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Host–Guest Chemistry of a New Class of Macrocyclic Multidentate Lewis Acids Comprised of Carborane-Supported Electrophilic Mercury Centers†

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Abstract: The synthesis and characterization of a family of carborane-supported macrocycles containing electrophilic mercury centers is described. These compounds are multidentate Lewis acids which have been demonstrated to bind anions such as Cl^-, Br^-, I^-, and *closo*-$B_{10}H_{10}^{2-}$ as well as uncharged nucleophilic species. The lithium salts of the anionic complexes $[(1,2\text{-}C_2B_{10}H_{10}Hg)_4X_n]Li_n$ (**1**·X_nLi_n; X = Cl, Br, $n = 1$; X = I, $n = 1$ or 2) were synthesized from the reaction of *closo*-$1,2\text{-}Li_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with HgX_2 (X = Cl, Br, and I) in 70–80% yields. The free host [12]mercuracarborand-4 (**1**) was obtained by the removal of halide ions from **1**·I_2^{2-} with AgOAc. The molecular structures of **1**·ClLi, (**1**·Br)$_2$-(benzo[15]crown-5)$_3$·$Li_2(H_2O)_2$, and **1**·$I_2(AsPh_4)_2$ have been determined from single-crystal X-ray diffraction studies. **1**·ClLi crystallizes in the tetragonal space group $P4/mcc$, $a = 14.3233(8)$ Å, $c = 11.2641(7)$ Å, $V = 2311$ Å^3, $Z = 2$ ($^1/_8$ of the tetramer per asymmetric unit), $R = 0.041$, $R_w = 0.060$. (**1**·Br)$_2$(dibenzo[15]crown-5)$_3$·$Li_2(H_2O)_2$ crystallizes in triclinic space group $P\bar{1}$, $a = 11.3204(4)$ Å, $b = 22.7459(8)$ Å, $c = 27.8148(9)$ Å, $\alpha = 86.5346(9)°$, $\beta = 86.218(1)°$, $\gamma = 88.640(1)°$, $V = 7132$ Å^3, $Z = 2$, $R = 0.039$, $R_w = 0.050$. **1**·$I_2(AsPh_4)_2$ crystallizes in monoclinic space group $P2_1/n$, $a = 9.518(2)$ Å, $b = 30.516(6)$ Å, $c = 15.531(4)$ Å, $\beta = 99.331(6)°$, $V = 4451$ Å^3, $Z = 2$, $R = 0.045$, $R_w = 0.053$. The structures and bonding observed in these complexes of host **1** are discussed. A ^{199}Hg NMR spectroscopic study demonstrated that **1**·I^- and **1**·I_2^{2-} were formed upon the sequential addition of iodide ion to an acetone solution of **1**. An octaethyl derivative of **1** was synthesized from $[(1,2\text{-}C_2B_{10}H_8Et_2Hg)_4\cdot I_2]Li_2$ (**2a**·I_2Li_2), which was originally obtained from the reaction of *closo*-$1,2\text{-}Li_2\text{-}9,12\text{-}Et_2\text{-}1,2\text{-}C_2B_{10}H_8$ with HgI_2. **2a** crystallizes in tetragonal space group $P\bar{4}2_1c$, $a = 14.806(1)$ Å, $c = 13.5141(9)$ Å, $V = 2962$ Å^3, $Z = 2$, $R = 0.052$, $R_w = 0.058$. The absence of coordinating solvents allows the formation of supramolecular species **2a**·$(9\text{-}I\text{-}12\text{-}Et\text{-}1,2\text{-}C_2B_{10}H_{10})_2$ and **2a**·$(9,12\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10})_2$, the former of which crystallizes in the monoclinic space group $P2_1/c$, $a = 12.828(1)$ Å, $b = 22.650(2)$ Å, $c = 14.698(1)$ Å, $\beta = 108.541(2)°$, $V = 4049$ Å^3, $Z = 2$, $R = 0.059$, $R_w = 0.059$ and the latter of which crystallizes in $P2_1/c$, $a = 12.768(2)$ Å, $b = 22.907(4)$ Å, $c = 14.589(3)$ Å, $\beta = 108.202(3)°$, $V = 4053$ Å^3, $Z = 2$, $R = 0.064$ $R_w = 0.081$. In addition, molecular aggregates of *closo*-$B_{10}H_{10}^{2-}$ (**10**) with **1** and **2a** were studied. **2a**·**10**$_2(MePh_3P)_4$ crystallizes in the triclinic space group $P\bar{1}$, $a = 15.583(2)$ Å, $b = 15.861(2)$ Å, $c = 16.045(2)$ Å, $\alpha = 67.831(4)°$, $\beta = 70.713(4)°$, $\gamma = 86.371(4)°$, $V = 3457$ Å^3, $Z = 1$, $R = 0.056$, $R_w = 0.064$. The template effect observed in the synthesis of the mercuracarborand hosts is discussed, along with the structures and bonding present in the host–guest complexes mentioned above.

Introduction

Since the synthesis of crown ethers and the discovery of their complexing properties toward alkali metal cations in 1967,[1] host–guest chemistry has developed rapidly[2] and now includes ancillary fields of study such as supramolecular chemistry, biomimetic chemistry, and materials science.[3] In contrast to the extraordinary achievements of cation complexation in host–guest chemistry, only relatively recently has anion complexation by compounds containing electron-deficient atoms such as boron,[4] mercury,[5] tin,[6] and silicon[7] received attention, although anion-inclusion complexes were observed as early as 1968.[8a] At that time it was reported that halide ions could be encapsulated by the so-called "in–in" isomers of protonated bicyclic diamine hosts via electrostatic and hydrogen bond interactions.[8a] Since that time several protonated, charged and spherical tricyclic cryptands and tricyclic quaternary ammonium[8] cages have been synthesized as well as

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† Dedicated to Professor Donald J. Cram on the occasion of his 75th birthday.

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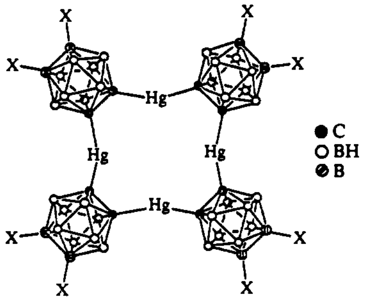
the planar diprotonated sapphyrin dication[9] which characteristically bind halide ions through electrostatic or hydrogen bond interactions. Such intermolecular noncovalent interactions between host and guest molecules play a central role not only in synthetic host–guest complexes and self-assembling supramolecular arrays but also throughout much of biomimetic and biological chemistry.[3] In addition, these interactions provide the basis for the development of chemical sensors, chromatography, catalysis, and novel materials.[10] Systems which have been most studied so far generally utilize electrostatic forces, induced dipole interactions, dispersion forces, charge-transfer interactions, and hydrogen bonding between the host and guest. Recently reported electrophilic hosts which employed boron,[4] mercury,[5] tin,[6] and silicon[7] atoms as binding sites interact with anion guests through coordinate covalent bond formation and offer new prospects for selective molecular recognition, anion transport, and the catalytic activation of electron-rich organic and inorganic substrates. Thus, the synthesis and application of Lewis acid hosts has provided coordinate covalent bond interactions to the general area of host–guest chemistry.

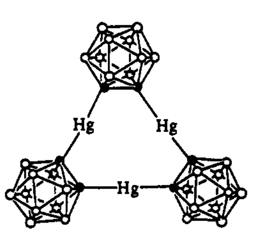
Linear mercuric ion derivatives, with two empty mercury p-orbitals, exhibit Lewis acidity toward a variety of ligands and nucleophiles. Mercuric halides are known to form HgX_2L in argon matrices where L = CO, NO, N_2, or unsaturated hydrocarbons[11a] and to form HgX_3^- and HgX_4^{2-} species with alkali metal halides in aqueous solution.[11b] Organomercury(II) compounds form anionic complexes with halides or pseudohalides in solution,[12] although no complexes have been isolated in the solid state due to their low stabilities. Recently, Wuest and coworkers described a series of complexes in which 1,2-phenylenedimercury dihalides are bidentate hosts and, unlike simple monodentate organomercuric halides, form stable complexes with added halide ions.[5] One such complex contains a chloride ion tetracoordinated by two 1,2-phenylenedimercury dichloride molecules (**4**),[5b] and it was pointed out that the stability of $\mathbf{4}_2\cdot Cl^-$ is due to the multiple coordination of Cl^- by four mercury centers. It has long been recognized that multiple complementary interactions between host and guest are of vital importance in the stabilization of host–guest complexes (e.g. the chelate effect). The additivity of *n* noncovalent interactions is reflected in the stability constant of a complex as the effect of individual interactions taken to the *n*th power.[10] It is thus not unusual that host–guest systems containing at least two binding centers have been designed, synthesized, and demonstrated to form isolable complexes. In addition, the preorganization of the host plays one of the key roles in determining the stability of host–guest complexes.[2a] The macrocyclic and cryptate effects have been advanced to explain the high stability of macrocyclic and cryptate host–guest complexes, respectively,[2] and these principles have recently been employed in the design of Lewis acid hosts. Thus, a series of tricyclic ditin Lewis acid hosts have been synthesized and are reported to form stable halide complexes both in solution and in the solid state[6a] while macrocycles containing three atoms of silicon or tin have been synthesized and are reported to transport anions through a liquid organic membrane.[6e,7a] Consequently, the design and synthesis of preorganized multidentate Lewis acid species will provide hosts which can both recognize and transport anions and other electron-rich moieties.

We recently reported the first example (**1**) of an important new class of *macrocyclic*, *multidentate*, and *electrophilic* host species.[13] The species [12]mercuracarborand-4 (**1**) is a charge-reversed analog of the well-known [12]crown-4 macrocycle. Species **2a** and **2b** are further examples of such "anti-crown" tetradentate Lewis acid hosts. Similarly, recently reported[13d] tridentate Lewis acid [9]mercuracarborand-3 (**3**) is an "anti-crown" of [9]crown-3. Recently, Shur and co-workers have reported the macrocyclic tridentate and pentadentate Lewis acid hosts **5** and **6** containing mercury-binding sites.[14] The mercury atoms in **1**–**6** display essentially linear and covalent bonding geometries as well as two empty p-orbitals capable of secondary coordinate covalent bond interactions with nucleophiles such as halide ions and coordinating organic solvents in the plane perpendicular to the linear primary bonds. Moreover, the mercury-binding sites in **1** and **2** are oriented such that their association with guests is maximized through the simultaneous and cooperative action of four Lewis acid–base interactions. We here report the synthesis and characterization of **1**, **2a**, and **2b** as well as certain of their complexes and related supramolecular chemistry.



1, X = H

2a, X = Et ; **2b**, X = I



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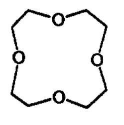
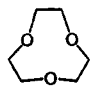
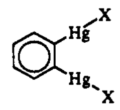


[12]crown-4



[9]crown-3



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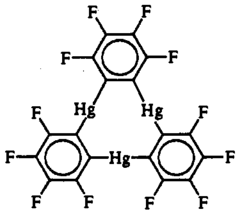

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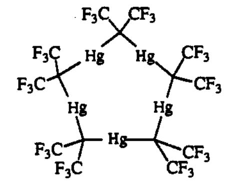

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Results

Synthesis of 1·XLi (X = Cl, Br). The icosahedral carborane *closo*-1,2-$C_2B_{10}H_{12}$ (or *o*-carborane) can be easily lithiated by *n*BuLi at its C–H vertices to give *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{10}$.[15]

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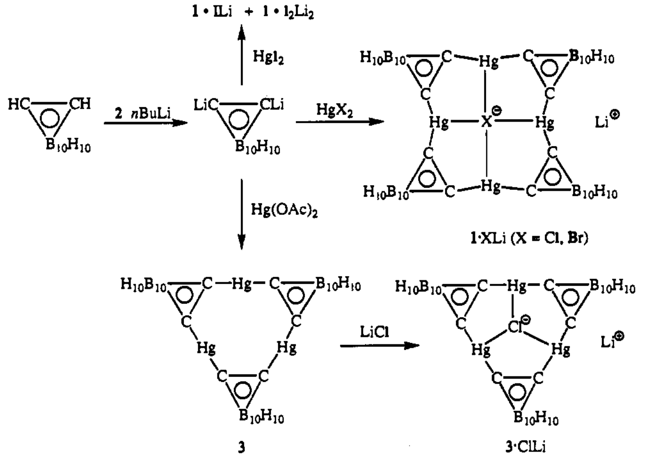
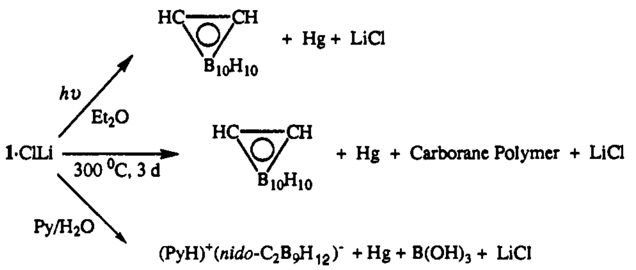
Scheme 1



Scheme 2



The reaction of mercuric halides with 1 mol equiv of *closo*-1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$ in dry Et$_2$O at room temperature under N$_2$ results in the formation of the cyclic tetramer **1**·XLi (X = Cl, Br), as shown in Scheme 1.

The anionic halide ion complexes of **1** are colorless and air-stable crystalline solids isolated in 75–85% yield. The species **1**·XLi are generally quite soluble in organic solvents with the exception of hydrocarbons, and they were characterized by ^{1}H, ^{13}C, ^{11}B, and ^{199}Hg NMR. The NMR data revealed that **1**·XLi (X = Cl, Br) has a highly symmetrical structure containing single types of both carbon and mercury atoms. The negative-ion FAB mass spectrum of **1**·ClLi exhibits an anion with an m/z envelope centered at 1406, which corresponds to **1**·Cl$^-$, while that of the **1**·BrLi complex was centered at m/z = 1450, the value which corresponds to **1**·Br$^-$. The observation of anionic host–guest complexes in mass spectroscopy demonstrates the high stability of these anion complexes.

Synthesis of 1·I$_n$Li$_n$ (n = 1, 2). The reaction of α-mercuric iodide with 1 mol equiv of *closo*-1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$ with vigorous stirring in dry Et$_2$O at room temperature results in the formation of iodide complexes of the cyclic tetramer, **1**·I$_n$Li$_n$ (n = 1, 2) (Scheme 1). A longer reaction time favors the formation of **1**·I$_2$Li$_2$. Complexes **1**·I$_2$Li$_2$ and **1**·ILi are colorless and air-stable crystalline solids isolated in 80% yield and characterized by ^{1}H, ^{13}C, ^{11}B, and ^{199}Hg NMR. The negative-ion FAB mass spectrum of **1**·I$_2$Li$_2$ is that of an anion with an m/z envelope centered at 1625, which corresponds to **1**·I$_2^-$; the spectrum of **1**·ILi exhibits an anion envelope centered at m/z = 1497, which corresponds to **1**·I$^-$. The species **1**·I$^-$ can be quantitatively converted to **1**·I$_2^{2-}$, since the sequential addition of nBu$_4$NI to an acetone solution of **1**·ILi results in the conversion of the monoiodide to the diiodide complex, as illustrated in Figure 9. The metathesis reaction of **1**·I$_2$Li$_2$ with [As(C$_6$H$_5$)$_4$]Cl gave **1**·I$_2$[As(C$_6$H$_5$)$_4$]$_2$ without halide ion exchange, and the ^{199}Hg and ^{11}B NMR spectra of the resulting **1**·I$_2$[As(C$_6$H$_5$)$_4$]$_2$ are identical to the corresponding spectra of **1**·I$_2$Li$_2$.

Chemical Stability of 1·XLi (X = Cl, Br). Like other organomercurials,[16] **1**·XLi species decompose upon prolonged heating at 300 °C or during UV irradiation in diethyl ether to form mercury, *o*-carborane, and carborane-containing polymers. In the presence of air and H$_2$O, **1**·XLi in pyridine slowly decomposes to Hg metal and *nido*-7,8-C$_2$B$_9$H$_{12}^-$, as shown in Scheme 2. Otherwise, **1** and its complexes are air-stable both in solution and in the solid state.

Synthesis of 1. The synthesis of **1** was achieved in 85–90% yield by the reaction of **1**·I$_2$Li$_2$ with 2 equiv of AgOAc in ethanol at room temperature (eq 1). The ^{1}H, ^{13}C, and ^{11}B NMR spectra

$$\mathbf{1}\cdot\mathrm{I_2Li_2} + 2\mathrm{AgOAc} \rightarrow \mathbf{1} + 2\mathrm{AgI} + 2\mathrm{LiOAc} \qquad (1)$$

of **1** were nearly identical with those of the halide ion complexes of this host. No resonances due to AcO$^-$ were observed, and all spectroscopic data confirmed that the macrocyclic structure of **1** was preserved following the removal of both iodide ions from **1**·I$_2$Li$_2$. The ^{199}Hg NMR spectrum of **1** exhibited a solvent-dependent peak at −1305 ppm in THF and at −1205 ppm in acetone. The reaction of **1**·I$_2$Li$_2$ with ethanolic AgNO$_3$ also produced a white solid which exhibited a ^{199}Hg NMR chemical shift at −1310 ppm in acetone and a ^{11}B NMR spectrum similar to that of **1**.

The synthesis of **1** is best achieved by the removal of iodide ions from **1**·I$_2$Li$_2$ or **1**·ILi with ethanolic AgOAc. The similar reaction of the chloride or bromide ion complexes of **1** with AgOAc resulted in incomplete precipitation of the halide ions and a low yield of **1**. Longer reaction times employed to increase the yield of **1** permitted the destructive oxidation of B–H bonds by Ag$^+$. Since OAc$^-$ does not bind to **1**, Hg(OAc)$_2$ was used in an attempt to synthesize **1** directly. However, the reaction of *closo*-1,2-Li$_2$-1,2-C$_2$B$_{10}$H$_{10}$ with Hg(OAc)$_2$ produced the cyclic trimer (C$_2$B$_{10}$H$_{10}$Hg)$_3$ (**3**) (Scheme 1).[13d] The template effect observed in the synthesis of mercuracarborand macrocycles will be discussed below. The sequential addition of nBu$_4$NI to **1** in acetone solution regenerates **1**·I$^-$ and **1**·I$_2^{2-}$ (eq 2), as demonstrated by ^{199}Hg NMR (Figure 9).

$$\mathbf{1} \xrightarrow{n\mathrm{Bu_4NI}} \mathbf{1}\cdot\mathrm{I}(n\mathrm{Bu_4N}) \xrightarrow{n\mathrm{Bu_4NI}} \mathbf{1}\cdot\mathrm{I_2}(n\mathrm{Bu_4N})_2 \qquad (2)$$

Synthesis of Octaethyl[12]mercuracarborand-4 (2a). To obtain [12]mercuracarborand-4 derivatives which were soluble in non-coordinating solvents, B-substituted *o*-carboranes were used to prepare the corresponding [12]mercuracarborand-4 derivatives. Thus, *closo*-9,12-Et$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**9**) was synthesized in moderate yield using a modification of the procedure of Jones and coworkers[55] by coupling EtMgBr with *closo*-9,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**7**) in the presence of a catalytic amount of (Ph$_3$P)$_2$PdCl$_2$/CuI. This reaction was accompanied by the formation of a small amount of *closo*-9-I-12-Et-1,2-C$_2$B$_{10}$H$_{10}$ (**8**). Both **7** and **9**[13e] are easily lithiated, and they react with α-HgI$_2$ to form the corresponding macrocycles. Thus **9** produces **2a**·I$_2$Li$_2$ and **2a**·ILi[13e] in a 2:1 ratio (determined by ^{199}Hg NMR spectroscopy), as depicted in Scheme 3. Similarly, **2b**·I$_2$Li$_2$ was synthesized in 90% yield from **7**. We have also converted *closo*-3-phenyl-1,2-C$_2$B$_{10}$H$_{11}$ to the corresponding tetrameric isomer mixture of halide ion complexes of *B*-tetraphenyl[12]mercuracarborand-4 species.[13f] The formation of tetrameric macrocycles appears to be a general reaction with these derivatized *o*-carboranes. All of these substituted [12]-mercuracarborand-4 hosts and their complexes are much more soluble in noncoordinating solvents than those derived from unsubstituted *closo*-1,2-C$_2$B$_{10}$H$_{12}$.

Host **2a** was synthesized from the reaction of ethanolic AgOAc with **2a**·I$_n$Li$_n$, in accord with Scheme 3, as an air-stable, white solid soluble in benzene, toluene, chloroform, and methylene chloride. The ^{199}Hg chemical shift of **2a** is solvent-dependent

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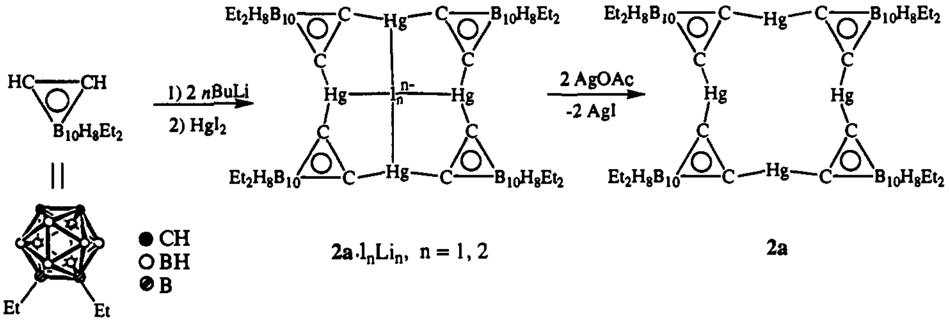
[16] Wardell, J. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 2, pp 863–978.

Scheme 3



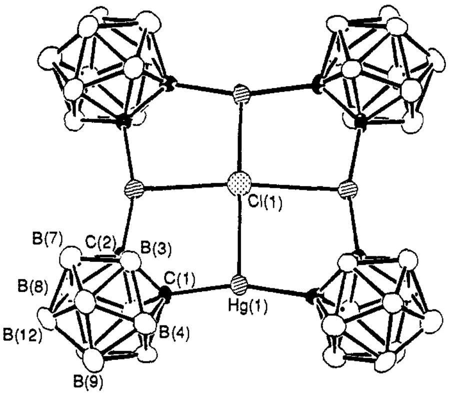
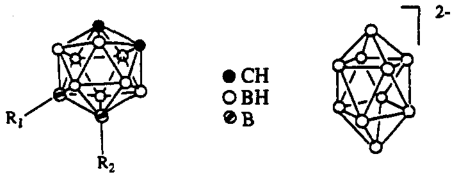


Figure 1. ORTEP representation of $1\cdot Cl^-$ with hydrogen atoms removed for clarity.

and ranges from −1221 ppm in $CDCl_3$ to −1200 ppm in benzene, which may be compared with the corresponding resonances of $2a\cdot I_2Li_2$ at −785 ppm and $2a\cdot ILi$ at −675 ppm in acetone. These values are quite similar to those of **1** and its iodide complexes.



$R_1 = R_2 = I$, 7
$R_1 = Et, R_2 = I$, 8
$R_1 = R_2 = Et$, 9

10

Complexation Studies of 2a with 7, 8, and [*closo*-$B_{10}H_{10}$]$^{2-}$ (10). To study the interaction of mercuracarborand hosts with weakly coordinated species, hosts soluble in noncoordinating solvents, such as **2a**, must be employed. Both $2a\cdot 7_2$ and $2a\cdot 8_2$ were isolated from mixtures of **2a** and **7** or **8** in methylene chloride in a 1:2 ratio while $2a\cdot 10_2(Ph_3MeP)_4$ was formed from $10(Ph_3MeP)_2$ and **2a** in a 1:1 ratio using CH_2Cl_2/CH_3CN solvent. The structures of complexes of $2a\cdot 7_2$, $2a\cdot 8_2$, and $2a\cdot 10_2(Ph_3MeP)_4$[13e] were determined by X-ray crystallography. These supramolecular complexes were studied in solution using ^{199}Hg and ^{11}B NMR, to be discussed below.

Structure of 1·ClLi. The structure of the anion $1\cdot Cl^-$ is presented in Figure 1, and selected bond distances and angles are listed in Table 1. The anion consists of four bivalent *closo*-1,2-$C_2B_{10}H_{10}$ cages linked by four Hg atoms in a cyclic tetramer with a chloride ion located in the center of the array and 2.944(2) Å from each Hg. The anion possesses crystallographically imposed C_{4h} symmetry with the four Hg atoms, eight cluster carbon atoms, and the eight boron atoms in the mirror plane. The chloride ion is displaced 0.383 Å above and below this plane, on the four-fold axis, with half occupancy of each of these two positions. Each Hg links carbon atoms of two carborane icosahedra with Hg–C distances of 2.105(13) and 2.080(13) Å, respectively. The Hg–C–C angles are 126.0(6) and 125.4(6)°, and the C–Hg–C angle is 162.0(3)°. The distance between the adjacent mercury atoms is 4.129(1) Å. In comparison, the cyclic trimer of 1,2-phenylenemercury, $(C_6H_4Hg)_3$, has a planar structure with an average C–Hg distance of 2.10 Å, a C–Hg–C angle of 177.7°, and a Hg–C–C angle of 120.5° for the orthorhombic crystal.[17] Similarly, trimeric **3** has a planar structure with a C–Hg–C angle of 177.1° and an average Hg- -Hg distance of 3.732 Å,[13d] which is longer than the van der Waals distance (3.46 Å).[18,19] The deviation from linear coordination of the mercury atoms in $1\cdot Cl^-$ is induced by strain in the tetramer ring. The average Hg–C–C angle of 125.7° in **1** is larger than that observed in the 1,2-phenylenemercury trimer (120.5°) and **3** (119.0°). However, this angle is much smaller than the ideal internal angle (135°) of a regular octagon. Therefore, displacement of the mercury centers toward the cavity of the ring occurs. The resulting conformation of the ring also maximizes the bonding between the chloride ion and the four mercury centers, and this deviation from linear mercury coordination requires the mixing of some additional p-character into the sp-hybrid mercury orbitals involved in bonding to carborane C-atoms. The nearly square planar coordination geometry observed for the chloride ion in $1\cdot Cl^-$ is unprecedented. The Hg–Cl distance of 2.944(2) Å is significantly shortened when compared with the van der Waals distance. The reported structure of the 1:2 adduct of chloride ion with 1,2-diphenylenedimercuric dichloride ($4_2\cdot Cl^-$) has two short Cl–Hg distances of 2.925 Å and two long Cl–Hg distances of 3.167 Å, respectively.[5b] Similarly, the pentacoordinated chloride complex $[(CF_2)_2CHg]_5Cl_2^{2-}$ ($6\cdot Cl_2^{2-}$) has Hg–Cl distances ranging from 3.089 to 3.388 Å.[14b]

Structure of 1·Br⁻. The structure of $1\cdot Br^-$ is presented in Figure 2a. Selected bond distances and angles are listed in Table 1. The unit cell contains four $(C_2B_{10}H_{10}Hg)_4$ hosts, each of which is complexed with a Br^- anion. These four anions are charge compensated by two dipositive cations, each containing two Li^+, three benzo[15]crown-5, and two H_2O molecules. In the cation, each Li^+ is coordinated to one benzo[15]crown-5 molecule and to one water molecule. Each of the two water molecules is hydrogen-bonded to the third crown ether molecule (Figure 2b). The asymmetric unit contains two nonequivalent bromide ion complexes of **1**. In each host, the four Hg atoms form a nearly perfect square with adjacent Hg- -Hg distances which range from 4.092(1) to 4.144(1) Å and Hg- -Hg- -Hg angles which range from 89.19(2) to 90.73(2)° with an alternation between obtuse and acute angles. The mercury atoms of each tetramer deviate from planarity by 0.006(1) and 0.002(1) Å. The Br^- ion occupies a central position either above or below this plane (half occupancy) at distances of 0.933, 0.999, 0.933, and 0.970 Å. There is a total

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[17] Brown, D. S.; Massey, A. G.; Wickens, D. A. *Acta Crystallogr.* **1978**, *B34*, 1695.

[18] Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 514.

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) in **1**·ClLi, **1**·$I_2(AsPh_4)_2$, and (**1**·Br)$_2$[(benzo[15]crown-5)$_3Li_2(H_2O)_2$][a]

		1·ClLi			
Hg1–Cl	2.944(2)	Hg1–C1	2.105(13)	Hg1–C2,2	2.080(13)
C1–C2	1.67(2)				
C1–Hg1–C2	162.0(3)	C1–C2–Hg1,2	125.4(6)	C2–C1–Hg1	126.6(6)
		(**1**·Br)$_2$[(benzo(15)crown-5)$_3Li_2(H_2O)_2$]			
Hg1–Br2	3.047(5)	Hg2–Br2	3.087(5)	Hg3–Br2	3.028(5)
Hg4–Br2	3.061(6)	Hg5–Br1	3.066(6)	Hg6–Br1	3.046(6)
Hg7–Br1	3.061(6)	Hg8–Br1	3.044(5)	Hg1–C1A	2.07(2)
Hg1–C2G	2.08(2)	Hg2–C2A	2.07(2)	Hg2–C1B	2.09(2)
Hg3–C2B	2.10(2)	Hg3–C1F	2.07(2)	Hg4–C2F	2.10(2)
Hg4–C1G	2.10(2)	Hg5–C1H	2.06(2)	Hg5–C2L	2.13(2)
Hg6–C2H	2.09(2)	Hg6–C1J	2.12(2)	Hg7–C2J	2.05(2)
Hg8–C2K	2.03(2)	Hg8–C2L	2.06(2)	C1A–C2A	1.65(3)
C1B–C2B	1.63(3)	C1F–C2F	1.65(3)	C1G–C2G	1.63(3)
C1H–C2H	1.66(2)	C1L–C2L	1.62(2)	C1K–C2K	1.63(3)
C1J–C2J	1.64(3)				
C1A–Hg1–C2G	162.6(7)	C2A–Hg2–C1B	163.0(7)	C2B–Hg3–C1F	163.0(7)
C2F–Hg4–C1G	162.6(7)	C1H–Hg5–C2L	162.7(7)	C2H–Hg6–C1J	164.2(7)
C2J–Hg7–C1K	162.8(7)	C2K–Hg8–C1L	162.9(7)		
		1·$I_2[AsPh_4]_2$			
Hg1–I1	3.774(1)	Hg1–I1,2	3.277(1)	Hg2–I1,2	3.304(1)
Hg2–I1	3.306(1)	Hg1–C1′	2.099(9)	Hg1–C01	2.095(9)
Hg2–C2′	2.101(9)	Hg2–C02,2	2.101(9)	I1–I1,2	3.969(1)
C1′–C2′	1.660(13)	C01–C02	1.638(13)		
C1′–Hg1–C01	158.1(4)	C2′–Hg2–C02,2	152.6(4)		

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

of four half-occupied Br^- positions in the asymmetric units, and only Br1 and Br2 are shown in Figure 2a. The average Hg–Br distance is 3.063(5) Å, which is much shorter than the Hg- -Br van der Waals distance of 3.68 Å (1.73 + 1.95).[18,19] The bromide ion complex of trimeric perfluoro-1,2-phenylenemercury has Hg- -Br distances ranging from 3.07 to 3.39 Å, and a diorganomercury bromide complex has Hg–Br distances of 3.187 and 2.981 Å.[5e] The geometrical parameters of the host **1** in **1**·Br^- are quite similar to those reported for **1**·ClLi (Table 1). The anion complexes stack along the *a* axis as shown in Figure 3 with alternating stacking distances of 5.57 and 5.74 Å, which is similar to the case observed for **1**·ClLi with a stacking distance of 5.63 Å.

Structure of 1·I_2[AsPh$_4$]$_2$. The structure of the anion **1**·I_2^{2-} is presented in Figure 4. Selected bond distances and angles are listed in Table 1. The dianion possesses crystallographically imposed inversion symmetry and consists of four bivalent 1,2-$C_2B_{10}H_{10}$ cages linked by four Hg atoms in a cyclic tetramer with iodide ions located both above and below the plane of the four mercury atoms and 1.962(1) Å from that plane but not equidistant from the four Hg atoms. The iodide atoms are equidistant from the two Hg(2) (3.304(1) and 3.306(1) Å), and each of the iodine atoms is nearer to one of the two remaining Hg atoms (3.277(1) Å) than to the other (3.774(1) Å). All distances are shorter than the van der Waals distance between Hg and I (3.89 Å).[18,19] In addition, the "sides" of the parallelogram formed by connecting the four Hg atoms are 3.921(1) and 3.963(1) Å, which are longer than the van der Waals separation (3.46 Å).[15] Angles about the Hg atoms to the two carborane carbon atoms are 152.6(4) and 158.1(4)°, which is the largest deviation from 180° yet observed in diorganomercurials, including those observed in **1**·Cl^- and **1**·Br^-. The large deviation observed in **1**·I_2^{2-} may be due to the distorted I–Hg interactions and I^-- - -I^- repulsion.

Structure of 2a. The structure of **2a** is presented in Figure 5, and selected bond distances and angles are listed in Table 2. The framework of molecule **2a** consists of four bivalent *closo*-9,12-Et_2-1,2-$C_2B_{10}H_8$ cages linked by C-vertices to four Hg atoms in a cyclic tetramer with crystallographically imposed S_4 symmetry and with the four Hg atoms roughly in a butterfly configuration. Certain structural features of **2a** are similar to those of the THF complex of **1**.[13c] Each Hg atom is located 0.326(1) Å from the least squares plane through the four Hg atoms. Each Hg in **2a** links carbon atoms of two carborane icosahedra with Hg–C distances of 2.06(2) (Hg1–C1) and 2.12 Å (Hg1–C2). The Hg–C–C angles are 120.3(13)° and 117.0(15)°, and the C–Hg–C angle is 170.5(9)°. The distance between adjacent mercury atoms is 3.775(2) Å, and the diagonal Hg- -Hg distance is 5.258(2) Å. The torsion angle involving Hg–C–C–Hg is 14°, which is significantly larger than those found in **1**·ClLi (0.0°) and **1**·I_2(AsPh$_4$)$_2$ (5.3(10)°) and smaller than that of **1**·(THF)$_4$·2H_2O (20°).[13c] The framework seen in **2a** has more linear Hg coordination than that in its halide ion complexes, and because the cycle is buckled, shorter Hg- - -Hg distances are observed in **2a** than in the planar complexed host. The Hg–C–C angles in **2a** are quite similar to those observed in **3** (118.5°)[13d] and (1,2-C_6H_4Hg)$_3$ (average 120.3(2)°),[17,20] both of which have linear mercury coordination. It is also noteworthy that the mercury atoms are bent toward the external coordinating THF molecules in **1**·(THF)$_4$·2H_2O,[13c] while the mercury atoms of the hosts present in **1**·ClLi[13a] and **1**·I_2(AsPh$_4$)$_2$[13b] are bent toward the cavity. Although two $CHCl_3$ molecules are present in each unit cell, no interaction is observed between the $CHCl_3$ and **2a**.

Structures of 2a·7$_2$ and 2a·8$_2$. The ORTEP representations of host–guest complexes **2a**·**8**$_2$ and **2a**·**7**$_2$ are shown in Figures 6 and 7, respectively. Selected bond distances and angles are listed in Table 2. The molecular aggregates have a crystallographically imposed inversion symmetry. Species **2a**·**8**$_2$ consists of a planar macrocyclic tetradentate Lewis acid host (**2a**) and two *closo*-9-I-12-Et-1,2-$C_2B_{10}H_{10}$ (**8**) carborane species. The complexed host consists of four bivalent *closo*-9,12-Et_2-1,2-$C_2B_{10}H_8$ cage fragments linked by four Hg atoms in a cyclic array with structural parameters similar to those observed in **1**·Cl^-. The planar host has an average Hg–C distance of 2.07(2) Å, an average C–C distance of 1.65(2) Å, and C–Hg–C angles of 163.9(10) and 167.1(10)°. The four Hg atoms are coplanar and arranged in a nearly perfect square. Guest **8** is coordinated to **2a** via the iodine atom of the former, which is 1.971(2) Å from the mercury plane. The Hg1–I9″ distances of 3.584(2) and 3.463(2) Å and Hg2–I9″ distances of 3.553(3) and 3.618(3) Å are shorter than the van der Waals distance of Hg- -I (ranging from 3.68 to 3.83 Å).[21] Complex **2a**·**7**$_2$ has structural features similar to those of **2a**·**8**$_2$, and only one of the iodine atoms of **7** is involved in

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(20) (a) Brown, D. S.; Massey, A. G.; Wickens, D. A. *Inorg. Chim. Acta* **1980**, *44*, L193. (b) Brown, D. S.; Massey, A. G.; Wickens, D. A. *Acta Crystallogr.* **1978**, *B34*, 1695.

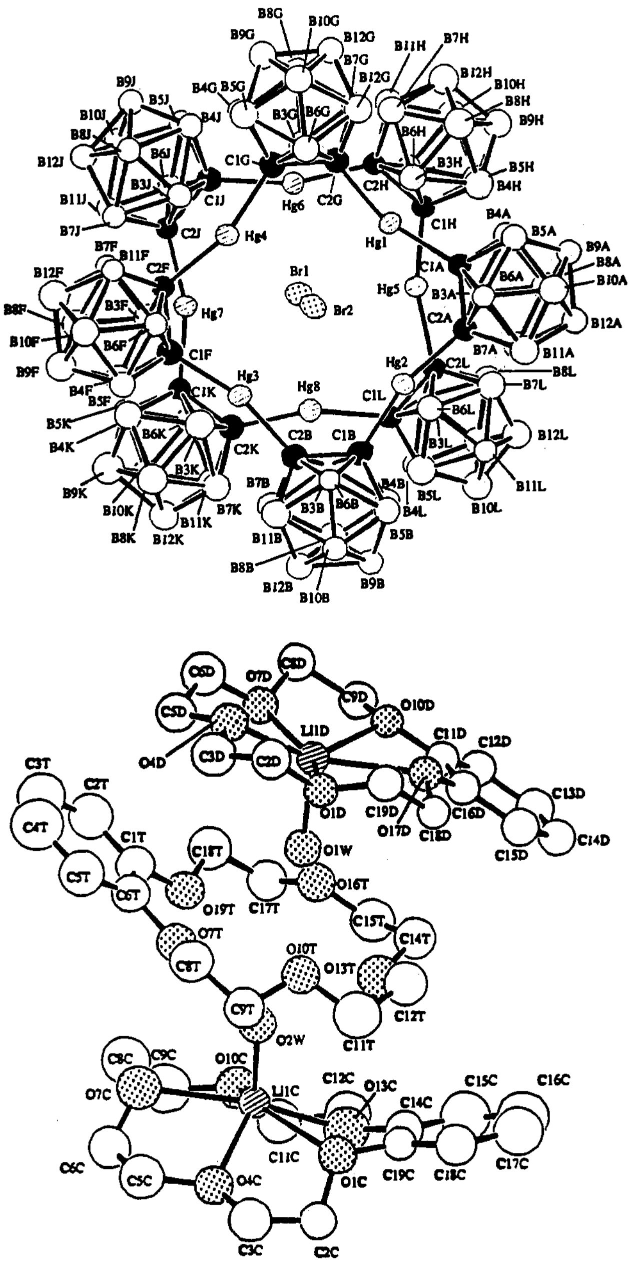

Figure 2. ORTEP representations of (a, top) two independent $1\cdot Br^-$ ions and (b, bottom) $[Li_2(H_2O)_2(benzo[15]crown\text{-}5)_3]^{2+}$ with hydrogen atoms removed for clarity.

complexation with host **2a**. The observed Hg–I distances are 3.445(2), 3.626(2), 3.620(2), and 3.549(2) Å, which are comparable to those found in $\mathbf{2a}\cdot\mathbf{8}_2$.

Even though weak, the Lewis base interaction of I-atoms of the *B*-iodocarboranes (**7** and **8**) with **2a** is sufficiently stabilizing to form the complex in which **2a** assumes a planar conformation with nonlinear Hg(II) centers. The electron donation of the iodine atom to the mercury atoms is assisted by the presence of a dipole in the *o*-carborane cage,[22] in which the B9 and B12 vertices are relatively electron-rich and the C1 and C2 vertices are electron-deficient.

Structure of $\mathbf{2a}\cdot\mathbf{10}_2(Ph_3MeP)_4$. An ORTEP drawing of $\mathbf{2a}\cdot\mathbf{10}_2$ is shown in Figure 8, and selected bond distances and angles are listed in Table 2. The tetraanionic aggregate with a crystallographically imposed inversion symmetry consists of a planar macrocyclic tetradentate Lewis acid host and two bicapped square antiprismatic *closo*-$B_{10}H_{10}^{2-}$ (**10**) ions. The complexed host

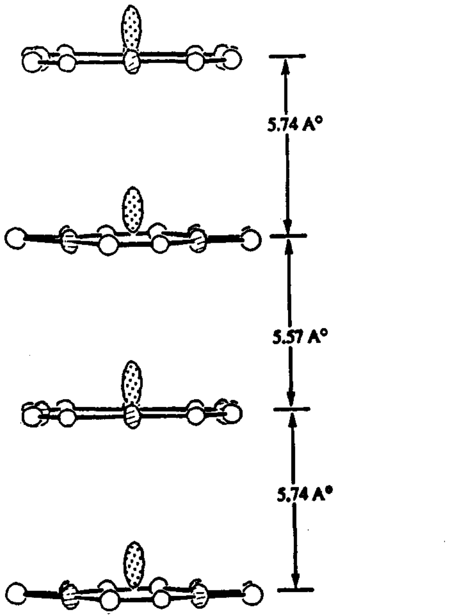

Figure 3. Stacking diagram of $1\cdot Br^-$ in the solid state with hydrogen and boron atoms removed for clarity. Open, striped, and dotted ellipsoids represent carbon, mercury, and bromine, respectively.

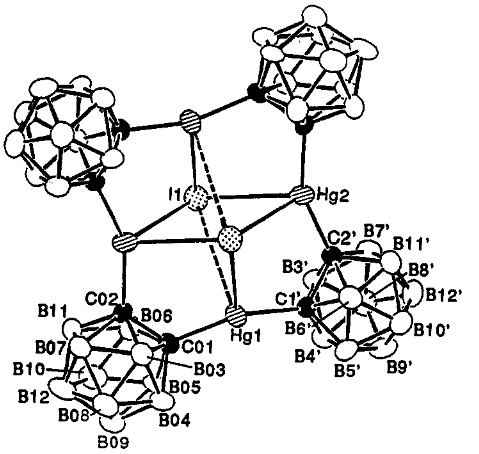

Figure 4. ORTEP representation of $1\cdot I_2^{2-}$ with hydrogen atoms removed for clarity.

consists of four bivalent *closo*-9,12-Et_2-1,2-$C_2B_{10}H_8$ cage fragments linked by four Hg atoms in a cyclic tetramer with structural parameters similar to those observed in $1\cdot Cl^-$ and $\mathbf{2a}\cdot\mathbf{8}_2$. The **10** components of the aggregate have a bicapped square antiprismatic structure, as expected. The eight apex–equatorial B–B distances of each complexed **10** average to 1.69(2) Å, the four equatorial–equatorial B–B distances adjacent to the host average to 1.84(2) Å, and the remaining four average to 1.85(2) Å. The remaining eight interactions across the equatorial belt of **10** average to 1.81(2) Å. All of these distances are quite similar to the values previously reported for $Cu_2B_{10}H_{10}$.[23] The bonding of **10** with **2a** consists of equatorial B–H–Hg three-center two-electron interactions with Hg–H distances ranging from 2.18 to 3.1 Å. Similar interactions were observed in $Cu_2B_{10}H_{10}$ with Cu–H distances of 1.7–2.2 Å.[23] The van der Waals distance of Hg- -H is 2.93 Å. The component borane cages are slightly tilted, one cage toward Hg1 giving a short Hg1–H4B (2.18 Å) and long Hg1,2–H2B (3.1 Å) and the second cage toward Hg1,2 in a symmetry related fashion.

^{199}Hg NMR Studies. The ^{199}Hg nucleus has a spin quantum number of $I = {}^1/_2$ and a moderately large natural abundance (16.9%). Consequently, ^{199}Hg NMR spectroscopy has been

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(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(22) Stanko, V. I.; Struchkov, Yu. T. *Zh. Obshch. Khim.* **1965**, *35*, 930.

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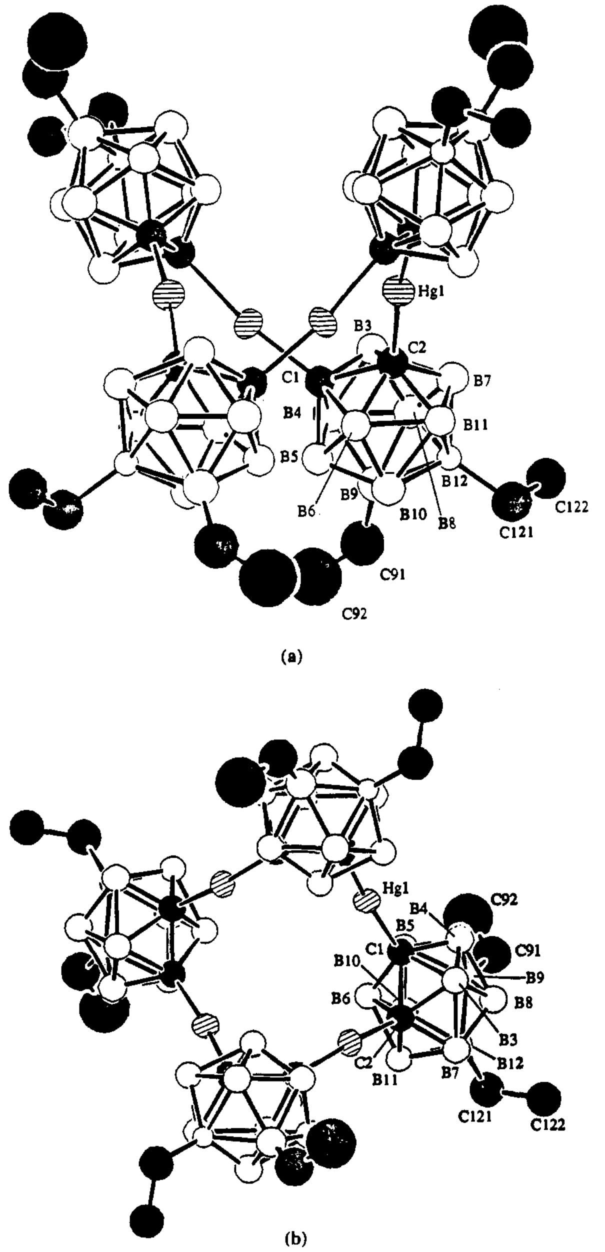

Figure 5. ORTEP representations of **2a** with hydrogen atoms removed for clarity: (a) side view; (b) top view.

employed in studies of biological systems and the interactions of organomercurials with a variety of bases and ligands.[24,25] The extreme sensitivity of ^{199}Hg chemical shifts to the immediate environment of Hg makes ^{199}Hg NMR very useful in the study of the system at hand and especially so since species **1–3** and their anion complexes have very similar ^{13}C and ^{11}B NMR spectra. Of principal interest here is the study of the interaction of hosts **1–3** with nucleophilic species in solution.

The ^{199}Hg NMR data of **1–3** and their anion complexes are listed in Table 3. The observed chemical shifts range from –1364 ppm for **3** in THF to –610 ppm for **2b**·I_2Li_2 in acetone. The chemical shifts of **1**, **2a**, and **3** are among the highest field chemical shifts reported[26] for diorganomercurials at –1300 in THF, –1221 in $CDCl_3$, and –1364 ppm in acetone-d_6, respectively, while linear [*closo*-1-(-1,2-$C_2B_{10}H_{11}$)]$_2$Hg has a chemical shift of –1332 ppm in acetone-d_6.[27] In comparison, diorganomercury compounds cover the range $\delta = 0$ (neat Me_2Hg) to –1187 ppm for [HgPh-(CBr_2Cl)] in DMSO (1 M).[25] Vinyl and aryl groups are known to cause higher shielding than alkyl groups in diorganomercurials, and Hg(tBu)$_2$ is the most highly shielded of simple dialkylmercurials with $\delta = -829$ ppm (50% in toluene).[28] It was pointed out that each successive substitution of methyl for hydrogen in one or both methyl groups of $HgMe_2$ gives incremental and additive shielding increases, $\Delta\beta = -148$ ppm. Therefore, in the case of dicarboranylmercurials, carborane cages might be responsible for the high shielding, since carborane carbon atoms are highly coordinated with a formal coordination number of six. In addition, the *closo*-1-(-1,2-$C_2B_{10}H_{11}$) group is strongly electron-withdrawing.[15]

Chemical shifts taken from Table 3 are **1**·ClLi, –1077 ppm; **1**·BrLi, –1010 ppm; **1**·ILi, –810 ppm; and **1**·I_2Li_2, –714 ppm in acetone. Similarly, **2a**·ILi and **2a**·I_2Li_2 have chemical shifts of –774 and –674 ppm in acetone, respectively. It is well-known that ^{199}Hg resonances of organomercurials exhibit large dependencies upon both solvent and concentration.[25,29] However, anion complexes of **1–2** have ^{199}Hg chemical shifts which are essentially independent of concentration and solvent identity at room temperature. This suggests that the solid-state structures of the **1**·X_n^{n-} ions (X = Cl, Br, $n = 1$; X = I, $n = 1, 2$) are maintained in solution with a planar host containing Hg atoms displaced toward the center of the tetrameric cycle. The carborane cages and halide ions virtually surround the mercury-binding sites in the anion complexes, and it is therefore unlikely that solvent molecules strongly coordinate to the Hg atoms of the cyclic host. The downfield shifts which occur upon complexation of halide ions to host **1** are 130, 200, and 390 ppm for Cl^-, Br^-, and I^- ions, respectively. Similar downfield shifts were also observed in RHgX and HgX_2 systems upon the formation of $RHgX_2^-$ and HgX_3^-. For halide complexes such as RHgX and HgX_2, the iodide ion complexes have chemical shifts upfield relative to those of the corresponding chloride ion complexes. It was therefore tentatively concluded that the shielding effect of halide ions has the order I > Br > Cl when halide ions are covalently bonded to mercury atoms, as observed in other metal halide complexes. However, upon the complexation of MeHgX with halide ions to form $MeHgX_2^-$, the chemical shift changes are about the same for iodide, bromide, and chloride with downfield shifts of 218, 227, and 208 ppm, respectively.[29] It appears that two factors influence the ^{199}Hg chemical shifts of $RHgX_2^-$. One is the shielding of the halide ion added to RHgX (secondary halide), and the other is the shielding of X^- present in the original RHgX. These two effects seem to cancel each other in the case of $MeHgX_2^-$, and therefore the downfield shifts are almost the same for X = Cl^-, Br^-, and I^-. Unlike previous studies, the study reported here employs the same host for complexation of different halide ions, and therefore the acidity of the host component remains constant. However, I^- is known to be a softer base than Cl^-, and Hg(II) is a soft acid.[31] Thus, the larger deshielding effect of I^- compared to Cl^- and Br^- for the **1**·X^- species is presumably due to stronger interaction between I^- and **1** and possibly the larger deshielding effect of the secondary bonded iodide ion to Hg(II). However, it is noteworthy that the additional deshielding provided by the second iodide ion in **1**·I_2^{2-} is only 96 ppm. Therefore, the

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in **2a**, **2a**·$\mathbf{7}_2$, and **2a**·$\mathbf{8}_2$(PMePh)$_4$[a]

		2a			
Hg1–C1	1.99(2)	Hg1–C2,2	2.12(2)	C1–C2	1.75(3)
C1–Hg1–C2,2	170.5(9)[a]	Hg1–C1–C2	120.0(15)		
		2a·$\mathbf{8}_2$			
Hg1–I9″	3.584(2)	Hg1–I9″,2	3.463(2)	Hg2–I9″,2	3.553(2)
Hg2–I9″	3.618(3)	B9″–I9″	2.27(4)		
Hg1–C1	1.99(2)	Hg1–C1A	2.04(2)	Hg2–C2A	2.13(2)
Hg2–C2	2.10(3)	C1–C2	1.71(3)	C1A–C2A	1.60(2)
C1–Hg1–C1A	163.9(10)	C2A–Hg2–C2	167.1(10)	C2A–C1A–Hg1	132(2)
C2–C1–Hg1,2	129.2(16)	C1–C2–Hg2,2	125.1(16)	C1A–C2A–Hg2	124.8(16)
		2a·$\mathbf{7}_2$			
Hg1–I12	3.445(2)	Hg1–I12,2	3.626(2)	Hg2–I12,2	3.620(2)
Hg2–I12	3.549(3)	B9E–I9	2,31(4)	B12E–I12	2.19(4)
Hg1–C1B	2.05(3)	Hg1–C1A	2.05(3)	Hg2–C2A	2.04(3)
Hg2–C2B	2.10(2)	C1B–C2B	1.69(4)	C1A–C2A	1.73(4)
C2B–Hg1–C1A	161.6(10)	C2A–Hg2–C1B	165.1(10)	C2A–C1A–Hg1	127(2)
C2B–C1B–Hg2	126.3(17)	C1A–C2A–Hg2,2	128(2)	C1A–C2A–Hg1,2	127.1(16)
		2a·$\mathbf{10}_2$(PMePh$_3$)$_4$			
Hg1–C1	2.077(11)	Hg1–C1′	2.076(12)	Hg2–C2,2	2.112(13)
Hg2–C2′	2.129(12)	C1–C2	1.63(2)	C1′–C2′	1.66(2)
Hg1–H4B	2.18(2)	Hg1,2–H2B	3.1(1)	Hg2,2–H3B	2.84(12)
Hg2–H5B	2.75(12)	Hg1,2- -B2B	3.49(1)	Hg2,2- -B3B	3.56(1)
Hg2- -B5B	3.56(1)	Hg1- -B4B	3.55(1)		
C1–Hg1–C1′	164.6(4)	C2′–Hg2–C2,2	157.5(5)	C2–C1–Hg1	126.4(7)
Hg1–C1′–C2′	128.8(8)	Hg2–C2′–C1′	121.9(7)	C1–C2–Hg2,2	125.5(8)
Hg1–H4B–B4B	141(8)	Hg1,2–H2B–B2B	117(9)	Hg2–H5B–B5B	112(8)
Hg2,2–H3B–B3B	121(8)				

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

contribution of deshielding by halide ions to the ^{199}Hg NMR spectra should be interpreted with caution.

Previous studies of halide exchange and complexation of mercuric complexes have shown that fast exchange, compared to the NMR time scale, was always observed.[30] For example, mixtures of HgCl$_2$ and HgBr$_2$ in ethanol gave only a single peak at an intermediate position between those characteristic of HgCl$_2$ and HgBr$_2$. In contrast to these observations, mixtures of **1**·ClLi and **1**·BrLi in acetone exhibit two discrete resonances which correspond to the two individual complexes. Consequently, the exchange between chloride and bromide ions complexed to **1** is too slow to produce a single time-averaged ^{199}Hg NMR signal. Similarly, a mixture of **1**·ILi and **1**·I$_2$Li$_2$ displays two characteristic ^{199}Hg resonances during the conversion of **1**·I$^-$ to **1**·I$_2^{2-}$ by the addition of *n*Bu$_4$NI to a solution of **1**·ILi (Figure 9). The characteristic solvent- and concentration-independent ^{199}Hg chemical shift of each of these complexes in solution allows the study of halide ion exchange and association with **1** in solution although more than one species is present under these conditions.

Anion Complexation. The conversion of **1** to **1**·I$_2^{2-}$ was studied by ^{199}Hg NMR spectroscopy. The incremental addition of *n*Bu$_4$NI to an acetone-*d*$_6$ solution of **1** results first in the formation of **1**·I$^-$, followed by **1**·I$_2^{2-}$, as demonstrated by the ^{199}Hg NMR spectra shown in Figure 9 and in accord with Scheme 5. When more than 2 equiv of *n*Bu$_4$NI was added to the acetone-*d*$_6$ solution of **1**, no further change in the spectrum was observed, proving that **1**, in agreement with the solid-state structure of **1**·I$_2^{2-}$, is not capable of hosting more than two iodide ions. We thus suggest that the solid-state structure of **1**·I$_2^{2-}$ is largely maintained in solution. It is also suggested that **1**·I$_2^{2-}$ is sufficiently stable that its exchange with bulk iodide ions is sufficiently slow to not be observed by NMR. In the case of 1,2-phenylenedimercuric dichloride, the addition of chloride anion shifted the ^{199}Hg resonance downfield and only a single resonance was observed, even though more than one species was believed to be present in the solution.[5a]

Unlike **1**·I$_2^{2-}$, **1**·X$^-$ (X = Cl, Br) exchange with added chloride or bromide ions is observed by ^{199}Hg NMR. As shown in Figure 10, the addition of Ph$_4$AsCl to an acetone solution of **1**·ClLi results in line broadening of the single resonance, which can be explained by the fast exchange of chloride ions between mercury-binding sites, as observed in the case of tricyclic tin hosts, with fluoride ion exchanging between two tin sites.[6a] Since chloride ion is much smaller than iodide ion, it is unlikely, because of mutual repulsion between the two chloride ions, for the hypothetical chloride ion exchange intermediate **1**·Cl$_2^{2-}$ to have a structure analogous to that of **1**·I$_2^{2-}$. A possible structure for an exchange intermediate might contain a buckled host which binds chloride ions located outside the cavity (Scheme 4) in a fashion similar to that of the THF molecules in **1**·(THF)$_4$(H$_2$O)$_2$.[13c] This host conformation would allow chloride ions to rapidly migrate between the four mercury atoms, and **1** could accommodate as many as four bidentate chloride ions for exchange with bulk chloride ion. A similar structure with chloride ion bridging two mercury atoms was observed in **4**$_2$·Cl$^-$.[5b] It was also reported,[5a] as a consequence of a ^{199}Hg NMR study, that the **4**·Cl$^-$ complex is present in solution with Cl$^-$ held in a bidentate fashion by **4**.

The addition of 1 equiv of *n*Bu$_4$NI to **1**·ClLi in acetone results in the formation of **1**·I$_2^{2-}$ instead of **1**·I$^-$, as detected by ^{199}Hg NMR. Only the one resonance characteristic of **1**·I$_2^{2-}$ was observed along with an uneven baseline. Equilibria possibly present in such a solution are shown in eqs 3–5. The apparent

$$\mathbf{1}\cdot\mathrm{Cl}^- + \mathrm{I}^- \rightleftharpoons \mathbf{1}\cdot\mathrm{I}^- + \mathrm{Cl}^- \qquad (3)$$

$$\mathbf{1}\cdot\mathrm{I}^- + \mathrm{Cl}^- \rightleftharpoons {}^1/_2\mathbf{1}\cdot\mathrm{I}_2^{\ 2-} + {}^1/_2\mathbf{1}\cdot\mathrm{Cl}^- + {}^1/_2\mathrm{Cl}^- \qquad (4)$$

$${}^1/_2\mathbf{1}\cdot\mathrm{Cl}^- + {}^1/_2\mathrm{Cl}^- \rightleftharpoons {}^1/_2\mathbf{1}\cdot\mathrm{Cl}_2^{\ 2-} \qquad (5)$$

rapid exchange, as described above, between **1**·Cl$^-$ and the produced chloride ion could result in the collapse of the peak expected for **1**·Cl$^-$. In another ^{199}Hg NMR experiment, the addition of 1 equiv of Ph$_4$AsCl to **1**·I(*n*Bu$_4$N) in acetone results in the formation of **1**·I$_2^{2-}$ (Scheme 5). These results indicate that **1**·I$_2^{2-}$ is the thermodynamically most stable complex present in these solutions. The high preferential stability of **1**·I$_2^{2-}$ may be attributed to the saturation of all available mercury p-orbitals

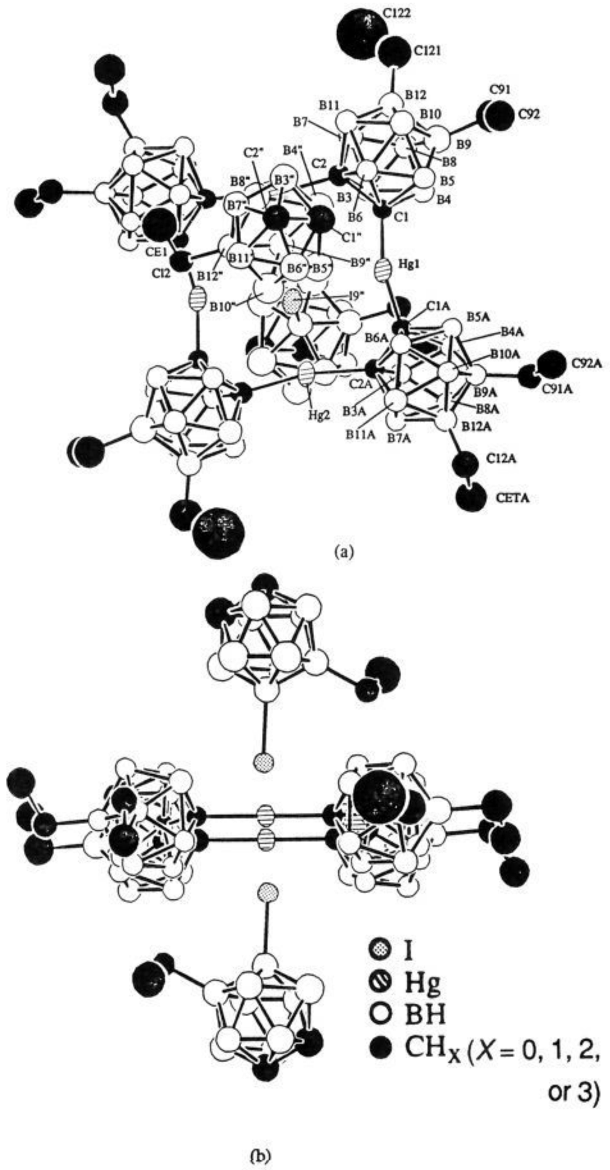


Figure 6. ORTEP representation of **2a**·**8**$_2$ with hydrogen atoms removed for clarity: (a) side view; (b) top view.

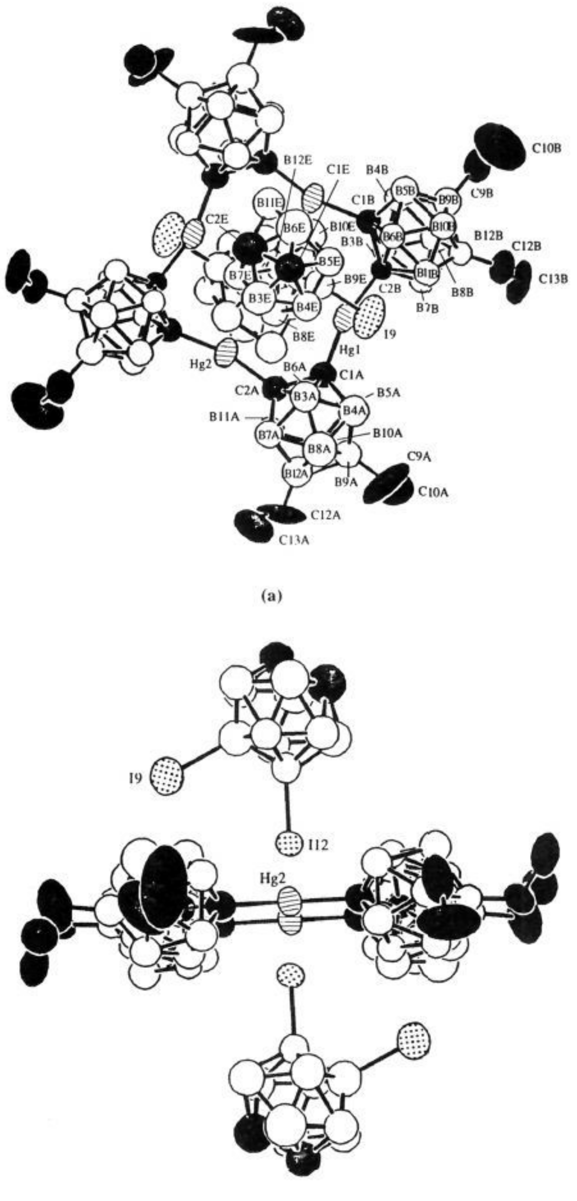


Figure 7. ORTEP representation of **2a**·**7**$_2$ with hydrogen atoms removed for clarity: (a) side view; (b) top view.

associated with the strong interaction between the soft Lewis acid, Hg(II), and the soft Lewis base, I$^-$.[31]

The high stabilities of the halide ion complexes of **1** coupled with their insolubility in water precluded the determination of equilibrium constants for complexation. The synthesis of water-soluble, hydrophilic [12]mercuracarborand-4 species will allow the required measurements to be made with accuracy.[13g]

Interaction of 8 with 2a in CHCl$_3$. The interaction of **8** and **2a** was studied by ^{199}Hg NMR. Upon addition of 1 equiv of **8** to the CDCl$_3$ solution of **2a**, line broadening of the resonance was observed, accompanied by a downfield shift of 5 ppm from that of **2a** to −1216 ppm. The line broadening could be explained by a weak interaction between **2a** and **8** which results in a rapid and reversible process (Scheme 5), since it is anticipated that the neutral **8** is a much weaker base than the halide ions.

Interaction of 10 with 1 and 2a in Solution. The intermolecular interaction of *closo*-$B_{10}H_{10}^{2-}$ (**10**) with [12]mercuracarborand-4 (**1**) and its octaethyl derivative (**2a**) was studied in organic solvents (acetone, CH$_2$Cl$_2$, and CH$_3$CN) using ^{11}B and ^{199}Hg NMR spectroscopy.[13e] The ^{11}B NMR spectrum of **10**(Ph$_3$MeP)$_2$ in CH$_2$Cl$_2$ exhibited two doublets at 0.83 and −27.3 ppm with a 1:4 ratio, corresponding to apical and equatorial boron atoms, respectively. Upon the addition of 1 equiv of **1** or **2a** in CH$_3$CN/CH$_2$Cl$_2$ (1:1), the doublet at −27.3 ppm splits into a broad singlet at −23.3 ppm and a sharp doublet of equal intensity at −26.9 ppm. These new resonances can be explained by the formation of 1:1 adducts of **10** with **1** or **2a** in which four equatorial BH groups of **10** simultaneously bond to four mercury atoms in **1** or **2a**, using B–H–Hg three-center two-electron bonds. No coupling of the ^{11}B nuclei with the protons or ^{199}Hg nuclei present in B–H–Hg bridges was observed.

The ^{199}Hg NMR spectrum of the 1:1 aggregate of *closo*-$B_{10}H_{10}^{2-}$ and **1** exhibits a resonance at −1002 ppm (Figure 11c) in CH$_3$CN/acetone (1:1), while the free host (**1**) itself appears at −1212 ppm (Figure 11a) in the same solvent. In comparison, **1**·Cl$^-$ and **1**·Br$^-$ in acetone exhibit resonances at −1077 and −1010 ppm, respectively. Two resonances which correspond to the 1:1 adduct and free **1** were observed when **10**(Ph$_3$MeP)$_2$ and **1** were combined in acetone/CH$_3$CN solution in a 1:2 ratio (Figure 11b), thus substantiating the suggestion that **10** cannot simultaneously bind two molecules of **1** in CH$_3$CN/acetone solution. Similarly,

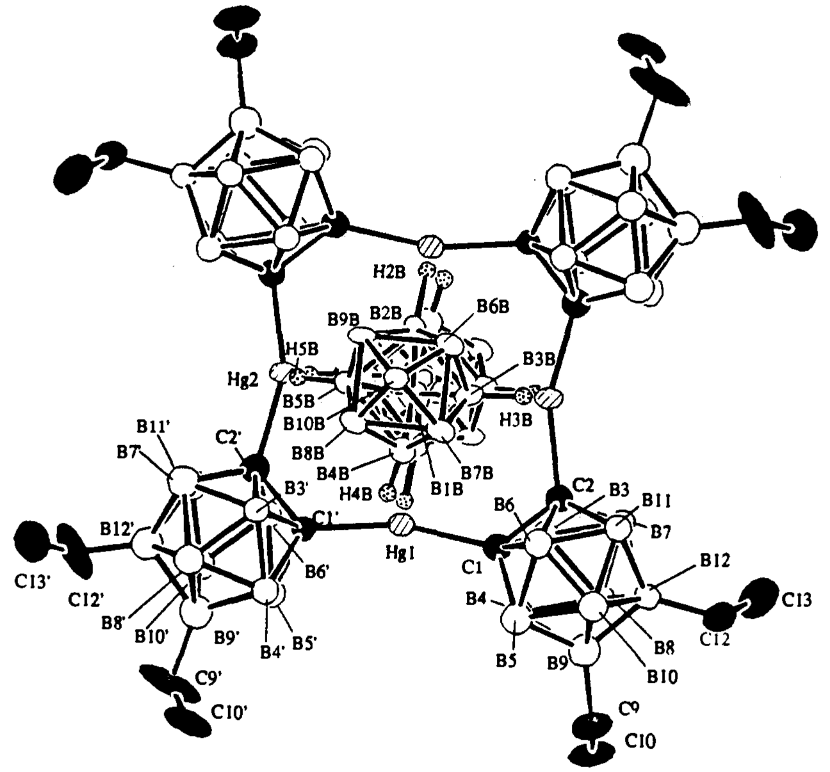


Figure 8. ORTEP representation of **2a**·**10**$_2$ with hydrogen atoms other than those in B–H–Hg bonds removed for clarity.

Table 3. ^{199}Hg NMR Chemical Shifts of **1**, **2a**, and **3** and Their Complexes[a]

compounds	δ (ppm)	ref
$(1,2\text{-}C_2B_{10}H_{11})_2Hg$	–1332[b]	27
1	–1300[b]	13c
1	–1212	13c
1·ClLi	–1077	13a
1·BrLi	–1010	this work
1·ILi	–810	13b
1·I_2Li_2	–714	13b
1·**10**	–1002[c]	13e
2a	–1200[d]	this work
2a	–1221[e]	this work
2a·ILi	–774	this work
2a·I_2Li_2	–674	this work
2a·**10**	–939	this work
2b·I_2Li_2	–610	this work
3	–1364	13d
3·ClLi	–1021	13d

[a] See Experimental Section for the experimental conditions. Acetone-d_6 was used as solvent unless otherwise stated, and all spectra were proton decoupled. [b] In THF. [c] In CH_3CN/acetone (1/1). [d] In benzene-d_6. [e] In $CDCl_3$.

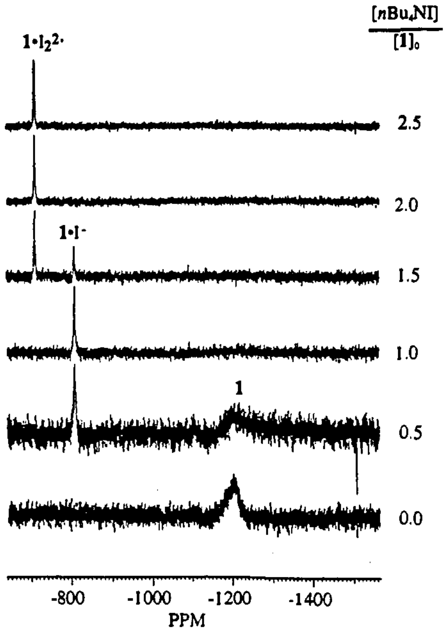


Figure 9. ^{199}Hg NMR spectra illustrating the sequential reaction of **1** with added *n*Bu_4NI in acetone solution.

2a·**10** in CH_3CN/acetone-d_6 displays a ^{199}Hg NMR resonance at –939 ppm. Addition of **10**$(Ph_3MeP)_2$ to this **2a**·**10**$(Ph_3MeP)_2$ solution results in no change of the chemical shift. The ^{11}B NMR of a 2:1 mixture of **10**$(Ph_3MeP)_2$ and **2a** in CH_3CN (Figure 12) exhibits a broad peak at –24.9 ppm and a doublet at –28.5 ppm. The broad peak is assigned to the equatorial boron atoms that provide binding to **2a**, and the doublet is assigned to a combination of resonances from the free **10** and the four remaining equatorial boron atoms which are not directly bonded to **2a** in the complex. The intensity ratio of these two peaks is 3:1, which is consistent with the fact that the acetonitrile solution contains equivalent quantities of **2a**·**10** and free **10**. The resonance observed at –0.5 ppm is assigned to apical boron atoms which are not affected upon complexation of **10** to **2a**. The other broad resonances are due to the BH vertices in **2a**. These NMR studies indicate that the **2a**·**20**$_1$ adduct is not present in detectable amounts in solution, even though in the solid state **2a**$(\mathbf{10})_2(Ph_3MeP)_4$ was crystallized from CH_3CN/CH_2Cl_2 solution.[13e] A similar result has been reported with a 1:1 mixture of $AsPh_4Cl$ and **4** in methylene chloride from which a 2:1 adduct, $(\mathbf{4}_2\cdot Cl)AsPh_4$, is precipitated upon the addition of hexane,[5a,5b] even though the 1:1 complex is the predominant species present in solution, as suggested by ^{199}Hg NMR. Thus far, all of the structurally characterized complexes of **1** or **2a**, with the single exception of **1**·Br$^-$, have crystallographically imposed inversion symmetry, and 2:1 complexes with **1** or **2a** preferentially crystallize when a choice exists.

Formation of 1·(phen)$_2$. Host **1** and 1,10-phenanthroline (phen) were combined in acetone solution in a ratio of 1:2. Colorless crystals subsequently formed upon evaporation of the solvent. The ^{1}H NMR spectrum of these crystals (acetone-d_6) exhibits

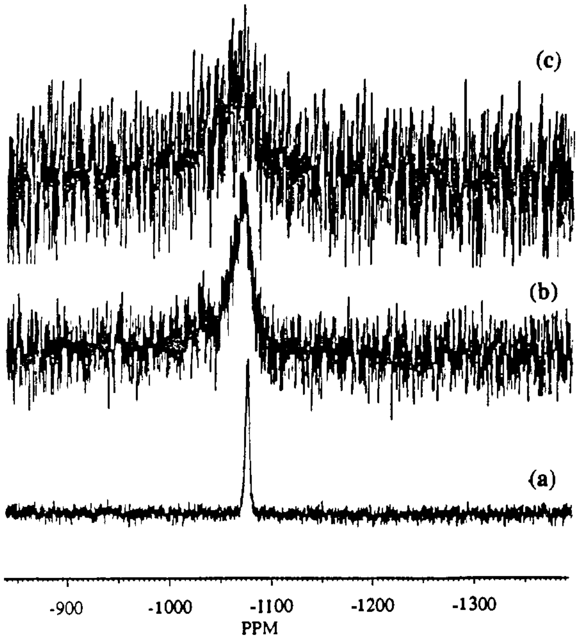
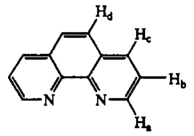


Figure 10. ^{199}Hg NMR studies on the addition of $(AsPh_4)Cl$ to **1**$\cdot Cl^-$ in acetone solution with $(AsPh_4)Cl$/**1**$\cdot Cl^-$ ratios of (a) 0.00; (b) 0.25; and (c) 0.50.

different chemical shifts of the phen protons when compared with those of free phen. A preliminary X-ray structure analysis proved that **1**$\cdot$(phen)$_2$ has a structure similar to that of **1**$\cdot$(THF)$_4$, as shown below. It is known that phen is capable of symmetrizing organomercury compounds such as RHgX. However, the reaction of phen with *closo*-1-(-1,2-$C_2B_{10}H_{11}$)HgX (X = halide) does not lead to symmetrization but to a series of phen adducts. It was suggested that the strong –I effect of the *closo*-1-(-1,2-$C_2B_{10}H_{11}$) cage favors the formation of Lewis acid–base adducts.[32]



	H$_a$	H$_b$	H$_c$	H$_d$
Phen	9.16 (dd)	7.72 (dd)	8.43 (dd)	8.11 (s)
1·(Phen)$_2$	9.05 (s,br)	7.88 (dd)	8.64 (d)	7.94 (s)

Discussion

Synthesis. The synthesis of **1**$\cdot$XLi (X = Cl, Br, I) is significant, since a macrocyclic multidentate Lewis acidic host, **1**, is efficiently produced in a single reaction. It is believed that halide ions function as templates which direct the assembly of tetrameric host macrocycles, since cyclic trimer **3** is formed in the absence of halide ion (Scheme 1). It is also observed that the reaction of *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{10}$ with mercuric halides gives higher yields of cyclic tetramer than the corresponding reaction with HgOAc, which yields cyclic trimer. The fact that cyclic tetramers are always isolated as their halide ion complexes supports the suggestion that[13a,d] halide ions exercise a template effect in the formation of such mercuracarborands. A reaction is described as being controlled by a kinetic template effect if it provides a route to a product that would not be formed in the absence of a template.[33] Consequently, the syntheses of **1**, **2a**, and **2b** arise from such kinetic template reactions. The species **1**$\cdot$ClLi might be formed via routes shown in Scheme 6. Attempts to synthesize **C** by the reaction of 2 equiv of $HgCl_2$ with *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{10}$ result in a mixture of products which includes **1**$\cdot$ClLi as a major and **F** as a minor component, as detected by ^{199}Hg NMR and negative-ion FAB mass spectroscopy. No **C** was detected in the mass spectrum of the product mixture. When an ethereal slurry of *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{10}$ was added to an ether solution of $HgCl_2$ at room temperature, **1**$\cdot$ClLi was still formed as a major product, which might indicate that the self-cyclization of **B** through **D** and **E** to **1**$\cdot Cl^-$ is faster than the reaction of $HgCl_2$ with the anion **B** to form **C**. The presence of Cl^- ion in **E** prevents its cyclization to form the cyclic trimer **3**, whose formation is favored in the absence of halide ion. The fact that the larger iodide ion serves as a template for the same cyclic tetramer as chloride ion indicates that mercuracarborand cycles larger than tetramers are probably too strained to allow facile formation by pathways similar to those of Scheme 6.

Failure to observe species **C** in the presence of excess $HgCl_2$ is not unexpected. It has been reported[34] that the reaction of *closo*-1-Li-1,2-$C_2B_{10}H_{11}$ with mercuric dihalides almost invariably produces symmetrical [*closo*-1-(-1,2-$C_2B_{10}H_{11}$)]$_2$Hg, even when the mercuric dihalide is present in large excess. Moreover, symmetrical [*closo*-1-(-2-Ph-1,2-$C_2B_{10}H_{10}$)]$_2$Hg only reacts with $HgCl_2$ in nitrobenzene at high temperature to slowly produce [*closo*-1-(-2-Ph-1,2-$C_2B_{10}H_{10}$)]HgCl in low yield.[35] These results were rationalized as being due to the high coordination number of carborane carbon vertices, steric hindrance of the icosahedral cage, and the electron-withdrawing properties of the carborane moiety. These chemical properties of the mercuric carboranes are ideally suited to the formation of symmetrical cycles such as **1** and **3**, as shown in Scheme 6, even though we observed the nonsymmetrical **F** as a minor product in the negative-ion FAB-MS.

Icosahedral *closo*-1,2-$C_2B_{10}H_{12}$ is known to be "aromatic", as is benzene, and benzene sweeps out a similar volume when it is rotated 180° about an in-plane axis. It is therefore noteworthy that the reaction of 1,2-dibromobenzene with sodium amalgam was initially reported to give hexameric *o*-phenylenemercury ($(C_6H_4Hg)_6$)[36a] on the basis of a solution molecular weight determination[37,38] and X-ray crystallography.[36b] However, it was later determined that *o*-phenylenemercury is actually trimeric and planar.[20] Although, in principle, hexameric and tetrameric *o*-phenylenemercury could exist, only the trimeric species was detected.[36c] Massey has approached the syntheses of hexameric and tetrameric *o*-phenylenemercury by modifying the electronic and/or steric properties of the constituent *o*-phenylene groups.[36c,d] In all cases only trimeric products were obtained. The reaction of 1,2-diiodotetrafluorobenzene with mercury at 200 °C yields tetrafluoro-*o*-phenylenemercury trimer **5**,[36c] which was recently found to bind halide ions[14a] in a fashion resembling that of mercuracarborands. The synthesis pathway leading to **5** is obviously quite different from that suggested in Scheme 6, in which the mercuric halide is the mercury source, rather than mercury metal and/or sodium amalgam, and the role of an anion template effect is not apparent in the syntheses of these *o*-phenylenemercury derivatives. Consequently, it may prove possible to prepare *o*-phenylenemercury tetramer from 1,2-$Li_2C_6H_4$[37,38] and mercuric halides. Previously, the reaction of 2,2′-dilithiobiphenyl ($Li_2C_{12}H_8$) with $HgCl_2$ was shown to produce the corresponding trimeric and tetrameric biphenylenemercury species.[36d]

Recently, Müller and his co-workers reported several examples of anion-directed self-assembly of inorganic O═VO_4 square pyramids to form cage hosts which encapsulate anionic guests

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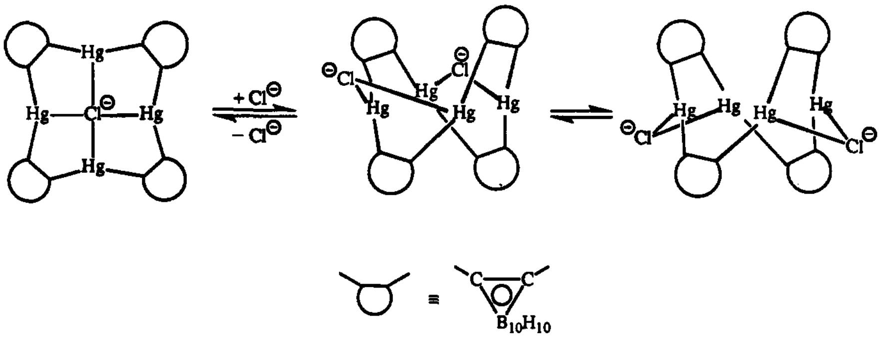
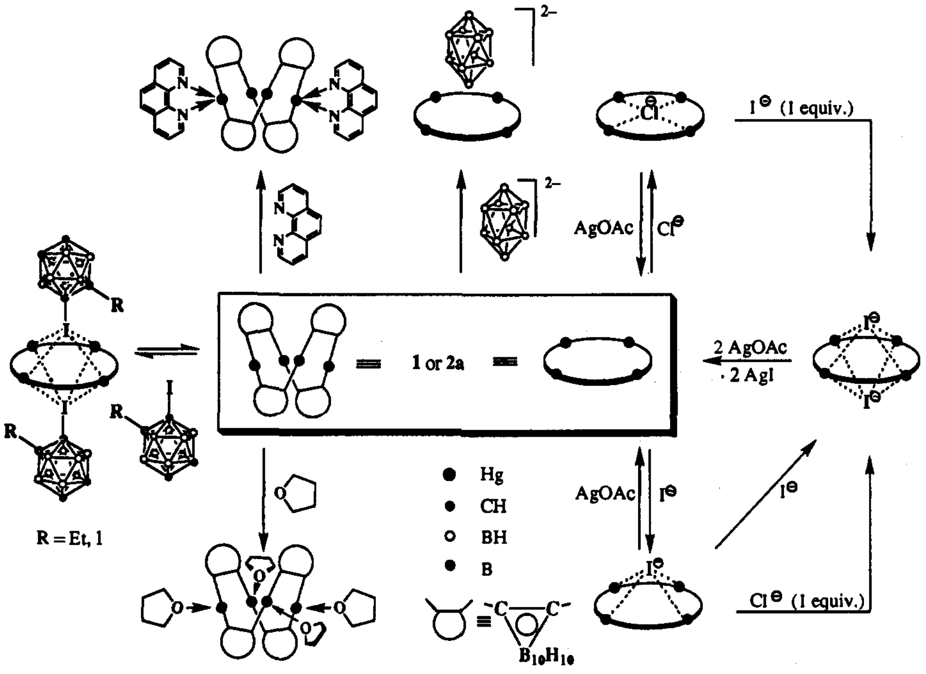
Scheme 4



Scheme 5



within polyhedral cages.[39] An "anion template" effect has recently been demonstrated in the synthesis of "expanded porphyrin" species in which higher yields of the macrocycle were achieved in the presence of added nitrate ion, although in the absence of nitrate the same macrocycle was formed, but in lower yields.[40,41]

Synthesis of Hosts 1 and 2a. The synthesis of free cyclic host species **1** and **2a** was achieved by reaction of their iodide ion complexes with silver ion to form AgI. Both silver nitrate and acetate were investigated, and the acetate was found to provide a superior Ag^+ source, since acetate ion does not coordinate to hosts **1** and **2a**. The product isolation steps must be rapidly completed to minimize the oxidation of carborane cages by Ag^+. The use of $AgNO_3$ produced **1** contaminated by nitrate ion.

Use of the *closo*-1,2-Carborane Cage in Host Construction. The utilization of *closo*-1,2-carborane cages in the construction of **1**–**3** is structurally similar to the use of arylene units in benzocrown ether hosts. The inductive electron-withdrawing nature of the bivalent *closo*-1,2-carborane moieties facilitates the synthesis of these new hosts and greatly increases the acidity of their component Hg(II) centers, which, in turn, enhances the stabilities of the mercuracarborand adducts. Mercuric carborane species are, in general, exceptionally stable. It was reported that $[closo\text{-}1\text{-}(\text{-}2\text{-Ph-}1,2\text{-}C_2B_{10}H_{10})]_2Hg$ fails to react either with hydrogen chloride in ethanol at the reflux temperature or with bromine after 10 h in boiling dichloromethane or benzene.[35] The

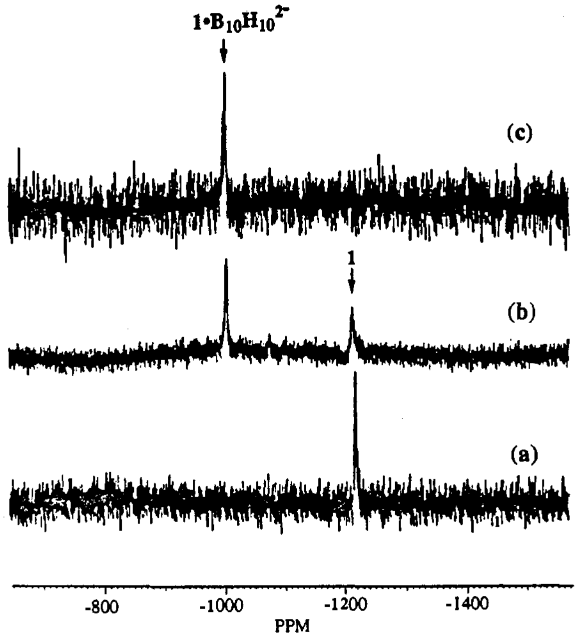


Figure 11. ^{199}Hg NMR studies on the addition of **10** to an acetone solution of **1** with **10**/**1** ratios of (a) 0.0; (b) 0.5; and (c) 1.0.

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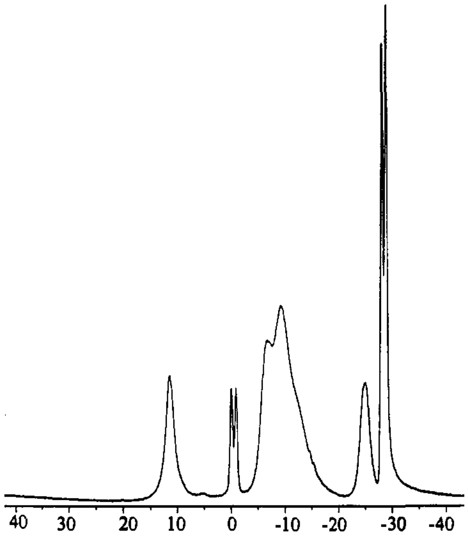


Figure 12. ^{11}B NMR spectrum of a 2:1 mixture of **10**$(Ph_3MeP)_2$ and **2a** in acetonitrile.

high thermal stability and insensitivity to electrophilic attack are attributed to the high coordination number of carborane carbon atoms, steric hindrance associated with carborane cages, and their characteristic -I effect. On the other hand, the Hg–C bonds of *closo*-1-(-1,2-$C_2B_{10}H_{11}$)-containing mercurials are susceptible to attack by strongly nucleophilic reagents such as $LiAlH_4$ and *n*BuLi, usually resulting in cleavage of the Hg–C bond. Since the carborane components of the mercuracarborands are three-dimensional cages, in their planar conformation compounds **1–3** provide a ring thickness of about 3 Å, which may inhibit the approach of reactants to the anion complexes of **1** and **2a**, thereby increasing their kinetic stabilities.

The possibility of functionalizing the carborane cage components of mercuracarborands provides many options in the design of hosts suited for a specific function. The quantitative synthesis of compound **9** has been reported by Li *et al.*[55] In contrast to this report, we recovered almost all the starting material, **7**, when attempting this reaction under the same conditions. Only upon the addition of copper(I) iodide as a cocatalyst could **9** be obtained in a moderate yield along with compound **8** as the major byproduct. We have demonstrated that the 9,12-substituted carborane cage can be used to form a hydrocarbon-soluble host (**2a**) and that the 3-phenyl-substituted carborane cage will form stereoisomeric and tetrameric hosts with sterically encumbered cavities.[13f]

Structural Comparisons among Mercury-Containing Hosts. Cyclic oligomers of the $(1,2\text{-}C_6H_4Hg)_n$ series were predicted to be stable for values of $n = 3, 4, 6,$ and 8 using Dreiding models,[36c,d] assuming all C–Hg–C angles were 180° and the Hg- -Hg distances were ≥3.5 Å. Only the trimer $(1,2\text{-}C_6H_4Hg)_3$ has been structurally characterized.[20] The 1,2-phenylenemercury trimer has linear C–Hg–C angles, 0° Hg–C–C–Hg torsion angles, and Hg- - -Hg distances of 3.57 Å. In comparison, trimeric **3** has essentially linear C–Hg–C angles, 2° Hg–C–C–Hg torsion angles, and Hg- -Hg distances of 3.729 and 3.734 Å.[13d] However, despite having linear C–Hg–C angles and adjacent Hg- -Hg distances of 3.775 Å, tetrameric **1**·$(THF)_4(H_2O)_2$ and **2a** have Hg–C–C–Hg torsion angles of 10 and 20°, respectively. Consequently, the tetrameric cycles are expected to be strained and thermodynamically less stable than the planar trimeric cycle. Upon complexation of nucleophilic guests at the center of the host, **1** and **2a** both adopt a planar configuration with nonlinear C–Hg–C angles ranging from 152.6(4)° in **1**·$I_2(AsPh_4)_2$ to 162.0(3)° in **1**·ClLi. These are the most distorted examples of Hg(II) linear coordination to be found in any diorganomercurial.[16] In addition, Hg–C–C angles (ca. 125°) observed in the anion complexes are distorted and larger than those (av. 119°) observed in **3**[13d] and (120.0(15)°) in free host **2a**. This type of distortion minimizes the deviation of C–Hg–C bonds from linearity. There is no significant difference in Hg–C bond distances for the organomercurial species listed in Table 4, even though the planar anion complexes of **1** and **2a** have nonlinear Hg(II) coordination. Shorter carborane C–C bonds are observed in these same complexes. The longer intracage C–C distances observed in **1**·$(THF)_4(H_2O)_2$ and **2a** might be due to the distorted coordination of carborane carbons, considering the large Hg–C–C–Hg dihedral angles observed in **1**·$(THF)_4(H_2O)_2$ and **2a**. In comparison with other host conformations, the strained planar conformation has the largest cavity (see Table 4 for Hg- -Hg distances), and four equivalent Lewis acid binding sites are positioned to provide the maximum complementary interaction with the guest. The resulting complexes are stable, although the host has an unfavorable planar conformation, which is compensated by strong host–guest interactions.

Qualitative Analyses of Guest–Host Bonding Interactions. In organomercury compounds, Hg(II) is normally sp-hybridized and forms two linear covalent bonds while retaining two empty and mutually perpendicular p-orbitals. The location of Cl^-, when placed within the host **1**, maximizes the cooperative interaction of four empty mercury orbitals with two filled p-orbitals originating at the chloride ion and essentially within the plane of the macrocycle. The trapped chloride ion is therefore bound to the host by a pair of three-center two-electron bonds (Chart 1A). Four empty p-orbitals perpendicular to the host ring are also present and arise from the set of four mercury atoms.

The bonding of two I^- ions to **1** in forming **1**·I_2^{2-} arises from the interaction of the filled p_x and p_y orbitals of both I^- 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_{Hg_2}–p_I–$p_{Hg_{2'}}$ three-center two-electron bonds are symmetrical while the remaining pair, p_{Hg1}–p_I–$p_{Hg1'}$, are unsymmetrical due to a lateral slippage of each guest I^- along its *x* axis. This distortion is thought to arise from *trans*-host repulsion of the filled p_z orbitals of each I^- guest, as depicted in the chart, since the I^-- -I^- distance in **1**·I_2^{2-} (3.969(1) Å) is shorter than the corresponding van der Waals distance (4.30 Å).

Related to iodide ion complexation in **1**·I_2^{2-} is the fact that each of the bonded iodine atoms present in pairs of **7** and **8** molecules apparently interact with **2a** via two equivalent three-center two-electron bonds (Chart 1C) in which R is *closo*-9-(-12-I-1,2-$C_2B_{10}H_{10}$) or *closo*-9-(-12-Et-1,2-$C_2B_{10}H_{10}$) and iodine is bound to B9 with an average Hg–I distance of 3.554(2) Å, which is longer than the similar interactions (3.277 and 3.305 Å) observed in **1**·I_2^{2-}. However, the van der Waals radius of iodine in **7** and **8** is expected to be significantly smaller than that in iodide ion because the latter bears a full negative charge. Since I^- is a more effective base than covalently bound iodine, the shorter I^-- -Hg interaction in **1**·I_2^{2-} is not unexpected. The Hg- -I distances in both **2a**·$\mathbf{8}_2$ and **2a**·$\mathbf{7}_2$ are shorter than the Hg- -I van der Waals distance, which is in the range 3.68–3.83 Å.[18,19,21] The *trans*-host I- -I distance (3.945 Å) in **2a**·$\mathbf{8}_2$ is close to that of the expected iodine van der Waals distance (3.90–4.20 Å), and therefore no apparent lateral slippage of the guests in **2a**·$\mathbf{8}_2$ is observed as in the case of **1**·I_2^{2-}.

Multiple binding is known to enhance the stability of host–guest complexes, and the principle of additive incremental binding has been applied to explain the increased stability of those complexes with a large number of redundant binding sites. For complex **2a**·$\mathbf{7}_2$, host–guest bonding could have involved both iodine atoms present in each **7** or only a single iodine atom, as observed. If both iodine atoms present in each **7** were to bind simultaneously to **2a**, each iodine center could only interact with a single mercury atom to form a two-center two-electron bond. A total of four such interactions would be present if two molecules of **7** bound to a single **2a**. When only one iodine atom from each of two **7**

Scheme 6

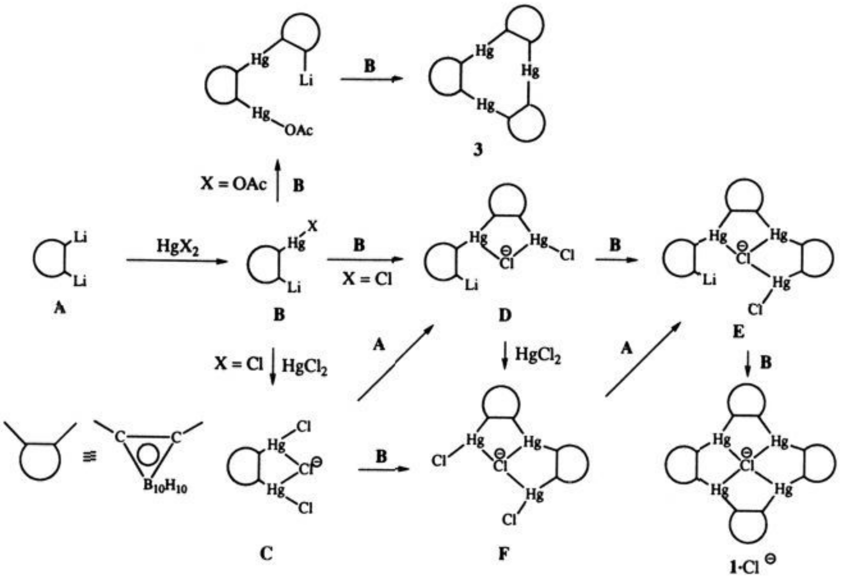
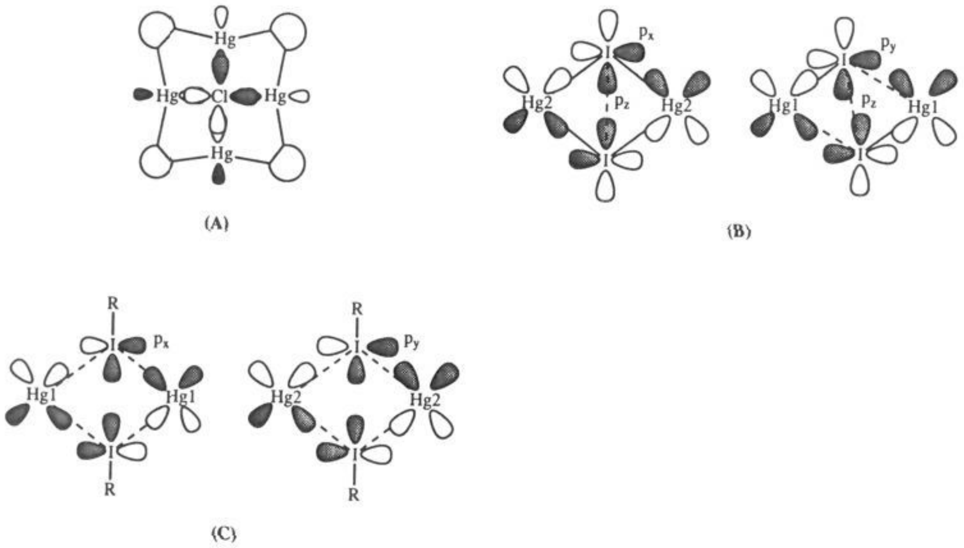


Table 4. Structural Comparison of Hosts **1**, **2a**, and **3** and Their Complexes Using Averaged Distances and Angles

compound	Hg–C (Å)	C–C (Å)	Hg- -Hg[a] (Å)	C–Hg–C (deg)	Hg–C–C (deg)	ref
$(o\text{-}C_6H_4Hg)_3$	2.10 (5)	1.43 (6)	3.57	178(2)	120(3)	17, 20
$(1,2\text{-}C_2B_{10}H_{11})_2Hg$	2.091 (2)	1.653 (6)		180.0	118.3(3)	27
3·$(CH_3CN)_3$	2.09 (2)	1.69 (3)	3.729(1)	177.1(9)	118.7(14)	13d
3·$(CH_3CN)_5$	2.10 (2)	1.67 (3)	3.734(1)	175.5(8)	119.3(13)	13d
1·$(THF)_4(H_2O)_2$	2.09 (9)	1.76 (3)	3.654(1)	167.7(8)	120.3(13)	13c
2a	1.99 (2)	1.75 (2)	3.775(2)	170.5(9)	120.0(15)	this work
1·ClLi	2.093 (13)	1.67 (2)	4.129(1)	162.0(4)	126.0(6)	this work
1·$I_2(AsPh_4)_2$	2.099 (9)	1.649 (13)	3.942(1)	155.3(4)	123.1(6)	this work
2a·**8**$_2$	2.07 (2)	1.65 (2)	4.183(2)	165.5(10)	127.8(17)	this work
2a·**10**$_2$	2.099 (12)	1.65 (2)	4.091(1)	161.1(5)	125.7(8)	this work

[a] Adjacent Hg- -Hg distances.

Chart 1



molecules is bound to **2a**, each iodine atom simultaneously interacts with four Hg centers and a total of four three-center two-electron interactions are present. The structure observed in the solid state is that in which molecule **7** has one iodine atom binding to **2a** while the remaining iodine atom is completely free, suggesting that maximum multiple binding and host–guest stereochemical congruency are dominant factors. Unlike purely electrostatic interactions, the coordinate covalent bonding discussed here is directional, and complementary orbital interactions provide the stabilization of supramolecular species such as **2a**·**7**$_2$ and **2a**·**8**$_2$.

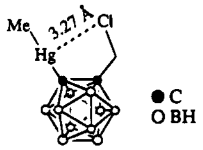
The interaction of each **10** ion with **2a** is a 4-fold bonding interaction between the host and guest. The *closo*-$B_{10}H_{10}^{2-}$ ions bind **2a** in **2a**·**10**$_2$ through four three-center two-electron B–H- -Hg interactions. The eight bonding electron pairs derived from the B–H σ-bonds of the two equatorial belts provided by the two

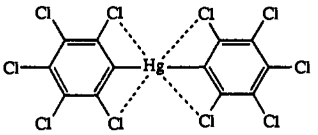
10 ions are donated to eight empty p-orbitals of the four Hg centers. Individually, these B–H- -Hg interactions are probably weak. However, the **2a**·**10** species is present in solution in the presence of acetonitrile, as detected by ^{11}B and ^{199}Hg NMR.

Supramolecular Chemistry. The successful construction of supramolecular systems based upon molecular recognition rests upon the existence of microenvironments with specific stereochemical and electronic features which provide complementarity between host and guest, as well as preorganization of those features responsible for chemical binding. The formation of supramolecules and ions such as **2a**·$\mathbf{7}_2$, **2a**·$\mathbf{8}_2$, and **2a**·$\mathbf{10}_2$ demonstrates the satisfaction of these requirements.

The macrocyclic and multidentate nature of **2a** provides stabilization of the molecular aggregates **2a**·$\mathbf{7}_2$ and **2a**·$\mathbf{8}_2$ through weak but complementary Lewis acid–base interactions with **7** and **8**, which are regarded as very weak bases. This characterization is possible, since the iodine atoms of **7** or **8** reside near the negative end of a strong dipole, induced by the C-atoms of the *closo*-1,2-$C_2B_{10}H_{10}$ cage, which enhances the nucleophilicity of the iodine atoms. The weak interactions between **7** or **8** and **2a** were amply demonstrated by ^{199}Hg NMR. Dissociation of these molecular aggregates occurs in $CHCl_3$ solution, which results in a broad ^{199}Hg NMR signal, and the chemical shift of the resulting resonance is only 5 ppm downfield from that of **2a** itself. However, both **2a**·$\mathbf{7}_2$ and **2a**·$\mathbf{8}_2$ are stabilized in the solid state.

Halocarbon coordination chemistry has recently attracted attention[42] because of interest in the binding of weakly basic ligands to metal ions and the possible activation of halocarbons toward substitution reactions. A number of iodocarbon complexes having cationic transition metal coordination centers such as $[RuCp(t\text{BuNC})(PPh_3)(MeI)][PF_6]$[43] and $[RuCp(CO)(PPh_3)(p\text{-}CH_3C_6H_4I)][PF_6]$[44] have been structurally characterized. In addition, a series of neutral silver(I) complexes with dichloromethane and 1,2-dichloroethane have been reported and structurally characterized in which the halocarbons function as bidentate ligands.[45] Bidentate coordination is viewed as the structural feature which stabilizes these complexes. To our knowledge, **2a**·$\mathbf{7}_2$ and **2a**·$\mathbf{8}_2$ are the first reported examples in which a neutral host molecule complexes with an uncharged iodine-containing guest. An intramolecular interaction between the chlorine atom and the mercury center present in *closo*-1-(-2-CH_2Cl-1,2-$C_2B_{10}H_{10}$)$HgCH_3$, shown below, has been reported with a Cl- -Hg distance of 3.27 Å.[46] This interaction is apparently due to both the favorable geometrical position of the Cl atom and the enhanced Lewis acidity of the Hg center bonded to the electron-withdrawing *closo*-1,2-carborane cage. It was also reported that *ortho*-chlorine atoms present in bis(pentachlorophenyl)mercury interact with the mercury center in an intramolecular fashion.[47]





The four-fold binding interaction of **10** and **2a**, discussed above, is believed to be responsible for the stabilization of molecular aggregate **2a**·$\mathbf{10}_2$. It has long been known that water-insoluble salts of **10** are formed with soft acid cations such as Ag^+, Cu^+, and Hg^{2+}.[48] Significant covalent interactions, characterized by IR spectroscopy[49] and X-ray crystallography,[23] were observed between these cations and **10**. Normal ionic salts (Na^+, K^+, $MePh_3P^+$) of **10** display a very strong IR absorption at about 2470 cm^{-1} (equatorial B–H stretch).[48] However, covalent **10**·Cu_2 exhibits this stretching mode as a broad band at 2100–2300 cm^{-1}.[49] In addition to the B–H stretching absorption at 2535 cm^{-1} (carborane B–H), **2a**·$\mathbf{10}_2(PMePh_3)_4$ displays a B–H stretching absorption at 2422 cm^{-1}, which corresponds to the equatorial B–H stretch of **10** in the aggregate (Nujol mull). Compared with B–H–M interactions observed in **10**-Cu_2, **10**·Ag_2, and **10**·Hg[48] as well as in $(PPh_3)_2CuB_3H_8$,[50] a weaker B–H–Hg interaction in **2a**·$\mathbf{10}_2$ is expected, since the Hg(II) centers in **1** and **2a** have no formal charge. The stability of species such as **2a**·$\mathbf{10}_2$ and **2a**·**10** must be due to the sterically complementary interactions of the host and guest; planar **1** and **2a** both have C_{4h} symmetry, and **10** has D_{4d} symmetry. As expected, ^{11}B NMR studies prove that **1** and **2a** do not interact with *closo*-$B_{12}H_{12}^{2-}$ of I_h symmetry, since this ion is less nucleophilic than **10** and sterically incompatible as well. Similarly, the icosahedral fragment, *nido*-7,8-$C_2B_9H_{12}^-$ does not react with **1** or **2a**.

Reorganization of Mercuracarborand Hosts Accompanying Complexation. One aspect of host–guest chemistry pertains to the reorganization of the host molecule upon complexation with its guest. Free host, [18]crown-6, has neither a "crown shape" nor a cavity, and only when the guest K^+ is complexed by the host, does a filled cavity develop.[51,52] In other words, the guest forces conformational reorganization upon the host during complexation. A similar reorganization occurs when Lehn's [2,2,2]cryptand complexes KI.[53] Compared with crown ethers and cryptands, solvated **1**[13c] and free **2a** are both relatively preorganized hosts equipped with a cavity in the uncomplexed state which is smaller than that observed in the complexed planar conformation. Upon complexation with anions, the reorganization of hosts **1** and **2a** involves the distortion of linear Hg coordination and an increase in Hg–C–C angles. The resulting planar conformation of the complex provides the largest possible cavity and positions the electrophile Hg-binding centers in such a way that they function in a cooperative manner. Mercuracarborands **1** and **2a** are unusual in their ability to accommodate guest species having a variety of steric requirements. Thus, when the guest is sufficiently small, as in the case of chloride ion, the strained planar host accommodates the ion within its cavity. When the guest is too large to fit into the available cavity volume, the anion is displaced from the plane of the ring, as observed with **1**·I_2^{2-}, **2a**·$\mathbf{7}_2$, **2a**·$\mathbf{8}_2$, and **2a**·$\mathbf{10}_2$. The two water molecules present in **1**·$(THF)_4(H_2O)_2$ are not bonded to the host, even though the H_2O molecules lie within the folded host.[13c]

Conclusions

A new class of macrocyclic multidentate Lewis acid hosts exemplified by **1**–**3** (mercuracarborands) has been discovered, and efficient procedures for the synthesis of these species have been developed. The results presented here prove (1) macrocyclic multidentate Lewis acid hosts **1** and **2a** could efficiently bind anions and nucleophilic species as well as extremely weak Lewis bases such as **7** and **8**; (2) the exceptional binding ability of **1** and **2a** is attributed to the preorganization, multiple binding, and

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host–guest complementarity observed in their host–guest complexes such as $\mathbf{2a}\cdot\mathbf{10}_2$; and (3) the *closo*-1,2-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 was demonstrated here and in previously reported work.[13f] Applications of mercuracarborands to molecular recognition, catalysis, and supramolecular chemistry await further development.

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were reagent grade and were distilled from appropriate drying agents before use. Diethyl ether was distilled from sodium benzophenone ketyl. Deuteriated solvents were obtained from Cambridge Isotope Laboratories. Mercuric chloride, mercuric bromide, mercuric iodide (Cerac), bis(triphenylphosphine)palladium dichloride, copper(I) iodide, *n*-butyllithium (2.5 M solution in hexane), and ethyl magnesium bromide (3.0 M solution in diethyl ether) (Aldrich) were used without further purification. $(Ph_3PMeP)_2(B_{10}H_{10})$ was prepared according to literature methods.[54]

Physical Measurements. IR spectra of KBr pellets were recorded with a Beckman FT-1100 instrument. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded with Bruker AF 200, AM 360, and AM 500 spectrometers, respectively. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to the residual protons and carbon atoms in deuteriated solvents. Chemical shift values for ^{11}B spectra were referenced relative to external $BF_3{\cdot}OEt_2$ (δ 0.0 ppm with negative δ values upfield). The ^{199}Hg {^{1}H} NMR spectra were recorded at 25 °C with a Bruker 500 spectrometer at 89.6 MHz by using broad-band decoupling. A 10-μs pulse width, a 3-s relaxation delay, and a 83333-Hz sweep width were used. Spectra were measured in 10-mm sample tubes, and the number of scans was determined by the intensity of the spectra. An average of 400 accumulations were taken. External 1.0 M PhHgCl in DMSO-d_6 solution was used as the reference at –1187 ppm[25] relative to neat Me_2Hg. All FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer.

1·ClLi. To an ethereal solution (50 mL) of 1,2-carborane (20.8 mmol, 3.00 g) at 0 °C was added *n*BuLi (43.7 mmol, 17.5 mL, 2.5 M in hexane), and the slurry was stirred at room temperature under argon. After 2 h, the mixture was treated with solid $HgCl_2$ (20.8 mmol, 5.65 g) and stirred overnight. The reaction mixture was then treated with 100 mL of H_2O, and the organic phase was washed three times with H_2O (100 mL) and dried over $MgSO_4$. The solvent was removed, and the residue was recrystallized from ether to give **1**·ClLi in 75% yield. Mp: >300 °C. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 25 °C): δ = 0.6–3.6 ppm. ^{13}C NMR (50 MHz, $(CD_3)_2CO$, decoupled) δ = 94 ppm. ^{11}B {^{1}H} NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}Et_2O$ external) δ = 0.3, –6.0, –8.3, –10.2 ppm. ^{199}Hg {^{1}H} NMR (acetone-d_6, 0.01 M, 25 °C) –1077 ppm. IR (KBr): ν (cm^{-1}) = 2056 (B–H). Negative-ion FAB: *m/z* 1407 ($\mathbf{1}{\cdot}Cl^-$, 100%), 1204 ($\mathbf{1}{\cdot}Cl^-$ – Hg, 2.5%), 1064 ($\mathbf{1}{\cdot}Cl^-$ – $HgC_2B_{10}H_{10}$, 18%). Anal. Calcd for $C_8H_{40}B_{40}ClLiHg_4$: C, 6.79; H, 2.85; B, 30.57; Hg, 56.78; Cl, 2.51. Found: C, 6.75; H, 2.73; B, 30.50; Hg, 57.10; Cl, 2.61.

1·BrLi. To an ethereal solution (50 mL) of 1,2-carborane (27.7 mmol, 4.00 g) at 0 °C was added *n*BuLi (58.3 mmol, 23.3 mL, 2.5 M in hexane), and the slurry was stirred at room temperature under argon. After 2 h, the mixture was treated with $HgBr_2$ (27.7 mmol, 10.0 g) and stirred overnight. The reaction mixture was then treated with 100 mL of H_2O, and the organic phase was diluted with 50 mL of ethyl ether, washed three times with H_2O (100 mL), and dried over $MgSO_4$. The solvent was removed, and the residue was recrystallized from ether to give **1**·BrLi in 77% yield. Mp: >300 °C. ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ = 0.6–3.6 ppm. ^{13}C NMR (50 MHz, $(CD_3)_2CO$, decoupled) δ = 94 ppm. ^{11}B {^{1}H} NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}Et_2O$ external) δ = 0.5, –6.0, –7.9 ppm. ^{199}Hg {^{1}H} NMR (89.6 MHz, 0.25 M in $(CD_3)_2CO$, 25 °C) δ = –1010 ppm. IR (KBr): ν (cm^{-1}) = 2056 (B–H). Negative-ion FAB: *m/z* 1450 ($\mathbf{1}{\cdot}Br^-$, 100%), 1109 ($\mathbf{1}{\cdot}Br^-$ – $HgC_2B_{10}H_{10}$, 30%).

$\mathbf{1{\cdot}I_2Li_2}$. To an ethereal solution (100 mL) of 1,2-carborane (34.67 mmol, 5.00 g) at 0 °C was added *n*BuLi (72.8 mmol, 29.0 mL, 2.5 M in hexane), and the slurry was stirred at room temperature under argon. After 2 h, the mixture was treated with red HgI_2 (34.67 mmol, 17.75 g) and stirred overnight (24 h). The reaction mixture was then treated with 100 mL of H_2O, and the organic phase was diluted with 50 mL of diethyl ether, washed three times with H_2O (100 mL), and dried over $MgSO_4$. The solvent was removed, and the residue was recrystallized from ether to give $\mathbf{1}{\cdot}I_2Li_2$ in 80% yield. Mp: >300 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.0–3.6 ppm. ^{13}C {^{1}H} NMR (90 MHz, acetone-d_6) δ = 95 ppm. ^{11}B {^{1}H} NMR (160 MHz, acetone) δ = 0.3, –7.5 ppm (4:6). ^{199}Hg {^{1}H} NMR (89.6 MHz, $(CD_3)_2CO$, 25 °C) δ = –714 ppm. IR (KBr): ν (cm^{-1}) = 2560 (B–H). Negative-ion FAB: *m/z* 1624 ($\mathbf{1}{\cdot}I_2^-$, 10%), 1497 ($\mathbf{1}{\cdot}I^-$, 100%), 1296 ($\mathbf{1}{\cdot}I^-$ – Hg, 95%), 1155 ($\mathbf{1}{\cdot}I^-$ – $HgC_2B_{10}H_{10}$, 30%).

$\mathbf{1{\cdot}I_2(AsPh_4)_2}$. Complex $\mathbf{1}{\cdot}I_2(AsPh_4)_2$ was prepared from the metathesis of $\mathbf{1}{\cdot}I_2Li_2$ with Ph_4AsCl in ethanol. The white solid was recrystallized from acetone. Anal. for $\mathbf{1}{\cdot}I_2[As(C_6H_5)_4]_2$. Calcd for $C_{56}H_{80}B_{40}As_2I_2Hg_4$: C, 28.12; H, 3.37; B, 18.08; I, 10.61; Hg, 33.55. Found: C, 27.86; H, 3.30; B, 17.92; I, 10.44; Hg, 33.70.

1·ILi. To an ethereal solution (100 mL) of 1,2-carborane (25.0 mmol, 3.6 g) at 0 °C was added *n*BuLi (52.4 mmol, 21.0 mL, 2.5 M in hexane), and the slurry was stirred at room temperature under argon. After 2 h, the mixture was treated with red HgI_2 (25.5 mmol, 11.36 g) and stirred for 1 h at room temperature, and then the reaction was quenched with 50 mL of H_2O. The aqueous layer was extracted with ethyl ether (3 × 100 mL). The combined organic phase was washed with water (3 × 100 mL) and dried over $MgSO_4$. The mixture was filtered, and the solid was dissolved in acetone and filtered. The solvent was removed, and the residue was titrated with pentane to give a white solid which was recrystallized from ether to give **1**·ILi in 80% yield. Mp: >300 °C. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 25 °C): δ = 1.0–3.6 ppm. ^{13}C {^{1}H} NMR (90 MHz, $(CD_3)_2CO$) δ = 94.5 ppm. ^{11}B {^{1}H} NMR (160 MHz, $(CH_3)_2CO$) δ = 0.2, –6.1, –8.4, –10.2 ppm (2:2:4:2). ^{199}Hg {^{1}H} NMR (89.6 MHz, $(CD_3)_2CO$, 25 °C) δ = –810 ppm. IR (KBr): ν (cm^{-1}) = 2562 (B–H). Negative-ion FAB: *m/z* 1497 ($\mathbf{1}{\cdot}I^-$, 100%).

1. Complex $\mathbf{1}{\cdot}I_2Li_2$ (10 g, 6.1 mmol) in 20 mL of ethanol was treated with AgOAc (2.14 g, 12.8 mmol) at room temperature, and a yellow precipitate immediately formed. After 5 min, the mixture was filtered, the solvent was removed, and the residue was recrystallized from diethyl ether to give **1** in 80% yield. Mp: >300 °C. ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ = 1.0–3.0 (B–H). ^{13}C {^{1}H} NMR (50 MHz, acetone-d_6, 25 °C, decoupled) δ = 93 (carborane C). ^{11}B {^{1}H} NMR (160 MHz, acetone) δ = 0.8, –6.0, –7.6, –9.6 ppm. ^{199}Hg {^{1}H} NMR (89.6 MHz, 0.05 M in acetone-d_6, 25 °C) δ = –1205 ppm. IR (KBr): ν (cm^{-1}) = 2556 (B–H).

***closo*-$\mathbf{9,12\text{-}Et_2\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (9).** Compound **9** was prepared by using a modified literature procedure.[55] A solution of EtMgBr (50.0 mmol, 16.7 mL, 3.0 M in diethyl ether) was added dropwise to a stirred THF solution (100 mL) of $9,12\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (10.0 mmol, 3.96 g) cooled in an ice/water bath, and the slurry was stirred at room temperature for 20 min. $(Ph_3P)_2PdCl_2$ (280 mg, 4% equiv) and CuI (76 mg, 4% equiv) were then added in a single portion. The reaction mixture was refluxed for 2 days. After removal of the solvent, 200 mL of diethyl ether was added to the residue and the excess EtMgBr was destroyed by slow addition of a dilute HCl solution. The organic phase was separated. The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with H_2O (3 × 50 mL) and dried over $MgSO_4$. The solvent was removed under vacuum. Flash silica gel column chromatography (1:1 methylene dichloride/pentane, R_f 0.92) gave 0.85 g (42%) of the titled compound as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.67, 2.27, 1.85, 1.30 (B–H), 3.38 (carborane, C*H*), 0.87 (m, CH_3), 0.69 (m, BCH_2) ppm. ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$) δ = 8.9, –9.2, –15.1, –17.0 ppm (2:2:4:2). A byproduct from the product mixture was separated (R_f 0.67) and characterized as ***closo*-$\mathbf{9\text{-}I\text{-}12\text{-}Et\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (8).** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.67, 2.27, 1.85, 1.30 (B–H), 3.38 (carborane, C*H*), 0.87 (m, CH_3), 0.69 (m, BCH_2) ppm. ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$) δ = 9.0, –7.0, –13.0, –14.0, –15.0 ppm (1:2:2:3:2).

$\mathbf{2a{\cdot}I_2Li_2}$. A solution of *n*BuLi (16.6 mmol, 6.65 mL, 2.5 M in hexane) was added to an ethereal solution (50 mL) of *closo*-$9,12\text{-}Et_2\text{-}1,2\text{-}C_2B_{10}H_{10}$[55] (8.0 mmol, 1.6 g) at 0 °C under nitrogen, and the slurry was stirred at room temperature. After 2 h, the mixture was treated with solid red HgI_2 (8.0 mmol, 3.63 g) and stirred overnight at room temperature. To the mixture was added 50 mL of H_2O, and the organic phase was washed three times with H_2O (50 mL) and dried over $MgSO_4$. The solvent was removed, and the residue was recrystallized from ether

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Table 5. Crystallographic Data

	1·ClLi	**1**·$I_2(AsPh_4)_2$	$(\mathbf{1}\cdot Br)_2Li_2(H_2O)_2$-(benzo[15]crown-5)$_3$	**2a**	**2a**·**10**$_2(Ph_3MeP)_4$	**2a**·**8**$_2$	**2a**·**7**$_2$
space group	$P4/mcc$	$P2_1/c$	$P\bar{1}$	$P\bar{4}2_1c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	14.3233(8)	9.518(2)	11.3204(4)	14.806(1)	15.583(2)	12.828(1)	12.768(2)
b (Å)		30.516(6)	22.7459(8)		15.861(2)	22.650(2)	22.907(4)
c (Å)	11.2641(7)	15.531(4)	27.8148(9)	13.5141(9)	16.045(2)	14.698(1)	14.589(3)
α (deg)			83.5246(9)		67.831(4)		
β (deg)		99.331(6)	86.218(1)		70.713(4)	108.541(2)	108.202(3)
γ (deg)			88.640(1)		86.371(4)		
V (Å^3)	2311	4451	7132	2962	3457	4049	4053
Z^a	2	2	2	2	1	2	2
density(calcd) (g/cm^3)	2.03	1.87	1.86	1.92	1.45	1.55	1.96
μ (cm^{-1})	133	83.4	91.8	104.9	45.1	79.6	90.9
temp (°C)	25	25	25	25	–117	25	25
scan rate (deg/min)	9.0	6.0	9.0	12.0	9.0	1.5	9.0
no. of unique reflcns	1608	10 252	18 651	1910	13 654	4647	7145
no. of obsd ($I > 3\sigma(I)$) reflcns	1207	5928	7914	1139	7609	1995	2753
2θ max (deg)	60	55	45	55	52	43	50
data collected	$+k, +k, +l$	$+h, +k, \pm l$	$+h, \pm k, \pm l$	$+h, +k, +l$	$+h, \pm k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$
no. of params refined	71	438	229 + 229 + 309	85	290 + 386	229	262
R, R_w, GOF^b	0.041, 0.060, 2.48	0.045, 0.053, 1.62	0.039, 0.050, 1.42	0.052, 0.058, 2.16	0.056, 0.064, 1.81	0.059, 0.059, 1.74	0.064, 0.081, 2.32

[a] Z = the number of molecules in the unit cell. [b] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$.

and hexane to give **2a**·I_2Li_2 in 90% yield (based on *closo*-9,12-Et_2-1,2-$C_2B_{10}H_{10}$). Negative-ion FAB: *m/z* 1849 (**2a**·I_2^-, 40%), 1722 (**2a**·I^-, 100%). ^{199}Hg{^{1}H} NMR (89.6 MHz, $(CD_3)_2CO$, 25 °C) δ = –674 ppm. ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ = 1.0–3.6 (B*H*), 0.74 (m, C*H*$_3$), 0.53 (m, BC*H*$_2$) ppm. ^{13}C {^{1}H} NMR (90 MHz, $(CD_3)_2CO$) δ 86.6 (carborane C), 13.8 (*C*H$_3$), 8.6 (broad, B*C*H$_2$) ppm. ^{11}B {^{1}H} NMR (160 MHz, Et_2O, BF_3·Et_2O external) δ = 10.8 (*B*Et$_2$), –6.5, –9.2 ppm (2:2:6). If the reaction mixture was quenched in 2–3 h, a mixture of **2**·I_2Li_2 and **2**·ILi (in a 2:1 ratio estimated by ^{199}Hg NMR with the chemical shift of **2**·ILi at –774 ppm) was isolated.

2a. Complex **2a**·I_2Li_2 (1.88 mmol, 3.5 g) in 5 mL of ethanol was treated with AgOAc (3.76 mmol, 0.63 g) at room temperature, and a yellow precipitate immediately formed. After 5 min, the mixture was filtered, the solvent was removed under vacuum, and the residue was triturated with pentane. The solid was then recrystallized from CH_2Cl_2/hexane to give **2** in 67% yield. ^{199}Hg{^{1}H} NMR (89.6 MHz, toluene/C_6D_6 (1:1), 25 °C) δ = –1221 ppm. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.0–3.6 (B*H*), 0.86 (m, C*H*$_3$), 0.74 (m, BC*H*$_2$) ppm. ^{13}C {^{1}H} NMR (90 MHz, $CDCl_3$) δ = 84.4 (carborane C), 13.4 (*C*H$_3$), 9.0 (broad, B*C*H$_2$) ppm. ^{11}B {^{1}H} NMR (160 MHz, CH_2Cl_2, BF_3·Et_2O external) δ = 8.9 (*B*Et$_2$), –8.5, –12.3, –14.9 ppm (2:2:4:2).

2b·I_2Li_2. A solution of *n*BuLi (5.25 mmol, 2.1 mL, 2.5 M in hexane) was added to an ethereal solution (50 mL) of *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (2.5 mmol, 1.0 g) at 0 °C under nitrogen, and the slurry was stirred at room temperature. After 2 h, the mixture was treated with solid red HgI_2 (2.1 mmol, 954 mg) and the mixture was stirred overnight at room temperature. The mixture was then treated with 50 mL of H_2O, and the organic phase was washed three times with H_2O (50 mL) and dried over $MgSO_4$. The solvent was removed, and the residue was recrystallized from ether and hexane to give **2b**·I_2Li_2 in 90% yield (based on *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$). Negative-ion FAB: *m/z* 2632 (**2b**·I_2^-, 40%), 2505 (**2b**·I^-, 100%). ^{199}Hg{^{1}H} NMR (89.6 MHz, $(CD_3)_2CO$, 25 °C) δ = 610 ppm. ^{11}B {^{1}H} NMR (160 MHz, Et_2O, BF_3·Et_2O external) δ = –2.7, –7.8, –12 (*B*I) ppm (2:6:2).

Solution and Refinement of Crystal Structures. All data were collected on automated diffractometers in the θ–2θ scan mode with Mo K_α radiation. Most of the data were collected on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Data for **2a**·**10**$_2(Ph_3MeP)_4$ were collected on a Picker FACS-1 modified by Professor C. E. Strouse. All calculations were performed using the DEC VAX 11/750 computer of the J. D. McCullough Crystallography Laboratory and the UCLA crystallographic programs. Data were corrected for Lorentz and polarization effects and for absorption and extinction. 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, SHELX76 (Sheldrick) crystal structure package, SHELX86 (Sheldrick) structure solution package, ABSCOR absorption correction based on psiscans, and ORTEP (Johnson). All structures were solved with use of heavy-atom methods unless otherwise noted. Reported R and R_w values are defined as GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. Scattering factors for hydrogen were obtained from Stewart *et al.*[56] and for other atoms were taken from the International Tables for X-ray Crystallography.[57] Details of the individual data collections are given in Table 5. The observed and calculated structure factors are given in Tables S-13–S-73 as supplementary material.

1·ClLi. A colorless crystal of **1**·ClLi grown from chlorobenzene was coated with epoxy and mounted on a glass fiber on a Huber diffractometer at 25 °C. The lattice constants were obtained from a least squares fit of 87 accurately centered reflections (8.0 < 2θ < 20.3). Data were collected at 25 °C in the θ–2θ scan mode. Of the 1608 unique reflections measured, 1207 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. The structure was solved by heavy-atom methods. Final positional and thermal parameters are listed in Tables S-11 and S-12 as supplementary material.

$(1\cdot Br)_2[Li_2(benzo[15]crown\text{-}5)_3\cdot 2H_2O]$. A colorless crystal, obtained from a THF/toluene solution, was sealed in a capillary and placed on a Huber diffractometer. Unit cell parameters were determined from a least squares fit of 108 accurately centered reflections. Data were collected at 25 °C. These dimensions and other parameters, including conditions of data collection, are summarized in Table 5. The intensities of three representative reflections did not decay during the course of the experiment (124.4 h). Atoms were located by use of heavy-atom methods. Br and Hg atoms were refined with anisotropic parameters. All other nonhydrogen atoms were refined with isotropic parameters. All phenyl and methylene hydrogens were included in calculated positions as members of rigid groups, C–H = 1.0 Å, angles 120° (phenyl) or H–C–H 109.5 (methylene). Other H atoms were included in located positions. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Terms for anomalous dispersion were applied for Hg and Br. The asymmetric unit also contains a molecule of toluene (methyl group not located, hydrogen atoms omitted) and two molecules of tetrahydrofuran with partial occupancy because they are disordered about centers of symmetry and another (ordered) molecule of tetrahydrofuran. No hydrogen atoms were included for any of the tetrahydrofuran molecules. Final positional and thermal parameters for nonhydrogen atoms are given in Tables S-21 and S-22 as supplementary material.

1·$I_2(AsPh_4)_2$. A colorless crystal, obtained from an acetone/ether solution, was coated with epoxy cement and placed on a Huber diffractometer. Unit cell parameters were determined from a least squares fit of 26 accurately centered reflections (9.6 < 2θ < 19.8°). These dimensions and other parameters, including conditions of data collection, are summarized in Table 5. Data were collected at 25 °C. Three intense reflections were monitored every 97 reflections to check stability. The

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[56] Stewart, R. F.; Davison, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[57] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

intensities of these reflections did not decay during the course of the experiment (136.6 h). Atoms were located by use of heavy-atom methods. Terms for anomalous dispersion were applied to the scattering of Hg, I, and As. All cation hydrogens were included in calculated positions as members of rigid C_6H_5 groups, C–C = 1.395 Å, C–H = 1.0 Å, angles = 120°. All carboranyl hydrogens were kept in located positions. No hydrogen atoms were included for the acetone. Hydrogen atoms were assigned isotropic displacement values based approximately upon the value of the attached atom. Final positional and thermal parameters for non-hydrogen atoms are listed in Tables S-31 and S-32 in the supplementary material.

2a. A colorless crystal, obtained from a $CHCl_3$ solution, was mounted on a fiber with epoxy cement and placed on a Huber diffractometer. Systematic absences were found for *hhl* reflections for which $l \neq 2n$, for 00l reflections for which $l \neq 2n$, and for *h*00 reflections for which $h \neq 2n$. Unit cell parameters were determined from a least squares fit of 76 accurately centered reflections. These dimensions and other parameters, including conditions of data collection, are summarized in Table 5. The intensities of three representative reflections did not decay during the course of the experiment (21.4 h). Atoms were located by use of heavy-atom methods. The unit cell consists of two tetrameric hosts (**2a**) with S_4 symmetry and two chloroform solvent molecules with the same symmetry (three Cl's disordered over four positions). All mercury atoms and chlorine atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. Most positions of H on the carborane ligand were located but were not refined. No H atoms have been included for the ethyl groups or for the solvent. H-atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Final positional and thermal parameters are listed in Tables S-41 and S-42 as supplementary material.

2a·8₂. A colorless crystal, obtained from a CH_2Cl_2/hexane solution, was mounted on a fiber with epoxy cement and placed on a Huber diffractometer. Systematic absences were found for *h*0*l* reflections for which $l \neq 2n$ and for 0*k*0 reflections for which $k \neq 2n$. Unit cell parameters were determined from a least squares fit of 51 accurately centered reflections. Three intense reflections were monitored every 97 reflections to check stability. The intensities of these reflections decayed 29% during the course of the experiment (181.7 h). Atoms were located by use of heavy-atom methods. Two of the ethyl groups were found to be disordered at the methyl carbon. Carbon atoms C92 and C92′ have occupancy factors of 0.4 and 0.6, respectively. CE1″ and CE2″ have occupancy factors of 0.5. Only Hg and I atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. Most positions of H's 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 atom. Anomalous dispersion terms were included for the scattering of Hg and I. Final positional and thermal parameters are listed in Tables S-51 and S-52 as supplementary material.

2a·7₂. A cut colorless crystal, obtained from CH_2Cl_2 solution, was coated with epoxy cement, and mounted on a fiber, and placed on a Huber diffractometer. Systematic absences were found for *h*0*l* reflections for which $l \neq 2n$ and for 0*k*0 reflections for which $k \neq 2n$. Unit cell parameters were determined from a least squares fit of 40 accurately centered reflections. Three intense reflections were monitored every 97 reflections to check stability. The intensities of these reflections decayed 8% during the course of the experiment (54.4 h). Atoms were located by use of heavy-atom methods. Only Hg, I, and seven ethyl C atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. One of the terminal C-atoms of an ethyl group is disordered and has been refined at half occupancy in two positions. With the exception of H on this disordered carbon atom, all ethyl hydrogens have been kept in calculated positions. Most positions of hydrogen 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 atom. Anomalous dispersion terms were included for the scattering of Hg and I. Final positional and thermal parameters are listed in Tables S-61 and S-62 as supplementary material.

2a·10₂(Ph₃MeP)₄. A colorless crystal, obtained from a CH_2Cl_2/CH_3CN solution, was mounted on a fiber with epoxy cement. Data were collected on a Picker FACS-1 diffractometer at −117 °C. Unit cell parameters were determined from a least squares fit of 45 accurately centered reflections. Atoms were located by use of heavy-atom methods. All phenyl, ethyl, and methyl C, P, Hg, and the ten B atoms of $B_{10}H_{10}^{2-}$ were refined anisotropically. All other non-hydrogen atoms were refined with isotropic parameters. Positional parameters for all hydrogen on B were refined. All other hydrogen were kept in calculated positions, C–H = 1.0 Å. No hydrogens were located on CH_3CN. All phenyl rings were treated as rigid groups, C–H = 1.0 Å, C–C = 1.395 Å, angles 120°. H-atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Final positional and thermal parameters are listed in Tables S-71 and S-72 as supplementary material.

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Supplementary Material Available: Tables of bond distances and angles, positional and equivalent isotropic thermal parameters, and anisotropic thermal parameters (69 pages); tables of observed and calculated structure factors (169 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.