measurements demonstrated that all three silver complexes shown in Figure 2C have very similar diffusion coefficients ($0.72 \pm 0.03 \times 10^{-5}$ cm^2 s^{-1}), indicating that they have similar molecular weights. More importantly, under the same conditions the diffusion coefficient of the free ligand **1** was found to be much higher in CD_3CN ($1.13 \pm 0.01 \times 10^{-5}$ cm^2 s^{-1}). These results indicate that these silver complexes are double-stranded in nature. As pointed out above, addition of a large excess of Ag^+ to the solution drove the equilibrium toward the trinuclear double-stranded helicate $[(\mathbf{2})_2Ag_3]^{3+}$(Figure 2D) which gave the expected ^{1}H and ^{13}C NMR spectra. These results seem to suggest that the silver helicate of **1** is more stable than the double-stranded silver helicate of **2**. However, it is known that 1,10-phenanthroline is a stronger complexant than 2,2′-bipyridine toward Ag^+, so the contrary is to be expected. It seems therefore that the apparent destabilization of the double-stranded helicate of **2** originates from steric rather than from electronic factors. The rigid all phenanthroline system **2** might lack some of the flexibility needed for the easy formation of the trinuclear double-stranded helicates.

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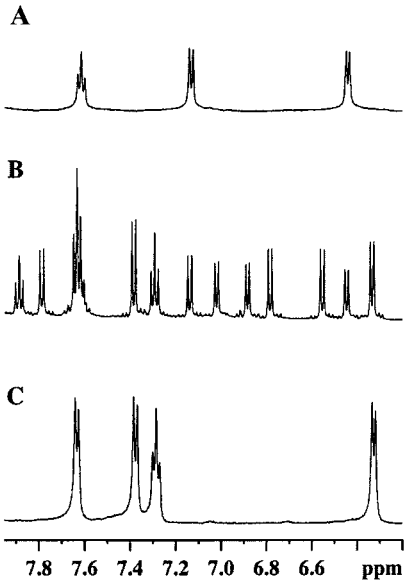

Figure 4. Enlarged high-field part of the aromatic region of the 500 MHz ^{1}H NMR spectra in DMSO-d_6 of the copper complexes obtained from a starting solution of (A) **1**, (B) a mixture of **1** and **4**, and (C) **4**.

Since the data clearly indicate that both **1** and **2** form the expected double-stranded helicates $[(\mathbf{1})_2Cu_3]^{3+}$ and $[(\mathbf{2})_2Cu_3]^{3+}$, we launched a series of experiments in which the starting solutions were mixtures of these new ligands and the known compounds **3** and **4**. These experiments were performed to evaluate the role of self-recognition in the formation of such double-stranded helicates. The most interesting mixture to follow consisted of ligands **2** and **3** that differ in all three binding sites.

Helicates from Mixtures of Ligands. The role of self-recognition in the self-assembly of such helicates was evaluated by analyzing the distribution of helicates obtained from mixtures of **1** with **4** and of **2** with **3**. Figure 4 shows the high-field part of the aromatic region in the 500 MHz ^{1}H NMR spectra of the homoleptic double-stranded copper complexes of **1** and **4** (Figures 4A and 4C, respectively) along with that of the copper complexes obtained from the mixture of **1** and **4** (Figure 4B). Figure 5 depicts the high-field portion of the aromatic region in the 500 MHz^{1}H NMR spectra of the double-stranded helicates of **2** and **3** (Figures 5A and 5C, respectively) along with the spectrum obtained by mixing the DMSO-d_6 solutions of $[(\mathbf{2})_2Cu_3]^{3+}$ and $[(\mathbf{3})_2Cu_3]^{3+}$. In both examples it is clear that the ^{1}H NMR of the mixtures are not a simple superposition of the spectra of the two homoleptic double-stranded helicates. In each case, additional peaks were observed in the ^{1}H NMR spectrum. These additional peaks were attributed to the heteroleptic double-stranded helicates, namely to $[(\mathbf{1/4})Cu_3]^{3+}$ and

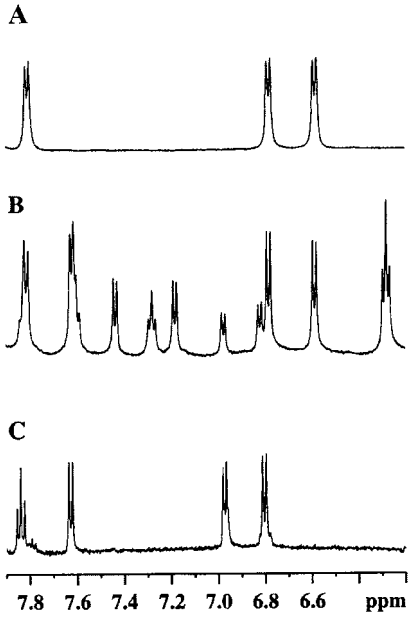

Figure 5. Enlarged high-field part of the aromatic region of the 500 MHz ^{1}H NMR spectra in DMSO-d_6 of (A) $[(\mathbf{2})_2Cu_3]^{3+}$ and (C) $[(\mathbf{3})_2Cu_3]^{3+}$. (B) The spectrum obtained a week after mixing the solutions shown in (A) and (C).

$[(\mathbf{2/3})Cu_3]^{3+}$. When the DMSO-$d_6$ solutions of $[(\mathbf{2})_2Cu_3]^{3+}$ and $[(\mathbf{3})_2Cu_3]^{3+}$ were mixed and followed by NMR spectroscopy, the $[(\mathbf{2/3})Cu_3]^{3+}$ peaks were apparent only at about 24 h after the mixing. Figure 5B shows the product distribution obtained 1 week after mixing. Two weeks after the mixing, the solution reached a steady state with the helicate distribution expected from simple statistics. It should be noted that when a similar experiment was performed with $[(\mathbf{2})_2Ag_3]^{3+}$ and $[(\mathbf{3})_2Ag_3]^{3+}$ in CD_3CN solution, the additional peaks corresponding to $[(\mathbf{2/3})Ag_3]^{3+}$ were observed as fast as we could measure the ^{1}H spectrum (about 20 min), reflecting the much higher lability of the silver helicates as compared with that of the copper helicates. The increased lability of the Ag^+ complexes is expected due to the weaker Ag−N bonds. It should be noted that these results clearly indicate that the formation of a mixture consisting of two homoleptic helicates and one heteroleptic helicate is thermodynamically favored in the above cases. Although ligand **3** contains three 2,2′-bipyridine binding sites and ligand **2** contains three 1,10-phenanthroline binding sites, a heteroleptic helicate is formed between the two ligands.

These NMR results were also corroborated by FAB mass spectrometry. For example, when the DMSO-d_6 solution of the copper helicates whose NMR spectrum is shown in Figure 5B was subjected to FAB-MS, the observed spectrum revealed three peaks with *m/z* of 1785, 1713, and 1641, corresponding to $[(\mathbf{2})_2Cu_3(PF_6)_2]^+$, $[(\mathbf{2/3})Cu_3(PF_6)_2]^+$, and $[(\mathbf{3})_2Cu_3(PF_6)_2]^+$, respectively (Figure 6).

Ligands **1**−**4** investigated in the present study all have similar structures and all form $[(\mathbf{L})_2Cu_3]^{3+}$-type helicates. Therefore, these ligands represent an ideal series of ligands for challenging the role of self-recognition in helicate self-assembly. In other words, these ligands can be used to address the question "how different should two ligands be for complete self-discrimination in their self-assembly to copper helicates?". Our results clearly indicate that even **2** and **3**, which have a similar structure, consisting of three 1,10-phenanthroline and three 2,2′-bipyridine binding sites, respectively, form a heteroleptic helicate. Additionally, even in this case, helicate distribution apparently follows statistical expectations.

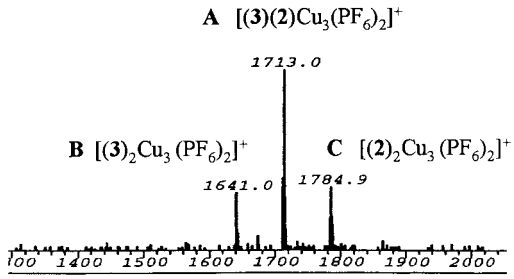

Figure 6. Partial FAB-MS spectrum of the DMSO-d_6 solution shown in Figure 5B. Only three peaks corresponding to the two homoleptic helicates and one heteroleptic helicate of **2** and **3** are observed.

The above results show that the self-assembly process of ligands **1**−**4** occurs with no significant self-recognition. In our systems both the number and the total length of these ligands is not very different. In addition, even the affinity of the different binding sites for Cu^+ is similar. Therefore, both the principle of maximum occupancy and the entropic factor predict a similar stability for the homoleptic and the heteroleptic helicates of these ligands.[23] Consequently, one might expect to obtain a heteroleptic helicate from mixtures of such ligands. Recently it was shown by electrochemical methods that the affinity of the 1,10-phenanthroline binding site for Cu^+ is around 10-fold greater than that of the 2,2′-bipyridine binding site in trinuclear copper helicates.[22] The formation of a heteroleptic helicates from the mixture **2** and **3** indicates that even three such differences are not sufficient to prevent the formation of such double-stranded heteroleptic helicate. These results indicate that our ability to construct supramolecular systems from "soups" of building units is still limited. This conclusion is in line with a recent report by the group of Lehn.[13b]

Conclusions

Ligands **1** and **2** self-assemble into double-stranded helicates of the $[(\mathbf{L})_2Cu_3]^{3+}$-type upon addition of Cu^+. Upon addition of Ag^+, **1** forms a trinuclear double-stranded helicate, whereas **2** affords a mixture of complexes that appear to be of double-stranded nature. A large excess of Ag^+ drives the equilibrium toward $[(\mathbf{2})_2Ag_3]^{3+}$. Complexation experiments show that whenever the starting solutions consist of a mixture of these ligands the self-assembly process proceeds without self-recognition and helicate distribution appears to follow simple statistics. We conclude that even ligands **2** and **3** which consist of three 1,10-phenanthroline and 2,2′-bipyridine binging sites, respectively, are not "sufficiently instructed" to preclude the formation of their heteroleptic helicate.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on an AC 200 or an ARX 500 Bruker spectrometer (Karlsruhe, Germany). The NMR spectra of the ligands and their complexes as well as the NMR diffusion measurements were all recorded

(22) Greenwald, M.; Wessely, D.; Katz, E.; Willner, I.; Cohen, Y. Submitted for publication.

(23) Williams, A. *Chem. Eur. J.* **1997**, *3*, 15.

on the ARX 500 NMR spectrometer as described previuosly.[21c–f] Chemical shifts are reported in ppm relative to the peak of the residual protonated solvents (δ DMSO-d_6 2.53, δ $CDCl_3$ 7.26). ^{13}C NMR chemical shifts are also reported in ppm relative to the solvent resonance (δ DMSO-d_6 39.5, δ $CDCl_3$ 77.0), and the spin−spin couplings are reported in hertz. Fast atomic bombardment mass spectra (FAB-MS) were recorded on a VG-AutoSpec M250 mass spectrometer (Manchester, U.K.) in *m*-nitrobenzyl alcohol (NBA) matrix. Melting points were all measured on a IA9100 melting point apparatus (Electrothermal, U.K.), and the values are not corrected.

The following compounds were prepared according to the literature. 1,10-Phenanthroline-2,9-dicarboxyaldehyde (**12**):[16b] mp 237 °C (lit. mp 231−232 °C[16b]). ^1H NMR (200 MHz, $CDCl_3$): 10.57 (s, 2H), 8.52 (d, 8.0, 2H), 8.39 (d, 8.0, 2H), 8.05 (s, 2H). 2,9-Bis(hydroxymethyl)-1,10-phenanthroline (**13**):[16b] mp 197 °C (lit. mp 197−198 °C[16b]). ^1H NMR (200 MHz, DMSO-d_6): 8.50 (d, 8.0, 2H), 7.95 (s, 2H), 7.90 (d, 8.0, 2H), 5.73 (t, 8.0, 2H), 4.9 (d, 8.0, 4H). We found that by continuing the reflux for 4 h instead of 2 h the yield increases the 80%−90%.

2,9-Bis(bromomethyl)-1,10-phenanthroline (**7**):[16b] mp 108−110 °C (lit. mp 110−111 °C[16b]). ^1H NMR (200 MHz, DMSO-d_6): 8.53 (d, 8.0, 2H), 8.01 (s, 2H), 7.94 (d, 8.0, 2H), 5.01 (s, 4H). 6,6′-Bis(bromomethyl)-2,2′-bipyridine (**6**):[8a] mp 182 °C (lit. mp 180−181 °C[8a]). ^1H NMR (200 MHz, $CDCl_3$): 8.38 (d, 8.0, 2H), 7.82 (t, 8.0, 2H), 7.47 (d, 6.0, 2H), 4.62 (s, 4H).

Synthesis. 2,9-Dimethyl-1,10-phenanthroline *N*-Oxide (8). Compound **8** was prepared as described[15] with the following modifications: 2,9-dimethyl-1,10-phenanthroline (**7**) (5 g, 0.024 mol) was dissolved in acetic acid (28 mL) and heated to 75 °C. Then 30% hydrogen peroxide (4.36 mL, 0.04 mol) was added. After 3.5 h of reflux, the mixture was cooled and added to a sodium carbonate solution (30 g in 270 mL of water). The resulting mixture was stirred for 30 min and then extracted with chloroform, dried, and evaporated, yielding 5.15 g of **8** (∼100% yield): mp 135 °C (lit. mp 131−132 °C[15]). ^1H NMR (200 MHz, $CDCl_3$): 8.13 (d, 8.0, 1H), 7.71 (s, 1H), 7.69 (s, 1H) 7.67 (d, 8.0, 1H), 7.63 (d, 8.0, 1H), 7.52 (d, 8.0, 1H), 2.94 (s, 3H), 2.78 (s, 3H).

2-(Acetoxymethyl)-9-methyl-1,10-phenanthroline (9). Compound **9** was prepared as decribed[15] with the only modification being that the crude was eluted after evaporation without any workup through a short alummina column with dichloromethane. The eluent was evaporated, yielding 3.8 g of **9** as a brown oil (59% yield).^1H NMR (200 MHz, $CDCl_3$): 8.30 (d, 8.0, 1H), 8.24 (d, 8.0, 1H), 7.79 (s, 2H), 7.72 (d, 8.0, 1H), 7.58 (d, 8.0, 2H), 5.64 (s, 2H), 2.99 (s, 3H), 2.2 (s, 3H).

2-(Hydroxymethyl)-9-methyl-1,10-phenanthroline (5). A solution of 1 N NaOH (14 mL) was added to a stirred solution of **9** (3.78 g, 0.0135mole) in ethanol (15 mL) at room temperature. The solution was stirred overnight, and then water was added. The ethanol was evaporated, and the water layer was extracted with dichloromethane (4 × 30 mL). The organic phase was dried with magnesium sulfate and evaporated, yielding 2.17 g of **5** as a brown powder (67% yield): mp 149−152 °C (lit. mp 153−158 °C[15]). ^1H NMR (200 MHz, $CDCl_3$): 8.23 (d, 8.0, 1H), 8.16 (d, 8.0, 1H), 7.76 (s, 2H), 7.58 (d, 8.0, 1H), 7.52 (d, 8.0, 1H), 5.11 (s, 2H), 2.92 (s, 3H).

6,6′-Dimethyl-2,2′-bipyridine (11). This compound was prepared as described[16a] with the following modifications: 1.4 M methyllithium (110 mL, 0.154 mol) was added to a stirred solution of 2,2′-bipyridine **10** (6 g, 0.038 mol) in dry THF (250 mL) cooled to −40 °C. The solution was stirred at this temperature for 1 h and then warmed to 0 °C. After 2 h at this temperature, the mixture was refluxed for 4 h. Then the reaction mixture was cooled and ice water (50 mL) was added. Following evaporation and extracteion with dichloromethane (4 × 60 mL), MnO_2 (100 g, Merck 805958) was added. After 30 min the mixture was dried with magnesium sulfate and filtered over Celite. The solvent was evaporated yielding 3.65 g of **11** as an orange powder (52% yield): mp 89−90 °C (lit. mp 89.5 °C[16c]). ^1H NMR (200 MHz, $CDCl_3$): 8.16 (d, 8.0, 2H), 7.68 (t, 8.0, 2H), 7.15 (d, 8.0, 2H), 2.62 (s, 6H).

Ligand Preparation. 6,6′-Bis[(2-methyl-1,10-phenanthroline-9-yl)methyleneoxymethylenyl]-2,2′-bipyridine (1): Butyllithium (1.6 M, 2.5 mL, 4 mmol) was added, using a syringe through a septum, to a solution of **5** (0.87 g, 3.8 mmol) dissolved in dry THF (200 mL) and cooled to −70 °C, under an argon atmosphere. After 30 min a solution of **6** (0.5 g, 1.4 mmol) in dry THF (30 mL) was added and the mixture was refluxed for 20 h. After evaporation, the crude solid was recrystallized from hot methanol, yielding 0.25 g of **1** (27% yield): mp 173 °C. ^1H NMR (500 MHz, $CDCl_3$): 8.29 (d, 8.2, H-11, 2H) 8.34 (d, 7.7, H-19, 2H), 8.15 (d, 8.1, H-4, 2H), 7.98 (d, 8.2, H-12, 2H), 7.83 (t, 7.7, H-18, 2H), 7.75 (s, H-7, H-8, 4H), 7.59 (d, 7.5, H-17, 2H), 7.51 (d, 8.1, H-3, 2H), 5.28 (s, H-14, 4H), 4.95 (s, H-15, 4H), 2.94 (s, H-1, 6H). ^{13}C NMR (500 MHz, DMSO-d_6): 159.9, 159.3, 157.7, 155.5, 145.3, 145.1, 137.5 (C-18), 136.9 (C-11), 136.5 (C-4), 128.0, 126.9, 126.1 (C-8), 125.5 (C-7), 123.7 (C-3), 121.4 (C-17), 120.7 (C-12), 119.9 (C-19), 74.5 (C-14), 74.2 (C-15), 29.7 (C-1). FAB-MS (DMSO, NBA): *m*/*z* 651.2 (**1**Na^+, 100%), 635 (**1**Li^+, 100%), 629.2 (**1**H^+, 10%).

2,9-Bis[(2-methyl-1,10-phenanthrolin-9-yl)methylenoxymethylenyl]-1,10-phenanthroline (2). Sodium hydride (143 mg, 3.3 mmol) was added to a stirred solution of **5** (785.5 mg, 3.3 mmol) in dry THF (50 mL) at room temperature under an argon atmosphere. After 1 h of stirring at this temperature, the mixture was warmed to 45 °C and **7** (600 mg, 1.65 mmol) dissolved in dry THF (20 mL) was added dropwise. Warming and stirring were continued for an additional 20 h, and the mixture was evaporated. The crude solid was eluted with a 1:1 chloroform:methanol solution through an LH-20 column. Trituration in hot *tert*-butyl ether gave 100 mg of **2** (10% yield): mp 215−220 °C (dec). ^1H NMR (500 MHz, DMSO-d_6): 8.63 (d, 8.0, H-18, 2H), 8.38 (t, 8.5, H-7, H-8, 4H), 8.08 (s, H-21, 2H), 8.04 (d, 8, H-17, 2H), 7.92 (d, 8.5, H-11, 2H), 7.87 (d, 8.5, H-4, 2H), 7.72 (d, 8, H-12, 2H), 7.66 (d, 8.5, H-3, 2H), 5.15 (s, H-15, 4H), 4.895 (s, H-14, 4H), 2.66 (s, H-1, 6H). ^{13}C NMR (500 MHz, DMSO-d_6): 158.6, 158.6, 158.4, 157.8, 144.5, 144.1, 137.4 (C-18), 136.9 (C-7), 136.5 (C-8), 127.9, 127.5, 126.6, 126.4 (C-21), 126.2 (C-11), 125.4 (C-4), 123.6 (C-3), 121.5, 120.6 (C-12), 73.3 (C-15), 72.9 (C-14), 24.9 (C-1). FAB-MS (DMSO, NBA): *m*/*z* 675.3 (**2**Na^+, 100%).

6″,6‴-Bis[(6-methyl-2,2′-bipyridin-6′-yl)methylenoxymethyl-yl]-2″,2‴-bipyridine (3).[8a] Compound **3**, known as BP_3, was prepared according to the literature, yielding the expected ^1H NMR spectrum: mp 232−233 °C (lit. mp 227−229 °C[8a]). ^1H NMR (500 MHz, CD_2Cl_2): 8.32 (d, 7.7, H-8, 4H), 8.19 (d, 7.7, H-5, 2H), 7.83 (t, 7.7, H-9, 4H), 7.68 (t, 7.7, H-4, 2H), 7.54 (d, 7.7, H-10 or H-15, 2H), 7.52 (d, 7.7, H-10 or H-15, 2H), 7.16 (d, 7.7, H-3, 2H), 4.85 (s, H-12 and H-13, 8H), 2.58 (s, H-1, 6H).

2,9-Bis[(6-methyl-2,2′-bipyridin-6′-yl)methylenoxymethyl-yl]-1,10-phenanthroline (4).[14] Compound **4** was prepared as previously described by us and gave the expected ^1H NMR spectrum: mp 141 °C (lit. 141−142 °C[14]). ^1H NMR (500 MHz, DMSO-d_6): 8.56 (d, 8.5, H-16, 2H), 8.33 (d, 7.6, H-8, 2H), 8.2 (d, 7.7, H-5, 2H), 8.02, 8.01, 8.00 (s, t, d, 7.5, 8.5, H-19, H-9, H-15, 6H), 7.82 (t, 7.7, H-4, 2H), 7.7 (d, 7.6, H-10, 2H), 7.32 (d, 7.7, H-3, 2H), 5.12 (s, H-13, 4H), 4.92 (s, H-12, 4H), 2.59 (s, H-1, 6H).

Complex Preparation. [(1)$_2$Cu$_3$(PF$_6$)$_3$]. A solution of $Cu(CH_3CN)_4PF_6$ (48.3 mg, 0.13 mmol) in acetonitrile (2 mL) was added to a solution of **1** (50 mg, 0.076 mmol) in dichloromethane (2 mL). The red solution obtained was stirred for 1 h and then evaporated. The crude product was triturated with a diethyl ether:dichloromethane (9:1) solution, followed by a solution of diethyl ether:acetonitrile (95:5). Finally, the product was dried (50 °C, 25mbar), yielding 40 mg of the complex as a red powder (53% yield): mp 240 °C (dec). ^1H NMR (500 MHz, DMSO-d_6): 8.82 (d, 8.0, H-4, 4H), 8.43 (d, 8.1, H-11, 4H), 8.36 (d, 8.9, H-8, 4H), 8.29 (d, 8.5, H-7, 4H), 8.27 (d, 9.2, H-19, 4H), 8.00 (d, 8.0, H-3, 4H), 7.61 (t, 7.7, H-18, 4H), 7.13 (d, 8.1, H-12, 4H), 6.44 (d, 7.42, H-17, 4H), 3.8 (AB, 13.3, H-15, 8H), 3.79 (AB, 17.4, H-14, 8H), 2.45 (s, H-1, 12H). ^{13}C NMR (500 MHz, DMSO-d_6): 157.7, 154.9, 154.23, 149.6, 141.9, 141.7, 137.9 (C-18), 137.52 (C-12), 137.36 (C-4), 127.92, 127.0 (C-7), 126.74 (C-8), 125.8, 125.8 (C-3), 122.8 (C-17), 122.6 (C-11),

120.9 (C-19), 71.2 (C-15), 70.7 (C-14), 25.5 (C-1). FAB-MS (DMSO, NBA): *m/z* 1737 ([(**1**)$_2$Cu$_3$(PF$_6$)$_2$]$^+$, 20%), 691 ([**1**Cu)]$^+$, 85%).

[(2)$_2$Cu$_3$(PF$_6$)$_3$]. A solution of Cu(CH$_3$CN)$_4$PF$_6$ (17.2 mg, 0.046 mmol) in acetonitrile (10 mL) was added to a suspension of **2** (20 mg, 0.03) in dichloromethane (10 mL). The red solution obtained was stirred for 1 h and then evaporated. The crude product was triturated with a diethyl ether:dichloromethane (9:1) solution and then with a diethyl ether: acetonitrile (95:5) solution. Finally the product was dried (50 °C, 25mbar), affording 29 mg of (**2**)$_2$Cu$_3$(PF$_6$)$_3$ as a red powder (98% yield): mp 243 °C (dec). ^{1}H NMR (500 MHz, DMSO-d_6): 8.82 (d, 8.0, H-4, 4H), 8.42 (s, H-21, 4H), 8.35 (d, 9.0, H-7, 4H), 8.29 (d, 8.0, H-18, 4H), 8.16 (d, 8.5, H-8, 4H), 8.0 (d, 8.0, H-3, 4H), 7.85 (d, 8.0, H-11, 4H), 6.8 (d, 8.0, H-17, 4H), 6.59 (d, 7.5, H-12, 4H), 3.87, 3.88 (AB, AB, 14.0, H-14, H-15, 16H), 2.37 (s, H-1, 12H). ^{13}C NMR (500 MHz, DMSO-d_6): 157.8, 154.9, 154.7, 141.9, 141.7, 141.2, 137.7 (C-4), 137.5, 136.7, 136.7 (C-11), 127.9, 127.6, 127.1 (C-7), 127.0 (C-18), 126.8 (C-8), 125.9 (C-3), 122.0 (C-17), 121.8 (C-12), 71.3, 71.1 (C-14, C-15), 25.6 (C-1). FAB-MS (DMSO, NBA): *m/z* 1785 ([(**2**)$_2$Cu$_3$(PF$_6$)$_2$]$^+$, 10%), 715 ([**2**Cu]$^{+2}$, 25%).

[(3)$_2$Cu$_3$(PF$_6$)$_3$]. This complex was prepared according to the literature[8a] and gave the expected ^{1}H NMR spectrum. ^{1}H NMR (500 MHz, DMSO-d_6): 8.48, 8.47 (d, d, 7.8, H-8, H-5, 8H), 8.37 (d, 7.9, H-17, 4H), 8.18 (t, 7.8, H-4, 4H), 8.07 (t, 7.8, H-9, 4H), 7.84 (t, 7.9, H-16, 4H), 7.63 (d, 7.8, H-3, 4H), 6.97 (d, 7.8, H-10, 4H), 6.81 (d, 7.9, H-15, 4H), 3.94, 3.92 (d, d, 13.4, H-12, H-13, 8H), 3.62, 3.57 (d, d, 13.4, H-13, H-12, 8H), 2.14, (s, H-1, 12H).

[(4)$_2$Cu$_3$(PF$_6$)$_3$]. This complex was prepared as described previously by us and gave the expected ^{1}H NMR spectrum.[14] ^{1}H NMR (500 MHz, DMSO-d_6): 8.70 (d, 8.1, H-16, 4H), 8.50 (d, 7.7, H-5, 4H), 8.50 (s, H-19, 4H), 8.21 (t, 7.7, H-4, 4H), 8.14 (d, 7.7, H-8, 4H), 7.64 (d, 7.7, H-3, 4H), 7.38 (d, 8.1, H-15, 4H), 7.29 (t, 7.7, H-9, 4H), 6.33 (d, 7.7, H-10, 4H), 4.2, 3.82 (AB, 13.4, H-13−13′, 8H), 3.86, 3.64 (AB, 13.4, H-12−12′, 8H), 2.10 (s, H-1, 12H).

[(1)$_2$Ag$_3$(CF$_3$SO$_3$)$_3$]. AgCF$_3$SO$_3$ (33.26 mg, 0.13 mmol) dissolved in acetonitrile (2 mL) was added to a solution of **1** (50 mg, 0.076 mmol) in chloroform (2 mL). After 1 h the mixture was filtered over Celite, evaporated, and triturated with a diethyl ether:dichloromethane (9:1) solution, followed by a solution of diethyl ether:acetonitrile (95:5). The solid was dried, affording 25 mg of the complex (40% yield): mp 230 °C (dec). ^{1}H NMR (500 MHz, DMSO-d_6): 8.73 (d, 8.2, H-4, 4H), 8.22 (d, 6.0, H-11, H-7, 4H), 8.06 (d, 8.8, H-7, 4H), 7.93 (d, 8.0, H-3, 4H), 7.64 (d, 8.0, H-19, 4H), 7.31 (d, 8.0, H-18, 4H), 7.08 (d, 8.0, H-12, 4H), 6.51 (d, 7.5, H-17, 4H), 4.24 (AB, 13.5, H-13, 8H), 3.28 (AB, 12.8, H-14, 8H), 3.5 (s, H-1, 12H). ^{13}C NMR (500 MHz, DMSO-d_6): 158.7, 155.9, 155.2, 148.9, 140.7, 138.8 (C-18), 138.2, 138.6 (C-4), 128.0, 127.0 (C-11), 127.2 (C-7), 126.1 (C-8), 125.3 (C-3), 123.5 (C-17), 123.1 (C-12), 122.3, 121.9 (C-19), 73.4 (C-14), 73.1 (C-15), 27.0 (C-1).

[(2)$_2$Ag$_3$(CF$_3$SO$_3$)$_3$]. A solution of AgCF$_3$SO$_3$ (33.2 mg, 0.13 mmol) in acetonitrile (2 mL) was added to a solution of **2** (50 mg, 0.076 mmol) in chloroform (2 mL). After 1 h the mixture was filtered over Celite, evaporated, and triturated with a diethyl ether:dichloromethane (9:1) solution and then with a diethyl ether:acetonitrile (95:5) solution. The solid was dried, giving 12.8 mg of yellow powder. The ^{1}H NMR spectrum of this powder in DMSO-d_6 was noninformative. Therefore, we dissolved the power in CD$_3$CN. Only after the addition of an excess of AgCF$_3$SO$_3$ to the NMR tube was a spectrum consistent with that of [(**2**)$_2$Ag$_3$]$^{3+}$ obtained. ^{1}H NMR (500 MHz, CD$_3$CN): 8.57 (d, 8.0, H-4, 4H), 8.16 (d, 8.0, H-7, 4H), 7.93 (broad s, H-21, 4H), 7.82 (d, 8.0, H-3, 4H), 7.79 (broad s, H-18, 4H), 7.74 (d, 9.0, H-8, 4H), 7.44 (d, 8.0, H-11, 4H), 6.67 (d, 7.5, H-17, 4H), 6.28 (d, 7.5, H-12, 4H), 4.24, 4.11 (AB, AB, 14.0, H-14, H-15, 16H), 2.57 (s, H-1, 12H). ^{13}C NMR (500 MHz,CD$_3$CN): 158.9, 155.5, 140.9, 139.9, 138.3 (C-4), 137.3 (C-11), 137.1 (C-3), 127.6, 127.4 (C-21), 127.2 (C-7), 126.9, 126.7 (C-8), 126.0 (C-18), 125.0, 122.2, 121.2 (C-17), 120.8 (C-12), 119.6, 72.1, 71.9 (C-14, C-15), 26.6 (C-1).

Competition Experiments. A typical procedure for the competition experiments was as follows: compounds **1** (30 mg, 0.0477 mmol) and **4** (28.8 mg, 0.0477 mmol) were carefully weighed and dissolved in dichloromethane (15 mL). Cu(CH$_3$CN)$_4$PF$_6$ (53.3 mg, 0.143 mmol) in acetonitrile (5 mL) was added at room temperature to the dichloromethane solution and stirred overnight. The solvent was evaporated, and the obtained solid was triturated with a diethyl ether:CH$_2$Cl$_2$ (9:1) (10 mL) solution followed by a solution of diethyl ether:CH$_3$CN (95:5) (10 mL). The product was dried and dissolved in DMSO-d_6 and analyzed by NMR spectroscopy. The same procedure was applied to **2** and **3**. In addition, in several experiments the DMSO-d_6 solutions of [(**2**)$_2$Cu$_3$]$^{+3}$ and [(**3**)$_2$Cu$_3$]$^{+3}$ or the CD$_3$CN solutions of [(**2**)$_2$Ag$_3$]$^{+3}$ and [(**3**)$_2$Ag$_3$]$^{+3}$ were mixed and followed by NMR spectroscopy and FAB mass spectrometry.

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