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Enhanced Silver Ion Binding to a Rigid Bisarene Molecular Cleft with Formation of Nonpolar Pleated Sheets through Non-Ionic Intermolecular Forces

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Silver ion complexation to bisarene ligands is enhanced by providing a conformationally rigid molecular cleft in the (*Z*)-acenaphthylene dimer **1**. NMR titrations were used to determine complexation constants *K* for a series of ligands in tetrahydrofuran solution, with $K = 4.9\ \mathrm{M}^{-1}$ for the Z dimer **1** and $0.4\ \mathrm{M}^{-1}$ for the E dimer **2**. Higher values of *K* were observed in $CDCl_3/CD_3OD$ 9:1 with $K = 38\ \mathrm{M}^{-1}$ for **1** and $K = 4.1\ \mathrm{M}^{-1}$ for **2**. In the solid state, isolated clusters of $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$ form a novel, pleated-sheet motif based on non-ionic interactions between clusters.

Introduction

The interaction between π electron systems and cations is an important noncovalent binding force both in biological and synthetic systems.[1,2] It is fundamental for metal-catalyzed organic synthesis as it has substantial impact on the reactivity of the coordinated organic species[3,4] and may constitute a powerful tool for the development of functional materials such as metal-binding polymer membranes,[5] sensors, and purification devices.[6] Of particular interest is the generation of defined structural motifs based on Ag^+−arene complexation,[7] where structurally very diverse complexes of corannulenes and flexible polyarenes, as well as calixarenes[8] and other heteroatom-containing ligands,[9] have been reported.

The π−cation interaction is ususally enhanced if the ligand provides a cavity with π-electron-rich domains suitably positioned for the intended guest. Thus, when designing arene-based host systems, the binding mode of the intended guest needs to be considered. The alkali-metal cations bind to arenes mainly via relatively weak electrostatic interactions, whereas the complexes to transition metals are much more stable due to arene−metal $\pi \rightarrow$ d donation and metal−arene d $\rightarrow \pi^*$ back-donation.[5,10] Cations with vacancies in their d orbitals may ligate the arenes in an η^3 fashion, whereas those with filled d orbitals such as Ag^+ prefer the less-symmetric η^1 or η^2 coordination.

Since most reported silver−arene host−guest systems are composed of conformationally flexible ligands or hosts with large cavity size as compared with the Ag^+ ion radius, we felt it tempting to investigate the binding properties of a small, rigid arene ligand. Whereas a conformationally flexible ligand might be able to bind a larger variety of ions and also be perceptive of induced fit, a rigid ligand should be

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restricted to a smaller selection of guests and hence be more selective. The smallest conceivable cavities are provided by (*Z*)-stilbenes, and many 1:1 complexes have been reported.[7] However, the (*Z*)-acenaphthylene dimer **1**, which might be regarded as a conformationally rigid structural analogue, has so far not been studied. It therefore constitutes an interesting model compound for a rigid arene ligand. The isomeric **2** should provide information on any cooperative effects of the arene walls.

Experimental Section

NMR spectra were recorded at 400 or 500 MHz (^{1}H) and at 376.3 MHz (^{19}F). Chemical shifts were indirectly referenced to TMS via the residual solvent signal (^{1}H, THF-d_8 at 3.58 (THF = tetrahydrofuran), $CDCl_3$ at 7.26) or the lock signal (^{19}F) at 25 °C on Varian Unity 400 or Inova 500 spectrometers. Spectral simulations of ^{1}H NMR spectra were performed using gNMR v. 4.1 (Cherwell Sci.). IR spectra were acquired for neat solid samples on a Perkin-Elmer Spectrum 100 instrument with UATR accessory. Electrospray mass spectrometry (ESI-MS) was performed on a Finnigan AQA mass spectrometer in ESI mode, positive ion detection, 15 V acceleration voltage, with direct injection of sample solutions. Analytical TLC was performed using pre-coated Merck Silica 60 F254 plates. For column chromatography, Matrex silica gel (60 Å, 35−70 μm) was used. Commercial reagents were purchased from Sigma-Aldrich and used without any further purification. Melting points were determined in open capillaries using a Stuart Scientific melting point apparatus SMP10 and are uncorrected.

Preparation of Acenaphthylene Dimers 1 and 2.[11] Commercial acenaphthylene (containing 20% acenaphthene, 11.3 g, ca. 56 mmol) was dissolved in dichloroethane (150 mL) and photolyzed under an argon atmosphere (medium-pressure Hg lamp, Duran glass jacket) for 67 h. Precipitated solid **A** (mainly E dimer, 3.29 g, max. 11 mmol) was filtered off, and the filtrate was evaporated to yield crystal/oil mixture **B** (8.05 g, max. 26 mmol). The solid **A** was recrystallized from benzene, yielding 1.14 g (3.7 mmol) of the pure E dimer **2**, mp = 308−310 °C (Lit.: 304−306 °C). The crystal/oil mixture **B** was washed with cyclohexane, leaving 2.79 g of a yellow-brown solid. Fractional crystallization of this solid from toluene produced acenaphthylene dimer with successively higher content of the Z isomer, and eventually 89 mg of **1** (0.3 mmol) of 99.6% purity (according to ^{1}H NMR) was obtained, mp = 237 °C (Lit.: 233.5−234.5 °C). ^{1}H NMR ($CDCl_3$ solution, 25 °C): **1**, $\delta = 7.19$ (dd, $J = 1.0$, 8.1 Hz, 4H, H-4), 7.14 (dd, $J = 6.6$, 8.1 Hz, 4H, H-3), 7.02 (dd, $J = 1.0$, 6.6 Hz, 4H, H-2), 4.84 (s, 4H, cyclobutyl); (THF-d_8 solution, 25 °C), 7.12 (dd, $J = 0.5$, 8.2 Hz, 4H, H-4), 7.07 (dd, $J = 6.9$, 8.2 Hz, 4H, H-3), 7.00 (dd, $J = 0.5$, 6.9 Hz, 4H, H-2), 4.82 (s, 4H, cyclobutyl); **2**, $\delta = 7.75$ (dd, $J = 0.9$, 8.1 Hz, 4H, H-4), 7.61 (dd, $J = 6.8$, 8.1 Hz, 4H, H-3), 7.53 (dm, $J = 6.7$ Hz, 4H, H-2), 4.09 (s, 4H, cyclobutyl).

Preparation of (*Z*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene (3). This compound was prepared according to a literature procedure by dimerization of *tert*-butyl phenyl ketone followed by photochemical isomerization of the resulting alkene (medium-pressure Hg lamp, quartz-glass jacket),[12] mp = 93−94 °C (Lit.: 89−90 °C). ^{1}H NMR ($CDCl_3$ solution, 25 °C): $\delta = 6.87$ (m, 4H, *o*-H), 6.78 (m, 2H, *p*-H), 6.65 (m, 4H, *m*-H), 1.25 (s, 18H, *t*-Bu).

NMR Titrations. To a solution of the ligand in THF-d_8 or $CDCl_3/CD_3OD$ (9:1) (ca. 0.7 mL, 5×10^{-3} M to 9×10^{-3} M), aliquots of a solution of a silver salt ($AgCF_3SO_3$ or $AgBF_4$, 0.15 M) in the same solvent were added. The total amount of ligand and of silver was determined by addition of a small quantity (ca. 20 mg) of 4-fluorobenzonitrile, followed by integration of the ^{1}H and ^{19}F NMR signals. Complexation stoichiometry and complexation constants were determined from Job and Scott plots. The reproducibility of K was estimated at ± 10% (at least two titrations). The chemical shift change for the signal of H-3 (i.e., H-5/H-9 in the crystallographic numbering scheme for $\mathbf{1}\cdot(AgCF_3SO_3)_2$), was followed for **1**, **2**, **4**, and **5**. The meta proton signal was followed for **3**. For more accurate determination of parameters, spectral simulations were also performed (full line-shape iteration for Lorentzian lines of 1.3 Hz width). For further information, see the Supporting Information.

ESI-MS Investigation. In a typical example, to a solution of ligand (**1** or **2**) in acetone/ethanol (1:1.5, 0.1 mL, ca. 1.6 μmol) was added a solution of $AgCF_3SO_3$ in the same solvent mixture (1.5 mL, 1.6 mmol Ag^+). A continuous flow of this mixture was introduced into the mass spectrometer using the direct sample infusion device.

Preparation of Crystalline (*Z*)-Acenaphthylene Dimer—Silver Complex $[\mathbf{1}\cdot(\mathbf{AgCF_3SO_3})_2]_2$. A solution of (*Z*)-acenaphthylene dimer (24.7 mg, 81.2 μmol) in an acetone/THF mixture (1:1, 1 mL) was mixed with a solution of silver trifluoromethanesulfonate (21 mg, 81.2 μmol) in acetone (0.3 mL). The resulting, clear mixture was layered with *n*-hexane (1 mL) in a screw-cap vial and stored at room temperature in the dark. Crystals started to appear at the wall in the region of the boundary layer after 1 day. After 6 days, the solution was removed, and the vial was rinsed with *n*-hexane (3 × 1 mL). Faintly yellowish, rhomboedric crystals, mp = 175−185 °C (dec to black solid). For FTIR data, see the Supporting Information.

Crystal data for $\mathbf{1}\cdot(AgCF_3SO_3)_2$: $C_{26}H_{16}Ag_2F_6O_6S_2$, $M_r = 818.25$, faintly yellow, rhomboedric crystals, $0.14 \times 0.10 \times 0.08$ mm^3, monoclinic, space group $C2/c$, $a = 16.6087(2)$ Å, $b = 17.43310(10)$ Å, $c = 18.4130(2)$ Å, $\alpha = 90°$, $\beta = 102.5420(10)°$, $\gamma = 90°$, $V = 5204.10(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.089$ g/cm^3, absorption coefficient = 1.752 mm^{-1}, $\theta = 1.90−25.35°$, $F(000) = 3200$, $T = 297(2)$ K, R1 = 0.0787, wR2 = 0.1504. Independent reflections = 4767 [R(int) = 0.0603], restraints = 0, parameters = 395.

A Siemens SMART CCD area-detector diffractometer was used, with Mo Kα radiation, wavelength = 0.71073 Å, multiscan, *SADABS* (Sheldrick, 2002). The structures were solved using direct methods, refined with the *SHELX* software package, and refined with full-matrix least-squares treatment on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure−factor calculations.

Results and Discussion

Photodimerization of acenaphthylene (**4**) gave a mixture of Z and E isomers[11] (**1** and **2**, respectively, Chart 1), which could be separated by repeated crystallization. The reference ligand (*Z*)-1,2-di-*tert*-butyl-1,2-diphenylstilbene (**3**) was obtained from dimerization of *tert*-butyl phenyl ketone followed by photochemical isomerization of the resulting alkene.[12]

Since the comparison of complexation constants K for weakly binding ligands requires that any desolvation penalties can be accounted for,[10] a direct comparison is possible

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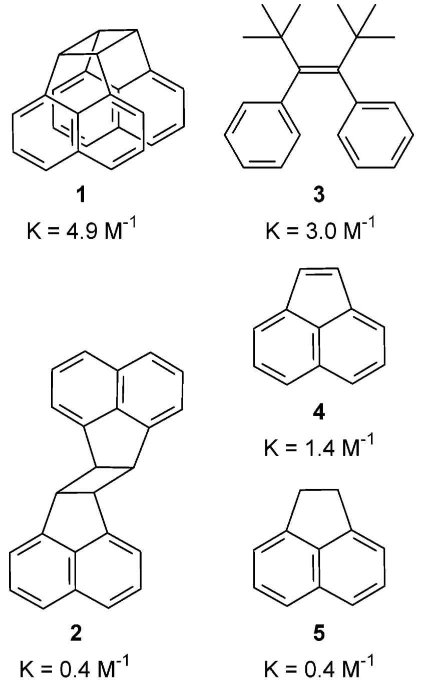
Chart 1. Ligands and Values for *K* Based on the Equilibrium $Ag^+ + L \leftrightarrows [Ag{\cdot}L]^+$ in THF at 25 °C



only if the same solvent has been used. THF was used to provide the sufficient solubility of all species. Complexation constants were determined via NMR titrations, recording chemical shift changes of ligand proton resonances upon the addition of a $AgCF_3SO_3$ solution to solutions of **1**−**5**.[13] Values for *K* based on the equilibrium $Ag^+ + L \leftrightarrows [Ag{\cdot}L]^+$ are reported in Chart 1.

The cofacial diarenes **1** and **3** show the strongest complexation to the Ag^+, with *K* values of 4.6 and 3.0 M^{-1}, respectively. These values are approximately 1 order of magnitude larger than those for the non-cofacial diarene **2** and the monoarene **5** (0.4 M^{-1}) and clearly demonstrate the cooperative binding effect of two suitably positioned arene moieties. Ligand **4**, with an additional C═C bond, exhibits an intermediate value of 1.4 M^{-1}. Binding of Ag^+ to this double bond is unlikely, as it is not observed in the crystal structure.[14] We attribute the larger *K* value of ligand **4** compared with that of **2** and **5** to an increased polarizability of **4**. Ligand **3** also has an alkene unit, but it is sterically shielded from the cation bound to the aromatic rings. Therefore, its larger *K* when compared with that of **4** should be due to the cooperative effect of Ag^+ binding to two opposite phenyl rings. Finally, we attribute the larger complexation constant for **1** as compared to **3** to the rigidity of **1** and the resulting preorganization.

The formation of complexes with higher stoichiometry such as $[Ag_2L]^{2+}$ can be neglected since the concentrations of $[AgL]^+$ are low and the complexation constants *K* are small in THF solution.[15,16] Direct comparisons with reported complexation constants in other solvents are not possible due to solvation effects. Much larger values for silver−arene complexes have been reported in other solvents. Typically, ligands resembling **3** have *K* values ranging from several hundred to thousand M^{-1} in chloroform or dichloromethane/methanol.[7a,17] This can be explained by the considerable differences between these solvents and THF regarding, e.g., donor numbers.[15,18] In keeping with these findings, we observed higher *K* values for silver ions in a different solvent mixture ($CDCl_3$/CD_3OD 9:1), while retaining the stronger binding to the rigid ligand **1**, namely, $K = 38$ M^{-1} for **1** and 4.1 M^{-1} for **2**. A reliable complexation constant for **3** could not be obtained due to its limited solubility.

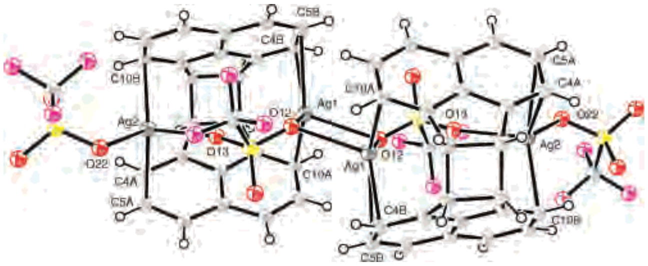
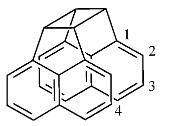
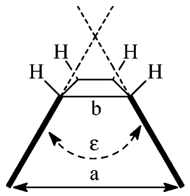


Figure 1. Structure of $[\mathbf{1}{\cdot}(AgCF_3SO_3)_2]_2$ cluster in the unit cell, showing the two different types of Ag^+ ions. The chain of Ag^+ and $CF_3SO_3^-$ ions runs parallel with the crystallographic *b* axis. *ORTEP* plot[22] showing displacement ellipsoids at the 40% probability level.

Table 1. Geometry for Selected Ligands in Silver Complexes



1



	ϵ (deg)	*a*/Å	*b*/Å
1[23]	55.41	5.730	1.571
$[\mathbf{1}{\cdot}(AgCF_3SO_3)_2]_2$	66.29	6.117	1.575
$[\mathbf{5}{\cdot}AgSO_3CF_3]_2$[14]	62.03[a]	3.880[a]	

[a] Different tilt of rings.

Silver ion complexation may also be detected by ESI-MS. This has been proposed as a method for analytical detection of hydrocarbons.[19] Recently, complexation between various cations and arenes has been studied,[8,20] including determination of relative complexation constants.[21] Thus, when solutions of **1** or **2** and a silver salt were subjected to ESI-MS, a peak at $m/z = 411$ displaying the silver isotope pattern indicated the presence of $(\mathbf{1}{\cdot}Ag)^+$ or $(\mathbf{2}{\cdot}Ag)^+$. Furthermore,

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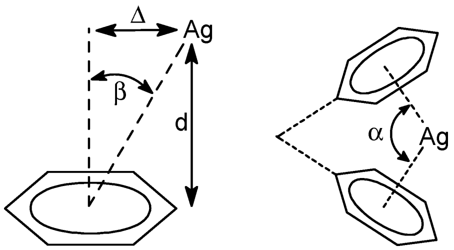
Table 2. Parameters Related to the Ag^+ Binding Geometry in Silver−Arene Complexes[a]



	α	Δ (η^1 side)	Δ (η^2 side)	*d* (η^1 side)	*d* (η^2 side)	*β* (η^1 side)	*β* (η^2 side)
1-Ag(1) (inner)	113.71	1.56	1.22	2.42	2.39	32.68	27.01−27.61
1-Ag(2) (outer)	113.71	1.40	1.06	2.52	2.47	28.11−29.27	22.82−25.38
5-Ag[14]	117.97[b]	1.43−1.46[b]		2.38−2.40[b]		30.99−31.37[b]	
typical values[7a]	130 or 155 ± 3	1.53 ± 0.2		2.41 ± 0.05		32 ± 3	

[a] Distance from ring plane *d*, displacement from ring center Δ, angular parameter *β*, and grab angle α. Distances are in Å. [b] Different tilt of rings.

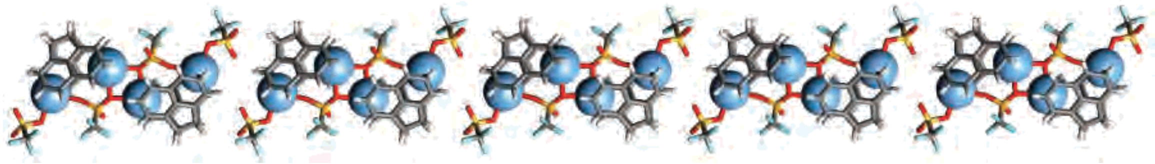


Figure 2. Columnar arrangement of five clusters in the crystal lattice of $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$ parallel with the crystallographic *b* axis. Note the absence of ionic interactions between clusters.

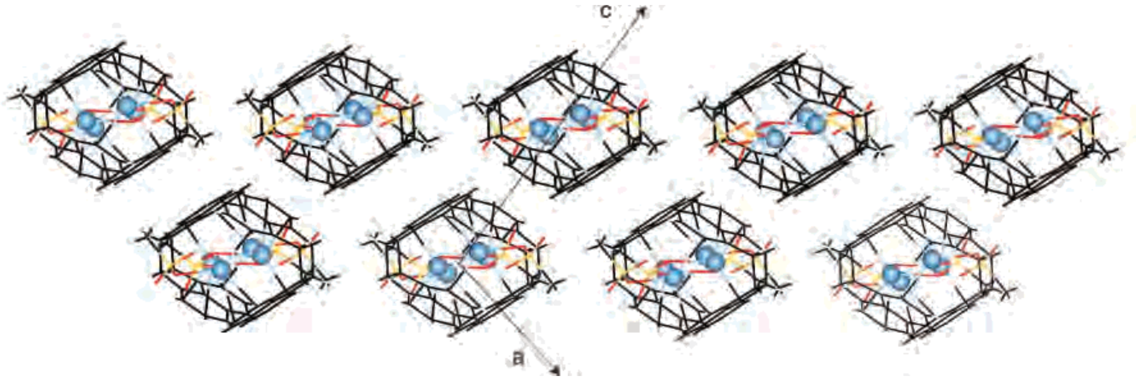


Figure 3. Pleated sheets of columns in the crystal lattice of $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$. The sheets are arranged in a plane at a 45° angle between the crystallographic *a* and *c* axes. View is along the *b* axis.

the peak for $(\mathbf{1}\cdot Ag)^+$ was of higher intensity than that for $(\mathbf{2}\cdot Ag)^+$ under all tested conditions, using THF, acetone/ethanol, or methanol/cyclohexane (6:4) as solvent and $AgCF_3SO_3$, $AgBF_4$, or $AgNO_3$ as silver salt. It should be emphasized, however, that the observation of these ions per se does not prove their existence other than under ESI conditions.

A complex of different stoichiometry than that derived from the NMR titrations was observed in the solid state. The crystal structure shows the presence of isolated clusters with composition $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$, where each ligand **1** binds two silver ions, one of which (Ag-1) is in the center of the cluster, while the other one (Ag-2) is in a terminal position (Figure 1). Two center $CF_3SO_3^-$ anions link the cluster components together, constituting a $CF_3SO_3^-{-}Ag^+{-}CF_3SO_3^-{-}(Ag^+)_2{-}CF_3SO_3^-{-}Ag^+{-}CF_3SO_3^-$ chain of ions. The cluster has *C*2 symmetry (space group *C*2/*c*).

Upon binding to Ag^+ ions, the cavity provided by the ligand **1** is widened considerably (Table 1). The angle ϵ between the two naphthalene walls increases from 55.41° for free ligand **1**[23] to 66.29° in the complex, which still is considerably smaller than the typical angle between rings in *cis*-stilbenoid ligands (71−91°).[10] The distance (a) between peri carbons (C-4) increases from 5.730 to 6.117 Å. Furthermore, the length (b) of the cyclobutane bonds linking the two halves of the ligand is slightly increased. The binding of Ag^+ to the inside of the cavity instead of the outside

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despite this considerable distortion indicates the importance of the cooperative effect.

Parameters regarding the geometry around the Ag^+ ions in the complex $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$ are summarized in Table 2 and compared to typical values reported for other silver−arene complexes.[7a] The two silver ions, Ag-1 and Ag-2 (inner and outer positions in the cluster, Figure 1), bind differently. Both coordinate in η^1 fashion to one side and in η^2 fashion to the other side of the cleft (ideal values are $\Delta = 1.40$ Å for η^1 and $\Delta = 1.20$ Å for η^2 hapticity).[10] At the η^2 side, the distance to the ring plane (Δ) is much closer than in typical silver−arene complexes. This is also indicated by the variation of the angular parameter β, which is at 27.01−27.61° (Ag-1, η^2-coordinated ring) vs 32.68° (Ag-1, η^1-coordinated ring) and at 22.82−25.38° (Ag-2, η^2-coordinated ring) vs 28.11−29.27° (Ag-2, η^1-coordinated ring). Silver−carbon distances range from 2.343 to 2.654 Å. Finally, the grab angle α is measured at 113.71°, due mostly to the rigidity of the ligand **1**. For comparison, in the complex of **5** with $AgClO_4$, two silver ions bind to two **5** molecules but are oriented more to the inside of the organic ligands.[14] Here, silver−carbon distances are between 2.44 and 2.51 Å. The silver complexation is characterized by parameters $d = 2.40$−2.38 Å, $\Delta = 1.43$−1.46 Å, and $\beta = 30.99$−31.41°, with a grab angle α of 117.97°.

In the crystal lattice of $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$, we find a columnar arrangement of cluster chains connected by CF_3−cyclobutane ring interactions (Figure 2). The polar, ionic groups are shielded within the clusters. This is in contrast with observations on other silver−arene complexes, which commonly contain polymeric chains of alternating Ag^+ and counterions instead of the isolated sequence of eight ions per cluster of $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$.[7,14]

These columns constitute pleated-sheet-like structures (Figure 3). In the *a*-axis direction, the arrangement is stabilized by interactions between arene planes, resembling those found in graphite. The distance between sheets is 3.544 Å (intersecting *a* axis) to 3.674 Å (intersecting *c* axis), not much greater than that between the layers of graphite (3.354 Å).[24] Additional stabilization is provided by nonpolar interactions between outer CF_3 groups of the clusters.

In summary, the rigid, preorganized bisarene molecular cleft in ligand **1** results in enhanced silver ion complexation as well as a geometry of silver coordination that deviates considerably from previously reported typical values for polyaromatic ligands.[7,14] Also, a novel structural motif consisting of isolated clusters organized in nonpolar pleated sheets with π−π stacking distances resembling graphite is observed. This suggests the possible development of nonpolar silver ion containers for applications in, e.g., organometallic and materials chemistry.

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Supporting Information Available: Tables of NMR chemical shift variations of **1** upon silver complexation; ^1H NMR spectra of titration experiments; observed and simulated ^1H NMR spectra for **1**; IR spectra of **1** and $[\mathbf{1}\cdot(AgCF_3SO_3)_2]_2$; X-ray crystallographic data tables; and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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