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Silver(I) Complexation of (Poly)aromatic Ligands. Structural Criteria for Depth Penetration into *cis*-Stilbenoid Cavities

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Synopsis

Structural factors inherent to the bonding of silver(I) to arene ligands are thoroughly analyzed with the aid of the Cambridge Crystallographic Database; and the normal separation of Ag from the aromatic mean plane is found to be invariant for all silver/arene complexes independent of the hapticity, hybridization, or multiple coordination. Using this basic information, we can precisely predict the depth penetration of silver(I) into the aromatic clefts of various *cis*-stilbenoid ligands with a single parameter that measures the separation of the two cofacial aryl groups comprising the cleft.

Abstract
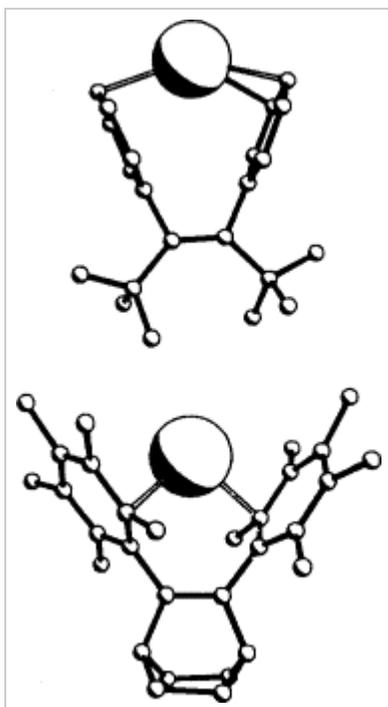
Silver(I) complexes with aromatic donors are thoroughly analyzed (with aid of the Cambridge Crystallographic Database) to identify the basic structural factors inherent to the bonding of an arene ligand. Most strikingly, the distance parameter d (which simply measures the normal separation of Ag from the mean aromatic plane) is singularly invariant at $d = 2.41 \pm 0.05$ Å for all silver/arene complexes, independent of the hapticity (η^1 or η^2), hybridization, or multiple coordination. As such, a systematic series of stilbenoid ligands has been successfully designed to precisely modulate the penetration of silver(I) into the ligand cleft, and a multicentered poly(arene) ligand (**X**) designed to form a one-dimensional assembly of Ag/arene units. Simply stated, the depth penetration of silver(I) into the aromatic cavities of various *cis*-stilbenoid donors can be precisely predicted with a single parameter γ that measures the separation of the two cofacial aryl groups comprising the cleft. This simple geometric consideration must be taken into account in any successful design of novel (poly)aromatic ligands for silver(I) complexation to constitute new molecular architectures.

Introduction

Among the various σ- and π-complexes of silver(I) with organic ligands,[1,2] those derived from arene donors have the desired structural diversity for the construction of organometallic (solid-state) devices

as electrical conductors, photoactive switches, chemical sensors, etc.[3,4] This possibility stems in large part from the active synthetic interest in polycyclic hydrocarbons that bear two or more aromatic groups in interesting arrays, including diarylalkanes (-alkenes and -alkynes), cyclophanes, tryptycenes, triangulanes, deltaphanes, cylindrophanes, etc.[5-7] Critical to crystal engineering is the spontaneous self-assembly of the active silver(I) center within a proscribed environment, whether it links a di- or trifunctional aromatic ligand in a polymeric (linear) structure or is encapsulated deep within a 3-dimensional cage such as a calixarene.[8,9] Despite numerous ingenious designs of novel ligands, however, the systematics for the precise placement of silver(I) has not evolved and it remains as a largely ad hoc operation.

To address this structural problem, we inquire as to the basic nature of the arene bonding to silver(I). Historically, Mulliken conceived the π-interaction of arene with silver(I) to be dominated by charge transfer;[10] but this formulation is not amenable to experimental test owing to the absence of distinctive (resolved) absorption bands in most (colorless) complexes.[11] The alternative Dewar–Chatt–Duncanson model is most widely accepted, and it predicts the η^2 bonding of silver(I) to a pair of ring carbon centers (arising from π-back-donation)[12] though it is not commonly observed.[13]

Our analysis initially considered (mono)benzenoid ligands with the thought that these may provide some clues for a better understanding of the general stereoelectronic requirements of silver/arene coordination that is unbiased by either distortion or steric hindrance introduced by the chemical linking of two or more aromatic groups. Indeed, a search through the Cambridge Crystallographic Database (CCD) reveals more than 70 entries of intermolecular structures of which more than half (40) involve two or three arene ligands bound to silver(I), independent of whether the arene/Ag molar ratios are less than 2:1 or 3:1.[14] Most importantly, the following three critical structural features are found to be inherent to all the silver/arene complexes of rather wide ligand diversity.

A. The separation of silver(I) from the mean plane of the coordinated benzene (see **I**) lies within a narrow range, being $d = 2.41 \pm 0.05$ Å, i.e., ±2% over all structures.

B. Silver(I) shows no preference toward either η^1 or η^2 coordination of arenes.[15] [Note that η^1 coordination is tantamount to σ-bonding of silver(I) to an arene center.] Most importantly, the position of Ag is always restricted to a narrow arc over the periphery of the coordinated benzene ring, and its (azimuthal) position can be quantitatively gauged by its deviation Δ from the centroid axis (see **I**). Indeed the angular parameter β and the linear Δ as measures of deviation show remarkable constancy with $\beta = 32° \pm 3°$ and $\Delta = 1.53 \pm 0.2$ Å over the range of all structures,[16] being only slightly subject to packing forces.


I   **II**
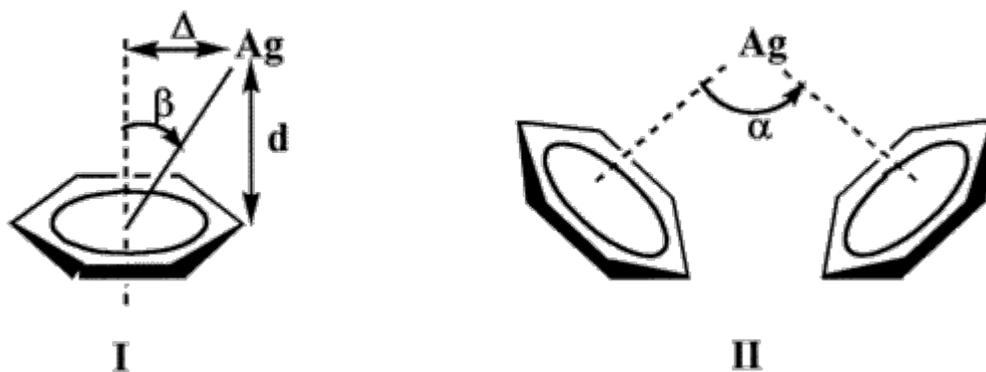
C. The "grab" angle α between the planes of the coordinated benzene (see **II**)[17] falls within three sharply delineated regions of 95°, 130°, and 155° (typically within ±3°) roughly corresponding to octahedral, tetrahedral, and linear hybridization of silver. Accordingly, the known silver/bis(monoarene) complexes can be divided into separate structural groups composed of three different coordination geometries, and they all abide by structural requirements A and B described above (for details see Table 4).

We believe that structural requirements A–C are equally applicable to cyclic (poly)arene ligands which have been elaborately designed to capture silver(I) deep within their cavities. Let us consider deltaphane **III** and (2.2.2)paracyclophane **IV** as illustrative examples[18] in which the size of the internal cavity matches the ionic radius of silver(I); and Ag^I was thus expected to occupy the center of the cavities and perfectly entombed within. However, NMR studies revealed a high kinetic lability of these complexes, and X-ray crystallography demonstrated the silver(I) contact to occur only with the carbon atoms of the upper rims of both cylinder-shaped donors and not in the middle of the cavity. Our more detailed consideration of the available crystallographic data revealed some large deviations of silver(I) from an expected ideal trigonal coordination (Table 1) and an unusually enhanced thermal motion of silver.[19] Such structural "anomalies" are easily accounted for and even predicted from structural facets A–C. For example, Ag^I sits over the rim of the coordinated benzene rings but at a distance a little too distant (d = 2.47 Å in **IV**) from the standard value of 2.41 Å. However, the principal reason for ineffective silver(I) coordination lies in the angular distortion of α, which is forced to be 120° instead of the desired value of α = 130°; and importantly the 3-fold symmetry of the (poly)arene ligand forces Ag to adopt an undesirable trigonal pyramidal coordination. As such, we conclude that the increased lability and thermal motion of silver(I) reflect a tendency to resolve this degenerate symmetry. The point is strongly supported by structural data on the less symmetrical homologue in which the additional methylene bridge removes the 3-fold symmetry.[20] As a result, Ag shifts aside (from the remaining mirror plane) to achieve the more natural (distorted) tetrahedral coordination. Even in this complex, however, the pair of potential minima are not well separated and three crystallographically independent units show different degrees of Ag deviation from the local mirror plane.
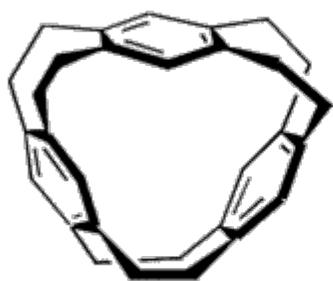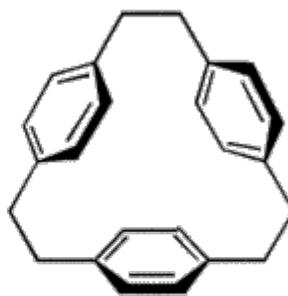
III   **IV.**

The same analyses of silver/arene complexes based on structural facets A–C of different macrocyclic aromatic ligands such as the calixarenes, other cyclophanes, etc. (for some details see Experimental Section) show why all previous attempts to totally encapsulate silver(I) heretofore have been unsuccessful. In order to achieve this goal, we identify the desirable structural features of the aromatic ligand to include two (not three) linked benzene rings so that the grab angle in the complex will be close to either 130° or 155° and the distance between benzene centers will not be less than 3.5 Å (but

not exceed 5 Å). Moreover, the local symmetry of the desired ligand should accord with the silver(I) coordination (e.g., 2-fold symmetry is allowed but not 3-fold) and possess only a narrow site wherein the steric limitations of silver(I) coordination are satisfied (since multiple or extended sites will reduce the efficiency of complexation).

A literature search revealed that these optimal structural features are inherent to the *cis*-stilbenoid ligand **V** previously utilized by Gano and co-workers[21] and its close bicyclic relative **VI** which we developed for nitrosonium complexation.[22]
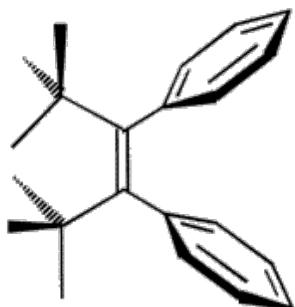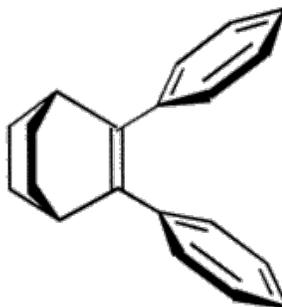
V   VI

Table 1. Geometrical Parameters of Silver(I)/Bis- and Tris(arene) Complexes with Polynuclear Tethered Ligands

Ar	AgX	Ratio Ar/A*	Ag...C*	Hapticity η	d (Å)	β (deg)	Δ (Å)	α (deg)	Coord.	Ref.
(CF₃ substituted borate)	Ag⁺	1:1	2.58/2.69	η²/η²	2.53	29	1.40	80	tetra-hedral	36
	C₆H₅I₂	(2:1)	2.51/2.57		2.43	30	1.41			
(bicyclic (CH₂)₂)	Ag-SO₃CF₃	1:1	2.48/-	η¹/η¹/η¹	2.46	32	1.51	119	trigonal	18
		(3:1)	2.41/-		2.39	33	1.54	121	pyram.	
			2.41/-		2.39	33	1.55	120		
(bicyclic (CH₂)₂)	Ag-SO₃CF₃ᵈ	1:1	2.56/2.63	η²/η²/η²	2.49	27	1.30	119	trigonal	18
		(3:1)	2.55/2.70		2.50	31	1.49	121	pyram.	
			2.62/2.63		2.50	31	1.51	120		
(bicyclic (CH₂)₂)	AgClO₄	1:1	2.54/2.67	η²/η²/η²	2.49	30	1.43	121	trigonal	19
		(3:1)	2.55/2.64		2.47	32	1.57	118	pyram.	
			2.57/2.62		2.48	30	1.43	120		
(bicyclic (CH₂)₂, Et)	AgSbF₆	1:1	2.51/2.62	η²/η²/η²	2.42	33	1.57	119	trigonal	39
		(3:1)	2.53/2.61		2.45	31	1.47	120	pyram.	
			2.51/2.58		2.41	33	1.59	120		
(polycyclic)	AgClO₄	1:1	2.59/-	η¹/η²	2.55	21	0.96	135	tetra-hedral	20
	1/3(H₂O)ᵉ	(2:1)	2.49/2.59		2.33	39	1.89			
(calixarene, OPr)₄ (cone)	Ag-SO₃CF₃	1:1	2.39/-	η¹/η¹	2.32	37	1.75	192	linear	8
		(2:1)	2.40/-		2.34	36	1.73			
(calixarene, OPr)₄ (paco)	Ag-SO₃CF₃	1:1	2.41/2.69	η¹·⁵/η¹·⁵	2.32	37	1.75	193	linear	8,9
		(2:1)	2.40/2.71		2.33	37	1.77			
(calixarene, OMe)₄ (paco)	AgNO₃	1:1	2.50/2.64	η¹·⁵/η²	2.37	37	1.79	193	linear	40
		(2:1)	2.53/2.55		2.40	34	1.64			
(azacalixarene NH)	Ag-SO₃CF₃	1:1	2.57/-	η¹/η¹	2.52	34	1.71	173	square planar	34
		(2:1)	2.55/-		2.53	32	1.57			
(cyclophane) : (benzene)	Ag-SO₃CF₃	1:2:2	2.54/-	η¹/η¹/η²	2.47	35	1.72	68.7	tetra-hedral	35
	H₂O	(3:1)	2.55/-		2.49	36	1.78	128.3ᶠ		
			2.46/2.51ᶠ		2.38ᶠ	29ᶠ	1.30ᶠ	136ᶠ		

ᵃ In parentheses: ratio between coordinated benzene rings and silver(I). ᵇ The symbol "-" means that all other distances Ag···C are larger than 2.71 Å ($r_{Ag} + r_C + 0.5$ Å). ᶜ "η¹·⁵" used for hapticities intermediate between η¹ and η². ᵈ Parameters are given only for one of four crystallographically nonequivalent units. ᵉ Parameters are given only for one of three crystallographically nonequivalent units. ᶠ With toluene molecule.

In these bis-arene ligands, the silver(I) complexation that occurs between the pair of (more or less) cofacial aryl groups will determine its penetration into the cleft. Although Gano and co-workers[21a] found that silver(I) sits somewhat outside the cleft formed by the cofacial phenyl groups in **V** (i.e., on the rim), we thought that the unique combination of steric and electronic factors in these *cis*-stilbenoid ligands can be optimized by (a) introduction of suitable (electron-donor) substituents on the aromatic complexing sites, (b) modulating the cleft opening by modification of the bicyclic bridge that controls the steric strain around the double bond, and (c) regulating the rotational freedom of the aryl groups with ortho substituents.

Results and Discussion

We focused in this study on four stilbenoid ligands in Chart 1 as prototypes for the study of silver(I) penetration into the ligand cavity. For comparison, data from Gano's ligand (1,2-di-*tert*-butyl-*cis*-stilbene, **V**) are also included.

Synthesis of the Stilbenoid Ligands. Ligands **VII**, **VIII**, and **X** were prepared by a general procedure described earlier based on the palladium-catalyzed coupling of a 1,2-dibromoalkene with an aryl Grignard reagent,[23] e.g., Ligand **IX** was prepared via the cycloaddition 1,5-cyclooactadiene and diphenylcyclopentadienone and isolated as colorless crystals in 62% yield.[24]
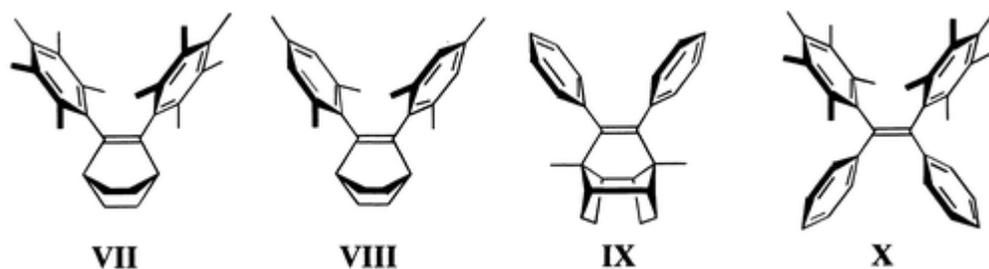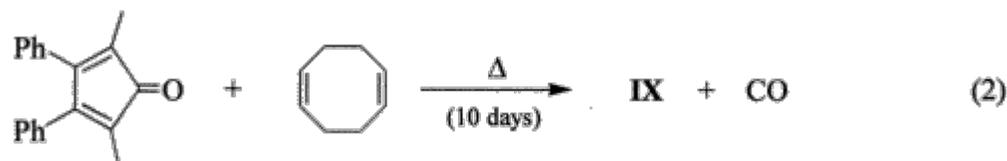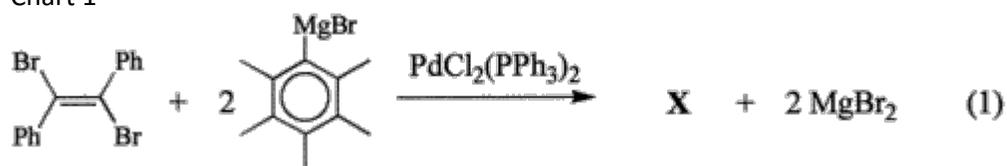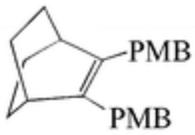

VII **VIII** **IX** **X**

Chart 1

$$Br\text{-}C(Ph)=C(Ph)\text{-}Br \quad + \quad 2 \text{ (aryl MgBr)} \quad \xrightarrow{PdCl_2(PPh_3)_2} \quad X \quad + \quad 2 \text{ MgBr}_2 \qquad (1)$$

$$\text{diphenylcyclopentadienone} \quad + \quad \text{COD} \quad \xrightarrow[\text{(10 days)}]{\Delta} \quad IX \quad + \quad CO \qquad (2)$$
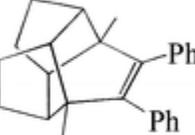
Cyclic Voltammetry of the Stilbenoid Ligands. The donor strengths of the stilbenoid ligands were evaluated by their reversible oxidation potentials.[25] Cyclic voltammetry carried out at a platinum anode showed reversible electrochemical behavior when a 5 mM solution in dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate was swept at 100 mV s^{-1}. The trend in the $E°_{ox}$ values listed in Table 2 followed the decreasing trend of the methylated benzenes established earlier.[26] As such, we conclude that they are largely unaffected by steric changes or the nature of the bicyclic bridge.

Table 2. Donor Strengths of Stilbenoid Ligands and Formation Constants of Their Complexes with Silver(I)

Stilbene[a]	$E°_{ox}$ (V vs SCE[b])	K_{form} (M^{-1})[c]
PMB / PMB	1.28	662 ± 10
Ph / Ph	1.52	527 ± 10
MES / MES	1.40	337 ± 10
Ph / PMB / Ph / PMB	1.30	-
Bu^t / Ph / Bu^t / Ph	-	3700 ± 300[d]
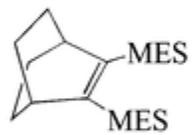
[a] PMB = pentamethylphenyl, Ph = phenyl, MES = mesityl, Bu^t = *tert*-butyl.[b] In dichloromethane at 25 °C.[c] In 3:1 v/v mixture of dichloromethane and methanol.[d] From Gano et al. in ref 21a.

Preparation and Isolation of Silver(I) Complexes with *cis*-Stilbenoid Ligands. A uniform procedure was followed in the preparation of the crystalline complexes by the dissolution of equimolar amounts of silver(I) trifluoromethanesulfonate (AgOTf) and the appropriate stilbenoid ligand in anhydrous tetrahydrofuran. The colorless solution was evaporated to dryness in vacuo, and the residue was redissolved in dichloromethane. The colorless solution was carefully layered with either *n*-hexane or toluene and allowed to deposit colorless crystals. The silver/stilbene complexes are stable at room temperature and showed no signs of decomposition over a period of months.

Evaluation of Formation Constants in Solution. The formation constants of the silver(I) complexes with ligands **VII−IX** were evaluated in a 3:1 v/v mixture of dichloromethane-d_2 and methanol-d_4 by the NMR method described earlier.[18,21a] The magnitudes of the K_{form} values in Table 2 are substantially larger than those of simple (mono)arene complexes ($K_{form} \sim 2.4–3.9$ M^{-1}in aqueous solutions),[27] but less than that [$K_{form} = (3.7 \pm 0.3) \times 10^3$ M^{-1}] obtained for **V** in pure chloroform by Gano and co-workers.[21a]

X-ray Crystallographic Structures of Silver(I) Complexes with Stilbenoids. Crystallographic data on the 1:1 silver(I)/stilbene complexes **VII−IX** were collected at low temperature (either 93 or 123 K) and refined to R1 ≤ 3.6%, and the pertinent structural parameters are listed in Table 3. As a basis for comparison, crystallographic data were also collected for the free (uncomplexed) ligands, and they are

available from the Cambridge Crystallographic Data Center together with those for their silver complexes.

The ORTEP structures for **VII–IX** are illustrated in Figures 1–3, respectively, and they uniformly show that Ag is incorporated within the cleft of the stilbenoid donors, and the bonding to both aromatic moieties is essentially the same (with a local 2-fold axis through the silver(I) ion and the middle of the C $\equiv$ C double bond), i.e., Although the silver(I) complex **VII** packs in the unit cell as single molecules and **VIII** and **IX** pack as dimeric units (with trifluoromethanesulfonato bridges), the basic structural unit illustrated by **XI** remains intact in all structures. However, the bonding of silver(I) to the aromatic moiety varies between η^1 and η^2 (see column 5, Table 3).

XI
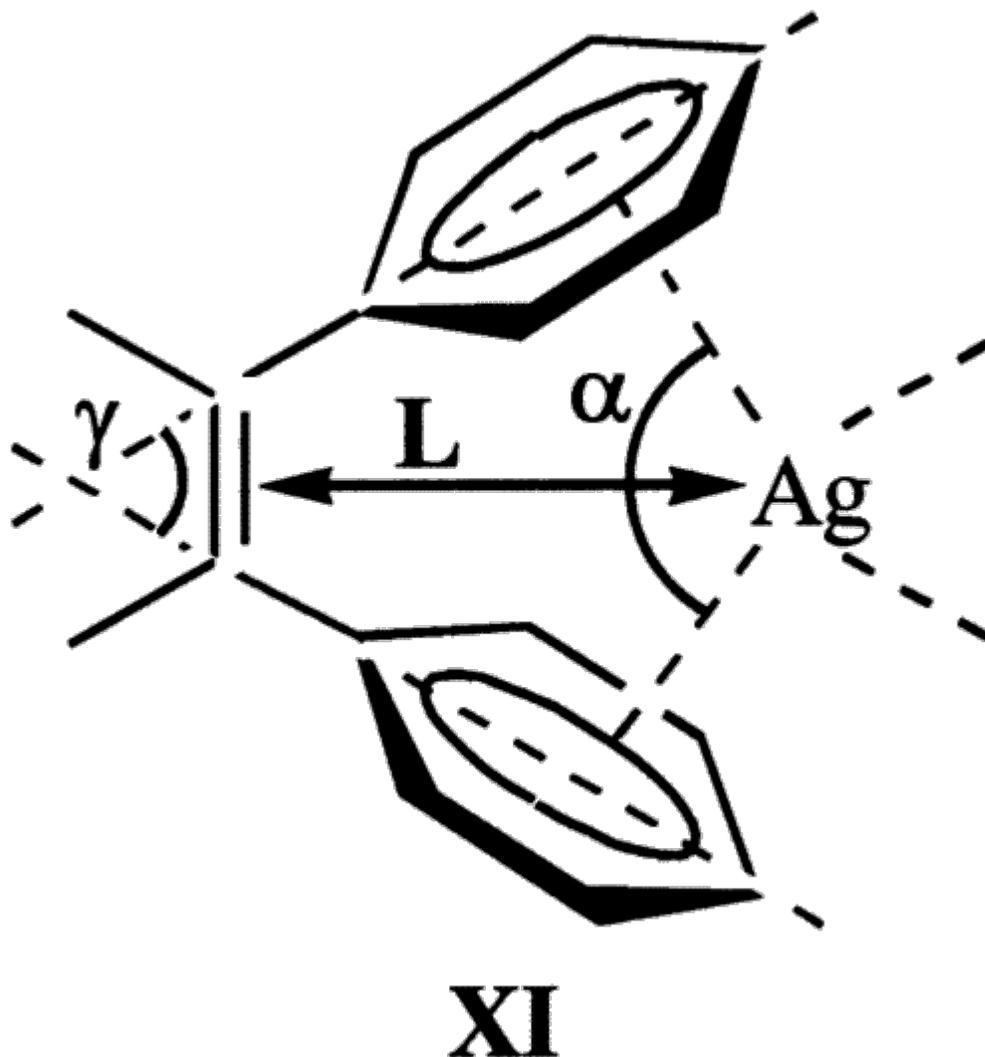
The most important structural parameter for this study is the distance between silver(I) and the olefinic center, which is given by the parameter **L** in structure **XI**. We consider the parameter L to be a reliable measure of the penetration of Ag into the donor cavity, and it is listed in the last column of Table 3. In the Ag complex **VII,** silver(I) penetrates deeply into the cleft, and the value of L is only 3.5 Å (more or less within van der Waals contact of silver cation and the double bond[28]). Such a close proximity occurs with the silver/arene bonding parameters α, β, and Δ of 113°, 24°, and 1.0 Å, which are significantly less than the optimal values of 130°, 32°, and 1.5 Å, as originally outlined in

structures **I** and **II** (vide supra). (Note that the silver/ arene separation as measured by *d* is the only structural parameter that remains invariant at 2.5 Å.)

Figure 1 ORTEP diagram of the monomeric [**VII**AgOTf(H_2O)] complex. Thermal ellipsoids are shown at the 50% probability level.

Figure 2 ORTEP diagram of the dimeric [**VIII**AgOTf(μ_2-OTf)(H_2O)Ag**VIII**] complex. Thermal ellipsoids are shown at the 50% probability level.

Figure 3 ORTEP diagram of the dimeric [**IX**Ag(μ_2-OTf)(μ_2-H$_2$O)OTfAg$\cdots$AgOTf(μ_2-H$_2$O)(μ_2-OTf)Ag**IX**] complex with an unusually short Ag$\cdots$Ag contact of 3.234(1) Å. Thermal ellipsoids are shown at the 50% probability level.

Table 3. Geometrical Parameters of Silver(I)/Bis(arene) Complexes with *cis*-Stilbenoid Ligands

Ar	AgX	Ratio Ar/Ag[a]	Ag...C[b]	Hapticity η[c]	d (Å)	β (deg)	Δ (Å)	γ[d] (deg)	α (deg)	L (Å)
VII	Ag-SO₃CF₃ H₂O	1:1 (2:1)	2.52/- (*o*) 2.55/2.70 (*o/i*)	$\eta^1/\eta^{1.5}$	2.48 2.47	24 20	1.10 0.90	91 (94)	113	3.47
VIII[e]	Ag-SO₃CF₃ ½H₂O	1:1 (2:1)	2.58/2.63 (*m/o*) 2.58/2.63 (*m/o*) 2.59/2.67 (*m/o*) 2.57/2.63 (*m/o*)	η^2/η^2 η^2/η^2	2.50 2.50 2.53 2.48	27 29 25 29	1.28 1.37 1.20 1.40	88 (91) 89 (91)	122 124	4.01 3.98
IX	Ag-SO₃CF₃ ½H₂O	1:2 (2:1)	2.52/- (*m*) 2.47/- (*m*)	η^1/η^1	2.51 2.45	29 30	1.38 1.41	79 (82)	133	4.45
X[f]	Ag-SO₃CF₃	1:2 (2:1)	2.44/- (*m*) 2.44/- (*m*) 2.55/2.71 (*m/o*) 2.55/2.71 (*m/o*)	η^1/η^1 $\eta^{1.5}/\eta^{1.5}$	2.35 2.35 2.51 2.51	39 39 25 25	1.90 1.90 1.17 1.17	77 (88) 85 (89)	140 125	4.82 4.07
V	Ag-SO₃CF₃	1:1 (2:1)	2.58/- (*p*) 2.51/2.58 (*m/p*)	η^1/η^2	2.58 2.44	25 29	1.19 1.36	71[21a] (74)[21c]	135	4.71

[a] In parentheses: ratio between coordinated benzene rings and silver(I). [b] The symbol "-" means that all other Ag$\cdots$C distances are larger than 2.71 Å ($r_{Ag} + r_C + 0.5$ Å). In parentheses: coordination site within Ph ring (ipso, ortho, meta, or para). [c] "$\eta^{1.5}$" used for hapticities intermediate between η^1 and η^2. [d] In parentheses: values for an uncomplexed ligand. [e] First two lines and last two lines refer to two symmetrically nonequivalent units, respectively. [f] First two lines: parameters with participation of unsubstituted Ph groups. Last two lines: with participation of methylated Ph groups.

The opposite extreme of silver penetration is found in Gano's silver(I) complex[21a] (L = 4.7 Å) in which Ag is situated on the rim at the very periphery of the bis(arene) complexing site. Although the bonding parameters of α = 135°, β = 25°, and Δ = 1.2 Å are close to optimal values (see structures **I** and **II**), silver coordination to arene is highly asymmetric with one benzene nucleus much more tightly bound than the other (see column 6, Table 3). This suggests a very shallow or wide shape of the potential energy minimum from silver(I) coordination [possibly with several minima that should reduce the

effectiveness of complex formation as described in the tris(arene) complexes above]. The systematic variation in depth of Ag penetration into the various stilbenoid clefts is illustrated in Figure 4.

V·Ag
($\gamma = 71°$)

IX·Ag
($\gamma = 80°$)

VIII·Ag
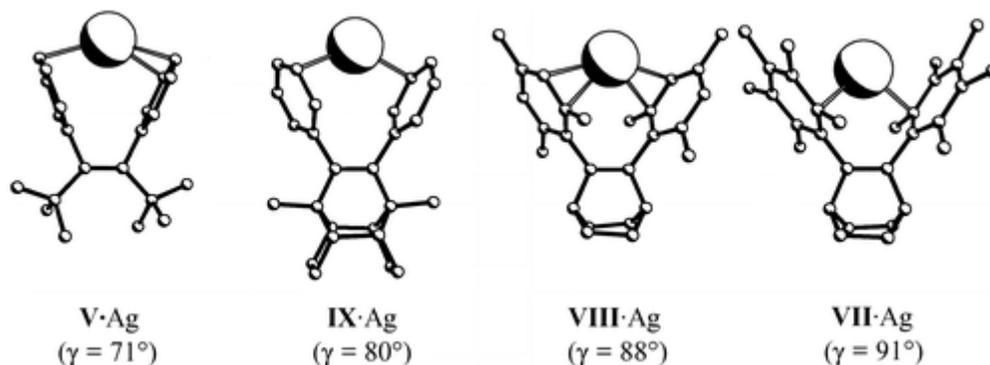($\gamma = 88°$)

VII·Ag
($\gamma = 91°$)

Figure 4 Progressive structural changes in silver(I)/stilbenoid complexes with increasing values of γ (cleft opening between benzene rings). See text and Table 3.

It is particularly important to note that the cleft between the phenyl groups of the *cis*-di-*tert*-butylstilbene in Gano's complex is the narrowest of all the stilbenoid ligands examined in this study. Let us therefore define γ as the cleft parameter for maintaining the dihedral angle α between the mean aromatic planes in stilbenoid ligands (see structure **XI**). If so, Figure 5dramatically illustrates the linear correlation that pertains between *L* (penetration) and γ (cleft).[29]In other words, the degree to which Ag penetrates the stilbenoid cavity is solely determined by the (dihedral) cleft angle, which modulates the precise location of Ag within the cavity. In essence, such a conclusion derives from the distance *d* as the *invariant parameter* for all silver/arene complexes. [Thus, it is easy to conclude that Ag will slide into the cleft (with a certain value of γ) up to an *L* at which the distance criterion (*d*) is fulfilled]. Minor adjustments of the ligand morphology to accommodate the *d* constant include a slight variation in the aryl twist angle (which in turn is influenced by ortho substituents) as well as some contraction of the cleft angle γ. The latter is indicated in Table 3 (column 9) by the comparative values of γ in the free ligand relative to that in the complex (always smaller). The hapticity of the silver/arene bonding is a "soft" parameter, and it is readily accommodated by changes in α, β, and Δ as listed in columns 10, 7 and 8.
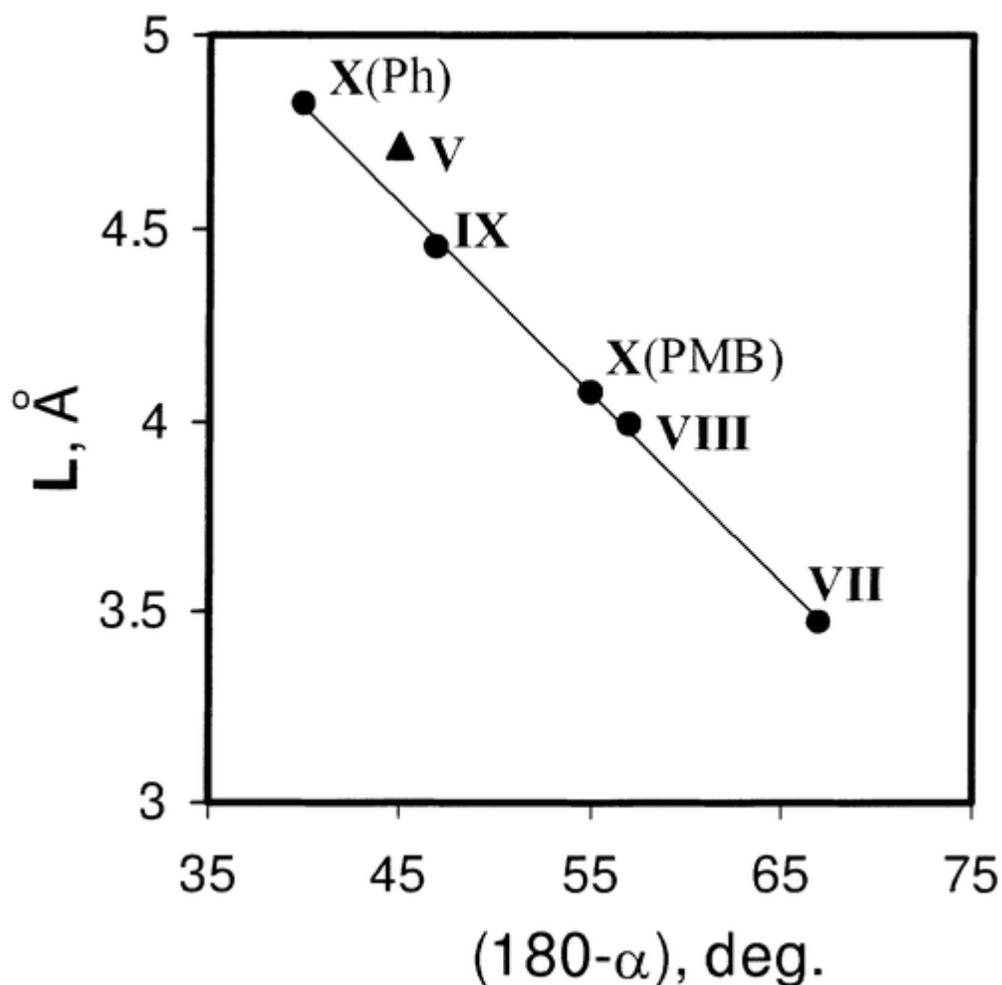
Figure 5 Silver penetration *L* (see structure **XI**) as a function of dihedral angle α between benzene rings (see structure **II**). Correlation factor for the linear approximation is *R* = 0.9995 (Gano's structure **V**·Ag was not included in the computation).

Silver(I) Complexes of Bifunctional Stilbenoid Ligands. Crystal engineering inherent to the encapsulation of silver(I) into the stilbenoid ligands can be extended to a polymeric chain by employing the bifunctional ligand **X** (see Chart 1). The synthesis of this tetraarylethylene followed from our earlier studies[30a] and involved the standard palladium-catalyzed coupling of 1,2-dibromostilbene with pentamethylphenylmagnesium bromide (compare eq 1). Indeed, X-ray crystallographic analysis shows that both pairs of *syn*-aryl groups are cofacially disposed about the ethylenic linkage in much the same manner as those in the *cis*-stilbenes **VII–IX**. Treatment of **X** with 1 equiv of silver trifluoromethanesulfonate in tetrahydrofuran and workup as described above yielded sharply melting colorless crystals of the silver(I) complex. X-ray crystallographic analysis of the silver(I) complex revealed the novel (linear) polymeric structure shown in Figure 6, in which each tetraarylethylene ligand is connected to two silver(I) in a regular alternating sequence with two different penetration distances characteristic of a pair of *syn*-phenyl groups (*L* = 4.82 Å) and *syn*-pentamethylphenyl groups (*L* = 4.07 Å).
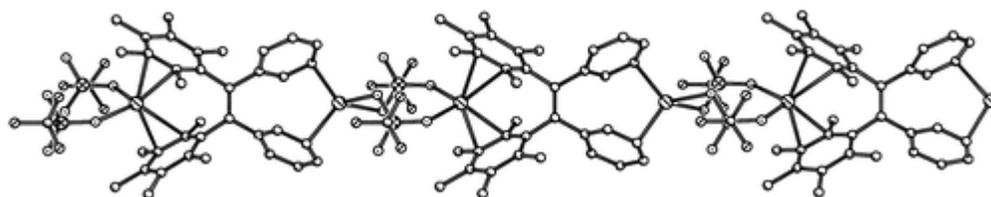
Figure 6 Infinite regular chain formed along 2-fold axis in structure **X**(AgOTf)$_2$. Note the head-to-tail arrangement and μ$_2$ bridging function of triflate ligands.

Despite the difference in the overall structure of the polymeric chain in Figure 6 from that in the stilbenoid mono- and dimeric analogues (Figures 1–3), the relevant penetrations of Ag into both clefts of **X** are unaffected. The latter is demonstrated by the exact inclusion of both sets of *L* and γ parameters for silver(I) complex **X** in the linear correlation shown in Figure 5. The latter confirms our above conclusion that the distance parameter *d* is the overriding factor that establishes the degree to which Ag can penetrate a stilbenoid cavity.

Conclusion

Structural analysis of a wide variety of both mono(arene) and poly(arene) complexes of silver(I) reveals a surprisingly consistent set of optimal (bonding) parameters: *d* = 2.4 Å, Δ = 1.5 Å, and α = 130° or 150° (within a rather narrow range) when 2-fold symmetry pertains in arene/Ag interactions. The hapticity (η^1 or η^2) is not a rigid bonding mode for silver(I), and a continuum of intermediate values (η$^{1.5}$) are commonly found. We hope these conclusions will aid in the appropriate design of poly(arene) ligands for effective silver(I) encapsulation.

Experimental Section

Materials. The 2,3-diphenylbicyclooctene derivative (**IX**, 9,12-dimethyl-10,11-diphenyltetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodec-10-ene) was prepared by heating a mixture of commercially available dimeric 3,4-diphenyl-2,5-dimethylcyclopentadienone (2.5 g, 10 mmol) and freshly distilled 1,4-cyclooctadiene (10 mL) in a sealed tube at 80 °C for 72 h. The excess 1,4-cycloocatadiene was removed in vacuo, and the chromatographic purification of the resulting crude syrup on silica gel, using a 1:1 mixture of hexane and ethyl acetate as an eluent, afforded the pure 2,3-diphenylbicyclooctene derivative **IX** in good yield (2.1 g, 62%); mp 142–144 °C (dichloromethane/ethanol); ^{1}H NMR (CDCl$_3$) δ 0.94 (s, 6H), 1.75 (br d, 4H), 1.82 (br s, 4H), 1.95 (br d, 4H), 6.88–7.07 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 22.97, 24.86, 45.63, 47.38, 125.11, 126.86, 130.02, 141.86, 142.18; GC–MS *m/z* 340 (M$^+$), 340 calcd for C$_{26}$H$_{28}$. An efficient general procedure for the synthesis of 2,3-bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (**VII**), 2,3-bis(2,4,6-trimethylphenylbicyclo[2.2.2]oct-2-ene (**VIII**), and 1,2-bis(pentamethylphenyl)-1,2-diphenylethylene (**X**) (mp 157–159 °C (dichloromethane–ethanol); ^{1}H NMR (CDCl$_3$) δ 2.05 (s, 12H), 2.12 (s, 6H), 2.15 (s, 12H), 7.08 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 16.46, 16.68, 20.07, 125.68, 127.22, 130.98, 131.79, 131.85, 132.83, 139.00, 141.59, 143.35; GC–MS *m/z* 470 (M$^+$), 470 calcd for C$_{36}$H$_{40}$) has been described previously.[23] Silver trifluoromethanesulfonate (Aldrich) was stored in a Vacuum Atmospheres HE-493 drybox kept free of oxygen.
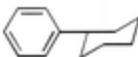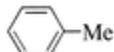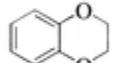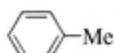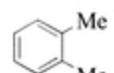
Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~20 vol %) until the acid layer remained colorless. After separation, it was

washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexane was distilled from P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH_2, the solvents were stored in the Schlenk flasks under an argon atmosphere.

Instrumentation. The ^{1}H and ^{13}C NMR spectra were obtained on a General Electric QE-300 FT NMR spectrometer. Electrochemical apparatus and the procedure for the determination of the oxidation potentials has been described elsewhere.[30b] The equilibrium constants for stilbenoid donor/silver complexes were determined according to a published procedure.[18,21a]

Preparation of Crystalline Stilbene/Silver Complexes. General Procedure. Equimolar solutions of CF_3SO_3Ag (0.2 mmol, 0.01 M) and of the stilbene (0.2 mmol, 0.01 M) in anhydrous tetrahydrofuran were mixed at 22 °C and under an argon atmosphere. After the mixture was stirred for 1 h at 22 °C, the solvent was removed in vacuo. The resulting solid was redissolved in dichloromethane. The cloudy solution was filtered through glass wool (under an argon atmosphere) and carefully layered with hexane. After standing for several days, the bilayeredmixture deposited colorless single crystals of high quality. Note that these silver/diaryl olefin complexes were stable at room temperature for months without showing any sign of decomposition.

Table 4. Comparison of the Geometrical Parameters of Silver(I)/Bis(arene) Complexes with Mononuclear Ligands

Ar	AgX	Ar/Ag	Ag...C[a]	Hapticity η[b]	d (Å)	β (deg)	Δ (Å)	α (deg)	Coordination	Ref.
(cyclooctene-phenyl)	AgClO$_4$	1:1	2.48/2.68 2.48/2.68	η$^{1.5}$/η$^{1.5}$	2.41 2.41	35 35	1.66 1.66	91	sq.pyr/ octah.	2c
(benzene)	AgClO$_4$	1:1	2.57/2.57 2.57/2.57	η^{2}/η^{2}	2.41 2.41	35 35	1.72 1.72	97	octah.	32
(benzene)	Ag-CH$_8$B$_9$F$_2$	2:1	2.47/2.52 2.49/2.65	η$^{1.5}$/η^{2}	2.36 2.45	34 31	1.59 1.49	128	tetrah.	41
(toluene –Me)	Ag-OTeF$_5$	2:1	2.49/2.70 2.44/2.63	η$^{1.5}$/η$^{1.5}$	2.46 2.41	29 28	1.36 1.29	132	tetrah.	42
(benzodioxane)	AgClO$_4$	2:1	2.47/2.57 2.47/2.57	η$^{1.5}$/η$^{1.5}$	2.39 2.39	32 32	1.50 1.50	132	tetrah.	43
(benzene)	Ag-CH$_{11}$B$_{11}$F	2:1	2.46/- 2.53/2.59	η^{1}/η^{2}	2.44 2.45	32 29	1.53 1.36	151	linear	44
(toluene –Me)	Ag-SO$_3$CF$_3$ (PtMe$_3$-SO$_3$CF$_3$)$_2$	2:1	2.39/2.57 2.39/2.68	η$^{1.5}$/η$^{1.5}$	2.34 2.36	32 30	1.45 1.35	155	linear	45
(o-xylene Me Me)	AgClO$_4$	2:1	2.44/2.53 2.49/2.57	η$^{1.5}$/η$^{1.5}$	2.39 2.40	31 32	1.43 1.47	158	linear	46
(benzene)	AgBF$_4$	3:1	2.48/- 2.49/- 2.53/2.54	η^{1}/η^{1}/η^{2}	2.47 2.45 2.41	34 35 32	1.67 1.73 1.50	92 128 131	tetrah.	33

[a] The symbol "-" means that all other Ag···C distances are longer than 2.71 Å (r_{Ag} + r_C + 0.5 Å). [b] "η$^{1.5}$" used for hapticities intermediate between η^1 and η^2.

X-ray Crystallography. The intensity data for all the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a 1K CCD detector using Mo Kα radiation (λ = 0.71073 Å), at −180 °C unless otherwise specified. The structures were solved by direct methods[31] and refined by a full-matrix least-squares procedure with IBM Pentium and SGI O$_2$computers. (The details of the X-ray structure of various compounds are on deposit and can be obtained from Cambridge Crystallographic Data Center, U.K.) **2,3-Bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (VII)/Ag$^+$CF$_3$SO$_3^-$ Complex.** Brutto formula: C$_{30}$H$_{40}$·CF$_3$SO$_3$Ag·H$_2$O, MW = 675.58, monoclinic, space group $P2_1/c$, at −150 °C a = 17.0787(3) Å, b = 14.5611(3) Å, and c = 12.6883(4) Å, β = 111.754(1)°, D_c = 1.531 g cm^{-3}, V = 2930.7(1) Å^3, Z = 4. The total number of reflections measured was 24367, of which 12740 reflections were symmetrically nonequivalent. Final residuals were R1 = 0.0228 and wR2 = 0.0554 for 11322 reflections with I > 2σ(I). **2,3-Bis(2,4,6-trimethylphenyl)bicyclo[2.2.2]oct-2-ene (VIII)/Ag$^+$CF$_3$SO$_3^-$ Complex.** Brutto formula: 2C$_{27}$H$_{32}$·2CF$_3$SO$_3$Ag·H$_2$O, MW = 1220.93, triclinic, space group $P\bar{1}$, a = 12.8222(7) Å, b = 13.9994(7) Å, and c = 15.5853(8) Å, α = 94.850(1)°, β = 93.037(1)°, γ = 106.372(1)°, D_c = 1.534 g cm^{-3}, V = 2643.0(2) Å^3, Z = 2. The total number of reflections measured was 36667, of which 22079 reflections were symmetrically nonequivalent. Final residuals were R1 = 0.0356

and wR2 = 0.0801 for 15475 reflections with $I > 2\sigma(I)$. **9,12-Dimethyl-10,11-diphenyltetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodec-10-ene (IX)/Ag$^+$CF$_3$SO$_3^-$ Complex.**Brutto formula: $C_{26}H_{28} \cdot 2CF_3SO_3Ag \cdot H_2O$, MW = 872.38, monoclinic, space group $P2_1/n$, a = 6.1411(8) Å, b = 36.618(5) Å, and c = 13.486(2) Å, β = 100.599(3)°, D_c = 1.944 g cm^{-3}, V = 2981.0(7) Å^3, Z = 4. The total number of reflections measured was 33402, of which 9115 reflections were symmetrically nonequivalent. Final residuals were R1 = 0.0492 and wR2 = 0.1108 for 5849 reflections with $I > 2\sigma(I)$. **1,2-Bis(pentamethylphenyl)-1,2-diphenylethylene (X)/Ag$^+$CF$_3$SO$_3^-$ Complex.** Brutto formula: $2C_{38}H_{40} \cdot 2CF_3SO_3Ag$, MW = 986.56, monoclinic, space group $C2/c$, a = 19.5429(5) Å, b = 14.1980(4) Å, and c = 16.4689(5) Å, β = 123.8240(10)°, D_c = 1.726 g cm^{-3}, V = 3796.2(2) Å^3, Z = 4. The total number of reflections measured was 26514, of which 8222 reflections were symmetrically nonequivalent. Final residuals were R1 = 0.0191 and wR2 = 0.0502 for 7282 reflections with $I > 2\sigma(I)$.
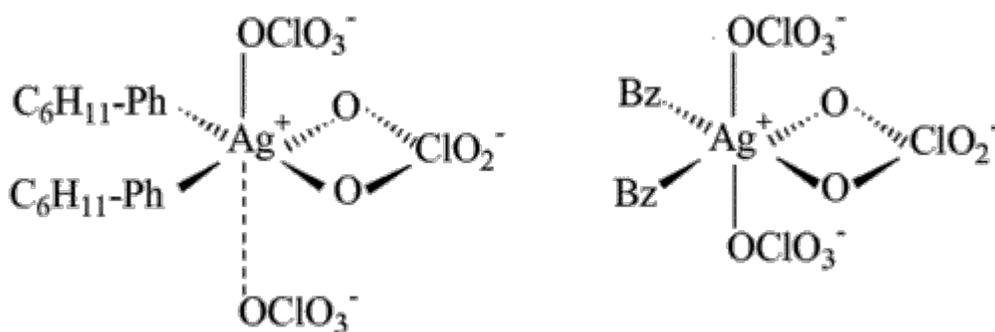
Neutral 9,12-Dimethyl-10,11-diphenyltetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodec-10-ene (IX). Brutto formula: $C_{26}H_{28}$, MW = 340.48, triclinic, space group $P\bar{1}$, a = 5.9876(2) Å, b = 11.6951(4) Å, and c= 13.9555(5) Å, α = 76.047(1)°, β = 81.328(1)°, γ = 83.152(1)°, D_c = 1.211 g cm^{-3}, V = 934.06(6) Å^3, Z = 2. The total number of reflections measured was 13264, of which 7886 reflections were symmetrically nonequivalent. Final residuals were R1 = 0.0458 and wR2 = 0.1247 for 6677 reflections with $I > 2\sigma(I)$.
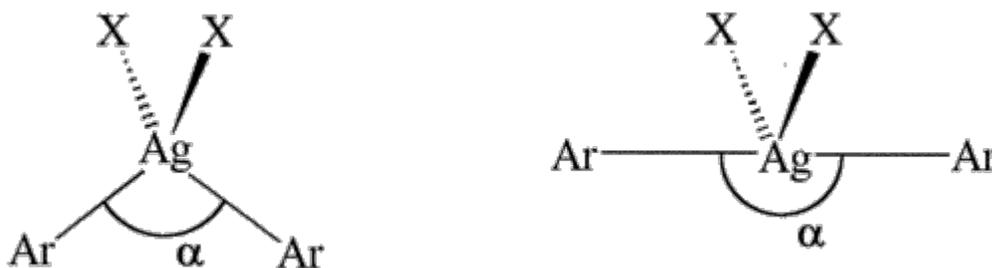
Neutral 1,2-Bis(pentamethylphenyl)-1,2-diphenylethylene (X). Brutto formula: $C_{36}H_{40}$, MW = 472.68, monoclinic, space group $P2_1/c$, a = 17.0401(5) Å, b = 9.6913(3) Å, and c = 17.3737(5) Å, β = 106.389(1)°, D_c = 1.141 g cm^{-3}, V = 2752.5(1) Å^3, Z = 4. The total number of reflections measured was 33158, of which 11876 reflections were symmetrically nonequivalent. Final residuals were R1 = 0.0428 and wR2 = 0.0668 for 8426 reflections with $I > 2\sigma(I)$. (Note that X-ray structure data for the neutral stilbenoid donors **VII** and **VIII** are published elsewhere.[22,23])

Structural Analysis of Silver(I) Complexes of (Mono)arenes. Silver(I) complexes of simple benzenoid donors fall into three classes with α = 95°, 130°, and 155° (typical deviation ±3°).

The first group of the complexes, with $\alpha \cong$ 95°, is composed of silver/arene complexes having the stoichiometric ratio of 1:1. These crystals have coordinationally active atoms (typically oxygens) in the counteranions, and, as a result, the silver(I) ion has a trend toward higher coordination numbers. For example, in the phenylcyclohexane/AgClO$_4$ complex with α = 91.5° (entry 1, Table 4), the silver(I) ion has a coordination number of 5.[2c] In the benzene/AgClO$_4$ complex with α = 96.9° (entry 2, Table 4), the silver(I) ion has a coordination number of 6.[32] In the first case, the silver(I) ion has a coordination intermediate between square pyramidal and octahedral, and in the second case, a distorted octahedral coordination: The observed α values in these complexes are those required for a nondistorted octahedral coordination and hybridization of the silver(I) ion. The 1:1 stoichiometry of these complexes results in a μ^2 functionality of coordinated benzene rings and leads to formation of polymeric chains (...Ar...Ag...Ar...Ag...) in their crystals.

OClO₃⁻ ... Ag⁺ ... structure (C₆H₁₁-Ph ligands, ClO₂⁻)

$C_6H_{11}\text{-Ph} \cdots Ag^+ \cdots O \cdots ClO_2^-$ with $OClO_3^-$ above and below

$Bz \cdots Ag^+ \cdots O \cdots ClO_2^-$ with $OClO_3^-$ above and below

All known silver/bis(monoarene) complexes with a 2:1 stoichiometry only have α values of either ~130° or ~150° and coordination number 4. This corresponds either to a distorted tetrahedral silver(I) coordination/hybridization (generic value α = 109.5°) or to a distorted linear coordination/hybridization (generic value α = 180°) with additional coordination in the equatorial plane: We could find no structures that deviate perceptibly from either one of these two types of coordination, and this indicates that they correspond to two relatively sharp potential energy minima. We also were unable to find any factors other than crystal packing forces to make one or another coordination the most favorable in particular crystals. We conclude that potential energies of the corresponding coordination/electron states of silver(I) are nearly equivalent.

[Diagram: X X above Ag, Ar and Ar below with angle α (distorted tetrahedral)]

[Diagram: X X above Ag, Ar—Ag—Ar linear with angle α]

There is only one example known of a silver/tris(monoarene) complex with a 3:1 stoichiometry (entry 9, Table 4).[33] Remarkably, its structure also follows all the regularities found for other silver/bis(monoarene) complexes (including values of the α angles).

Structural Analysis of Calixarene and Other Polyaromatic Complexes of Silver(I). The principal rationale for the use of calixarene ligands is the favorable distance (about 5 Å) between opposed benzene rings, which is well suitable for silver(I) intercalation if one consider only its ionic radius. However, a scrupulous analysis of the resulting structures (entries 7–9, Table 1) shows that the steric conditions for silver/arene complexation are not completely met in these complexes. In particular, the α angle has an unfavorable value of ~193° that is far from the optimal value ~155°:As a result, the angular distortion results in a large separation of opposed aryl groups in the uncomplexed calixarene donor. A more detailed consideration of the geometric features shows that the distance between upper rims of the benzene rings that participate in the silver(I) coordination is 5.5 Å in uncoordinated calixarene but only 4.5 Å in the complexed one. [Such a contraction is required to maintain an optimal separation d = 2.41 Å between the silver(I) ion and the coordinated benzene nuclei since this can be achieved only by rotation (clamping) of the benzene rings toward each other.] In the resulting configuration, these rings are inclined toward the center of the cavity and cause the "inverted" distortion of the α angle (note in the uncomplexed donor they are inclined outward from the cavity): To relieve this angular distortion, the silver(I) ion moves outward from the cavity (toward the

equatorial oxygen ligands), and this causes increased values of $\Delta \sim 1.75$ Å (typical value 1.55 Å) and $\beta \sim 37°$ (typical value 32°) in these calixarene complexes.
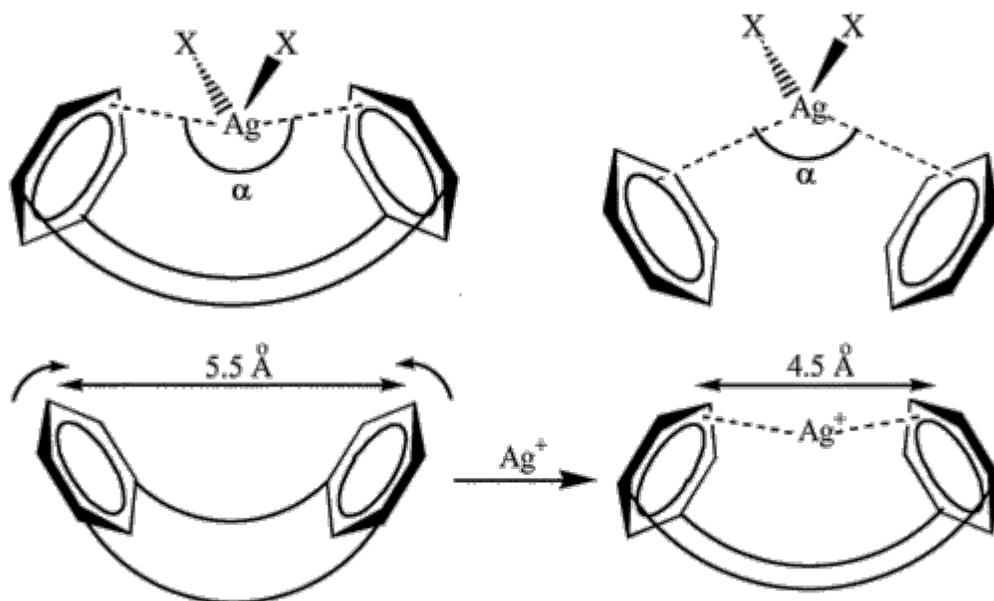
In a less conformationally rigid but topologically closely related cyclophane donor,[34] the "inversion" of the α angle over 180° is avoided ($\alpha = 172.5°$), but the presence of coordinationally active amino nitrogens in the bridges of the molecule forces an atypical square-planar coordination of silver(I) that does not favor an effective silver(I) complexation. (Compare the similar consequences of trigonal symmetry degeneration in the deltaphane complexes above.)
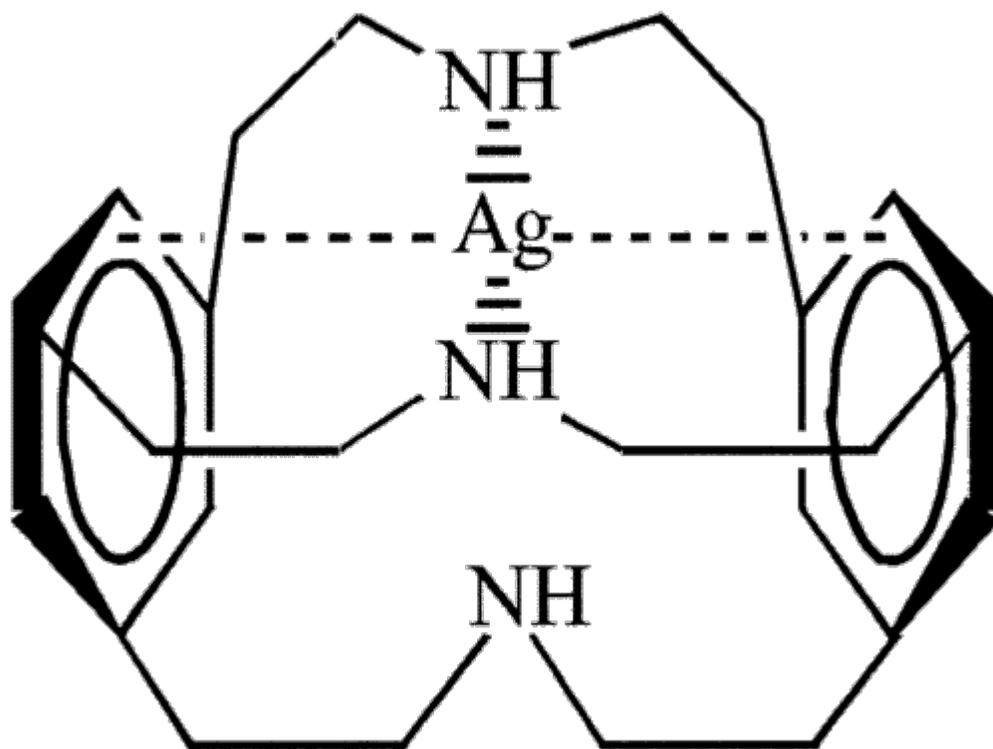

There has also been an attempt to use a larger box-shaped poly(arene) moiety for silver(I) complexation[35] that actually failed owing to steric restrictions: The silver(I) ion in this complex cannot

coordinate to the opposed benzene rings which are too distant (the separation is ~8 Å), and instead, it coordinates to two neighboring arene groups under very unfavorable geometrical conditions (entry 11, Table 1). The generally constrained situation is relieved only by participation of an additional toluene solvate that coordinates to the silver(I) ion at much more characteristic geometric values.
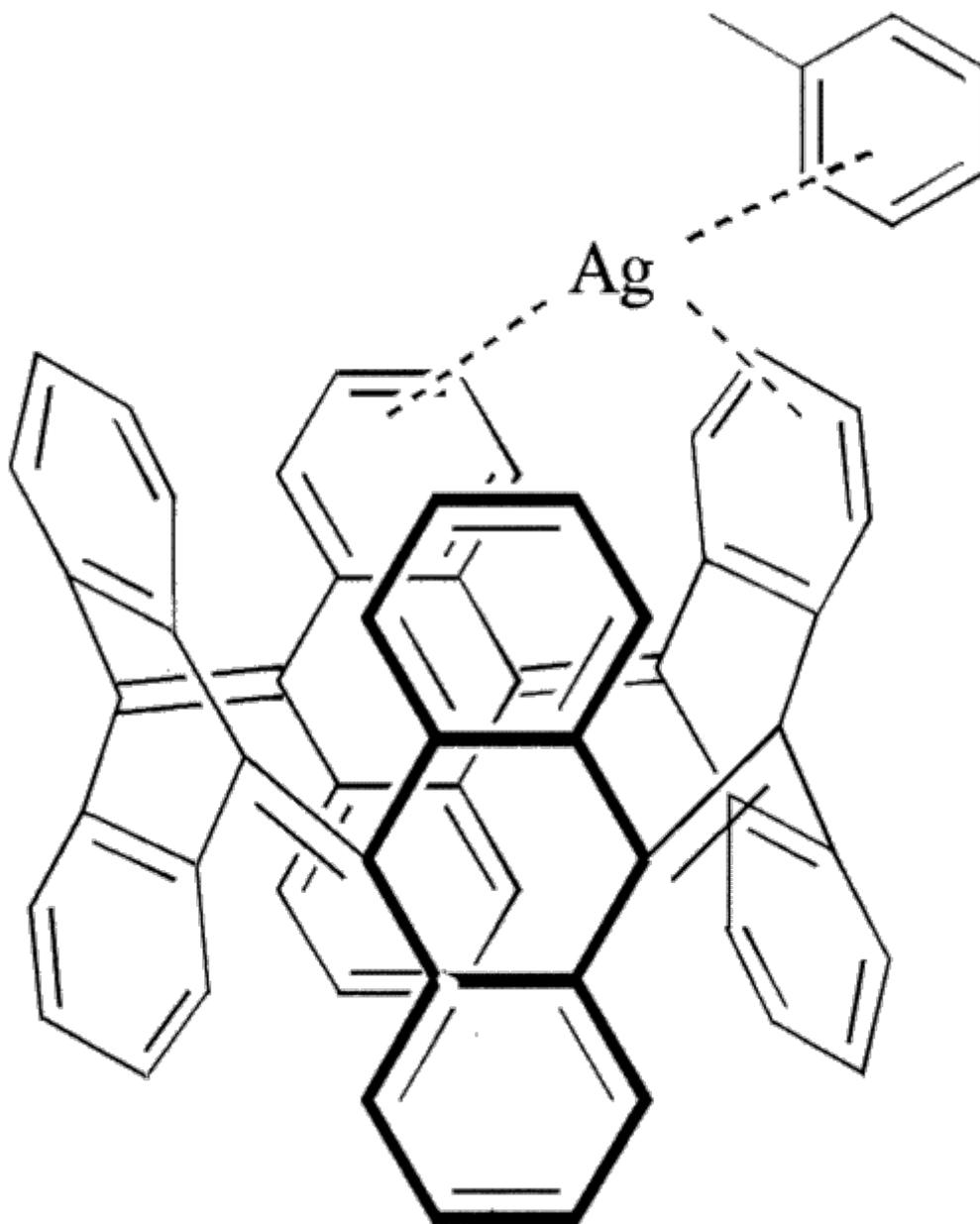
A relatively straightforward attempt was undertaken in a silver(I) tetraarylborate complex (entry 1, Table 1)[36] in which the multidentate arene substrate functions also as the counteranion. The latter greatly increases the total strength of the silver–ligand interactions due to contribution of Coulombic forces. Indeed in this complex, the silver(I) cation deeply penetrates into the central boron cleft of the anion giving short contacts with the ipso and ortho carbons of two of the four aryl groups. However, the $Ag^+ \cdots Ar$ separations (2.43 and 2.53 Å) are unexpectedly longer than the standard value (2.41 Å), and the silver(I) ion is strongly shifted toward the axes of the benzene rings (Δ = 1.40 and 1.41 Å instead of the optimal 1.53 Å value). These structural features indicate that the Coulombic attraction

Ag$^+$···B$^-$ takes a place, but at the expense of substantial distortions in the silver/arene coordination. A conflict between Coulombic and coordination interactions results in a general hindering of the system that is not satisfactory for effective complexation. The most apparent manifestation of this conflict is a very much contracted α angle at the silver(I) ion (80.2°) that is incompatible with the 4-coordinated silver/arene complexes,[37] being far from the optimal 130° or 155° values. Such a contracted value of α is forced by the tetrahedral angle ($\gamma \sim 109°$) between the axes of the coordinated benzene rings; and it cannot be further extended beyond 70° (180° − γ) without even more severe distortions in silver(I) coordination:[38]
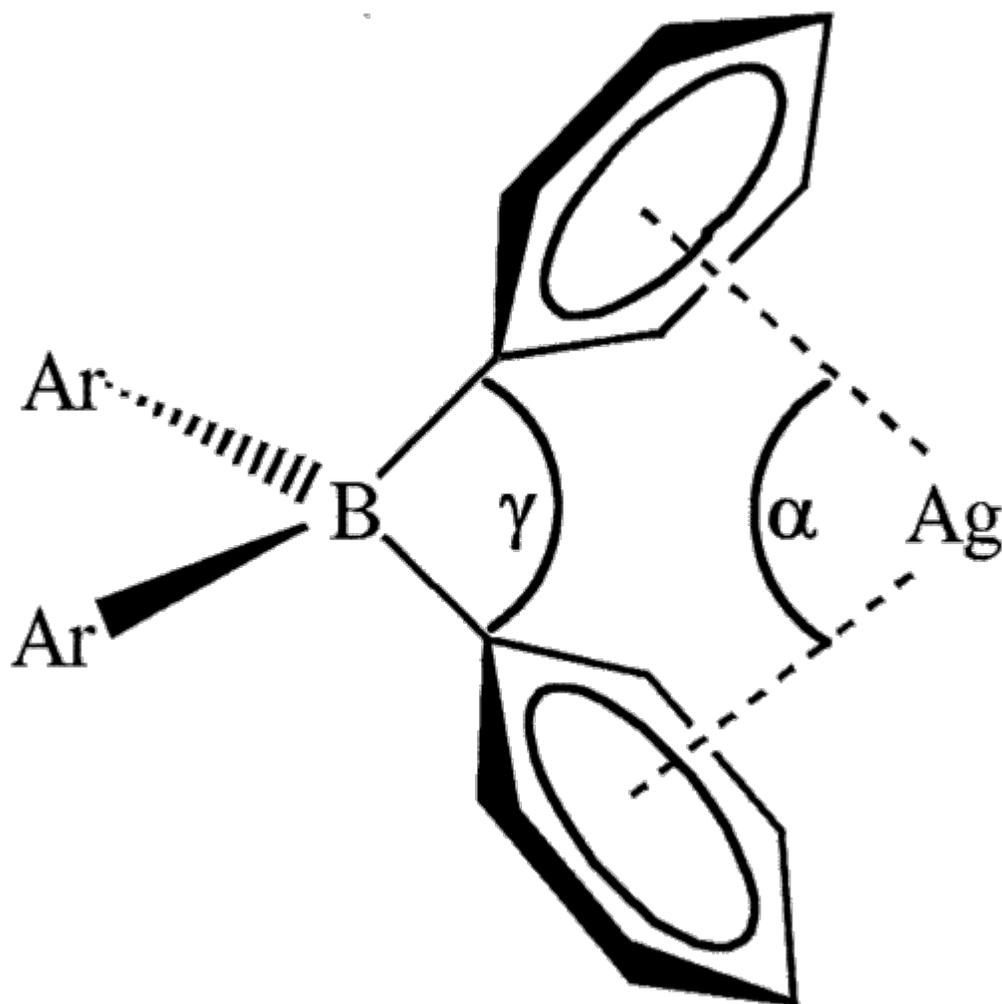
Acknowledgment

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[11]The relevant charge-transfer band overlays the local band of the aromatic donor and is unresolved.

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[13]Silver(I) nearly always coordinates to aromatic molecules in an unsymmetrical fashion.[2b] See also a trenchant analysis by Shelly et al.: Shelly, K.; Finster, D. C.; Scheidt, W. R.; Reed, C. A. *J*. *Am*. *Chem*. *Soc*.**1985**, *107*, 5955.

[14]For the relevant references, see Table 4.

[15]In the known structures,[14] silver(I) coordination varies continuously between the η^1 and η^2 modes, with a wide range of intermediate hapticities indicated as $\eta^{1.5}$ in Table 4.

[16]Ideal values are Δ = 1.40 Å if Ag is located directly over a ring carbon (η^1 coordination) or 1.20 Å if it sits astride the CC bond (η^2 coordination). In real structures, Ag is always slightly shifted (by 0.1–0.3 Å) outside the benzene rim.

[17]More precisely, α is the angle subtended by the normals to the mean planes of the two benzenoid rings.

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[29]The "cleft" angle γ of the stilbenoid ligand closely correlates with the "grab" angle α associated with the silver(I) coordination. Thus, if the benzene rings are turned orthogonal relative to the central double bond, γ = 180° − α. In the complexes investigated, γ ≅ 210° − α because of some twist of the benzene rings.

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