Molecular Devices

A Molecular Ball Bearing Mediated by Multiligand Exchange in Concert**

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There is much interest in the development of devices based on molecular motion similar to that seen in living organisms.[1–3] A variety of chemical bonding patterns have been extensively utilized so far for the realization of such molecular devices at the molecular level: for example, covalent bonding for a controlled rotation through single bonds[4,5] and photoisomerized double bonds[6] as well as noncovalent bonding for the formation of interlocked architectures such as rotaxanes[1,7] and catenanes.[8,9] Among the possible modes of noncovalent bonding, metal coordinative bonding shows particular promise for the fabrication of rotational devices, as evidenced by recent excellent reports on mononuclear bisporphyrinate double-decker complexes[10,11] and a functionalized ferrocene derivative.[12] Herein we present a novel rotational device, a molecular ball bearing mediated by metal ions, which is quantitatively formed as a thermodynamically favorable product from three Ag^+ ions and disk-shaped tris-monodentate and hexa-monodentate ligands through a heterotopic, self-assembly process. In the device the three Ag^+ ions serve as the balls for the relative rotational motion of the two disk-shaped ligands by allowing their efficient rotation through a combination of intramolecular, reversible multipoint ligand exchange and flip motions that act in concert.

In a preliminary study we recently constructed a sandwich-type trinuclear Ag^+ complex $[Ag_3(\mathbf{2})_2]$ using two disk-shaped, tris-monodentate thiazolyl ligands **2**. In this complex, each Ag^+ ion is bound by the two thiazolyl nitrogen donors of the two ligands, and all the monodentate ligand rings attached to **2** tilt toward the same direction to form a helical structure. This arrangement is further accompanied by a 120° flipping rotation of the ligands as a result of the *P* versus *M* equilibrium.[13] This system was further advanced to a heterogeneous Ag^+-mediated association of a hexa-monodentate and a tris-monodentate thiazolyl ligands, **1** and **2**, respectively, to form a heterotopic trinuclear complex $[Ag_3(\mathbf{1})(\mathbf{2})]$.[14] In this complex all three nitrogen donors of the tris(thiazolyl) ligand **2** and every alternate nitrogen donor atoms of the hexa(thiazolyl) ligand **1** participate in the complexation with the three Ag^+ ions in a linear coordination geometry (Figure 1b). This heterotopic complex is quantitatively formed by a simple mixing of **1** and **2** in a 1:1 ratio in the presence of three equivalents of Ag^+ ions in CD_3OD. Moreover, the variable-temperature (VT) ^1H NMR spectroscopic studies strongly suggested that the intramolecular three-point ligand exchange occurred in concert between the two disk-shaped ligands (namely, $\boldsymbol{M} \rightleftharpoons \boldsymbol{P}$ in Figure 2).[15] In an $\boldsymbol{M} \rightarrow \boldsymbol{P}$ conversion, for example, alternate coordinatively free ligand rings of **1** (rings B, D, and F) in ***M*** (with *M* configuration) rotates clockwise and then comes close to the neighboring Ag^+ ion and ligand exchange finally leads to ***P*** (with *P* configuration), presumably through formation of a three-coordinate transition state. The thiazolyl rings B, D, and F independently coordinate to each Ag^+ ion in the structure ***P***. The $\boldsymbol{M} \rightarrow \boldsymbol{P}$ metal–ligand exchange converts an Ag^+-mediated pair of ligands from a ring 1-Ag-A, 3-Ag-E, and 5-Ag-C in ***M*** into a ring 1-Ag-B, 3-Ag-F, and 5-Ag-D in ***P***. A 60° rotation from ***M*** to $\boldsymbol{M'}$ is realized if a subsequent rewinding of complex ***P*** by the flip motion that maintains the linked three pairs take place (Figure 2). Further motions in the clockwise direction as well as in the reverse direction ($\boldsymbol{M'} \rightarrow \boldsymbol{P}$ and $\boldsymbol{P} \rightarrow \boldsymbol{M}$) should occur with equal probability. Therefore, sequential metal–ligand exchanges and flip motions occurring in concert finally give rise to the full relative rotation between the two disk-shaped ligands **1** and **2**.

The previous VT ^1H NMR study of the $[Ag_3(\mathbf{1})(\mathbf{2})]$ complex revealed the 60° relative rotational oscillation of the two disk-shaped ligands mediated by multipoint metal–ligand exchanges ($\boldsymbol{M} \rightleftharpoons \boldsymbol{P}$ in Figure 2).[15] We thus examined the dynamic behavior of a similar heterotopic $[Ag_3(\mathbf{1})(\mathbf{5})]$ complex formed from **1** and a tris(thiazolyl) ligand **5** with a C_{2v} symmetry (Figure 3) to obtain evidence for the free

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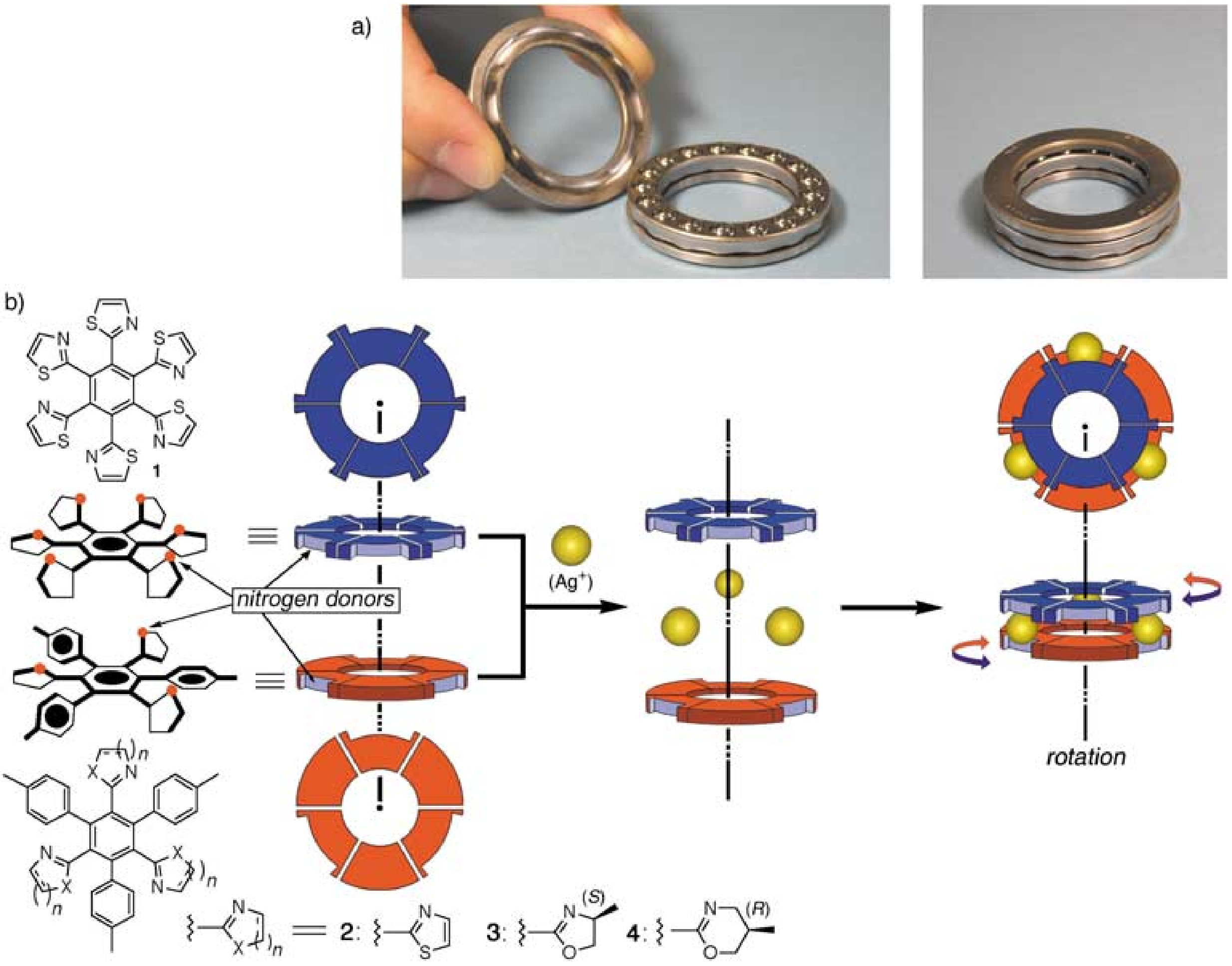

Figure 1. a) A thrust ball bearing, b) the envisioned scheme of the rotation with molecular ball bearings and the disk-shaped ligands used in this study.

rotation of the two disks by the mechanism shown in Figure 2. If the relative rotation between the two disk-shaped ligands **1** and **5** is faster than the NMR timescale, the symmetry of the signals for **1** would not be affected by the less-symmetrical **5** and, as a result, only one set of thiazolyl proton signals should be observed in the spectrum. In the case of slower or no relative rotation, on the other hand, four sets of inequivalent thiazolyl proton signals for rings I–IV should appear for **1**. The quantitative formation of the $[Ag_3(\mathbf{1})(\mathbf{5})]$ complex was unambiguously evidenced by ^{1}H NMR spectroscopy (Figure 3c) and ESI-TOF mass spectrometric measurements in CD_3OD (m/z 529.9, 842.4, 1779.9: dideuterated $[Ag_3(\mathbf{1})(\mathbf{5})]^{3+}$, $[Ag_3(\mathbf{1})(\mathbf{5})(CH_3SO_3)]^{2+}$, and $[Ag_3(\mathbf{1})(\mathbf{5})(CH_3SO_3)_2]^{+}$, respectively).[16] Upon complexation, the aromatic H^g, H^h, H^i, and H^j protons of **5** were divided into two sets as a consequence of the formation of a sandwich complex in which the inner and outer aromatic protons are inequivalent. This result indicates that the intermolecular ligand exchanges between Ag^+ complexes are slower than the NMR timescale at 293 K,[17] and that the following dynamic spectral changes should, therefore, arise from intramolecular motions. At 293 K, the H^a and H^b protons of **1** were observed as one set of signals at $\delta = 7.90$ and 7.67 ppm, respectively (Figure 3c), which indicates that the six thiazolyl rings of **1** in the $[Ag_3(\mathbf{1})(\mathbf{5})]$ complex are equivalent. This result reveals that the two disk-shaped ligands connected by three Ag^+ ions rotate freely and faster than the NMR timescale at 293 K. In contrast, cooling the sample to 213 K resulted in the H^a resonances dividing into three distinct signals in a 1:2:3(1:2) ratio (Figure 3g), thus showing that the thiazolyl rings of **1** are inequivalent as a consequence of the slower relative rotation of the opposite ring **5**. These results taken together lead us to conclude that the intramolecular relative rotation between the two disk-shaped ligands in $[Ag_3(\mathbf{1})(\mathbf{2})]$ and $[Ag_3(\mathbf{1})(\mathbf{5})]$ takes place in concert, and that the three Ag^+ ions positioned between the tris- and hexa-monodentate ligands can act as both couplers and mediators for the rotational motion.[18]

To investigate the rotation mechanism in detail, optically active tris-monodentate nitrogen ligands (*S*)-**3** and (*R*)-**4** were used in the VT ^{1}H NMR study, in the expectation that the *P*- and *M*-helical isomers could be distinguished as diastereomers at low temperatures. The tris(oxazolyl) and tris(oxazinyl) ligands **3** and **4**, respectively, were found to heterogeneously associate with **1** in the presence of three equivalents of Ag^+ ions, as observed with **2**. The quantitative formation of $[Ag_3(\mathbf{1})(\mathbf{3})]$ and $[Ag_3(\mathbf{1})(\mathbf{4})]$ were similarly confirmed by the

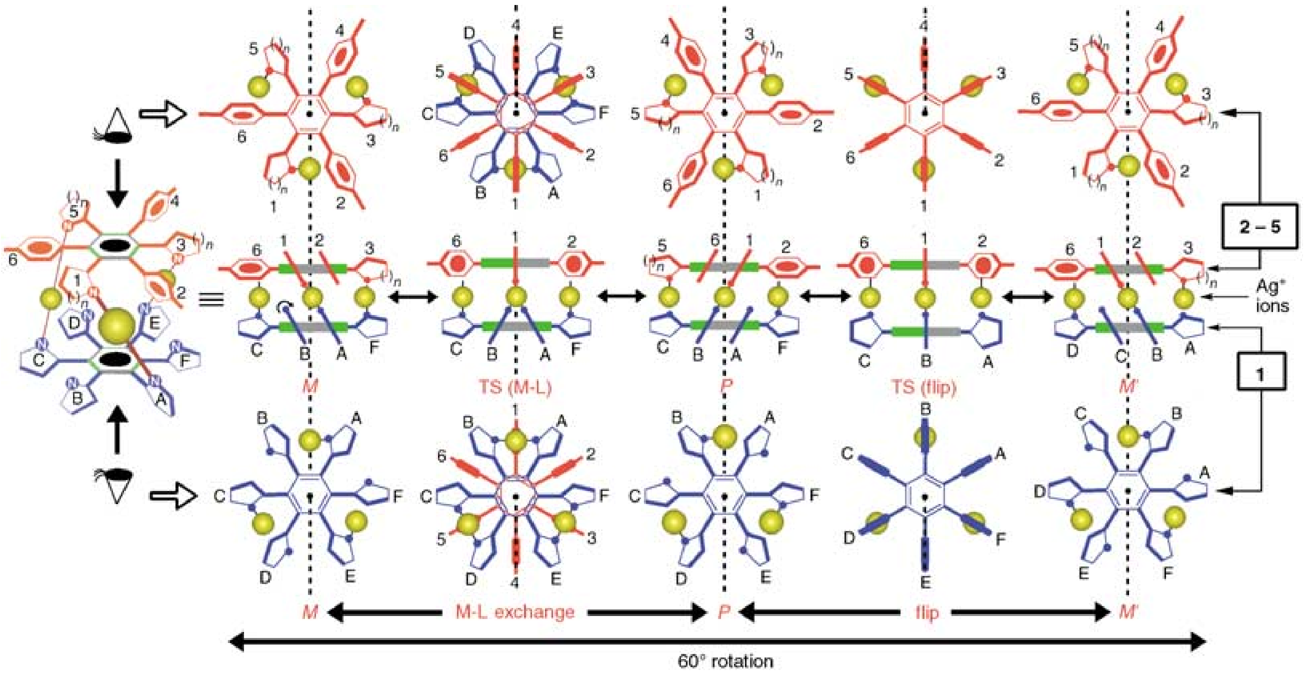

Figure 2. A plausible rotation mechanism of the Ag$^+$ sandwich complex with the aid of the metal–ligand (M-L) exchange and flip motion. In the M-L exchange from ***M*** to ***P***, the binding pairs of the rings between the two ligands through Ag$^+$ ions change from 1-A, 3-E, and 5-C in ***M*** to 1-B, 3-F, and 5-D in ***P*** with a conversion of the helicity from *P* into *M*. The subsequent flip motion maintaining the binding pairs converts the chirality of the structure from ***P*** into ***M′***. A combination of concerted M-L exchange at the three Ag$^+$ centers (***M***$\rightleftharpoons$***P***) and a flip motion (***P***$\rightleftharpoons$***M′***) finally allows a 60° rotational motion. Sequential M-L exchanges and flip motions results in the relative free rotation between the two disk-shaped ligands.

^{1}H NMR spectroscopic and ESI mass spectrometric measurements.[16] The proton signals for the six thiazolyl rings of **1** were equivalent in both [Ag$_3$(**1**)(**3**)] and [Ag$_3$(**1**)(**4**)] complexes at 293 K, thus indicating their faster rotation relative to the NMR timescale (Figure 4a, f). Cooling the sample of [Ag$_3$(**1**)(**3**)] to 213 K resulted in the thiazolyl proton signals for H^a and H^b being divided into two sets ($\delta = 7.85$, 7.76 (overlapped), and 7.59 ppm), while the signals of the tris-monodentate ligand **3** did not show any changes, probably because the metal–ligand exchange becomes slower than the NMR timescale while the flip motion is still faster (Figure 4e). These results suggest that the energy barrier of the metal–ligand exchange $\Delta G^{\ddagger}_{\text{M-L}}$ is greater than that of the flip motion $\Delta G^{\ddagger}_{\text{flip}}$.[19] In contrast, each signal of both the thiazolyl protons of **1** and the aromatic protons of **4** were divided into two sets at temperatures around 223 K in the case of the [Ag$_3$(**1**)(**4**)] complex (Figure 4i). Four sets of signals for the thiazolyl protons of **1** and two sets of signals for **4** were observed at 203 K (Figure 4k),[20] which indicates that the coordinating and uncoordinating thiazolyl rings of the hexa-monodentate ligand **1** are distinguishable in both the *P* and *M* diastereomers of the [Ag$_3$(**1**)(**4**)] complex because both the metal–ligand exchange and the flip processes are slower. From these spectral changes we concluded that $\Delta G^{\ddagger}_{\text{flip}}$ is equal to or greater than $\Delta G^{\ddagger}_{\text{M-L}}$ in [Ag$_3$(**1**)(**4**)] ($\Delta G^{\ddagger}_{\text{flip}} \geq \Delta G^{\ddagger}_{\text{M-L}}$). In such a case, at temperatures at which the flip motion becomes slower than the NMR timescale but the metal–ligand exchange is still faster, the *P* and *M* isomers can not be observed separately because of the rapid intraconversion through the metal–ligand exchange process (***M***$\rightleftharpoons$***P*** in Figure 2). Therefore, the NMR signals do not show any significant changes. Furthermore, cooling down the solutions to temperatures at which the metal–ligand exchange becomes slower than the NMR timescale should result in the signals for the hexa-monodentate ligand **1** and the tris-monodentate ligand **4** being divided simultaneously. In fact, the energy difference between the metal–ligand exchange and the flip motion was affected by the nature of the monodentate ligand rings bound to the Ag$^+$ ions. The destabilization of the transition state in the flip motion was particularly noticeable for the [Ag$_3$(**1**)(**4**)] complex containing the six-membered ligand rings of **4**. Such a marked tendency is consistent with our previous findings.[13] These results suggest that the rate or frequency of their rotation is controllable through the effect of the size of the tris-monodentate ligands on the flip processes.

In summary, we have established a quantitative formation of a novel molecular thrust ball bearing consisting of three Ag$^+$ ions as balls and two disk-shaped multi-monodentate ligands as nanosized bearings. This molecular ball bearing allows the relatively free rotation of two ligands connected by three Ag$^+$ ions that is mediated by sequential, multiligand exchanges and flip motions occurring in concert. Finally, a rotational rate (approximately 8000 rotations per second at 298 K) was obtained for [Ag$_3$(**1**)(**2**)] from the VT ^{1}H NMR study.[20] Furthermore, the energy barriers between the $P \rightarrow M$ and the $M \rightarrow P$ processes in ball bearings using chiral ligands could be differentiated from each other as a result of the difference in stability between the *P* and *M* diastereomers. Such ball bearings could work as parts of chiral molecular motors which make unidirectional rotation feasible in a controlled manner with the aid of external energy sources.

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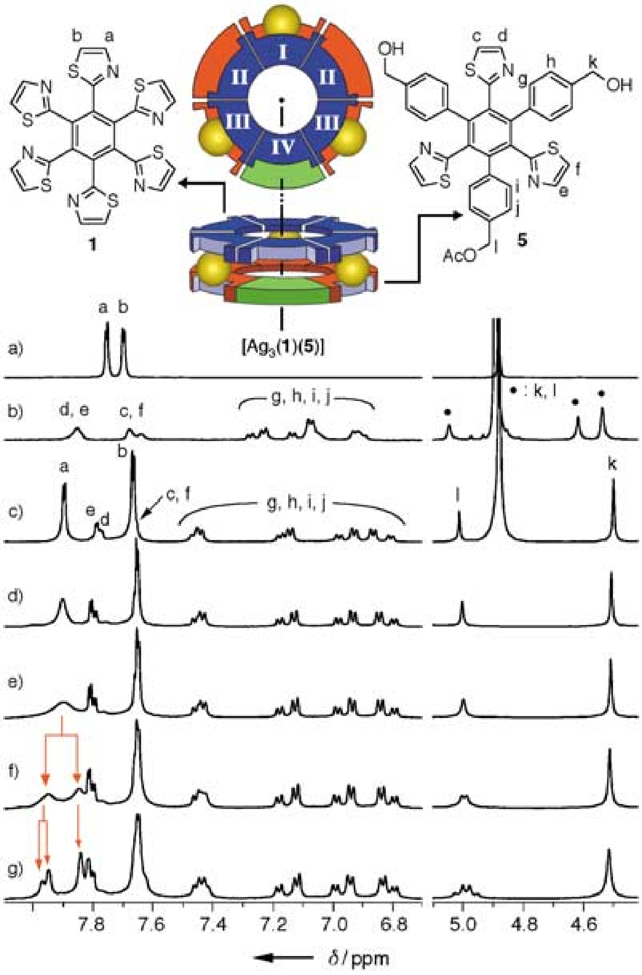

Figure 3. ^{1}H NMR spectra (500 MHz, CD$_3$OD): a) **1** + 3 equiv of AgCH$_3$SO$_3$,b) [Ag$_3$(**5**)$_2$] at 293 K, c) [Ag$_3$(**1**)(**5**)] at 293 K, d) [Ag$_3$(**1**)(**5**)] at 243 K, e) [Ag$_3$(**1**)(**5**)] at 233 K, f) [Ag$_3$(**1**)(**5**)] at 223 K, g) [Ag$_3$(**1**)(**5**)] at 213 K.

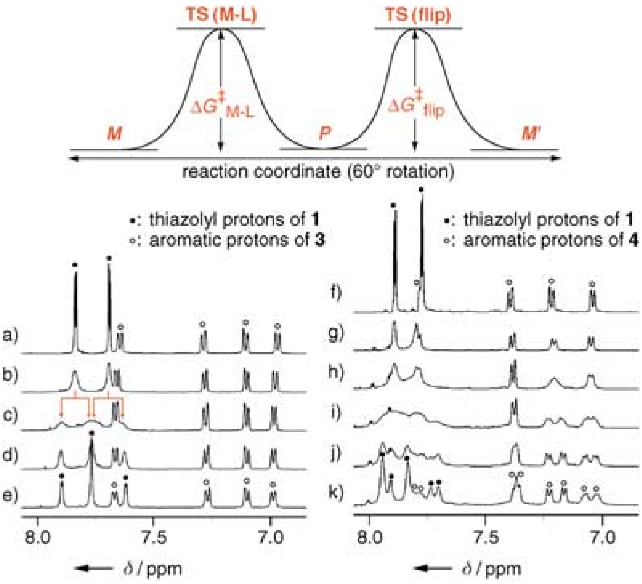

Figure 4. Schematic representation of a reaction coordinate for 60° rotation, and partial ^{1}H NMR spectra (500 MHz, CD$_3$OD) of [Ag$_3$(**1**)(**3**)] (a)–(e) and [Ag$_3$(**1**)(**4**)] (f)–(k). a) 293 K, b) 253 K, c) 233 K, d) 223 K, e) 213 K, f) 293 K, g) 243 K, h) 233 K, i) 223 K, j) 213 K, k) 203 K.

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[15] The ^{1}H NMR spectrum of [Ag$_3$(**1**)(**2**)] showed only one set of the thiazolyl protons of **1** ($\delta = 7.90$ (d, $J = 3.3$ Hz, 6H), 7.64 ppm (d, $J = 3.3$ Hz, 6H)) above 263 K. Upon cooling the sample down to 213 K the thiazolyl signals were divided into two sets ($\delta = 7.96$ (d, $J = 3.3$ Hz, 3H), 7.83 (d, $J = 3.3$ Hz, 3H), 7.64 (d, $J = 3.3$ Hz, 3H), 7.62 ppm (d, $J = 3.3$ Hz, 3H)), whereas the signals of **2** did not show any changes. The VT ^{1}H NMR results of the [Ag$_3$(**1**)(**2**)] and the discussion on the energy barrier of the metal–ligand exchange are described in detail in ref. [14].

[16] See Supporting Information.

[17] In the ^{1}H NMR titration studies using **1** and **5**, the signals of [Ag$_3$(**1**)(**5**)] and [Ag$_3$(**5**)$_2$] ([**5**] > [**1**]) or those of [Ag$_3$(**1**)(**5**)] and unidentified Ag$^+$ complexes with **1** ([**5**] < [**1**]) were independently observed. These results also support the relatively slow intermolecular ligand exchanges in the Ag$^+$ complexes.

[18] The relatively free rotation of the two disks in the ball bearings contains every rotational motion produced by the combination of the metal–ligand exchange and the flip motion between the *P* and *M* isomers, such as a 360° full rotation and a back and forth movement.

[19] In the chiral [Ag$_3$(**1**)(**3**)] and [Ag$_3$(**1**)(**4**)] complexes, the stabilities of the *P* and *M* isomers would be different from each other for each case, and therefore the energy barriers of both the

metal–ligand exchange and the flip motion from P to M ($\Delta G^{\ddagger}_{\text{M-L}(P\rightarrow M)}$ and $\Delta G^{\ddagger}_{\text{flip}(P\rightarrow M)}$) should be different from those of M to P ($\Delta G^{\ddagger}_{\text{M-L}(M\rightarrow P)}$ and $\Delta G^{\ddagger}_{\text{flip}(M\rightarrow P)}$, respectively; namely, $\Delta G^{\ddagger}_{\text{M-L}(P\rightarrow M)} \neq \Delta G^{\ddagger}_{\text{M-L}(M\rightarrow P)}$ and $\Delta G^{\ddagger}_{\text{flip}(P\rightarrow M)} \neq \Delta G^{\ddagger}_{\text{flip}(M\rightarrow P)}$). Here we discuss the relative energy differences between the energy barriers of the ligand exchanges and the flip motions using the greater one in each motion.

[20] Four sets of thiazolyl signals for the [Ag_3(**1**)(**4**)] complex at 203 K were confirmed by its H-H COSY spectrum, as shown in the Supporting Information.

[21] From the VT ^{1}H NMR studies for the molecular motion of the [Ag_3(**1**)(**2**)] complex, in which the metal–ligand exchange is the rate-determining step ($\Delta G^{\ddagger}_{\text{M-L}} \gg \Delta G^{\ddagger}_{\text{flip}}$), the rate constant of the intramolecular ligand exchange at 298 K can be calculated to be approximately 49000 s^{-1}.[14] The rate of a single 360° rotation is at least six times greater than the rate of metal–ligand exchange, and hence the maximum rotation rate can be estimated to be about 8000 rps.