Molecular Gears

Quantitative Formation of Sandwich-Shaped Trinuclear Silver(I) Complexes and Dynamic Nature of Their $P\rightleftharpoons M$ Flip Motion in Solution**

*Shuichi Hiraoka, Koji Harano, Takaaki Tanaka, Motoo Shiro, and Mitsuhiko Shionoya**

There has been much interest in developing artificial helical structures by synthetic oligomers[1] or metal–ligand complexes[2] closely related to those present in natural biomolecules such as DNA and proteins. In general, helical structures potentially undergo molecular motions such as folding[3] and $P\rightleftharpoons M$ conversion.[4,5] The $P\rightleftharpoons M$ conversion is well-known in natural systems, for example, the dynamic behavior of DNA helices between the right-handed B and left-handed Z forms.[6] Such $P\rightleftharpoons M$ dynamic processes are currently attracting considerable attention from a viewpoint of the development of molecular machines.[7]

Our strategy reported herein is directed toward the flip motion of the helical structures of trinuclear Ag_3L_2 complexes with disk-shaped ligands that bear three coordination sites (Figure 1). The ligands contain three monodentate ligands and three *p*-tolyl groups attached to the central benzene ring; the three *p*-tolyl groups are introduced to force the neighboring flat metal ligands out of the plane of the central aromatic ring. Such ligands self-assemble to form sandwich-shaped architectures with appropriate metal ions (e.g. Ag^+) favoring linear coordination geometry.[8] For example, in the Ag_3L_2 complexes, all the exterior rings should tilt in the same direction and result in the formation of helical structures with *P* and *M* geometries, between which flip motions may take place and allow the ring rotation with retention of the coordination bonds. Herein we describe the quantitative formation of sandwich-shaped trinuclear Ag^+ complexes with two disk-shaped ligands that bear three thiazolyl (**1**) or 2-pyridyl groups (**2**) as the coordination sites. The helical structure of the resulting entity $Ag_3\mathbf{1}_2$ was determined by X-ray single-crystal analysis, and variable-temperature ^1H NMR measurements revealed that the dynamic behavior (i.e. $P\rightleftharpoons M$ flip motion) of these complexes is remarkably affected by the ring size of the ligands attached to the central benzene ring.

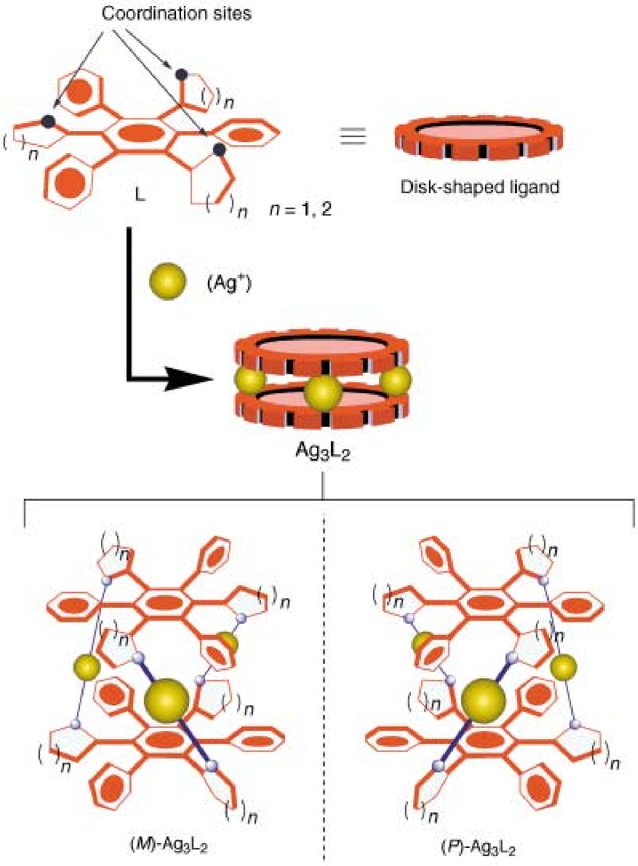
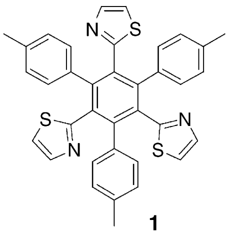


Figure 1. Schematic representation of the formation of sandwich-shaped trinuclear Ag_3L_2 complexes using disk-shaped tridentate ligands.



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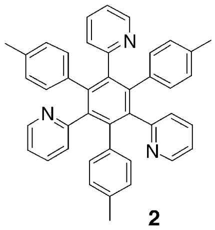

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Evidence for the formation of sandwich-shaped Ag^+ complexes from a mixture of tridentate ligands **1** or **2**[9] and AgOTf (2:3) in $CHCl_3/CH_3OH$ was obtained by electrospray ionization time-of-flight (ESI TOF) mass spectrometry.[10] The ESI mass spectrum of a mixture of **1** and AgOTf (**1**/AgOTf 2:3) exhibited a main peak at *m*/*z* 777.2, which is attributed to cationic $[Ag_3\mathbf{1}_2\cdot(OH)\cdot(H_2O)]^{2+}$. Similarly, the spectrum of a mixture of **2** and AgOTf (**2**/AgOTf 2:3) showed a main peak at *m*/*z* 759.4, which corresponds to $[Ag_3\mathbf{2}_2\cdot(OH)\cdot(H_2O)]^{2+}$. These data indicate that trinuclear $Ag_3\mathbf{1}_2$ and $Ag_3\mathbf{2}_2$ complexes were formed in solution.

The ^1H NMR spectrum of a mixture of **1** and AgOTf (2:3) in $CDCl_3/CD_3OD$ (1:1) was highly symmetrical except for the

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[*] Prof. M. Shionoya, Dr. S. Hiraoka, K. Harano, T. Tanaka
Department of Chemistry, Graduate School of Science
The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5841-8061
E-mail: shionoya@chem.s.u-tokyo.ac.jp
Dr. M. Shiro
Rigaku Corporation
3-9-12 Matsubaracho, Akishima, Tokyo 196-8666 (Japan)

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signals for the aromatic protons of the *p*-tolyl substituents (H^c and H^d in Figure 2b). This spectral pattern indicates that the outer (H^{c1} and H^{d1}) and the inner protons (H^{c2} and H^{d2}) of the *p*-tolyl rings are not equivalent as a result of the formation of a sandwich-shaped $Ag_3\mathbf{1}_2$ complex. In contrast, the thiazolyl protons H^a and H^b provide only one set of signals with downfield shifts as a result of complexation ($\Delta\delta = 0.35$–0.50 ppm). Further addition of AgOTf (up to 3 equiv) did not change the spectrum at all, although the amount is enough for the formation of polymeric structure $(Ag_3\mathbf{1})_n$. These results suggest that only either the N or the S donor atoms of the thiazolyl ligands coordinates to the Ag^+ ion, thus leading to the quantitative formation of a higher-symmetry sandwich-shaped $Ag_3\mathbf{1}_2$ complex.

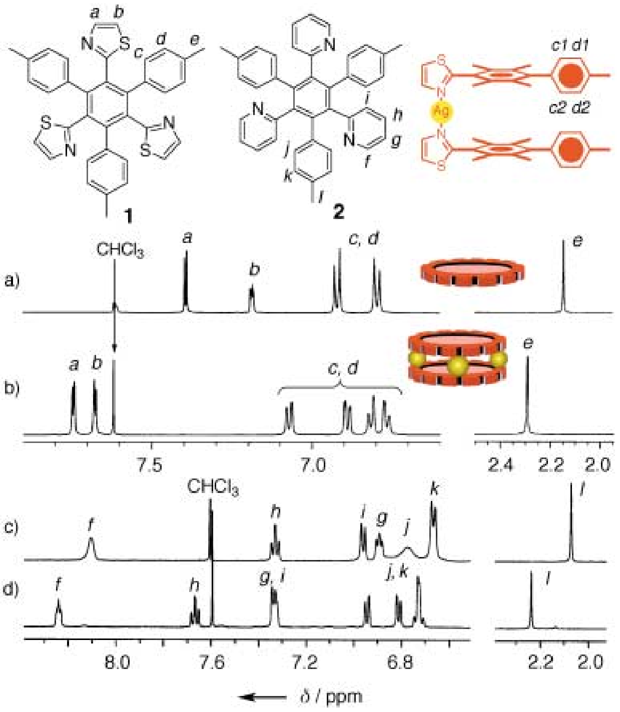

Figure 2. ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ (1:1)) spectra of the Ag^+ complexes with **1** and **2**; a) [**1**] = 14.0 mM, b) [**1**] = 14.0 mM and [AgOTf] = 20.9 mM, c) [**2**] = 8.2 mM, and d) [**2**] = 8.2 mM and [AgOTf] = 12.3 mM.

The ^1H NMR spectrum of a mixture of **2** and AgOTf (2:3) in a $CDCl_3/CD_3OD$ (1:1) showed a similar pattern (Figure 2d). All the signals for the ligand part of the Ag^+ complex are shifted downfield relative to those for the ligand **2** itself, and those for the aromatic protons of the *p*-tolyl groups (H^e and H^f) were not equivalent. Notably, the formation of both Ag^+ complexes ($Ag_3\mathbf{1}_2$ and $Ag_3\mathbf{2}_2$) is quantitative and is complete within a few minutes at room temperature (by NMR spectroscopic analysis).

The helical structure of the trinuclear complex $Ag_3\mathbf{1}_2$ was determined by X-ray crystallographic analysis (Figure 3).[11,12] Three Ag^+ ions are held between the two ligands **1** facing each other to provide a sandwich-shaped structure, and each Ag^+ ion is linearly coordinated by the two thiazolyl nitrogen atoms of both ligands with N–Ag bond lengths from 2.16(4) to 2.25(0) Å. The distance between the two central aromatic rings arranged face to face is approximately 5.4 Å, which is significantly longer than that for aromatic π–π stacking. In addition, the two ligands **1** are offset by 60° to form a helical structure in which the three N–Ag–N linkages are almost parallel to each other but twisted from the helix axis by approximately 30°. Notably, the crystal was obtained as a racemate of the *P* and *M* forms.

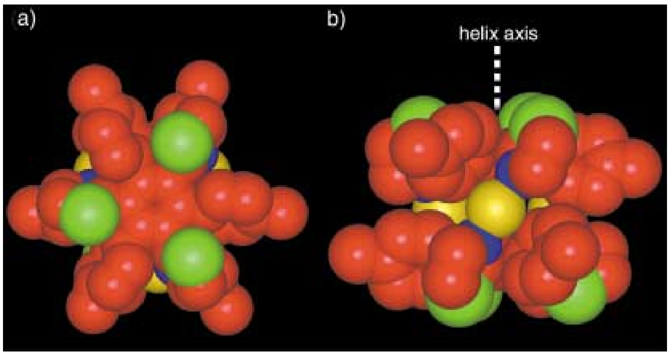

Figure 3. Crystal structure of $Ag_3\mathbf{1}_2$ in the *P* form: a) top view and b) side view. Color labels: Ag yellow, C red, N blue, S green.

The X-ray crystallographic analysis thus revealed that the sandwich-shaped Ag^+ complexes in the *P* and *M* forms have helical structures in the solid state. To verify the equilibria between the *P* and *M* isomers in solution, chiral counter-anions, Δ-tris(tetrachlorobenzenediolato)phosphate(V) (Δ-TRISPHAT),[13] were used for ^1H NMR spectroscopic studies. Upon addition of $[n\mathrm{Bu}_4\mathrm{N}]$[Δ-TRISPHAT] (3 equiv) to Ag^+ complexes ($Ag_3\mathbf{1}_2\cdot(OTf)_3$ and $Ag_3\mathbf{2}_2\cdot(OTf)_3$), $Ag_3\mathbf{1}_2\cdot(\Delta\text{-TRISPHAT})_3$ and $Ag_3\mathbf{2}_2\cdot(\Delta\text{-TRISPHAT})_3$ were isolated in 67% and 94% yields, respectively.

The signals of the *P* and *M* isomers were separated (1:1 ratio) without chiral induction in the ^1H NMR spectrum of $Ag_3\mathbf{2}_2\cdot(\Delta\text{-TRISPHAT})_3$ in $[D_6]$acetone/$CDCl_3$ (2:1) at 303 K (Figure 4b). This result indicates that the flip motion between (*P*)- and (*M*)-$Ag_3\mathbf{2}_2$ complexes is slow on the NMR timescale. Upon heating to 328 K, the signals almost coalesced, which indicates that the $P \rightleftharpoons M$ flip motion of $Ag_3\mathbf{2}_2$ is fast on the NMR timescale above 328 K (Figure 4a).

In the case of the $Ag_3\mathbf{1}_2\cdot(\Delta\text{-TRISPHAT})_3$ complex, the $P \rightleftharpoons M$ flip motion readily takes place even at 303 K. The signals for $Ag_3\mathbf{1}_2\cdot(\Delta\text{-TRISPHAT})_3$ in $[D_6]$acetone/$CDCl_3$ (2:1) did not split at all into two sets for the *P* and *M* isomers (Figure 4c). On the other hand, upon cooling the sample to 253 K, two sets of signals for H^a, H^b, and one of the *p*-tolyl protons appeared in a 7:6 ratio with low chiral induction;[14] these signals correspond to the (*P*)- and (*M*)-$Ag_3\mathbf{1}_2\cdot(\Delta\text{-TRISPHAT})_3$ complexes (Figure 4d).[15] Thus, the $Ag_3\mathbf{1}_2$ complex can flip between the *P* and *M* forms rapidly on the NMR timescale even at 303 K. The differences found in the dynamic features of the $Ag_3\mathbf{1}_2$ and $Ag_3\mathbf{2}_2$ complexes probably arise from the difference in the size of the ligands attached to the central aromatic ring. The $Ag_3\mathbf{2}_2$ complex with six-membered pyridine rings is likely to have more geometrical constraints than the $Ag_3\mathbf{1}_2$ complex with five-membered

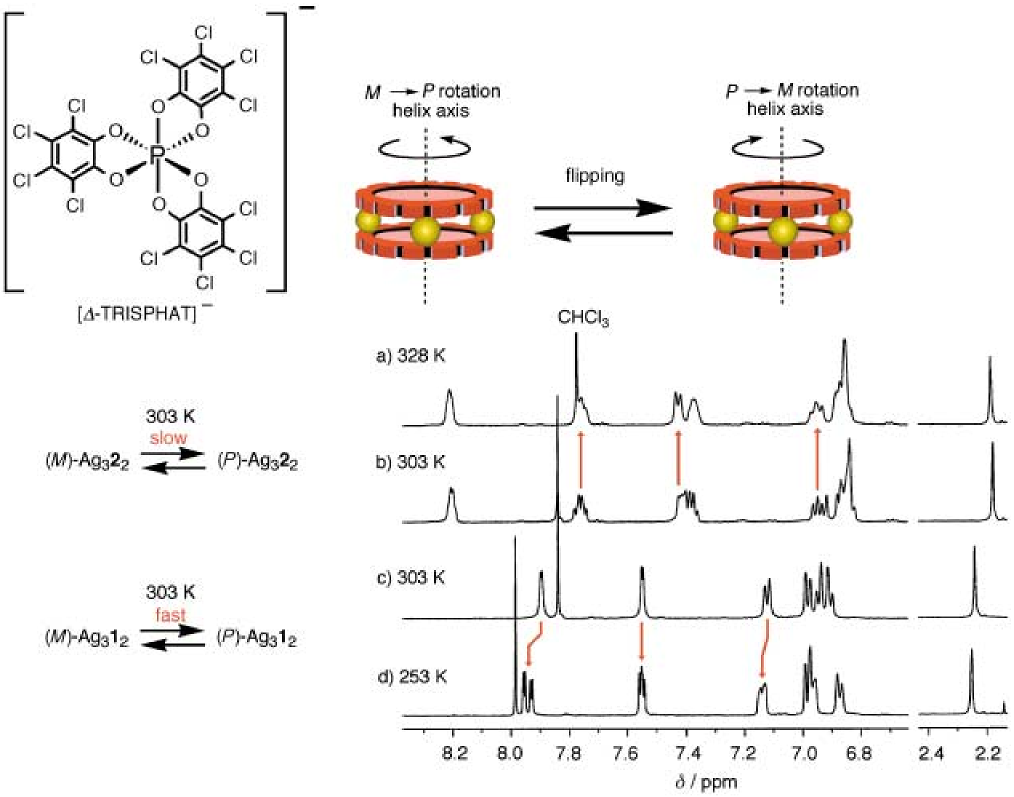

Figure 4. ^{1}H NMR spectra (500 MHz, [D$_6$]acetone/CDCl$_3$ (2:1)) of Ag$_3$**2**$_2$·(Δ-TRISPHAT)$_3$ and Ag$_3$**1**$_2$·(Δ-TRISPHAT)$_3$ complexes. a) Ag$_3$**2**$_2$·(Δ-TRISPHAT)$_3$ at 328 K, b) Ag$_3$**2**$_2$·(Δ-TRISPHAT)$_3$ at 303 K, c) Ag$_3$**1**$_2$·(Δ-TRISPHAT)$_3$ at 303 K, d) Ag$_3$**1**$_2$·(Δ-TRISPHAT)$_3$ at 253 K.

thiazole rings. Therefore, the transition state of the flip motion (Figure 5) in which all the N–Ag–N linkages are parallel to the helix axis would be rather destabilized in the Ag$_3$**2**$_2$ complex. As the result, the energy barrier of the flip motion in Ag$_3$**2**$_2$ complex should be larger than that in the Ag$_3$**1**$_2$ complex. Therefore, $P \rightleftharpoons M$ flipping is allowed in the Ag$_3$**1**$_2$ complex, whereas such a motion is restricted in the Ag$_3$**2**$_2$ complex at 303 K. The flip motion potentially contains a concerted twist motion of the twelve aromatic rings with a reversible change in the distance between the two central benzene rings (less than 1 Å). Moreover, the flip motion includes a relative 120° rotation between the two disk-shaped ligands connected by Ag$^+$ ions: In the P isomer, a thiazole ring (ring 1) and a p-toluene ring (ring 6) are placed face to face; after the $P \rightarrow M$ rotation, the thiazole ring (ring 1) lies opposite a different p-toluene ring (ring 2) (Figure 5).

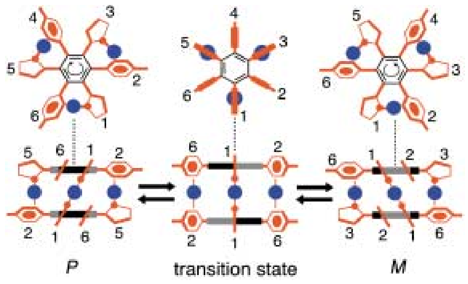

Figure 5. Proposed mechanism for the $P \rightleftharpoons M$ flip motion between sandwich-shaped Ag$^+$ complexes.

In summary, the present study demonstrates the quantitative formation of sandwich-shaped Ag$^+$ complexes from disk-shaped tridentate ligands **1** (or **2**) and Ag$^+$ ions both in solution and in the solid state. Variable-temperature ^{1}H NMR measurements with chiral counterparts revealed the existence of P and M helical structures of these complexes in solution, thus providing information on their dynamic behavior. Moreover, the $P \rightleftharpoons M$ flip motion of these complexes was found to depend strongly on the size of the ring of the metal ligands. Studies into chiral induction with this system are currently underway.

Experimental Section

Typical procedure**:** AgOTf (3.1 mg, 12.6 μmol) was added to a solution of ligand (8.4 μmol) in CDCl$_3$/CD$_3$OD (1:1; 0.6 mL), and the mixture was kept at room temperature for 5 min. The ^{1}H NMR spectrum showed the quantitative formation of the Ag$_3$L$_2$ complex.

Ag$_3$**1**$_2$·(OTf)$_3$: ^{1}H NMR (500 MHz, CDCl$_3$/CD$_3$OD (1:1)): δ = 7.73 (d, J = 3.4 Hz, 6H), 7.69 (d, J = 3.4 Hz, 6H), 7.06 (d, J = 7.8 Hz, 6H), 6.88 (dd, J = 1.5, 7.8 Hz, 6H), 6.81 (d, J = 7.6 Hz, 6H), 6.76 (d, J = 7.6 Hz, 6H), 2.29 ppm (s, 18H); ^{13}C NMR (125 MHz, CDCl$_3$/CD$_3$OD (1:1)): δ = 168.2, 145.3, 142.4, 140.3, 133.1, 132.8, 131.0, 129.6, 128.9, 127.6, 124.5, 120.3 (q, J = 319.3 Hz), 20.6 ppm; MS (ESI TOF; CH$_3$OH): m/z = 777.2 [Ag$_3$**1**$_2$·(OH)·(H$_2$O)]$^{2+}$. Crystallization of a 3:2 complex of AgOTf with **1** in a mixture of CHCl$_3$ and CH$_3$OH afforded colorless block crystals suitable for X-ray crystallographic analysis.

$Ag_3\mathbf{2}_2\cdot(OTf)_3$: ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ (1:1)): $\delta =$ 8.24 (m, 6H), 7.67 (ddd, $J = 1.4$, 7.8, 7.8 Hz, 6H), 7.34–7.33 (m, 12H), 6.94 (d, $J = 8.0$ Hz, 6H), 6.84 (d, $J = 8.0$ Hz, 6H), 6.74 (d, $J =$ 7.8 Hz, 6H), 6.71 (d, $J = 7.8$ Hz, 6H), 2.24 ppm (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (1:1)): $\delta = 158.6$, 151.5, 142.6, 140.3, 139.4, 139.1, 133.9, 131.34, 131.27, 131.1, 128.9, 128.7, 123.6, 120.7 (q, $J =$ 319.3 Hz), 20.9 ppm; MS (ESI; CH_3OH): $m/z = 759.0$ $[Ag_3\mathbf{2}_2\cdot(OH)\cdot(H_2O)]^{2+}$. The $Ag_3\mathbf{2}_2$ complex formed from **2** (11.9 mg, 20.5 µmol) and $AgCH_3SO_3$ (6.2 mg, 30.8 µmol) in a mixed solution of H_2O and CH_3OH was isolated as PF_6 salts (14 mg, 71 %). Elemental analysis: calcd for $[Ag_3\mathbf{2}_2][PF_6]_3[CH_3OH]$: C 52.35, H 3.61, N 4.30; found: C 52.35, H 3.67, N 4.33.

$Ag_3\mathbf{1}_2\cdot(\Delta$-TRISPHAT$)_3$ and $Ag_3\mathbf{2}_2\cdot(\Delta$-TRISPHAT$)_3$. $[n\mathrm{Bu}_4N][\Delta$-TRISPHAT] were prepared according to reference [13b]: A solution of $[n\mathrm{Bu}_4N][\Delta$-TRISPHAT] (3 equiv relative to the silver(I) complex) in $CHCl_3$ was added to $Ag_3\mathbf{1}_2\cdot(OTf)_3$ (4.6 µmol) or $Ag_3\mathbf{2}_2\cdot(OTf)_3$ (8.6 µmol) in $CHCl_3/CH_3OH$ (1:1) prepared as described above. A colorless precipitate was collected, washed with CH_3OH and $CHCl_3$, and dried in vacuo to obtain $Ag_3\mathbf{X}_2\cdot(\Delta$-TRISPHAT$)_3$ ($\mathbf{X} = \mathbf{1}$ or **2**) as a colorless solid, which was used for further ^1H NMR spectroscopic studies. $Ag_3\mathbf{1}_2\cdot(\Delta$-TRISPHAT$)_3$: 12.0 mg (3.1 µmol, 67 %). Elemental analysis: calcd for $[Ag_3\mathbf{1}_2][\Delta$-TRISPHAT$]_3[H_2O]_3$ ($C_{126}H_{60}Ag_3Cl_{36}N_6O_{21}P_3S_6$): C 39.01, H 1.56, N 2.17; found: C 39.18, H 1.91, N 1.96; $Ag_3\mathbf{2}_2\cdot(\Delta$-TRISPHAT$)_3$: 30.7 mg (8.1 µmol, 94 %). Elemental analysis: calcd for $[Ag_3\mathbf{2}_2][\Delta$-TRISPHAT$]_3[H_2O]_4$ ($C_{138}H_{74}Ag_3Cl_{36}N_6O_{22}P_3$): C 42.93, H 1.93, N 2.17; found: C 42.95, H 2.14, N 2.02.

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[9] For the preparation of **1** and **2**, see Supporting Information. Their ^1H NMR spectra showed only one set of highly symmetrical signals over a wide temperature range (223–293 K), probably as a result of the rapid exchange between a possible statistical mixture of racemic diastereomers.

[10] ESI TOF mass spectra of $Ag_3\mathbf{1}_2$ and $Ag_3\mathbf{2}_2$ are reported in the Supporting Information.

[11] Crystal data for $Ag_3\mathbf{1}_2\cdot(OTf)_3\cdot(CH_3OH)_5\cdot(H_2O)_2$: $C_{80}H_{78}Ag_3F_9N_6O_{16}S_9$, $M = 2162.66$, colorless block ($0.25 \times 0.25 \times 0.05$ mm^3), orthorhombic, $Pna2_1$, $a = 24.508(2)$ Å, $b = 23.017(2)$ Å, $c =$ 15.984(8) Å, $V = 9016(1)$ Å^3, $Z = 4$, $T = -180$ °C, $\rho_{calcd} =$ 1.59 g cm^{-3}, $F(000) = 4376.00$, $\mu(Mo_{K\alpha}) = 9.36$ cm^{-1}, a total of 14229 unique reflections ($2\theta_{max} = 60.1°$) were measured. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. Full-matrix least-squares refinement on F^2 (1102 variable parameters) converged to $R_1 = 0.0601$, $wR_2 = 0.1550$ ($I > 2\sigma(I)$). CCDC-202447 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] X-ray crystallographic analysis data of crystals obtained from a mixture of AgOTf and **2** (3:2) in $CHCl_3/CH_3OH$ were not fully refined owing to the disorder of the solvent and anion molecules, although the sandwich-shaped skeleton of $Ag_3\mathbf{2}_2$ structure was obtained preliminarily.

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