

# ACCOUNTS of CHEMICAL RESEARCH<sup>®</sup>

JULY 1997

Registered in U.S. Patent and Trademark Office; Copyright 1997 by the American Chemical Society

## Recognition of Electron-Donating Guests by Carborane-Supported Multidentate Macrocyclic Lewis Acid Hosts: Mercuracarborand Chemistry

M. FREDERICK HAWTHORNE\* AND ZHIPING ZHENG

*Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095*

Received September 4, 1996

### Background

Since the synthesis of crown ethers and the discovery of their complexing properties toward alkali metal cations in 1967,<sup>1</sup> host-guest chemistry has developed rapidly and now includes ancillary fields of study such as supramolecular chemistry, biomimetic chemistry, and materials science.<sup>2</sup> In contrast to the extraordinary achievements of cation complexation in host-guest chemistry, anion

complexation by artificial receptors remained largely undeveloped, although anion-inclusion complexes were observed as early as 1968.<sup>3</sup> This hiatus is largely due to the peculiarities (as compared with cations) associated with most anions, namely, their larger sizes, various geometries, larger free energies of solvation, and the limited pH range in which they exist, resulting in great difficulty in designing hosts for selective anion complexation.

With the importance of anion complexation and related chemistry being recognized, an upsurge of interest in this discipline has recently become apparent.<sup>4</sup> A variety of receptor molecules have been devised, and various anion-binding strategies have been exploited which yield a plethora of novel structures of possible biological and chemical significance.<sup>2</sup> Along this line, our laboratory,<sup>5</sup> as well as others,<sup>6</sup> has been engaged for a number of years in the design and synthesis of novel host molecules for anion complexation. Highlights of our studies in the field of anion complexation by multidentate macrocyclic Lewis acid hosts such as **1** and **2** (Figure 1) will be presented in this Account, with particular emphasis given to the design of the hosts and the selection of anions required to produce defined complexes having predetermined solubilities. These macrocycles are comprised of three or more mercury atoms interlinked by the same number of icosahedral *o*-carborane cages and are referred to as "mercuracarborands".

Before embarking on this tour, it is worthwhile to mention the stereoelectronic properties of icosahedral carborane isomers<sup>7</sup> as well as the Lewis acidity of the mercury(II) binding sites.<sup>5,6</sup> Each of the three isomeric

M. Frederick Hawthorne is a native of Kansas. He obtained his B.A. degree from Pomona College in 1949 and his Ph.D. in organic chemistry with D. J. Cram at UCLA in 1953. After postdoctoral work with George S. Hammond and several years in industry with Rohm and Haas he became Professor of Chemistry at the University of California, Riverside, in 1962, and he later returned to UCLA in that same capacity in 1969. He has been Editor-in-Chief of *Inorganic Chemistry* since 1969. He is the recipient of many honors including election to the National Academy of Sciences, to the American Academy of Arts and Sciences, and as a Corresponding Member of the Goettingen Academy of Sciences. Most recently (1997) he was the recipient of the National Academy of Sciences Award in Chemical Sciences. His research interests lie at the interfaces of inorganic, organic, and biochemistry and most often involve the elaboration of polyhedral borane and carborane chemistry as a central theme.

Zhiping Zheng was born in Fujian, China, in 1967 and obtained his B.S. and M.S. degrees from Peking University. He continued his graduate training in the United States, first at Tulane University and then under the guidance of Professor Hawthorne at UCLA where the work described in this Account was carried out. After receiving his Ph.D. in 1995, he became a postdoctoral fellow with Professor Richard H. Holm at Harvard University. He is just beginning an independent academic career at the University of Arizona.

- (1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
- (2) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995; pp 1–9.
- (3) Park, C. H.; Simmons, H. E. *J. Am. Chem. Soc.* **1968**, *90*, 2431–2432.
- (4) For recent reviews on anion complexation chemistry, see: (a) Kaufmann, D. E.; Otten, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1832–1834. (b) Dietrich, B. *Pure Appl. Chem.* **1993**, *65*, 1457–1464.
- (5) (a) Hawthorne, M. F.; Yang, X.; Zheng, Z. *Pure Appl. Chem.* **1994**, *66*, 245–254. (b) Yang, X.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142–7159.
- (6) (a) Vaugeois, J.; Simard, M.; Wuest, J. D. *Coord. Chem. Rev.* **1995**, *145*, 55–73. (b) Shur, V. B.; Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T.; Volkonsky, A. Yu.; Solodova, E. V.; Panov, S. Yu.; Petrovskii, P. V.; Vol'pin, M. E. *J. Organomet. Chem.* **1993**, *443*, C19–C21.
- (7) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970; pp 54–66.

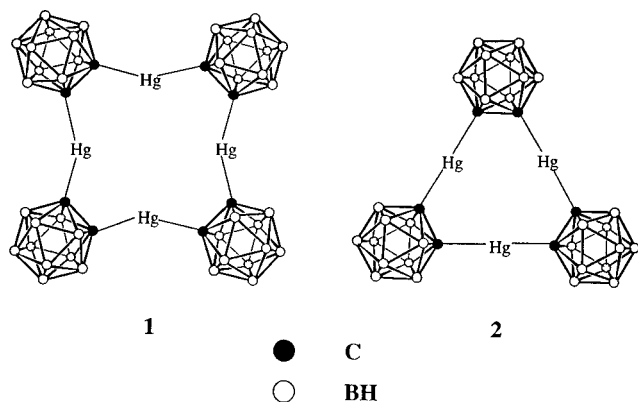


FIGURE 1. Representations of unsubstituted [12]mercuracarborand-4 (1) and [9]mercuracarborand-3 (2).

$C_2B_{10}H_{12}$  carboranes has two moderately acidic CH vertices which are easily deprotonated and subsequently functionalized using electrophilic reagents. The 10 BH vertices present in each of the icosahedral carborane isomers have an electrophilic substitution chemistry in many ways reminiscent of arenes. Thus, most reactions which occur at the boron vertices do not affect the carbon vertices, and *vice versa*. The rigid three-dimensional icosahedron holds substituents in well-defined spatial relationships, and most transformations maintain the integrity of the underlying geometry.

The metal centers of organomercury(II) compounds, with two empty p orbitals, exhibit Lewis acidity toward a variety of ligands and nucleophiles. Compared with other possible Lewis acid host molecules which contain tin, boron, and silicon atoms, mercury centers provide several unique features as electrophilic binding sites. First, in diorganomercury compounds, Hg(II) forms two essentially colinear primary  $\sigma$  bonds, and it retains appreciable Lewis acidity in the plane perpendicular to these primary  $\sigma$  bonds through the use of empty p orbitals. Second, the linear geometry around Hg sites allows its inclusion in cyclic structures equipped with a spacious cavity which can accommodate large guests such as inorganic anions. Finally, the Hg(II) species are stable in the presence of air and water and soluble in most organic solvents, thus facilitating the study of their coordination chemistry.

### Unsubstituted Mercuracarborands

Reaction of *closo*-1,2-Li<sub>2</sub>-1,2- $C_2B_{10}H_{10}$  with Hg(II) salts results in the self-assembly of cyclic arrays composed of alternating carborane icosahedra and mercury atoms linked by C–Hg–C moieties (Scheme 1).<sup>5</sup>

In the design of these molecules, both the electron-withdrawing character of the *o*-carborane cage and the close geometric similarity of the *ortho*-positions of the icosahedron with those of the planar benzene ring are exploited. The relatively positive carbon vertices of the icosahedra activate the mercury centers as Lewis acids, thereby enhancing the ability of the cycles to function as hosts to anionic and other electron-rich guests. The usual tools of <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy are uninformative regarding host–guest complexation since they undergo little change regardless of the presence or absence of host–guest association. However, <sup>199</sup>Hg NMR

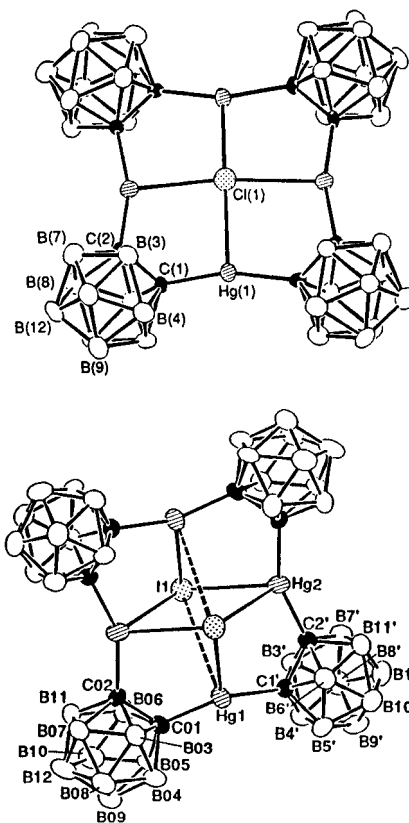
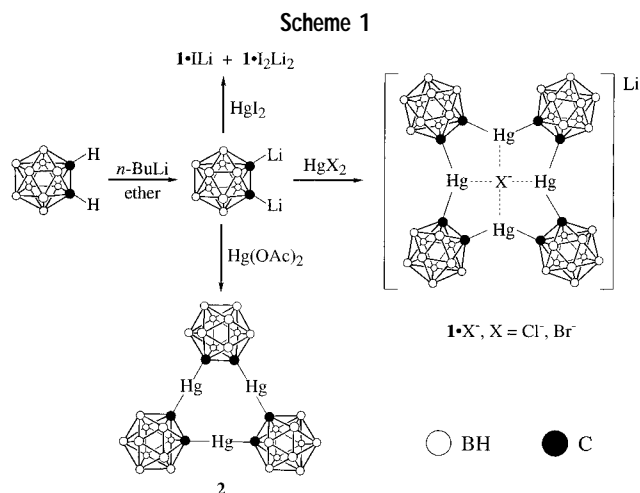


FIGURE 2. Molecular structure of  $1\text{-Cl}^-$  (A, top) and  $1\text{-I}_2^{2-}$  (B, bottom). spectroscopy<sup>8</sup> is very sensitive to changes in the immediate environment around the mercury atom, and we have found it to provide useful information regarding the strength of the interaction between the guest and the host species. Structural characterization of both the hosts and their complexes with various guest species is dependent upon single-crystal X-ray diffraction studies.

The crystal structures of  $1\text{-Cl}^-$  and  $1\text{-I}_2^{2-}$  are shown in Figure 2. Both structures display the simultaneous and cooperative complexation of the halide ion(s) by the mercuracycle. The Hg–X distances (X<sup>−</sup> = halide ion) are much shorter than the sum of the corresponding van der Waals radii,<sup>9</sup> revealing strong interactions between the Hg atoms and the coordinated halide(s). Figure 3 is a space-filling representation of  $1\text{-Cl}^-$ .

(8) Sen, M. A.; Wilson, N. K.; Ellis, P. D.; Odom, J. D. *J. Magn. Reson.* **1975**, *19*, 323–336.

(9) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

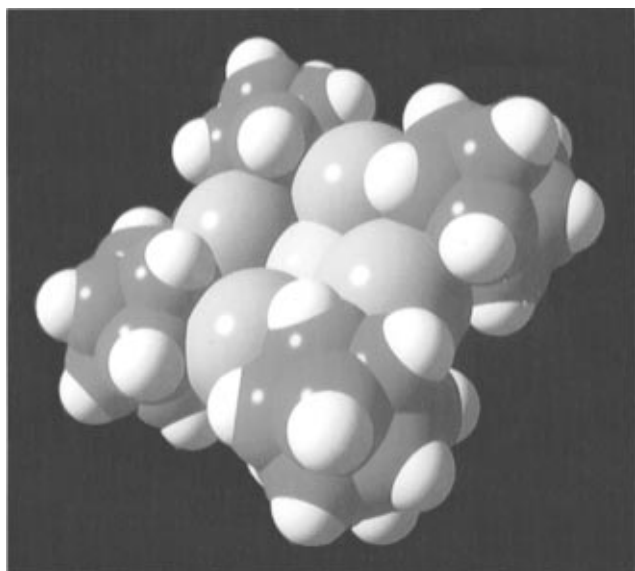


FIGURE 3. Space-filling illustration of  $1 \cdot \text{Cl}^-$  showing the coordinated square planar chloride ion.

The iodide ions present in  $1 \cdot \text{I}_2^{2-}$  can be removed quantitatively from the tetrameric complex by reaction with two or more molar equivalents of silver acetate, thereby precipitating silver iodide (Scheme 2).<sup>10</sup> The acetate ion is bulky and charge-diffuse and exhibits no coordination to the host species. Removal of the silver salt by filtration followed by an aqueous wash allowed the isolation and characterization of compound **1**. Species **1**, crystallized from tetrahydrofuran (THF) as  $1 \cdot (\text{THF})_4 \cdot (\text{H}_2\text{O})_2$  (Figure 4), exhibits a buckled conformation which facilitates the coordination of THF to the mercury centers and encloses the two water molecules. The primary mercury coordination is less distorted from linearity in **1** than in its halide ion complexes.

The decomplexation process can be reversed, in discrete stages, by the sequential addition of iodide ion to regenerate the diiodide complex. This process was monitored by  $^{199}\text{Hg}$  NMR titration experiments (*vide infra*). The complex can then be regarded as an "iodide reservoir" with a maximum capacity of two iodide ions per host molecule.

### Anion Template Effects during the Synthesis of Mercuracarborand Complexes

Metal ions, by functioning as templates for the synthesis of a variety of macrocyclic receptors, have played an indispensable role in the development of host-guest chemistry.<sup>11</sup> Although the utilization of metal ions for this purpose is widespread, the phenomenon of an anion serving as a template is very rare.<sup>12</sup> The organization of oxovanadium-organophosphonate clusters around chloride anions has recently been reported,<sup>13</sup> and the utilization of anions such as  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{N}_3^-$ , and  $\text{NO}_3^-$  for the construction of poly(oxovanadate) cages has also

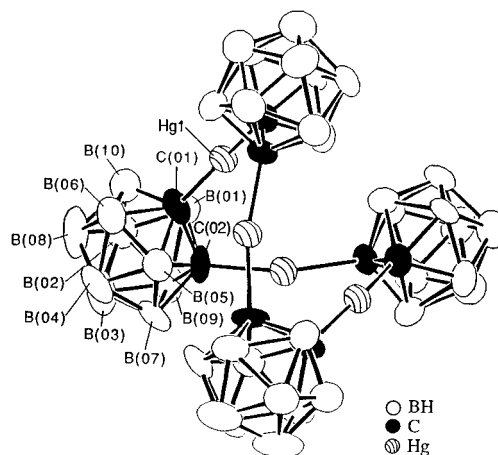
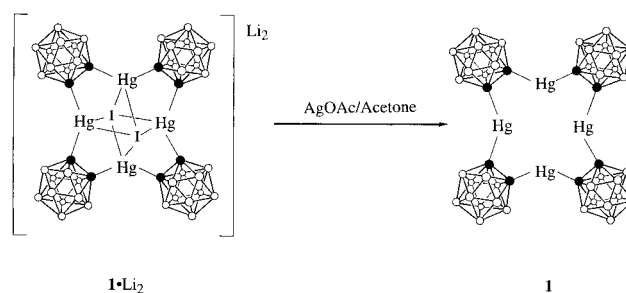


FIGURE 4. Molecular structure of  $1 \cdot (\text{THF})_4 \cdot (\text{H}_2\text{O})_2$  with THF and  $\text{H}_2\text{O}$  molecules removed for clarity.

Scheme 2



been described by Müller and co-workers.<sup>14</sup> In the absence of the anionic species encapsulated within the cage, the architecture of these systems would not develop in either case.<sup>15</sup> In neither complex could the anionic guest be removed, and hence it 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.<sup>16</sup>

The formation of a tetrameric cyclic host such as **1**, encapsulating a halide ion, is unexpected since the trimeric [9]mercuracarborand-3, **2**, has less angle strain than **1** and, *a priori*, should be the preferred product. It was subsequently revealed that the anions associated with the Hg(II) source profoundly affected the ring size of the resulting mercuracarborand species.<sup>5</sup> Thus, use of a mercury salt with a noncoordinating anion, such as acetate, in the reaction with *closo*-1,2- $\text{Li}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  affords cyclic trimer (**2**) having no associated guest.<sup>17</sup> The efficient assembly of halide ion complexes of the stereochemically less favored tetrameric macrocycle and the formation of a virtually strainless cyclic trimer utilizing mercury acetate led to the conclusion that the anion exercises a kinetic template effect<sup>18</sup> in the construction

(10) Yang, X.; Johnson, S. E.; Kahn, S.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 893–896.

(11) Hoss, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 375–384 and references therein.

(12) Mitchell, P. H. *Nature* **1990**, *348*, 15–16.

(13) Salta, J.; Chen, Q.; Chang, Y.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 757–760.

(14) Müller, A.; Rohlfing, R.; Krickemeyer, E.; Penk, M.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 909–912 and references therein.

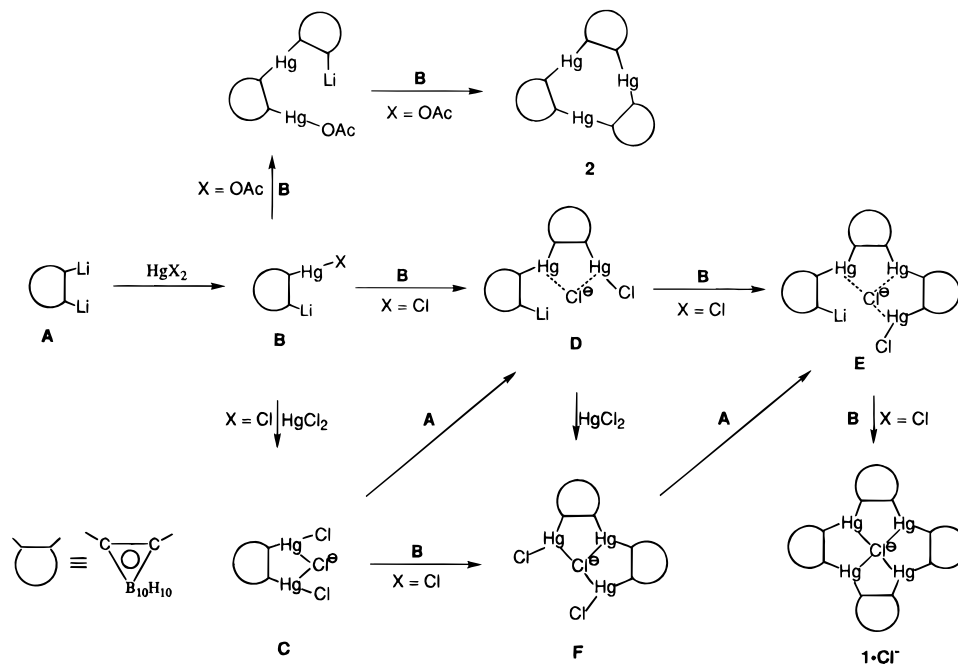
(15) Müller, A. *Nature* **1991**, *352*, 115.

(16) Sessler, J. L.; Mody, T. D.; Lynch, V. *J. Am. Chem. Soc.* **1993**, *115*, 3346–3347.

(17) Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 193–195.

(18) Template effects are classified as either thermodynamic or kinetic. Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469–475.

Scheme 3



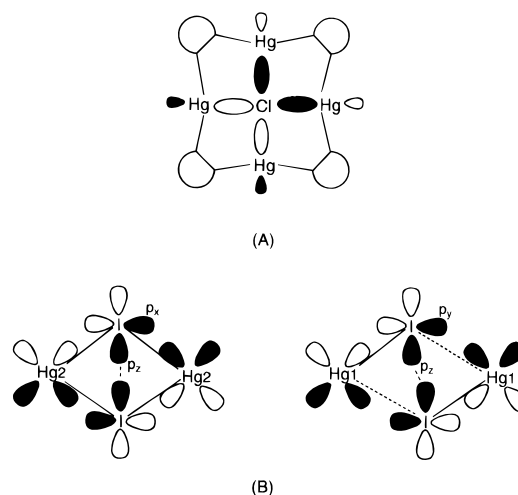
of such mercuracarborands. To operate as a kinetic template, the halide ion must be a stabilizing component in product-determining transition states,<sup>18</sup> and the tetrameric cycle is therefore not formed as a free host appropriate for the later complexation of the halide ion, but as the halide ion complex.

On the basis of these considerations, a reaction route to species  $\mathbf{1}\cdot\text{ClLi}$ , as shown in Scheme 3, was postulated to rationalize the template effects provided by the halide ion(s).<sup>5</sup> Attempts to synthesize **C** by the reaction of 2 equiv of  $\text{HgCl}_2$  with *closo*-1,2- $\text{Li}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  result in a mixture of products which includes  $\mathbf{1}\cdot\text{ClLi}$  as a major component and **F** as a minor component, as demonstrated by <sup>199</sup>Hg NMR and negative ion FAB mass spectroscopy. No **C** was detected in the mass spectrum of the product mixture. The presence of  $\text{Cl}^-$  ion in **E** prevents its cyclization to form the cyclic trimer **2**, whose formation is favored in the absence of a halide ion. Thus, the halide ion accelerates the assembly and cyclization of the intermediates leading to the tetramers and at the same time inhibits cyclic trimer formation by stabilizing **E** with respect to spontaneous cyclization.

In  $\mathbf{1}\cdot\text{ClLi}$ , one of the two empty and mutually perpendicular p orbitals at each Hg interacts in a three-center manner with one of the set of two filled and in-plane p orbitals of the chloride ion, maximizing the cooperative and simultaneous interaction of the trapped guest and the Hg atoms. The chloride ion is therefore bound to the host by a pair of three-center two-electron bonds (Chart 1A). Being unused, four more empty p-orbitals, one from each Hg atom, are perpendicular to the plane of the host ring.

The bonding of two iodide ions in  $\mathbf{1}\cdot\text{I}_2^{2-}$  arises from the interaction of the filled  $p_x$  and  $p_y$  orbitals of both iodide ions with a total of eight empty Hg p orbitals with four each directed 45° above and below the plane of the host (Chart 1B). Two of the resulting  $p_{\text{Hg}2}-p_{\text{I}}-p_{\text{Hg}2}$  three-center two-electron bonds are symmetrical while the remaining pair  $p_{\text{Hg}1}-p_{\text{I}}-p_{\text{Hg}1}$  are unsymmetrical due to a

Chart 1



lateral slippage of each guest iodide along its x axis and in opposite directions. This distortion is believed to arise from trans-host repulsion of the filled  $p_z$  orbitals of each  $\text{I}^-$  guest, as depicted in the chart, since the  $\text{I}^- \cdots \text{I}^-$  distance in  $\mathbf{1}\cdot\text{I}_2^{2-}$  (3.969(1) Å) is shorter than the corresponding van der Waals distance (4.30 Å). However, the fact that the larger iodide ion serves as a template for the same cyclic tetramers as chloride ion indicates that  $\mathbf{1}\cdot\text{I}_2^{2-}$  is possibly formed from  $\mathbf{1}\cdot\text{I}^-$  in a manner similar to that depicted in Scheme 3.

Lending further support to the anion template hypothesis is the fact that the use of mercuric thiocyanate as the mercury source provides the pentameric species  $[(\text{C}_2\text{B}_{10}\text{H}_{10}\text{Hg})_5\cdot(\text{SCN})]\cdot\text{Li}$  and  $\{(\text{C}_2\text{B}_{10}\text{H}_{10}\text{Hg})_5\cdot[\text{Hg}(\text{SCN})_3]\cdot\text{Li}\}$ .<sup>19</sup> It is not yet known how the  $\text{SCN}^-$  and  $\text{Hg}(\text{SCN})_3^-$  ions interact with the macrocycle Hg centers since the molecular structures of these complexes are not yet available. However, without an appropriate template anion, neither the tetrameric nor the pentameric structures are developed, as demonstrated.

(19) Zheng, Z.; Hawthorne, M. F. Unpublished results.

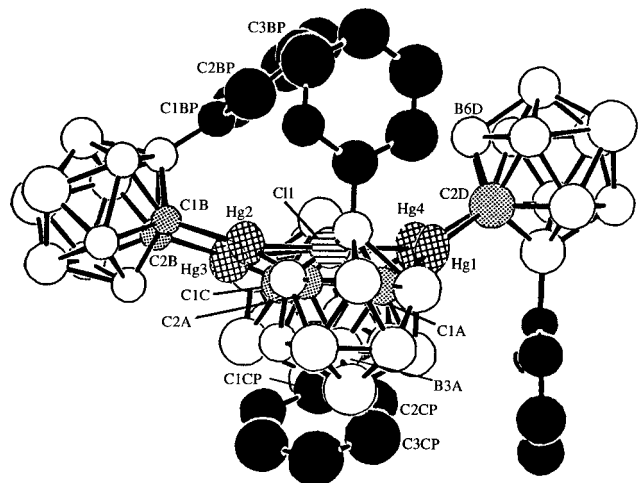


FIGURE 5. Molecular structure of the 1,2-alternate  $[(3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_9\text{-Hg})_4]\cdot\text{Cl}^-$ .

### Mercuracarborands with a Sterically Encumbered Cavity

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. For spherical anion guests, 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  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions, although these anions are markedly different in size and it is impossible to identify the specific roles of individual halide ions (*vide supra*). One way to unambiguously demonstrate the necessity 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 by stereochemical means.

It was demonstrated previously that removal of a B-H vertex adjacent to the two carbon atoms in *closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  (i.e., at either the 3- or 6-position) and replacement with a B-phenyl vertex yields *closo*-3-( $\text{C}_6\text{H}_5$ )-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ,<sup>20</sup> which can then be used to synthesize a number of isomeric phenyl-substituted derivatives of **1** in which the central cavity containing the halide ion has varying degrees of steric protection.<sup>21</sup> Upon formation of the mercuracarborand around a central chloride ion, four stereoisomers are possible depending upon whether the phenyl group on each of the carboranes is "up" or "down" relative to its neighbors. We have structurally characterized three of the isomeric chloride ion complexes (Figures 5–7); the fourth, in which all the phenyl substituents are located on the same side of the host, does not form due to severe steric constraints. When mercuric iodide was employed in the cyclization reaction, the only product isolated was the isomer having four phenyl groups arrayed about the periphery of the host cavity in an up, down, up, down fashion (Figure 8). Thus, the relative orienta-

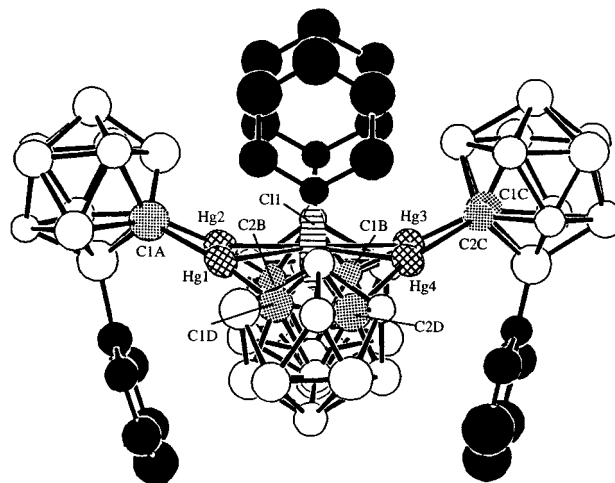


FIGURE 6. Molecular structure of the 1,3-alternate  $[(3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_9\text{-Hg})_4]\cdot\text{Cl}^-$ .

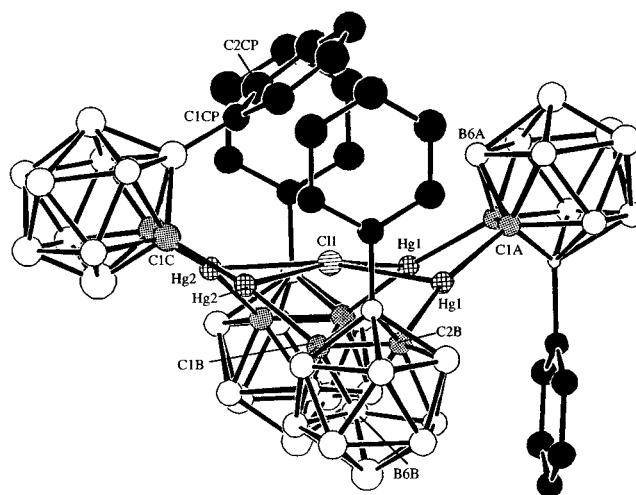


FIGURE 7. Molecular structure of the partial cone  $[(3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_9\text{-Hg})_4]\cdot\text{Cl}^-$ .

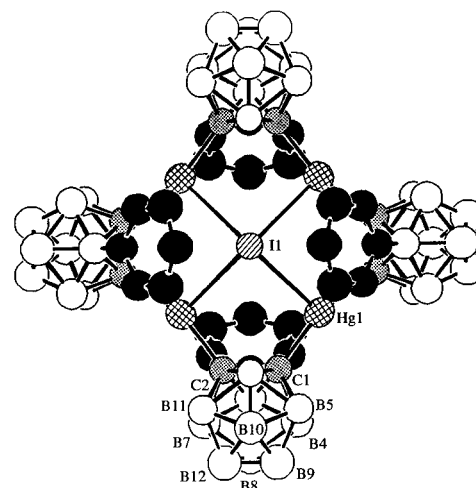
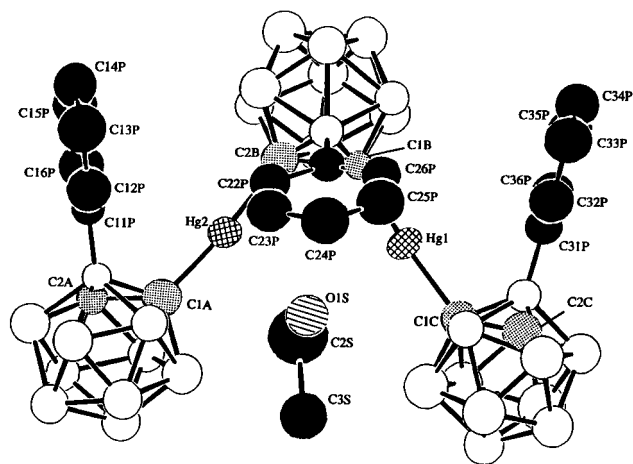


FIGURE 8. Molecular structure of the 1,3-alternate  $[(3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_9\text{-Hg})_4]\cdot\text{I}^-$ .

tions of the phenyl substituents of the component carborane cages are dependent upon the identity of the individual halide ion templates, as observed. Consequently, observation of the distribution of the possible isomers formed in the assembly of the cyclic host offers a useful probe of the templating effects of the different

(20) Wegner, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 896–901.

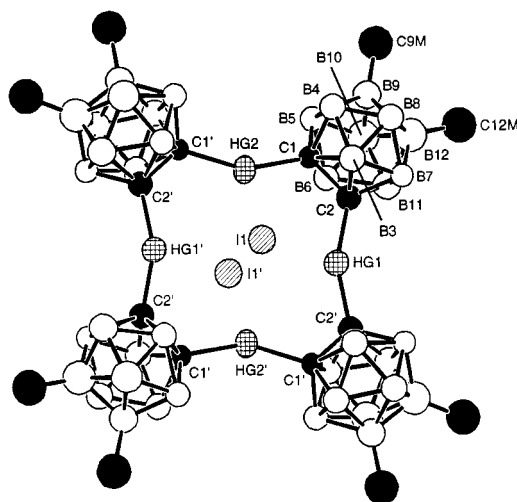
(21) Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 5105–5113.

FIGURE 9. Molecular structure of  $3 \cdot (\text{C}_2\text{H}_5\text{OH})$ .

halide ions; the much smaller chloride ion (ionic radius 1.80 Å for  $\text{Cl}^-$  vs 2.15 Å for  $\text{I}^-$ ) appears to provide less steric bias in the orientation of the phenyl substituents. The product-determining transition state for the formation of the only observed iodide isomer, 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.

The isolation of an acyclic mercury-containing intermediate present 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. Such an acyclic host, **3**, comprised of two mercury atoms and three carborane units, has been prepared by the reaction of *closo*-3-phenyl-1,2-Li<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>9</sub> with Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>. Compound **3** 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 (Figure 9). 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 triphenyl-substituted [9]mercuracarborand-3. Crystallographic data<sup>21</sup> also suggest the presence of a pair of intramolecular edge-to-face aromatic–aromatic interactions<sup>22</sup> which assist the stabilization of such a structure in the solid state.

It is clear that a cyclic tetramer would not be formed without stabilizing template formation and that the product distribution can be controlled by using different templates. The complexation of halide ion with electrophilic Hg centers compensates for energetically unfavorable features 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.

(22) Hunter, A. C. *Chem. Soc. Rev.* **1994**, 101–109.FIGURE 10. Molecular structure of  $4 \cdot \text{I}_2^{2-}$ .

### Hydrocarbon-Soluble Mercuracarborands

During the investigation of mercuracarborand chemistry, it was observed that the parent unsubstituted hosts are quite soluble in a variety of organic electron-donor solvents, but lack solubility in noncoordinating solvents such as hydrocarbons. Such solvent coordination mitigates the potential usefulness of mercuracarborands as Lewis acid catalysts.<sup>23</sup> A possible approach to rectify this problem is to modify the supporting carborane cages with lipophilic substituents. A number of methods are known by which selected B–H vertices of the carborane cage can be replaced with B–R vertices, where R is an alkyl or aryl group.<sup>24</sup> Although the mercuracarborands and their halide complexes based on the use of *closo*-3-phenyl-1,2-Li<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>9</sub> are more soluble in weak and noncoordinating solvents than their unsubstituted counterparts, the stereoisomeric nature of the products coupled with their sterically hindered binding sites makes such species unattractive as potential catalysts. Alternatively, substituents can be introduced in a symmetrical manner to the 9- and 12-positions of the icosahedron, the points farthest removed from the carbon vertices present at positions 1 and 2. Upon formation of the substituted mercuracarborand, these substituents are directed outward from the cage and have no stereochemical influence upon host–guest interactions.

Formation of a variety of hydrocarbon-soluble mercuracarborand hosts has been achieved, and their interactions with simple halide ions, nucleophilic solvent, and solute molecules have been studied.<sup>25</sup> As an example, the diiodide ion complex of mercuracarborand with eight methyl substituents has the expected structure shown in Figure 10 ( $4 \cdot \text{I}_2^{2-}$ ).

It has been found that substitution of methyl and ethyl groups has a beneficial effect on the solubility of the host–guest complexes; the mercuracycles as well as their halide ion complexes are soluble not only in the coordinating

(23) Frost, C. G.; Williams, J. M. J. *Contemp. Org. Synth.* **1995**, 2, 65–83.(24) (a) Zheng, Z.; Wei, J.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, 34, 2095–2100. (b) Zakharkin, L. I.; Kovredou, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Zh. S. *J. Organometal Chem.* **1982**, 226, 217–222. (c) Li, J.; Logan, C. M.; Jones, M., Jr. *Inorg. Chem.* **1991**, 30, 4866–4868.(25) Zheng, Z.; Knobler, C. B.; Mortimer, M. D.; Kong, G.; Hawthorne, M. F. *Inorg. Chem.* **1996**, 35, 1235–1243.

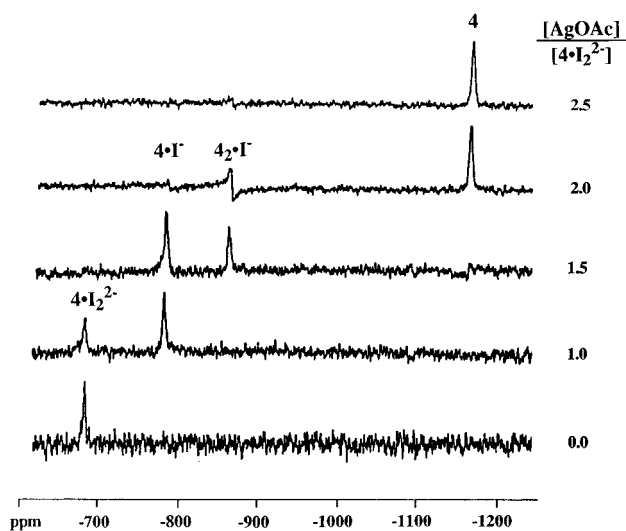


FIGURE 11.  $^{199}\text{Hg}$  NMR spectra showing the effects of incremental addition of silver acetate to  $4\cdot\text{I}_2\text{Li}_2$  in acetone solution.

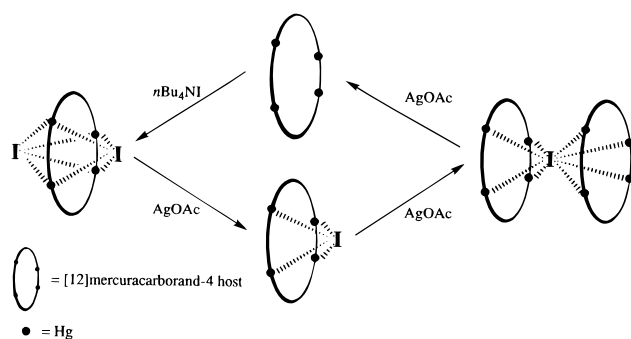


FIGURE 12. Proposed species present during progressive decomplexation of host–diiodide complexes with silver acetate.

solvents required for their unsubstituted congener but also in methylene chloride, toluene, and to a lesser extent benzene, making them more tractable for further reactions and reducing the need for polar, coordinating solvents which tend to mask subtle interactions between the hosts and weakly coordinating guests.

Preparation of the free host **4** from its iodide complex was carried out in a fashion similar to the method reported for **1** (*vide supra*). Progressive removal of the iodide ions from the complex  $4\cdot\text{I}_2\text{Li}_2$  by incremental addition of silver acetate, monitored by  $^{199}\text{Hg}$  NMR, revealed that intermediate species are formed which are quite distinct in the NMR spectrum, proving that they are stable on the NMR time scale. The results of the progressive decomplexation of  $4\cdot\text{I}_2\text{Li}_2$  by silver acetate are shown in Figure 11.

The species responsible for the resonance at  $-765$  ppm is assumed to be the monoiodo complex  $4\cdot\text{I}\text{Li}$ , and it is probable that the signal at  $-846$  ppm arises from a sandwich structure  $4_2\cdot\text{I}\text{Li}$ , in which a single iodide ion is coordinated simultaneously to two mercuracarborand hosts. After the addition of a total of two and one-half molar equivalents of silver acetate, only the decomplexed host remains, as shown by the single resonance at  $-1145$  ppm in the NMR spectrum. A schematic diagram of the various complexes and their interconversions is given in Figure 12.

Several attempts were made to isolate the intermediate complexes prepared by progressive decomplexation moni-

tored by  $^{199}\text{Hg}$  NMR, but crystallization from the filtered solutions containing the desired intermediates yielded either diiodide complexes or an unusual structure having a surprising stoichiometry of  $4_3\cdot\text{I}_4\text{Li}_4$ , which is depicted in Figure 13. The latter structure takes the form of a “short stack” of three host molecules alternating with four iodide ions. The molecular aggregate has a 4-fold axis of symmetry running through the iodide atoms and a center of symmetry. None of the iodide ions are “slipped” from the central axis of the aggregate, reflecting that they are not forced into sufficiently close proximity for iodide–iodide repulsions to come into play. It would seem to be incorrect to regard the stack as a single large host–guest complex. It is instead best described as comprising three separate monoiodide complexes and a very loosely coordinated iodide ion. There seems to be no evidence of such a species being present in solution, and it is presumably a solid state construct favored for reasons of lattice energetics and solubility.

The reaction of *closo*-1,2- $\text{Li}_2$ -9,12- $(\text{CH}_3)_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_8$  with mercuric acetate results in the formation of  $[(\text{CH}_3)_2\text{-C}_2\text{B}_{10}\text{H}_8\text{Hg}]_3$  (**5**), a hexamethyl derivative of **2**.<sup>26</sup> The trimeric structure of **5** was confirmed by X-ray crystallography and is shown in Figure 14.

The complexation behavior of **5** toward halide ions was studied by  $^{199}\text{Hg}$  NMR spectroscopy. Interestingly, stepwise addition of halide ion salts to an acetone solution containing free host **5** does not result in the formation of discrete sets of signals as observed in  $^{199}\text{Hg}$  NMR studies of the tetrameric mercuracarborands. Instead, only a single resonance is observed after each addition of the halide salt even though more than one species is believed to be present in the solution. This suggests that at room temperature the observed  $^{199}\text{Hg}$  resonances are time-averaged and result from ion exchange processes which are faster than the NMR time scale both between the individual halide ion and its complexes and between the complexes themselves. The guest/host ratio of the resulting complexes has been established to be 1, 2, and 2 for chloride, bromide, and iodide ions, respectively, as can be seen clearly from the corresponding titration curves (Figure 15).

Overall, it appears that the attachment of alkyl substituents to those boron vertices of the carborane cage which are quite distant from the mercury atoms has relatively little effect on the coordinating properties of the mercuracarborands, while having significant effects on the solubilities of the various substituted hosts and their complexes. However, a definite, if small, trend can be discerned in the  $^{199}\text{Hg}$  NMR data indicating that the degree of coordination of guests to the mercury atoms decreases with increasing alkyl substitution.

As an extension of host–guest chemistry, the supramolecular interactions of the unsubstituted host **1** and its alkyl-substituted mercuracarborands with weakly nucleophilic guests such as carborane derivatives (*closo*-9-I-12-Et-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  and *closo*-9,12- $\text{I}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ )<sup>5b</sup> and polyhedral borane anions (*closo*- $\text{B}_{10}\text{H}_{10}^{2-}$ , *closo*- $\text{B}_{10}\text{I}_{10}^{2-}$ , and

(26) Zinn, A. A.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 70–74.

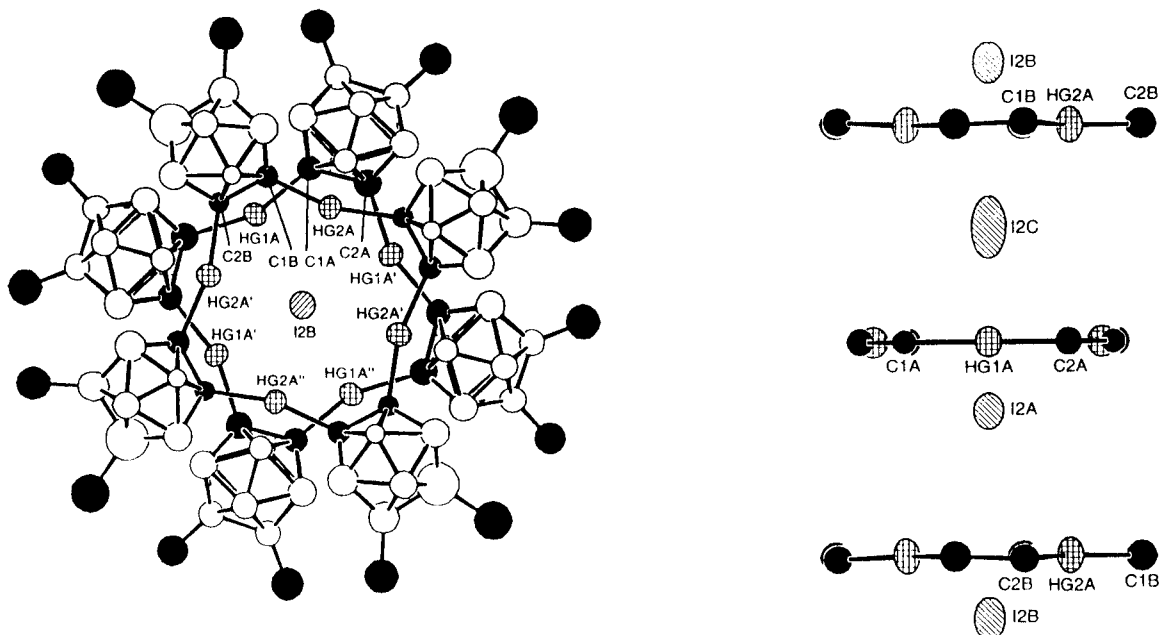


FIGURE 13. Molecular structure of  $4_3 \cdot I_4^{4-}$ : (A, left) top view, (B, right) side view with boron, methyl carbons, and hydrogen atoms removed for clarity.

*closo*- $B_{12}H_{12}^{2-}$ )<sup>5,25,27</sup> have been investigated. Although more than one molar equivalent of the anions was added in each case, evidence for only a monoadduct was observed in solution. Figure 16 shows the results of one such sequential addition of  $(Ph_3MeP)_2(B_{10}H_{10})$  to host **1** in acetone solution. Similar results were obtained with host **6**, an octaethyl-substituted derivative of **1**, in acetone solution.

The crystal structures of  $6 \cdot (closo-B_{10}H_{10}^{2-})_2$  (Figure 17) and two other supramolecular aggregates demonstrated the preferential crystallization of bisadducts. Each of the two *closo*- $B_{10}H_{10}^{2-}$  ions uses four equatorial B–H vertices to form a set of four three-center two-electron Hg–H–B bonds to the mercury atoms of the cycle in the solid state.<sup>27</sup>

## Mercuracarborands Characterized by B–Hg Bonds

Complementing the studies of the mercuracarborands incorporating C–Hg bonds, we have also succeeded in forming mercuracycles with B–Hg bonds. Through the use of a procedure which is synthetically different, but results in a structurally analogous product, it is possible to synthesize the “inside-out” mercuracarborand **7** (Scheme 4).<sup>28</sup>

The <sup>199</sup>Hg NMR resonance arising from **7** (Figure 18) exhibits a very broad heptet with relative line intensities of 1:2:3:4:3:2:1, consistent with the coupling of each mercury atom to two boron atoms (<sup>11</sup>B, 80.4%,  $I = 3/2$ , and <sup>10</sup>B, 19.6%,  $I = 3$ );<sup>29</sup> the relaxation of the two quadrupolar boron nuclei gives rise to the extremely broad lines, and the fine structure of the coupling between <sup>199</sup>Hg and <sup>10</sup>B ( $2nI + 1 = 13!$ ) is not observed.

(27) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 4904–4905.

(28) Zheng, Z.; Diaz, M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 12338–12339.

(29) Harris, R. K., Mann, B. E., Eds. *NMR and the Periodic Table*; Academic Press: London, 1978; p 195.

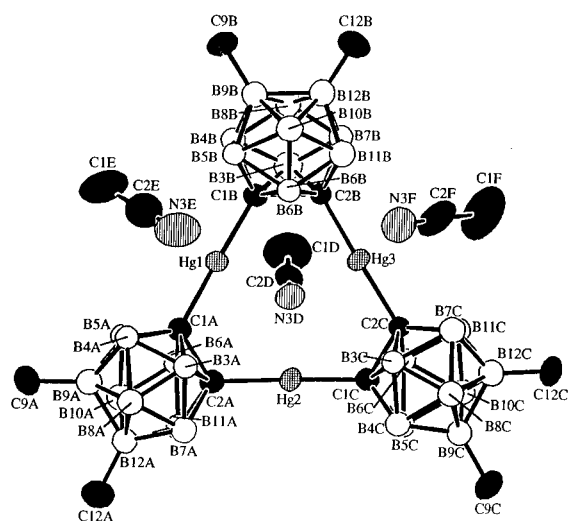
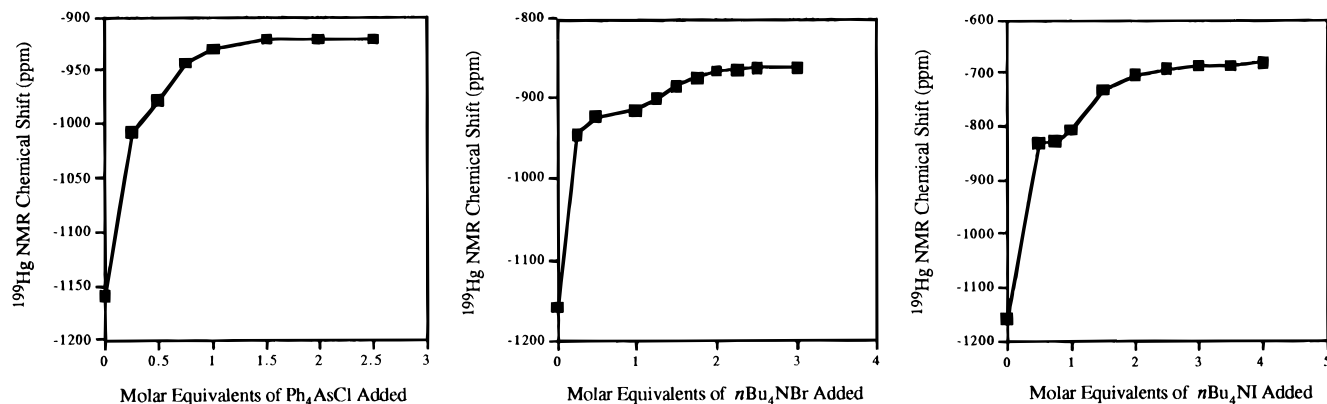
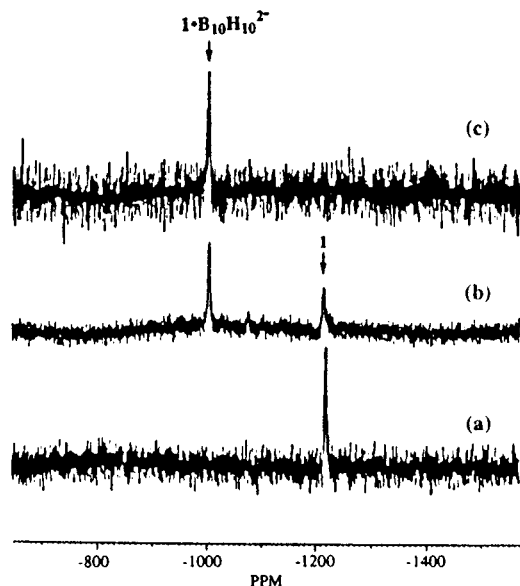
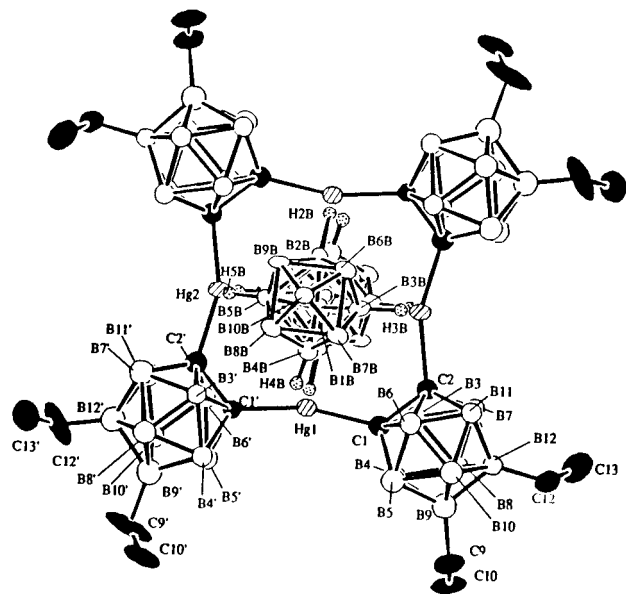


FIGURE 14. Molecular structure of  $5 \cdot (CH_3CN)_3$ .

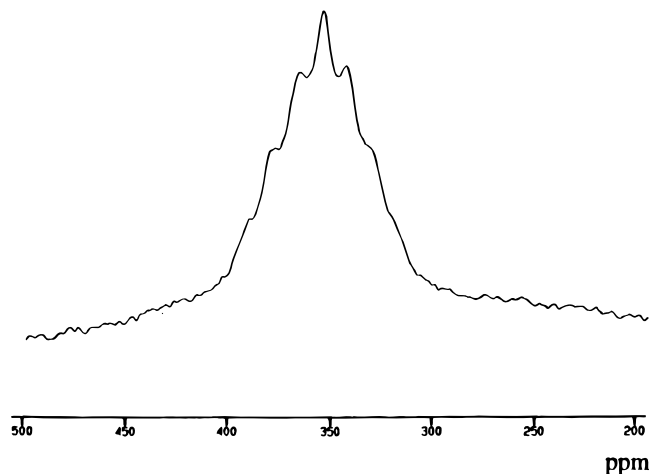
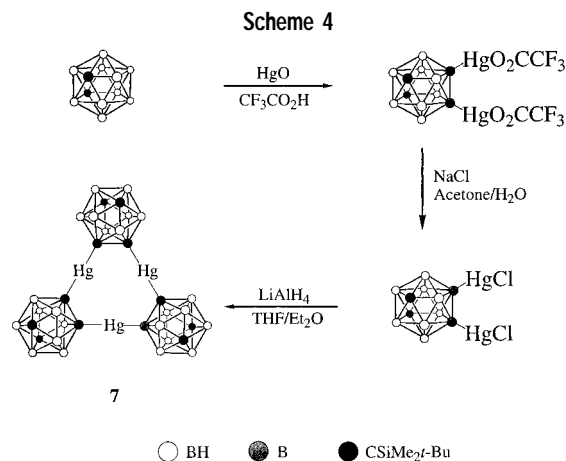
The molecule consists of three *closo*-1,7- $C_2B_{10}H_{10}$  icosahedra linked by the same number of mercury atoms through B–Hg–B structural motifs in a cyclic trimer (Figure 19). Unlike the trimeric mercuracarborands **2** and **5**, which contain *closo*-1,2-carborane cages, the exocyclic *tert*-butyldimethylsilyl substituents do not lie in the plane of the Hg atoms, but are directed both above and below the cycle.

Use of boron vertices as skeletal connectors frees the easily functionalized carbon vertices for further chemistry, and this simple change of the mode of mercury–cage bonding from Hg–C to Hg–B clearly reverses the electronic demand upon the mercury centers and thus reduces the coordinating properties of the host. Attempts to induce complexation of various guest species with compound **7**, including halide and thiophenolate ions, were unsuccessful. Presumably, the strong electron-donating effect of the 9- and 10-B vertices deactivates the mercury centers toward complexation with Lewis bases. By contrast, addition of a halide ion to **5**, a C-carboranyl




 FIGURE 15.  $^{199}\text{Hg}$  chemical shift of **5** against the molar equivalents of halide ion salts added.

 FIGURE 16.  $^{199}\text{Hg}$  NMR titration of **1** with  $(\text{Ph}_3\text{MeP})_2(\text{B}_{10}\text{H}_{10})$  in acetone solution with  $(\text{Ph}_3\text{MeP})_2(\text{B}_{10}\text{H}_{10})/1$  molar ratios of (a) 0.0, (b) 0.5, and (c) 1.0.

 FIGURE 17. Molecular structure of  $6 \cdot (\text{B}_{10}\text{H}_{10}^{2-})_2$ .

analog of **7**, causes a significant downfield shift of the  $^{199}\text{Hg}$  resonance (up to 452 ppm) due to the formation of the corresponding halide ion complex. These results


 FIGURE 18.  $^{199}\text{Hg}$  NMR spectrum of **7** in dichloromethane.


dramatically demonstrate the range of electronic properties available through selective carborane substitution. Despite showing no coordinating properties toward electron-rich species, the B–Hg–B motif appears to be more robust toward nucleophilic attack than its C–Hg–C counterpart. In the presence of the thiophenolate ion, mercuracarborands containing C–Hg bonds are eventually decomposed, whereas **7** is stable under these conditions.

During the preparation of the known compound *closo*-9- $\text{CF}_3\text{CO}_2\text{Hg}$ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ,<sup>30</sup> a byproduct, **8**, having the

(30) Bregadze, V. I.; Kampel, V. TS.; Godovikov, N. N. *J. Organomet. Chem.* **1976**, *112*, 249–251.

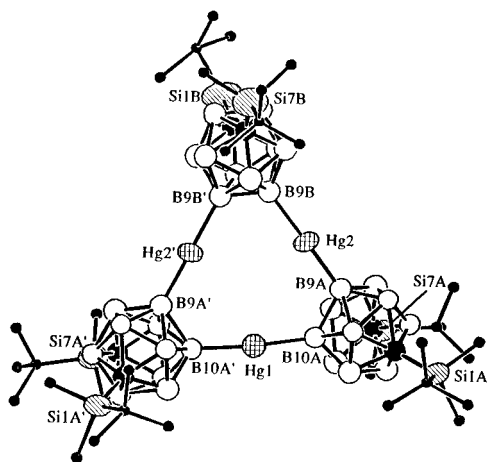


FIGURE 19. Molecular structure of 7.

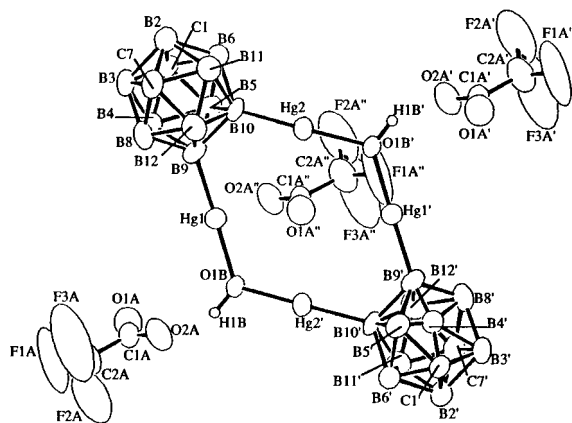


FIGURE 20. Molecular structure of 8.

structure presented in Figure 20 was obtained.<sup>31</sup> The complex consists of two inversion-related *closo*-1,7-carborane cages linked by two Hg(OH)<sub>2</sub> segments through four B–Hg bonds. Each of the four trifluoroacetate ions (the fourth is not shown) interacts with the macrocyclic host through either hydrogen bonding or Hg–O interactions using only one of its two oxygen atoms and with a second cycle using the remaining oxygen. In other words, each trifluoroacetate ion is shared by two mercury cycles, and a self-assembled polymeric 1:2 (mercury cycle to trifluoroacetate ion) complex with two trifluoroacetate anions is formed in the crystalline solid as shown in Figure 21.

### Concluding Remarks

A new family of macrocyclic multidentate Lewis acid hosts (mercuracarborands) has been discovered, and efficient

(31) Zheng, Z.; Knobler, C. B.; Curtis, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 432–435.

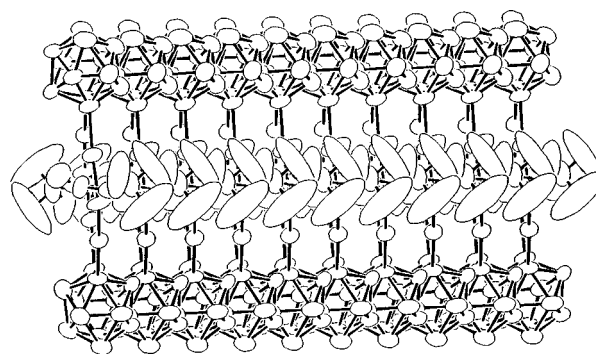


FIGURE 21. Lattice orientation of 8 showing the presence of polymeric chains in the solid state.

procedures for the synthesis of these species have been developed. This family of macrocycles incorporates carborane cages linked by an equal number of mercury atoms in which the Hg atoms serve as Lewis acid centers for binding electron-rich guest species. The results presented in this Account prove (1) macrocyclic multidentate Lewis acid hosts of this type could efficiently bind anions and nucleophilic species as well as extremely weak Lewis bases, (2) the exceptional binding ability of mercuracarborands is attributed to the preorganization, multiple binding, and host–guest complementarity observed in their host–guest complexes, and (3) the icosahedral carborane cage plays a crucial role as a structural unit in the formation of these macrocyclic hosts by stabilizing the host superstructure and by enhancing the electron deficiency of the electrophilic Hg(II) binding sites.

The ability of mercuracarborands to be selectively modified by the judicious choice of substituents is amply demonstrated in this Account. Applications of mercuracarborands to molecular recognition, catalysis, and supramolecular chemistry await further development.

*The authors thank the National Science Foundation for their support of the research described here, Dr. Carolyn B. Knobler for her splendid crystallography which has continually oriented our research, and Dr. Xiaoguang Yang for the earliest work with mercuracarborands in our laboratory. In addition, we thank our many colleagues and research group members who have directly and indirectly contributed to the success of the chemistry described here. The color photo shown in Figure 3 was prepared from crystallographic data by Darren M. Ricciardi of Imperative Images, Inc. We thank Dr. David Harwell and Mrs. Margaret B. Bird for their assistance with the manuscript and illustrations.*

AR9501479