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Stereoselective Anion Template Effects: Syntheses and Molecular Structures of Tetraphenyl [12]Mercuracarborand-4 Complexes of Halide Ions

Zhiping Zheng, Carolyn B. Knobler, and M. Frederick Hawthorne*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024

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Abstract: The synthesis and characterization of the chloride and iodide ion complexes of a set of isomeric hydrophobic tetraphenyl [12]mercuracarborand-4 hosts having sterically encumbered cavities are described. These compounds $[(3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9Hg)_4]\cdot XLi$ (**3**$\cdot$XLi, X = Cl^- and I^-) were prepared by the reaction of the corresponding mercuric halides with *closo*-3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$. The presence of phenyl substituents in this system requires the existence of isomers in which the phenyl substituents are arrayed about the periphery of the host cavity. Three of four possible stereoisomers of the chloride ion complex were detected by HPLC analysis of the reaction mixtures, separated by recrystallization, identified as the desired species by the negative ion FAB mass spectrum, and structurally characterized by crystallography. X-ray diffraction data are as follows: **3a**$\cdot$ClLi (1,2-alternate structure with phenyl substituents in an "up", "up", "down", "down" fashion): monoclinic, space group *P2/a*, $a = 24.080(1)$ Å, $b = 13.4509(8)$ Å, and $c = 26.054(2)$ Å, $\beta = 99.488(2)°$, $V = 8323$ Å^3, $Z = 4$, $\varrho_{calcd} = 1.61$ g cm^{-3}, $R = 0.056$, $R_w = 0.067$. **3b**$\cdot$ClLi (1,3-alternate structure; phenyl substituents "up", "down", "up", "down"): triclinic, space group $P\bar{1}$, $a = 12.8692(9)$ Å, $b = 18.126(1)$ Å, and $c = 18.309(1)$ Å, $\alpha = 114.593(2)°$, $\beta = 100.016(2)°$, and $\gamma = 97.259(2)°$, $V = 3729$ Å^3, $Z = 2$, $R = 0.076$, $R_w = 0.097$. **3c**$\cdot$ClLi (partial cone structure; phenyl substituents "up", "up", "up", "down"): monoclinic, space group *Cm*, $a = 16.405(2)$ Å, $b = 18.928(3)$ Å, and $c = 10.409(1)$ Å, $\beta = 112.610(4)°$, $V = 2984$ Å^3, $Z = 2$, $\varrho_{calcd} = 1.91$ g cm^{-3}, $R = 0.032$, $R_w = 0.045$. This molecule has a mirror plane. In contrast to these results, only one of four possible stereoisomers of the iodide ion complex was detected by HPLC analysis of the reaction mixtures. This species, **3b**$\cdot$ILi, was found to be a 1,3-alternate structure by X-ray analysis (phenyl substituents "up", "down", "up", "down") and was further characterized by multinuclear NMR and negative ion FAB mass spectroscopy. Crystal data: tetragonal, space group $I4_1/amd$, $a = 17.520(2)$ Å, $c = 35.432(5)$ Å, $V = 10876$ Å^3, $Z = 4$, $\varrho_{calcd} = 1.23$ g cm^{-3}, $R = 0.069$, $R_w = 0.095$. Molecular modeling results preclude the formation of analogous 1,2-alternate or partial cone structures of the iodide ion complex. An acyclic host, **4**, having two Lewis-acidic mercury atoms and three carborane units was prepared by reacting 3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$ with $Hg(O_2CCH_3)_2$. This species forms a 1:1 complex with ethanol in the solid state. Crystal data for **4**$\cdot$(C_2H_5OH): monoclinic, space group $P2_1/c$, $a = 14.542(4)$ Å, $b = 17.861(5)$, $c = 20.701(6)$ Å, $\beta = 99.04(1)°$, $V = 5310$ Å^3, $Z = 4$, $\varrho_{calcd} = 1.21$ g cm^{-3}, $R = 0.072$, $R_w = 0.083$. The halide ion-specific kinetic template effects displayed by Cl^- and I^- ions during the stereoselective cyclization reaction are discussed.

Introduction

It has been known for decades that suitable metal ions can promote cyclization leading to the synthesis of macrocycles. In these syntheses, the cationic metal ion functions as a template for the construction of the macrocyclic host.[1] In the absence of an appropriate metal cation, the substrate may react in a variety of undesirable ways. Consequently, this so-called "template effect" has played an indispensable role in the development of host–guest chemistry by facilitating the synthesis of a variety of macrocyclic host molecules. Although the utilization of metal ions for this purpose is widespread, the phenomenon of an anion serving as a template is very rare.[2] The organization of oxovanadium–organophosphonate clusters around chloride anions has recently been reported[3] and the utilization of anions such as Cl^-, CO_3^{2-}, ClO_4^-, N_3^-, and NO_3^- for the construction of polyoxovanadate cages has also been described by Müller and co-workers.[4] In the absence of the anionic species encapsulated within the cage, the architecture of these systems would not develop in either case.[5] In neither complex could the anionic guests be removed from the vanadium oxide host–guest complex, and the anion is an integral part of the overall structure it assists in forming. An anion template effect has also been demonstrated in the synthesis of "expanded porphyrin" species in which increased yields of the macrocycle were achieved in the presence of added nitrate ion.[6]

Our interest in the host–guest chemistry of anion complexation[7] began with studies of a novel class of macrocyclic multidentate Lewis acid hosts[8] (**1** and **2**) (Figure 1) comprised of carborane-supported electrophilic mercury centers.[9] Initial studies were focused primarily upon the halide ion complexes

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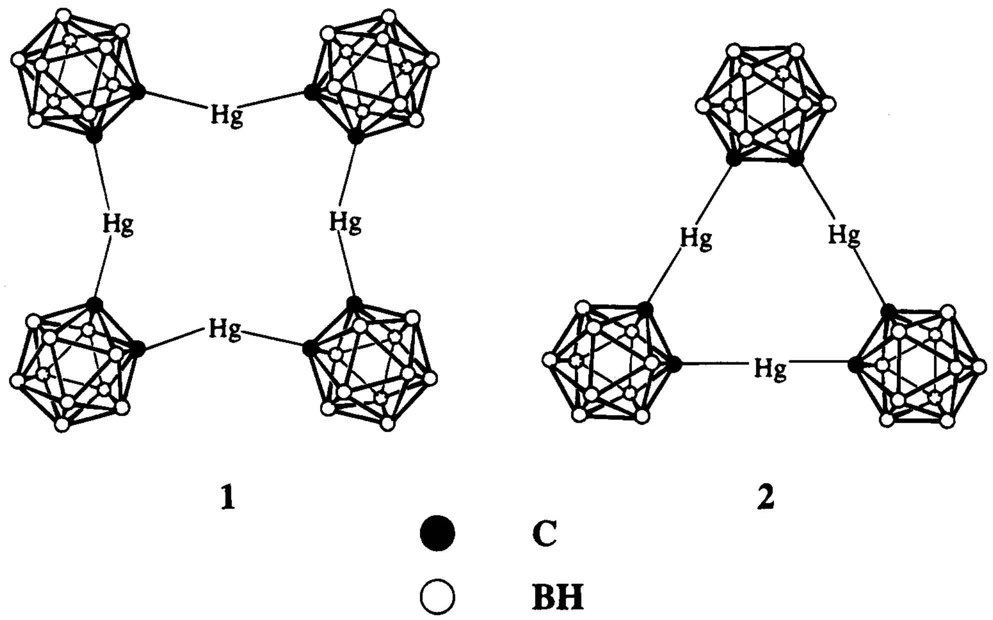

Figure 1. Representations of unsubstituted [12]mercuracarborand-4 (**1**) and [9]mercuracarborand-3 (**2**).

of the neutral tetrameric host molecule **1**, which were prepared through the reaction of *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{12}$[10] with the mercuric ion salts of the corresponding halide ion. The formation of such a tetrameric cyclic host encapsulating a halide ion is unexpected since the trimeric [9]mercuracarborand3 (**2**)[11] has less angle strain than **1** and, *a priori*, should be the preferred product. Addition of silver acetate to the halide complexes of the tetrameric mercuracarborand host removed the halide ion(s) and afforded the free host molecule **1**.[9a,c−e] The high-yield synthesis of the halide ion complexes of the stereochemically less favored tetrameric macrocycle led to the conclusion that the halide ion exercises a template effect in the construction of such mercuracarborand species.[9,11]

A key concept in host−guest chemistry is the structural match in size and shape of host and guest leading to the property of selectivity.[12] For spherical anions, the most important characteristic is the match between anion and macrocycle cavity diameters. Interestingly, the formation of a tetrameric mercuracarborand host seems to be a general result for Cl^-, Br^-, and I^- ions although these anions are markedly different in size and it is impossible to identify the specific roles of individual halide ions. One way to unambiguously demonstrate the utility of these anions as templates in the syntheses of mercuracarborand halide ion complexes is to devise a model system in which the interaction of the developing host and its template halide ion can be recognized by a dependence of product distribution (kinetic control) upon halide ion identity. This goal has been achieved, as described herein.

Throughout the development of mercuracarborand chemistry,[9] it has become obvious that the parent unsubstituted hosts are quite soluble in a variety of organic electron-donor solvents, but they lack solubility in hydrocarbons. Such solvent complexation mitigates the potential usefulness of mercuracarborands as Lewis acid catalysts.[13] Based upon these solubility characteristics as well as the mechanistic considerations presented above, a model mercuracarborand system has been designed and synthesized in which each of the component *o*-carborane cages is substituted with a phenyl group in the 3-position:[14] adjacent to both of the two neighboring carbon atoms and in the periphery of the host cavity. It was anticipated that this new system would exhibit two useful characteristics: (1) The tetraphenyl-substituted mercuracarborand isomers and their anion complexes would be soluble in a variety of noncoordinating solvents due to their increased lipophilicity. (2) The presence of the 3-phenyl-substituted carborane cages would allow the possible existence of four stereoisomers upon the formation of a tetrameric mercuracarborand, a situation very similar to that observed in calix[4]arene chemistry (Figure 2).[15] Consequently, the characteristic steric interactions between halide ion templates of different sizes and the peripheral phenyl substituents combined with intramolecular interactions between the phenyl groups could exert stereochemical control of the isomeric mercuracarborand product mixtures, thus demonstrating

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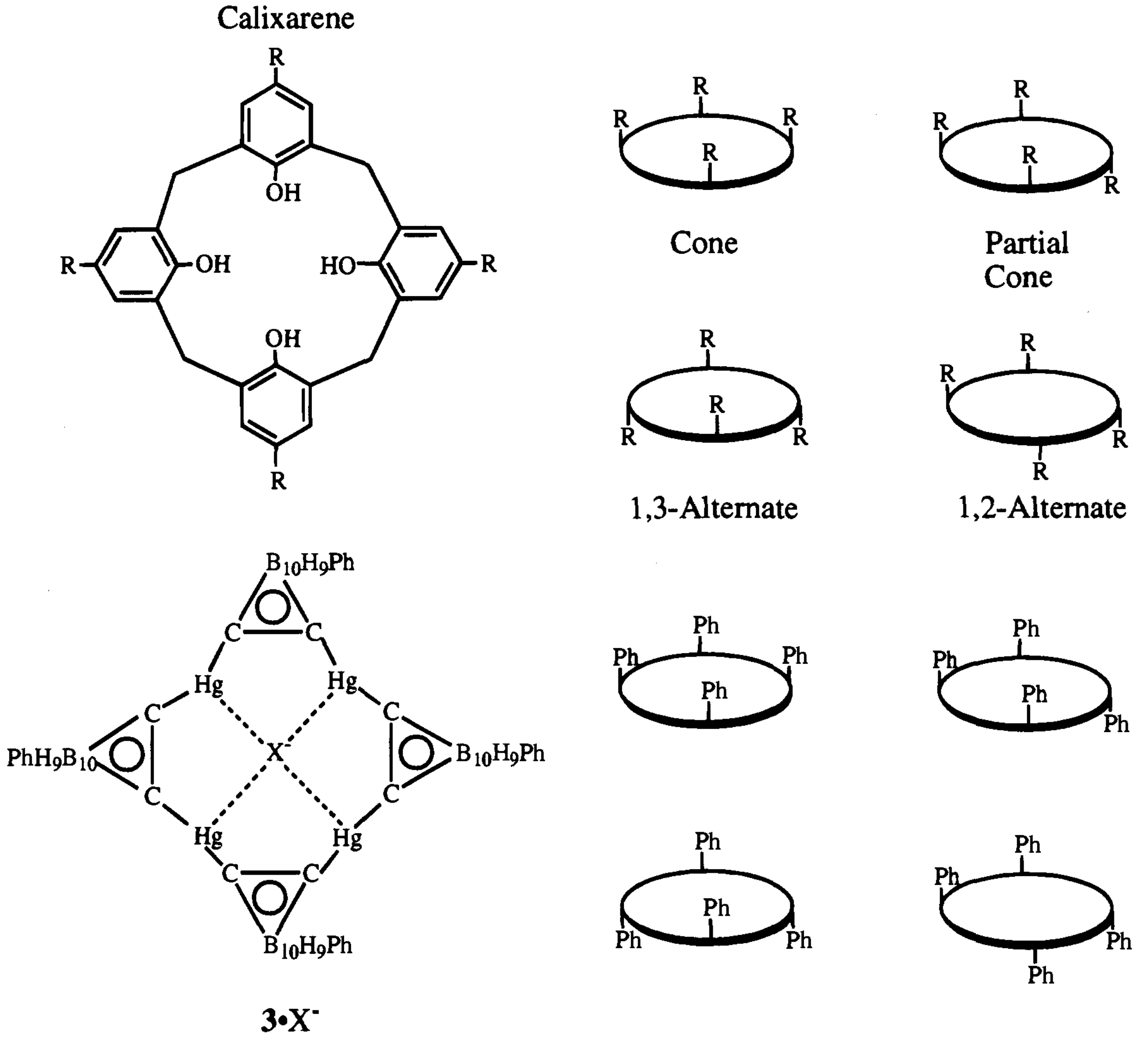

Figure 2. Schematic representations of the stereoisomers possible in the conceptually related halide ion complexes of tetraphenyl [12]-mercuracarborand-4 ($3 \cdot X^-$) and para-substituted calix[4]arene systems.

through differences in product isomer distributions the presence of halide ions in the competing product-determining transition states. In addition, the subtle isomeric structural variations observed here provide a more complete understanding of the interactions between these Lewis acid hosts and their anionic guests. A preliminary report of certain aspects of this work was previously published.[16]

Results and Discussion

Synthesis. (a) The Reaction of *closo*-3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$ with $HgCl_2$. Deprotonation of *closo*-3-Ph-1,2-$C_2B_{10}H_{11}$[14] is easily accomplished with *n*-butyllithium to give *closo*-3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$.[10] Reaction of the latter species with 1 mol equiv of mercuric chloride in diethyl ether at ambient temperature results in the formation of a mixture of lithium salts of the isomeric chloride complexes of cyclic tetramers as a colorless, air- and moisture-stable crystalline solid in 80% yield. The negative ion FAB mass spectrum of this product mixture is consistent with an anion having an *m/z* envelope centered at 1711, which corresponds to a tetrameric anionic complex of the chloride ion, $[(C_6H_5)C_2B_{10}H_9Hg]_4 \cdot Cl^-$ ($3 \cdot Cl^-$). In contrast with the corresponding unsubstituted species described previously,[9f] the product is very soluble in methylene dichloride and somewhat soluble in chloroform, benzene, and toluene. A recent report[9a] described the conversion of *closo*-9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$ to the corresponding hydrocarbon soluble halide ion complexes of *B*-octaethyl [12]mercuracarborand-4 species.

The ^1H, ^{13}C, and ^{199}Hg[17] NMR spectra of $3a \cdot Cl^-$ all indicated that the product was a mixture of isomers. Both the ^1H and ^{13}C NMR spectra exhibited complex multiplets characteristic of a phenyl group while the ^{199}Hg NMR spectrum of the same sample was also complex due to the presence of isomers. Further evidence for the presence of isomers was provided by HPLC analysis of the product mixture in which only three major peaks were detected. Recrystallization procedures successfully separated the three isomers, and the samples corresponding to the observed HPLC peaks all exhibited the same negative ion FAB mass spectrum with an *m/z* envelope centered at 1711. The molecular structures of these three stereoisomers were determined by single-crystal X-ray diffraction studies discussed below. In order to unambiguously assign the HPLC trace to the corresponding isomers, single crystals from X-ray diffraction studies of both the 1,2-alternate (**3a** $\cdot Cl^-$; phenyl groups up, up, down, down with respect to the cavity) and the 1,3-alternate (**3b** $\cdot Cl^-$; phenyl groups up, down, up, down) isomers were subject to HPLC analysis. Each species resolved into a single peak with the same retention time as the first (rt = 3.16 min) and second (rt = 3.48 min) peaks of the reaction mixture

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Table 1. Crystal Data and Data Collection Parameters

	3a · ClLi	**3b** · ClLi	**3c** · ClLi	**3b** · ILi	**4** · (C_2H_5OH)
formula	$C_{32}H_{56}B_{40}Hg_4ClLi$	$C_{32}H_{56}B_{40}Hg_4ClLi$	$C_{32}H_{56}B_{40}Hg_4ClLi$	$C_{32}H_{56}B_{40}Hg_4ILi$	$C_{26}H_{50}B_{30}Hg_2O$
mol wt	1717.2	1717.2	1717.2	1808.7	1103.5
crystal system	monoclinic	triclinic	monoclinic	tetragonal	monoclinic
crystal dimens, mm	0.20 × 0.15 × 0.25	0.20 × 0.25 × 0.20	0.14 × 0.11 × 0.54	0.12 × 0.15 × 0.15	0.15 × 0.15 × 0.18
space group	$P2/a$	$P\bar{1}$	Cm	$I4_1/amd$	$P2_1/c$
a, Å	24.080(1)	12.8692(9)	16.404(2)	17.520(2)	14.542(4)
b, Å	13.451(8)	18.126(1)	18.928(3)	35.432(5)	17.861(5)
c, Å	26.054(2)	18.309(1)	10.409(1)		20.701(6)
α, deg		114.593(2)			
β, deg	99.488(2)	100.016(2)	112.610(4)		99.04(1)
γ, deg		97.259(2)			
V, Å^3	8323	3729	2984	10876	5310
Z	4	2	2	4	4
density (calcd), gcm^{-3}	1.61	*a*	1.91	1.23	1.21
T, K	298	298	156	298	298
radiation, λ (Å)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)
μ, cm^{-1}	74.2	*a*	103.3	59.3	29.2
no. of unique reflcns	10898	12056	4479	4222	9887
no. of obsd reflcns ($I > 3\sigma(I)$)	3181	4855	3478	733	3219
no. of parameters refined	344	287 + 58 (two blocks)	167	58	233
2θ max (deg)	45	50	45	60	51
R	0.056	0.076	0.032	0.069	0.072
R_w	0.067	0.097	0.045	0.094	0.083
GOF	1.86	2.79	1.62	3.24	2.11

[a] Because of the uncertainty about the solvent content, these values cannot be determined. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

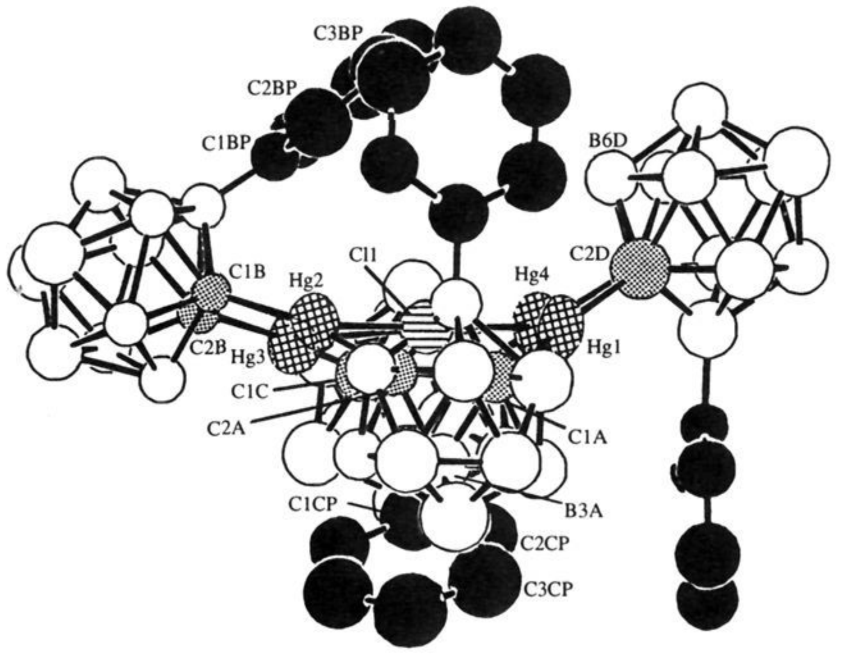

Figure 3. ORTEP plot of the 1,2-alternate $[(3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9\text{-}Hg)_4]\cdot Cl^-$ anion, **3a** · Cl^-, with the labeling scheme. Hydrogen atoms are omitted for clarity.

chromatogram. Consequently, the third peak observed with the reaction mixture must be attributed to the partial cone structure (**3c** · Cl^-; phenyl groups up, up, up, down).

(b) The Reaction of *Closo*-3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$ with HgI_2. The iodide ion complex of the same mercuracarborand has been prepared in 85% yield from *closo*-3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$ and HgI_2. The negative ion FAB mass spectrum of the resulting product mixture confirmed the presence of an anion with an *m*/*z* envelope centered at 1803 corresponding to $[(C_6H_5)C_2B_{10}H_9Hg]_4\cdot I^-$ (**3** · I^-). The complex **3** · I^- was purified by recrystallization from diethyl ether–pentane. The ^1H NMR spectrum contained clearly resolved multiplets expected for monosubstituted phenyl groups from 7.29 to 7.78 ppm. A singlet at 100.1 ppm was identified in the ^{13}C NMR spectrum as arising from the carborane carbon atoms. The ^{199}Hg NMR spectrum of the sample exhibited only one resonance at −910 ppm. All of these data revealed that this complex was highly symmetrical and contained single types of phenyl substituents, carborane carbon atoms, and mercury centers. Although four peaks have been identified from the HPLC trace, only one of them corresponded to the iodide complex **3** · I^- of the tetrameric cyclic host based upon their negative ion FAB mass spectra. The remaining three peaks were attributed to acyclic fragments, the chloride ion complex (**3** · Cl^-), and the iodide ion complex of a phenyl-substituted pentameric host, $[(C_6H_5)C_2B_{10}H_9Hg]_5\cdot I^-$, for which an *m*/*z* envelope centered at 2221 was found. However, the simplicity of the NMR spectra suggested that these undesired species were present in negligible amounts. The 1,3-alternate structure of this iodide ion complex (**3b** · I^-) was confirmed by X-ray diffraction studies.

Crystal and Molecular Structures. Molecular structure analyses for the halide ion complexes of the stereoisomeric tetraphenyl [12]mercuracarborand-4 hosts have been carried out along with that of an acyclic product, **4** · (C_2H_5OH), discussed below. A summary of these crystallographic data is presented in Table 1, and atomic coordinates and isotropic thermal parameters are provided in the supplementary material along with stereodrawings, complete atom number schemes, and full listings of bond distances and angles.

The structures of the chloride ion complexes of the three isomeric hosts, namely **3a** · Cl^-, **3b** · Cl^-, and **3c** · Cl^-, are shown in Figures 3, 4, and 5, respectively. They share a common feature: a chloride ion is located in the cavity formed by four divalent *closo*-3-Ph-1,2-$C_2B_{10}H_9$ cages linked by four Hg atoms. Although the four Hg atoms are essentially coplanar[18] and almost precisely equidistant from their nearest neighbors, the isomeric tetraphenyl hosts in these complexes are not planar metallacycles as in the case of **1** · Cl^-;[9f] rather, they are saddle-shaped regardless of the orientation of the phenyl substituents. This distortion from planarity is obviously due to the mutual steric interaction of the peripheral phenyl substituents (especially those opposed to one another), which must also be responsible for the absence of the highly-strained cone isomer (Figure 2). All structural parameters involving Cl^- ions and Hg atoms are very consistent among these three species. The average Hg–Cl^- distances span the range 2.75–2.90 Å. All of these values are noticeably shorter than those found in **1** · Cl^- (average Hg–

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[18] The Hg atoms are coplanar in both **3b** · I^- and **3c** · Cl^-, while those in **3a** · Cl^- and **3b** · Cl^- deviate from their least-squares plane by 0.069 and 0.003 Å, respectively.

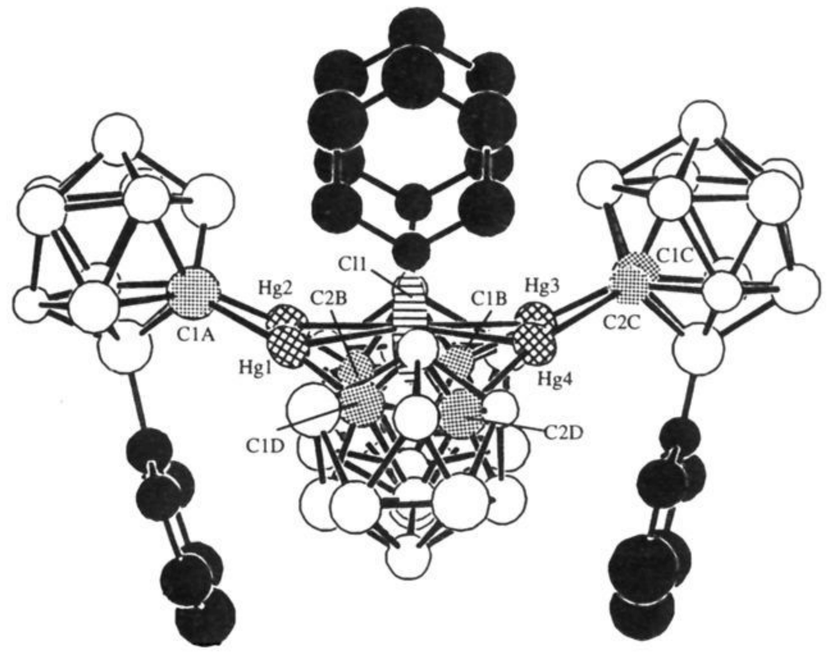

Figure 4. ORTEP plot of the 1,3-alternate $[(3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9\text{-}Hg)_4]\cdot Cl^-$ anion, **3b**$\cdot Cl^-$, with the labeling scheme. Hydrogen atoms are omitted for clarity.

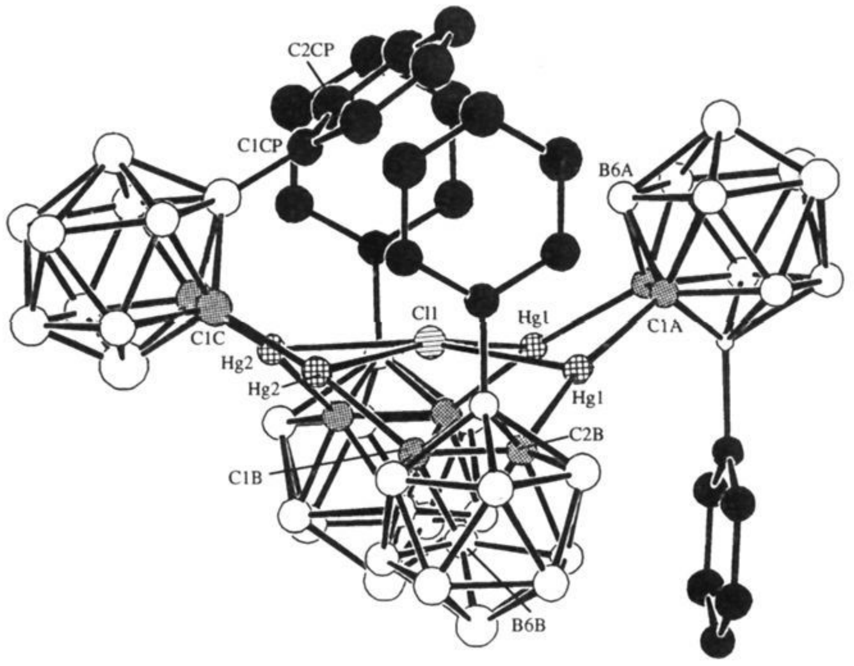

Figure 5. ORTEP plot of the partial cone $[(3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9\text{-}Hg)_4]\cdot Cl^-$ anion, **3c**$\cdot Cl^-$, with the labeling scheme. Hydrogen atoms are omitted for clarity.

Cl^- 2.94 Å) and are much smaller than the sum of the van der Waals radii of Hg (1.73 Å)[19] and Cl (1.80 Å)[20] atoms. The Hg−Hg distances fall into two sets, namely those involving adjacent Hg atoms, 3.93−4.06 Å, and those involving the diagonal Hg atoms, 5.58−5.74 Å. These values are also somewhat shorter than those in **1**$\cdot Cl^-$ (average 4.13 and 5.84 Å, respectively). The more condensed molecular structures of these isomers of **3**$\cdot Cl^-$, as compared with **1**$\cdot Cl^-$, are also shown by the distances of the more restricted chloride ion to the plane defined by the four Hg atoms. These values are 0.053, 0.12, and 0.255 Å for **3a**$\cdot Cl^-$, **3b**$\cdot Cl^-$, and **3c**$\cdot Cl^-$, respectively, and are much shorter than the corresponding distance in **1**$\cdot Cl^-$ (0.383 Å).[9f] Selected bond distances and angles for **3a**$\cdot Cl^-$, **3b**$\cdot Cl^-$, and **3c**$\cdot Cl^-$ are given in Table 2.

The molecular structure of **3b**$\cdot I^-$, illustrated in Figure 6, is composed of four divalent *closo*-3-Ph-1,2-$C_2B_{10}H_9$ cages linked by four Hg atoms in a cyclic tetramer and an iodide ion located in the center of the array 3.125(5) Å from each mercury. The four Hg atoms are coplanar and placed at the corners of a perfect square with a Hg−Hg distance of 4.052(2) Å. The iodide ion is displaced 1.25 Å above or below the plane of the four mercury atoms with half occupancy in each of these two positions, while its nearest equivalent is 1.962 Å in **1**$\cdot I_2^{2-}$. The Hg−I distance of 3.125(5) Å is significantly shorter than the van der Waals distance between Hg (1.73 Å) and I (2.15 Å).[20] This value is also smaller than corresponding Hg−I^- distances found in the diiodide complex of the unsubstituted [12]mercuracarborand-4, **1**$\cdot I_2^{2-}$ (3.28−3.77 Å).[9e] The compactness of the structure of **3b**$\cdot I^-$ is illustrated not only by this shorter Hg−I bond distance and the shorter distance of the iodide ion from the Hg_4 plane of the macrocycle but also by the absence of a diiodide complex corresponding to **1**$\cdot I_2^{2-}$ derived from **3b**. The formation of such a diiodide complex would conflict with the steric requirements of the bulky phenyl substituents which do not allow any significant displacement of the iodide ion of the monoiodide complex from its crystallographic 2-fold symmetry axis. Consequently, the system is not able to accommodate the steric congestion derived from two iodide ions and four phenyl groups and no species corresponding to the diiodide complex of **3b** is formed. Selected bond distances and angles for **3b**$\cdot I^-$ are presented in Table 2. Again, the core structure of **3b**$\cdot I^-$ is a saddle-shaped 12-membered ring whose distortion from planarity is attributable to the steric interaction between mutually opposed pairs of phenyl substituents (Figure 7).

In summary, the stereochemical arrangement of the phenyl substituents determines the accessibility of the mercury centers to the halide ion guests. Data for the structural comparisons between **3a**$\cdot Cl^-$, **3b**$\cdot Cl^-$, **3c**$\cdot Cl^-$, and **1**$\cdot Cl^-$ as well as that between **3b**$\cdot I^-$ and **1**$\cdot I_2^{2-}$ are presented in Table 3.

Anion Template Effects during the Synthesis of Halide Ion Complexes of Tetraphenyl [12]Mercuracarborand-4 Isomers. It was previously observed that the anions associated with the Hg^{2+} source profoundly affected the size of the resulting mercuracarborand product species.[9a] When mercuric acetate was used, anion-free [9]mercuracarborand-3 (**2**) was the exclusive product, whereas the corresponding halide ion complexes of [12]mercuracarborand-4 were the sole products when mercuric chloride, bromide, or iodide was employed as the mercury source. It was previously postulated that the efficient assembly of halide ion complexes of the tetrameric mercuracarborand hosts must be due to the operation of a kinetic template effect[22,23] with the halide ion serving as template since the formation of a virtually strainless, and presumably more stable, cyclic trimer is favored in the absence of this effect[11] when mercuric acetate is employed in the cyclization reaction. Presumably, acetate ion is not an efficient template due to its bulk and dispersed charge. Lending further support to this hypothesis is the fact that the use of mercuric thiocyanate as the mercury source provides the pentameric species $[(C_2B_{10}H_{10}Hg)_5\cdot(SCN)]\cdot Li$ and $\{(C_2B_{10}H_{10}Hg)_5\cdot[Hg(SCN)_3]\}\cdot Li$.[24] In this case, both the geometry and size of the linear thiocyanate ion might be responsible for the unique formation of a pentameric structure. Unfortunately, it is not yet known how the SCN^- and $Hg(SCN)_3^-$ ions interact with the mercury centers present in the pentameric host since the molecular structures of these complexes are presently unknown. However, without an appropriate template anion, neither the tetrameric nor the pentameric structures are developed, as demonstrated.

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[23] Template effects are classified as either thermodynamic or kinetic. See ref 22.

[24] Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. Work in progress.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **3a** · Cl^-, **3b** · Cl^-, **3c** · Cl^-, and **3b** · I^-

		3a · Cl^-			
Hg(1)−C(1A)	2.06(4)	Hg(1)−C(2D)	2.04(4)	Hg(2)−C(1B)	2.10(3)
Hg(2)−C(2A)	2.08(4)	Hg(3)−C(1C)	2.17(4)	Hg(3)−C(2B)	2.11(3)
Hg(4)−C(1D)	2.07(4)	Hg(4)−C(2C)	2.10(4)	Hg(1)−Cl(1)	2.852(11)
Hg(2)−Cl(1)	2.832(10)	Hg(3)−Cl(1)	2.896(11)	Hg(4)−Cl(1)	2.790(10)
C(1A)−C(2A)	1.68(5)	C(1B)−C(2B)	1.68(4)	C(1C)−C(2C)	1.60(6)
C(1D)−C(2D)	1.69(5)				
C(1A)−Hg(1)−C(2D)	168.8(16)	Hg(1)−C(1A)−C(2A)	126(2)	Hg(2)−C(2A)−C(1A)	123(2)
Hg(4)−C(1D)−C(2D)	121(2)	Hg(1)−C(2D)−C(1D)	125(2)		
		3b · Cl^-			
Hg(1)−C(1A)	2.02(4)	Hg(1)−C(1D)	1.98(4)	Hg(2)−C(2B)	2.04(3)
Hg(2)−C(2A)	2.14(3)	Hg(3)−C(1B)	2.22(4)	Hg(3)−C(1C)	2.18(5)
Hg(4)−C(2D)	2.23(5)	Hg(4)−C(2C)	2.02(3)	Hg(1)−Cl(1)	2.847(15)
Hg(2)−Cl(1)	2.78(2)	Hg(3)−Cl(1)	2.829(14)	Hg(4)−Cl(1)	2.85(2)
C(1A)−C(2A)	1.70(6)	C(1B)−C(2B)	1.65(4)	C(1C)−C(2C)	1.77(5)
C(1D)−C(2D)	1.66(5)				
C(1A)−Hg(1)−C(1D)	167(2)	C(2A)−Hg(2)−C(2B)	166.2(13)	C(1C)−Hg(3)−C(1B)	165(2)
C(2D)−Hg(4)−C(2C)	162(2)	Hg(1)−C(1A)−C(2A)	122(3)	Hg(1)−C(1D)−C(2D)	136(3)
Hg(2)−C(2A)−C(1A)	124(2)	Hg(2)−C(2B)−C(1B)	128(2)	Hg(3)−C(1B)−C(2B)	119(2)
Hg(3)−C(1C)−C(2C)	121(3)	Hg(4)−C(2C)−C(1C)	123(2)	Hg(4)−C(2D)−C(1D)	112(3)
		3c · Cl^-			
Hg(1)−C(1A)	2.162(11)	Hg(1)−C(2B)	2.034(11)	Hg(2)−C(1B)	2.175(11)
Hg(2)−C(1C)	1.977(14)	Hg(1)−Cl(1)	2.745(4)	Hg(2)−Cl(1)	2.859(4)
C(1A)−C(1A,2)	1.662(16)[a]	C(1B)−C(2B)	1.642(16)	C(1C)−C(1C,2)	1.72(2)
C(1A)−Hg(1)−C(2B)	166.6(4)	C(2B)−C(1A)−Hg(1)	162.4(4)	C(1B)−Hg(2)−C(1C)	171.1(5)
Hg(1)−C(1A)−C(1A)	121.3(7)	Hg(1)−C(2B)−C(1B)	123.5(7)	Hg(2)−C(1B)−C(2B)	123.7(2)
Hg(2)−C(1C)−C(1C)	124.0(9)				
		3b · I^-			
Hg(1)−C(1)	2.10(4)	Hg(1)−I(1)	3.125(5)	C(1)−C(1,2)	1.64(5)
C(1)−Hg(1)−C(1,2)	162(2)	Hg(1)−C(1)−C(1,2)	125(2)		

[a] Atoms labeled with ",2" are in the positions related by the symmetry of the molecules.

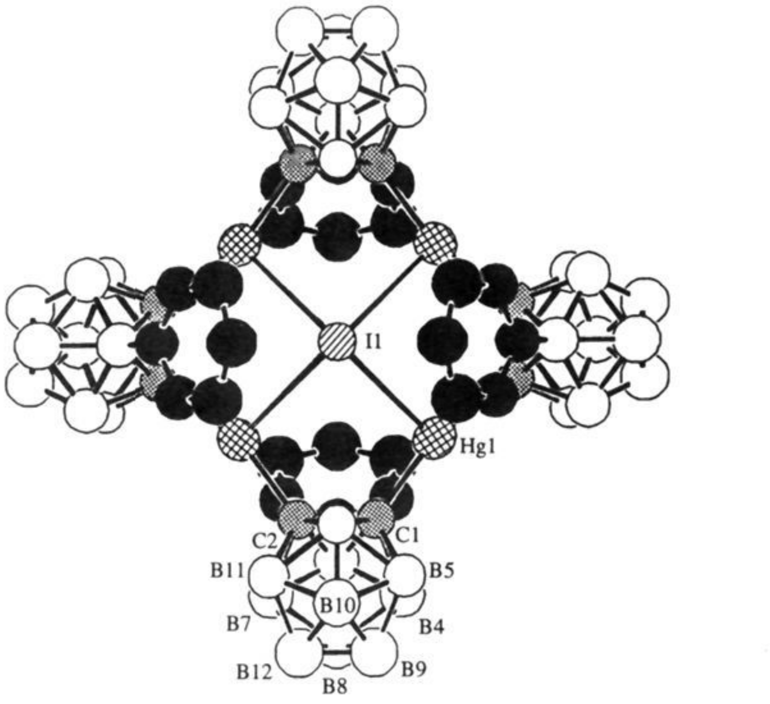

Figure 6. ORTEP plot of the 1,3-alternate $[(3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_9\text{-}Hg)_4]\cdot I^-$ anion, **3b** · I^-, with the labeling scheme. Hydrogen atoms are omitted for clarity.

The kinetic template effect, illustrated both previously[9a] and in this work, takes advantage of the molecular organization provided by the complexation of a halide ion with electrophilic mercury centers present in reaction intermediates. This chelation compensates for the energetically unfavorable features characteristic of these reactions such as the formation of nonlinear and strained C−Hg−C bonds, steric interactions between the complexed halide ions and the peripheral phenyl substituents, and the intramolecular repulsion among the phenyl groups.

Complementarity between the Halide Ions and the Encumbered Hosts Leading to the Formation of Stereoisomeric Complexes. To operate as a kinetic template, the halide ion must be a stabilizing component in product-determining transition states. Therefore, the tetrameric cycle is not formed as a free host appropriate for the later complexation of the halide ion, but the formation of the halide ion complex can be best described as halide ion-induced organization of the reactants as they proceed to products. It is suggested that a template effect of this origin involves the operation of topological (or linking) and metric (or relative size) factors between the interacting species.[22a] Thus, the relative orientations of the phenyl substituents of the component carborane cages will be characteristic of the individual halide ion templates. As a result, one or more isomeric complexes would be produced with stereoisomeric configurations that are complementary to the templating halide ion. This has been clearly shown by the fact that the reaction of the *closo*-3-Ph-1,2-Li_2-$C_2B_{10}H_9$ reagent with $HgCl_2$ produced three stereoisomers while only the 1,3-alternate isomer was formed with HgI_2. The much smaller chloride ion (ionic radius 1.80 Å for Cl^- *vs* 2.15 Å for I^-) appears to provide

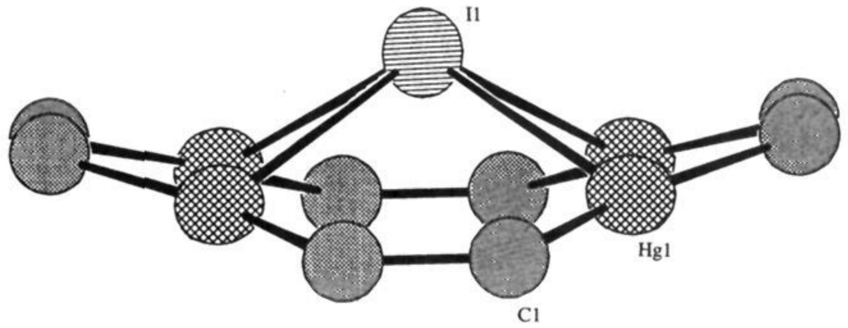

Figure 7. Side view of **3b** · I^- showing only the 12-membered ring and the complexed iodide ion (one of the two possible locations) for clarity.

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(25) The mercury atom tends to form two essentially colinear primary bonds in the structure of a typical Hg(II) complex and the molecule retains appreciable Lewis acidity in the plane perpendicular to these primary bonds, allowing secondary bonding interactions through the use of empty p orbitals. See ref 8a and the references therein.

Table 3. Structural Comparison of **1**·ClLi, **1**·$I_2(AsPh_4)_2$, **3a**·ClLi, **3b**·ClLi, **3c**·ClLi, and **3b**·ILi Using Averaged Distances and Angles

compd	Hg−X (Å)	Hg- -Hg[a] (Å)	C−Hg−C (deg)	Hg−C−C (deg)	X- -P[b] (Å)	ref
1·ClLi	2.944(2)	4.129(1)	162.0(4)	126.0(6)	0.383	9a
3a·ClLi	2.843(11)	4.021(2)	168.8(16)	123.8(2)	0.053	this work
3b·ClLi	2.827(8)	3.990(2)	165.1(5)	123.1(3)	0.12	this work
3c·ClLi	2.802(4)	3.929(1)	165.6(4)	123.1(8)	0.255	this work
1·$I_2(AsPh_4)_2$	3.415(1)	3.942(1)	155.3(4)	123.1(6)	1.962	9a
3b·ILi	3.125(5)	4.052(3)	162(2)	125(2)	1.25	this work

[a] Adjacent Hg- -Hg distance. [b] Distance of X^- from the mean plane formed by the four Hg atoms.

Table 4. Selected Interatomic Distances (Å) in Molecular Modelings of **3a**·ILi and **3c**·ILi

	3a·ILi		
I[a]- -C(1CP)	2.70	I- -C(2CP)	2.53
I- -C(3CP)	2.62	I- -B(3A)	3.10
I′[a]- -C(1BP)	2.68	I′- -C(2BP)	2.56
I′- -C(3BP)	2.69	I′- -B(6D)	3.18
	3c·ILi		
I- -C(1CP)	2.58	I- -C(2CP)	2.81
I- -B(6A)	3.17		
I′- -B(6B)	2.91	I′- -H(6B)	2.06
	Sum of van der Waals Radii (Å)[b]		
I- -C	3.87	I- -H	3.35
I- -B	4.28		

[a] I and I′ represent the iodide ions above and below the plane (Figure 3 and Figure 5) formed by the four Hg atoms, respectively. In both simulative structures, the I−Hg distance assumes a value of 2.937 Å as found in the structure of **3b**·ILi. [b] The van der Waals radii of C (1.72 Å), H (1.20 Å), and I (2.15 Å) are taken from ref 20, and that of B (2.13 Å) from ref 21.

less steric bias in the orientation of the phenyl substituents. Scrutiny of the structures of all halide ion complexes revealed that although the chloride ion is always bound to the four mercury centers in a surprising almost square-planar manner, the iodide ion is too large to occupy the center of the mercuracycle and is displaced above or below the Hg_4 macrocycle plane. The product-determining transition state for the formation of the only observed iodide isomer, **3b**·I^-, the 1,3-alternate structure, presumably minimizes the steric congestion between the iodide and the phenyl substituents to an extent not possible in the transition states leading to the other possible stereoisomers.

Molecular Modeling of the Iodide Ion Complexes of the 1,2-Alternate and the Partial Cone Host Isomers. In order to lend further credence to the concept that kinetic stereoisomer control is due to template ion size differences, a molecular modeling experiment was carried out to evaluate the severity of steric congestion between iodide ion and the phenyl substituents in both the 1,2-alternate and the partial cone structures (Figure 2). In the experiment, the framework of these two isomers was kept intact while an imaginary iodide ion was put into a position either above or below the plane defined by the four Hg atoms. It was assumed that the Hg−I^- distance was 2.937 Å, the same as that found in **3b**·I^-. In the modeling of the iodide ion complex of the 1,2-alternate host, **3a**·I^-, the interatomic distances between the iodide ion and several phenyl carbons (C(1CP), C(2CP), C(3CP), C(1BP), C(2BP), and C(3BP)) and boron (B3A) and B(6D)) are much shorter than the sum of the van der Waals radii of the corresponding atoms and the structure is impossibly compressed. Similarly, very close contacts of the iodide ion and C(1CP), C(2CP), B(6A), B(6B), and H(6B) were found in the modeling of **3c**·I^-. Consequently, the existence of a 1,2-alternate or a partial cone structure for the iodide ion complex would require a prohibitive deformation or rearrangement of the macrocycle. A summary of the calculated distances between the iodide ion and relevant atoms is presented in Table 4.

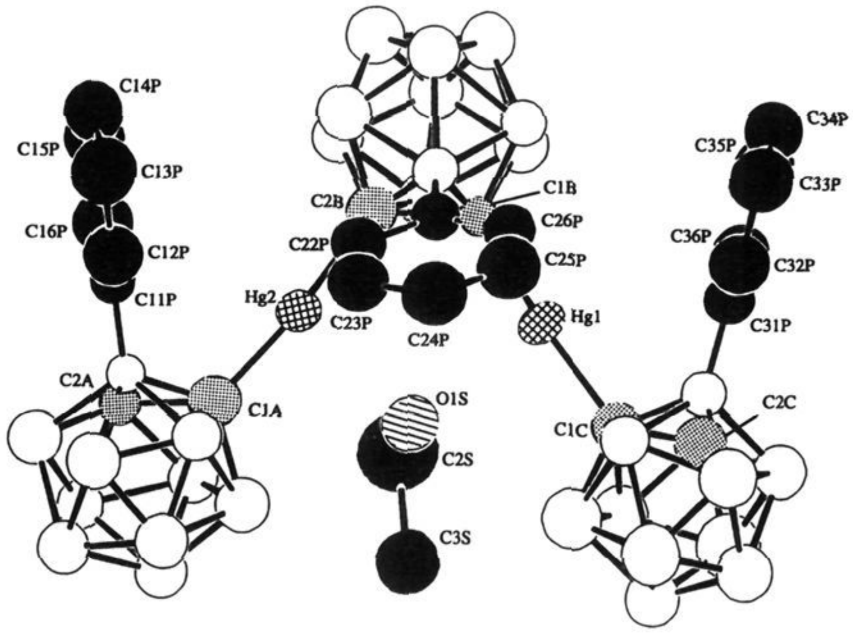

Figure 8. ORTEP plot of **4**·(C_2H_5OH), with the labeling scheme. Hydrogen atoms are omitted for clarity.

Supporting Evidence for Template Effects. Isolation of an acyclic mercury-containing intermediate in the cyclization reaction which itself functions as a host with the ability to coordinate anions or nucleophilic guests would provide strong evidence of the self-assembling nature of the overall cyclization reaction. Using a modular approach, such an acyclic host, **4**, has been prepared and structurally characterized. The reaction of the sterically encumbered *closo*-3-Ph-1,2-Li_2-$C_2B_{10}H_9$ reagent with $Hg(O_2CCH_3)_2$ produced the complex **4**·(C_2H_5OH), with two Lewis-acidic mercury atoms and three carborane units (phenyl substituted at the 3-position). This molecule coordinates a molecule of ethanol in the solid state and clearly resembles an intermediate expected in the self-assembly of the cyclic host around an anionic template. A view of the structure is presented in Figure 8. There are several noteworthy features in this structure: First, the distances between the oxygen atom of the ethanol molecule and the mercury atoms are 2.89 Å for O1S−Hg1 and 2.85 Å for O1S−Hg2. These values resemble those found in related complexes[8k,26] and are appreciably shorter than the sum of the van der Waals radii of Hg (1.73 Å) and O (1.40 Å)[20] atoms, indicating a fairly strong interaction. Secondly, the phenyl substituents are oriented in a “down”, “up”, “down” manner, which presumably minimizes steric congestion and supports the assumption that the steric interactions among the phenyl substituents themselves are quite important. The considerable strain energy resulting from steric interactions between these substituents impedes the formation of a phenyl-substituted [9]mercuracarborand-3. Carbon atoms C2A and C2C are located in such a way that their separation is maximized. Thirdly, the phenyl ring (C11P−C16P) on the left and the central phenyl group (C21P−C26P) exhibit a dihedral angle of 72.0° and have a center-to-center distance of 5.62 Å, while the phenyl group on the right (C31P−C36P) and the central aromatic ring are fixed in planes inclined 89.3° to each other, with a centroid−centroid separation of 5.54 Å (see Figure

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(26) Zheng, Z.; Knobler, C. B.; Curtis, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 432.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $\mathbf{4}\cdot(C_2H_5OH)$

	Interatomic Distances (Å)		
Hg(1)−C(1B)	2.05(2)	Hg(2)−C(2B)	2.02(3)
Hg(1)−C(1C)	2.12(3)	Hg(2)−C(1A)	2.02(3)
Hg(1)−O(1S)	2.89(2)	Hg(2)−O(1S)	2.85(2)
Hg(1)−Hg(2)	3.901(2)		
	Angles (deg)		
Hg(1)−C(1B)−C(2B)	124(2)	Hg(2)−C(1A)−C(2A)	120(2)
Hg(1)−C(1C)−C(2C)	118(2)	Hg(2)−C(2B)−C(1B)	121(2)
C(1A)−Hg(2)−C(2B)	171.9(13)	C(1B)−Hg(1)−C(1C)	172.2(2)
O(1S)−Hg(1)−C(1B)	91.8(9)	O(1S)−Hg(2)−C(1A)	93.3(10)
O(1S)−Hg(1)−C(1C)	95.3(9)	O(1S)−Hg(2)−C(2B)	94.8(10)

8). These crystallographic data suggest the presence of a pair of intramolecular edge-to-face aromatic−aromatic interactions[27] which help to stabilize such a structure in the solid state. Indeed, these values are within the range found for similar interactions[28] and the values (*vide supra*) are close to the 5.44 Å, 88° values for the interacting aromatic residues on peptide chains of the calcium-binding protein car parvalbumin.[29] Selected bond distances and angles for $\mathbf{4}\cdot(C_2H_5OH)$ are presented in Table 5.

Concluding Remarks. Several aspects of the present work are worthy of emphasis.

1. The reactions of *closo*-3-Ph-1,2-Li_2-1,2-$C_2B_{10}H_9$ with $HgCl_2$ and HgI_2 resulted in the formation of the corresponding stereoisomeric halide ion complexes of the expected tetraphenyl-substituted mercuracarborand host system. These complexes have enhanced solubility in hydrocarbons due to the presence of phenyl substituents as compared with their unsubstituted analogues.

2. The halide ion complexes derived from the stereoisomeric 3-phenyl [12]mercuracarborand-4 host species were isolated. Three isomers of the chloride ion complex were identified and structurally characterized, while only a single isomer was recognized when mercuric iodide was used as the mercury source. This clearly demonstrates that the distribution of product isomers is controlled by the identity of the halide ion and that the halide ion is present in the product-determining transition states. When mercuric acetate was employed in the cyclization reaction, an acyclic oligomer comprised of three 3-phenyl-substituted carborane cages connected by two Hg atoms was obtained. The absence of a cyclic trimer[9a] among the products of the mercuric acetate reaction, together with the unique halide ion-dependent distribution of stereoisomers formed in the present host system, suggests that interactions between the phenyl substituents and the complexed halide ion establish the stereochemistry of the final products, as does the mutual intramolecular steric repulsion among the phenyl groups if no effective anion template is available. These results also demonstrate that it is possible to modify the stereochemical properties of the electrophilic binding site of the host by the judicious choice of carborane substituents.

We believe this to be the first report of *anion-dependent control of stereochemistry developed during a template-mediated cyclization reaction.*

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Diethyl ether was distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Deuteriated solvents were obtained from Cambridge Isotope Laboratories. Mercuric acetate (Mallinckrodt), mercuric chloride (Mallinckrodt), mercuric iodide (Cerac), and *n*-butyllithium (2.5 M solution in hexanes) (Aldrich) were used as received. *closo*-3-Ph-1,2-$C_2B_{10}H_{11}$ was prepared according to the previously described procedure.[14]

Physical Measurements. Infrared spectra (Nujol) were recorded with a Beckman FT-1100 spectrometer. All NMR spectra were recorded at room temperature. The ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM 360 spectrometer and the $^{11}B\{^1H\}$ and $^{199}Hg\{^1H\}$ NMR spectra were obtained on an ARX 500 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to residual ^1H and ^{13}C present in deuteriated solvents. Chemical shift values for $^{11}B\{^1H\}$ spectra were referenced relative to external $BF_3\cdot Et_2O$ (0.0 ppm with negative value upfield). The $^{199}Hg\{^1H\}$ NMR spectra were measured in 10 mm sample tubes at 89.4 MHz by using broad band decoupling. External 1.0 M PhHgCl/DMSO-d_6 solution was used as the reference at −1187 ppm relative to neat Me_2Hg. All FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer. Separation of both the reaction mixtures was performed at 25 °C on a Beckman HPLC Model 110 A connected to a Hitachi Model 100-40 variable-wavelength absorbance detector. A Raman Microsorb-MV reversed-phase C_{18} column was employed for $\mathbf{3a}\cdot Cl^-$, $\mathbf{3b}\cdot Cl^-$, and $\mathbf{3c}\cdot Cl^-$ and a reversed-phase phenyl column for $\mathbf{3b}\cdot I^-$.

Synthesis. $\mathbf{3}\cdot Cl^-$. To an ethereal solution (20 mL) of *closo*-3-Ph-1,2-$C_2B_{10}H_{11}$ (2.3 mmol, 0.50 g) at 0 °C was added *n*-butyllithium (4.6 mmol, 1.8 mL, 2.5 M solution in hexanes), and the slurry was stirred at room temperature under argon. After 4 h, the mixture was cooled to 0 °C and treated with solid $HgCl_2$ (2.3 mmol, 0.62 g). The stirring was continued overnight as the mixture warmed up to room temperature. The reaction was then quenched with 20 mL of H_2O and the organic phase was separated. The water layer was extracted with diethyl ether (3 × 5 mL). The combined organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was triturated with pentane to give white crystalline solids of the corresponding chloride ion complexes in 80% yield. ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 1.0−3.6 (carborane B-H), 7.3−7.9 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (90 MHz, $(CD_3)_2CO$) δ 98.3, 99.0 (carborane), 128.6−133.6 (m, C_6H_5); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$) δ 0.7, −4.4, −8.4; $^{199}Hg\{^1H\}$ NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C) δ −991, −1002, −1010, −1039; IR (Nujol) v [cm^{-1}] 2563, 725, 700; negative ion FAB *m/z* 1711 (100%).

$\mathbf{3}\cdot I^-$. To an ethereal solution (20 mL) of *closo*-3-Ph-1,2-$C_2B_{10}H_{11}$ (2.3 mmol, 0.50 g) at 0 °C was added *n*-butyllithium (4.6 mmol, 1.8 mL, 2.5 M solution in hexanes), and the slurry was stirred at room temperature under argon. After 4 h, the mixture was brought back to 0 °C and treated with solid HgI_2 (2.3 mmol, 1.05 g). The stirring was continued overnight as the mixture warmed up to room temperature. The reaction was then quenched with 20 mL of H_2O and the organic phase was separated. The water layer was extracted with diethyl ether (3 × 5 mL). The combined organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was triturated with pentane to give white crystalline solids of the corresponding iodide ion complexes in 85% yield. ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 1.0−3.6 (carborane), 7.3−7.8 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (90 MHz, $(CD_3)_2CO$) δ 100.1 (carborane), 128.7−133.5 (m, C_6H_5); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$) δ 1.0, −3.5, −8.1; $^{199}Hg\{^1H\}$ NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C) δ −911; IR (Nujol) v [cm^{-1}] 2562, 725, 700; negative ion FAB *m/z* 1805 (100%), 2221 (pentamer$\cdot I^-$, 40%).

4. To an ethereal solution (20 mL) of *closo*-3-Ph-1,2-$C_2B_{10}H_{11}$ (2.3 mmol, 0.50 g) at 0 °C was added *n*-butyllithium (4.6 mmol, 1.8 mL, 2.5 M solution in hexanes), and the slurry was stirred at room temperature under argon. After 4 h, the mixture was brought back to 0 °C and treated with solid $Hg(O_2CCH_3)_2$ (2.3 mmol, 0.73 g). The stirring was continued overnight as the mixture warmed up to room temperature. The reaction was then quenched with 20 mL of H_2O and the organic phase was separated. The water layer was extracted with diethyl ether (3 × 5 mL). The combined organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was removed under

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vacuum. The residue was triturated with pentane to give white crystalline solids of the acyclic species **4** in 35% yield. ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 1.3–3.0 (carborane), 7.3–7.9 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (90 MHz, $(CD_3)_2CO$) δ 63.0, 93.0, 98.4, 129.8, 130.5, 133.3, 133.7; $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$) δ 1.5, −2.2, −4.5, −6.7, −8.9, −10.1; $^{199}Hg\{^1H\}$ NMR (89.4 MHz, $(CD_3)_2CO$) δ −1303; IR (Nujol) ν [cm^{-1}] 2562, 725, 700; HREIMS calcd for $C_{24}B_{30}H_{44}Hg_2$ 1058.5842, found 1058.5847.

HPLC Analysis. 3·Cl⁻. The HPLC analysis of the reaction mixture was performed at 25 °C using a C_{18} column (reversed-phase packing) with mixed acetonitrile and 0.1% trifluoroacetic acid (90:10, v/v) as eluent. A sample of **3**·ClLi was subject to HPLC analysis. Three HPLC peaks have been identified with the same negative ion FAB mass spectrum with *m/z* 1711 (100%). This value corresponds to the chloride ion complex of the tetraphenyl [12]mercuracarborand-4 host. In order to unambiguously assign these peaks to the corresponding isomers, single crystals of **3a**·ClLi (1,2-alternate) and **3b**·ClLi (1,3 alternate) dissolved in eluting solvent were injected into the HPLC column. Each species resolved into a single peak with the same retention time as the first (**3a**·ClLi, rt = 3.16 min) and second (**3b**·ClLi, rt = 3.48 min) peaks of the reaction mixture trace. Consequently, the third peak observed with the reaction mixture must be attributed to the isomer **3c**·ClLi (partial cone).

3·I⁻. The HPLC analysis of the reaction mixture was performed at 25 °C using a phenyl column (reversed-phase packing) with MeOH–H_2O (85:15) as eluent. Four peaks were identified and only one (rt = 5.94 min) corresponds to **3b**·I⁻ (negative ion FAB *m/z* 1803, 100%). The other three are due to an acyclic fragment, **3**·ClLi (*m/z* 1711, 100%), and the iodide ion complex of pentaphenyl [15]mercuracarborand-5 host (*m/z* 2221, 100%).

Solution and Refinement of Crystal Structures. All data were collected on automated diffractometers in the $\theta-2\theta$ mode with Mo Kα radiation. Data for **3a**·Cl⁻, **3b**·Cl⁻, and **3b**·I⁻ were collected on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Data for **3c**·Cl⁻ were collected on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Data for **4**·(C_2H_5OH) were collected on a Crystal Logic diffractometer. All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory using the UCLA crystallographic programs. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; SHELX76 (Sheldrick), crystal structure package; and SHELX86 (Sheldrick), crystal structure solution package; and ORTEP (Johnson). Reported R and R_w values are defined as $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. Scattering factors were obtained from Stewart *et al.*[30] for hydrogen and from the International Tables for X-ray Crystallography[31] for other atoms. Details for individual data collections are given in Table 1. The observed and calculated structure factors are provided in the supplementary material along with atomic coordinates, isotropic thermal parameters, and full listings of bond distances and angles.

Data were collected in the $\theta-2\theta$ scan mode and corrected for Lorentz and polarization effects and for absorption and extinction. Atoms were located by use of heavy atom methods. Only Hg atoms for **3a**·Cl⁻, **3c**·Cl⁻, and **4**·(C_2H_5OH), Hg and Cl atoms for **3b**·Cl⁻, and Hg and I atoms for **3b**·I⁻ were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. All phenyl H were included in calculated positions as members of C_6H_5 rigid groups: C–C = 1.395 Å, C–H = 1.0 Å, angles = 120°. Most positions of H on the carborane ligand were located but were not refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atoms. Anomalous dispersion terms were included for the scattering of Hg and Cl in **3a**·Cl⁻, **3b**·Cl⁻, and **3c**·Cl⁻, Hg and I in **3b**·I⁻, and Hg only in **4**·(C_2H_5OH).

3a·Cl⁻ (1,2-alternate): colorless crystal, diethyl ether–pentane. The crystal contains four molecules of ether and one molecule of water per tetramer. No hydrogen positions were located for any of these molecules and some of the ether molecules were disordered.

3b·Cl⁻ (1,3-alternate): colorless crystal, methylene chloride–benzene. The crystal contains two molecules of water, two molecules of benzene or toluene, and one molecule of ether or pentane per tetramer. No hydrogen positions were located for the solvent molecules. Li was not located, but it is possibly disordered or could have been misidentified as oxygen of a water molecule.

3c·Cl⁻ (partial cone): colorless crystal, CH_2ClCH_2Cl–cyclohexane–1,2-dichlorobenzene.

3b·I⁻: colorless crystal, diethyl ether–pentane. The crystal contains three molecules of water per tetramer. No hydrogen positions were located for the water molecules. Li was not located, but it was possibly disordered.

4·(C_2H_5OH): colorless crystal, acetone–pentane–ethanol. The crystal contains four molecules of water per molecule of Hg complex. No hydrogen positions were located for the water molecules.

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Supplementary Material Available: Tables of position and thermal parameters, bond lengths and angles, and crystallographic data and an ORTEP view of **3a**·Cl⁻, **3b**·Cl⁻, **3c**·Cl⁻, **3b**·I⁻, and **4**·(C_2H_5OH) (46 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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