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Hydrocarbon-Soluble Mercuracarborands: Syntheses, Halide Complexes, and Supramolecular Chemistry

Zhiping Zheng, Carolyn B. Knobler, Mark D. Mortimer, Gapgoung Kong, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry, 405 Hilgard Avenue, University of California,
Los Angeles, California 90095-1569

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The syntheses of macrocyclic species composed of carborane derivatives joined *via* their carbon vertices by electrophilic mercury atoms are described. The reaction of *closo*-1,2-$Li_2[C_2B_{10}H_{10-x}R_x]$ with HgI_2 gives $Li_2[(1,2\text{-}C_2B_{10}H_{10-x}R_xHg)_4I_2]$ [R = Et, $x = 2$ ($\mathbf{5}\cdot I_2Li_2$); R = Me, $x = 2$ ($\mathbf{6}\cdot I_2Li_2$); R = Me, $x = 4$ ($\mathbf{7}\cdot I_2Li_2$)]. $\mathbf{6}\cdot I_2(K\cdot[18]$-dibenzocrown-6$)_2$ crystallizes in the monoclinic space group $C2/m$ [$a = 28.99(2)$ Å, $b = 18.19(1)$ Å, $c = 13.61(1)$ Å, $\beta = 113.74(2)°$, $V = 6568$ Å^3, $Z = 4$, $R = 0.060$, $R_w = 0.070$]; $\mathbf{7}\cdot I_2(NBu_4)_2$ crystallizes in the monoclinic space group $P2_1/c$ [$a = 12.77(1)$ Å, $b = 21.12(2)$ Å, $c = 20.96(2)$ Å, $\beta = 97.87(2)°$, $V = 5600$ Å^3, $Z = 2$, $R = 0.072$, $R_w = 0.082$]. The precursor to **7**, *closo*-8,9,10,12-Me_4-1,2-$C_2B_{10}H_8$ (**4**), is made in a single step by reaction of *closo*-1,2-$C_2B_{10}H_{12}$ with MeI in trifluoromethanesulfonic acid. The free hosts **5**, **6**, and **7** are obtained by reaction of the iodide complexes with stoichiometric quantities of AgOAc. A ^{199}Hg NMR study indicates that sequential removal of iodide from $\mathbf{5}\cdot I_2Li_2$ and $\mathbf{6}\cdot I_2Li_2$ with aliquots of AgOAc solution leads to formation of two intermediate host−guest complexes in solution, presumed to be **5**(**6**)ILi and $\mathbf{5}_2(\mathbf{6})_2\cdot ILi$. Crystals grown from a solution of $\mathbf{6}\cdot I_2Li_2$ to which 1 equiv of AgOAc solution had been added proved to be an unusual stack structure with the formula $\mathbf{6}_3\cdot I_4Li_4$ [tetragonal, $I4/m$, $a = 21.589(2)$ Å, $c = 21.666(2)$ Å, $V = 10098$ Å^3, $Z = 2$, $R = 0.058$, $R_w = 0.084$]. Addition of 2 equiv of NBu_4Br ion to **5** or **6** gives $\mathbf{5}\cdot Br_2(NBu_4)_2$ and $\mathbf{6}\cdot Br_2(NBu_4)_2$, respectively, while addition of 1 equiv of KBr to **6** forms $\mathbf{6}\cdot BrK$. $\mathbf{5}\cdot Br_2(NBu_4)_2$ crystallizes in the triclinic space group $P\bar{1}$, [$a = 10.433(1)$ Å, $b = 13.013(1)$ Å, $c = 15.867(2)$ Å, $\alpha = 91.638(2)°$, $\beta = 97.186(3)°$, $\gamma = 114.202(2)°$, $V = 1492$ Å^3, $Z = 1$, $R = 0.078$, $R_w = 0.104$]. The hosts **5** and **6** form 1:1 supramolecular adducts with the polyhedral anions $B_{10}I_{10}^{2-}$ and $B_{12}I_{12}^{2-}$ in solution.

Introduction

We have recently described the chemistry of a new class of Lewis acidic multidentate hosts containing electrophilic mercury atom centers connected by *closo*-1,2-$C_2B_{10}H_{10}$ icosahedra (Figure 1).[1] These "mercuracarborand" cyclic species can be regarded as charge-reversed analogs of the well-known crown ethers,[2] and they are observed to bind halide ions and weak nucleophiles with remarkable efficiency. Syntheses of the halide ion complexes of the tetrameric species [12]mercuracarborand-4 (**1**) are high-yield and relatively simple procedures. Removal of the halide guest generates the free host without associated degradation of the cycle.[1c,f] The host can subsequently form complexes with alternative guest species including other halide ions in a variety of stoichiometries, polyhedral borane dianions, or neutral solvent molecules.

A number of methods are known by which selected B−H vertices of the isomeric *closo*-$C_2B_{10}H_{12}$ carborane cages can be replaced with B−R vertices, where R is an alkyl or aryl group.[3] These modifications to the individual icosahedra can be carried forward into the design of mercuracarborand hosts with properties additional to those of the parent molecule. Thus, it is possible to remove a B−H vertex adjacent to the two carbon atoms in *closo*-1,2-$C_2B_{10}H_{12}$ (*i.e.* at either the 3- or 6-position) and replace it with a boron−phenyl vertex.[3a,b] The resulting compound can then be used to synthesize a number of stereoisomeric derivatives of **1** in which the central cavity containing the halide ion has varying degrees of steric protection.[4] Observation of which of the possible stereoisomers are formed in assembly of the cyclic host also offers a useful probe into the templating effects of the different halide ions and their

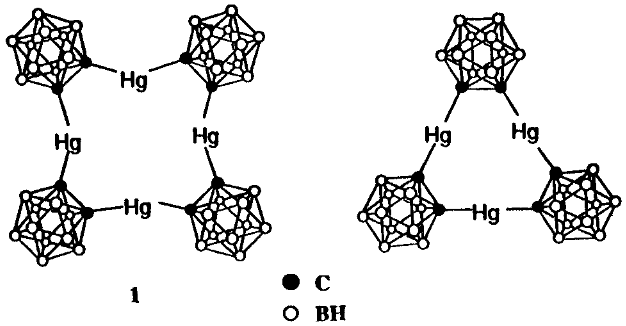

Figure 1. Unsubstituted [12]mercuracarborand-4 (**1**) and [9]mercuracarborand-3.

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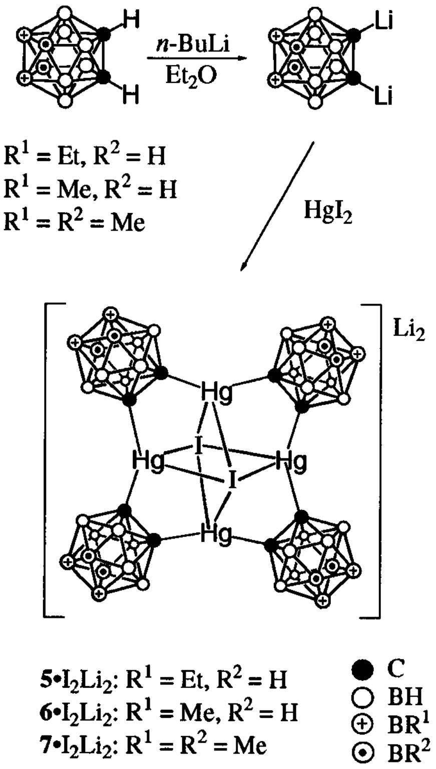
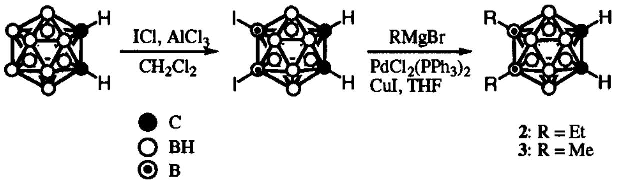
Scheme 1



Scheme 2

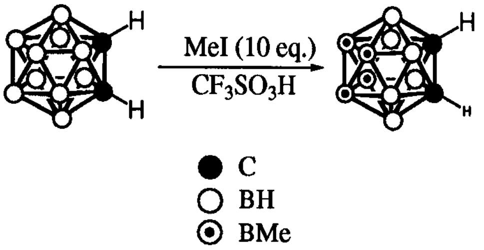


mechanistic consequences. Alternatively, substituents can be introduced to the 9- and 12-positions of the icosahedra, the vertices furthest removed from the carbon vertices.[3d,e] Upon formation of the mercuracarborand, the 9- and 12-substituents are directed outward about the periphery of the cycle and have no steric influence upon subsequent host–guest interactions. We have found that ethyl groups at these positions have a beneficial effect upon the solubility of the host–guest complexes, making them more tractable for further reactions and reducing the need for polar, coordinating solvents which tend to mask subtle interactions between the hosts and weakly coordinating guests.[1e,f] However, synthesis of *closo*-9,12-Et_2-1,2-$C_2B_{10}H_{10}$ is a relatively low-yield reaction, and we therefore have an interest in finding derivatives of *closo*-1,2-$C_2B_{10}H_{12}$ which can be made in high yield and which impart similar or improved solubility properties to host–guest complexes of which they are constituents. Furthermore, the Lewis acidity of the mercury centers in the host molecules derives largely from the inductive effect of the electron-deficient icosahedra. It is therefore reasonable to expect that the presence of electron-donating substituents on the cage will have an effect on the coordinating properties of the host. In this article, we describe the syntheses of a series of alkyl-substituted host molecules and studies on their binding characteristics with halide ions and polyhedral borane dianions.

Results and Discussion

Synthesis of Iodide-Complexed Mercuracarborands. The host complexes used in this study were synthesized as their diiodide complexes by reaction of the dilithio salts of *closo*-9,12-Et_2-1,2-$C_2B_{10}H_{10}$ (**2**), *closo*-9,12-Me_2-1,2-$C_2B_{10}H_{10}$ (**3**), and *closo*-8,9,10,12-Me_4-1,2-$C_2B_{10}H_8$ (**4**) with mercuric iodide (Scheme 1). The syntheses of compounds **2** and **3** have been previously reported[3d,e,5] and follow the common procedure of substituting two hydrogen atoms at boron vertices with iodine, followed by a palladium-catalyzed reaction with an alkyl Grignard reagent (Scheme 2). This two-step reaction is time-consuming and limited to two substituents per carborane cage, due to the deactivating effect of B–I vertices to further reaction with iodinating agents. It also has the disadvantage of a competing β-elimination reaction promoted by the palladium catalyst in the cases where the alkyl Grignard reagent has available β-hydrogen atoms. Thus, synthesis of **2** using ethylmagnesium bromide proceeds in only 30% yield, whereas the synthesis of **3** using methylmagnesium bromide may be achieved in 90% yield.[5]

Compound **4** was synthesized by a different method. The carborane *closo*-1,2-$C_2B_{10}H_{12}$ was reacted under reflux for 4 days with 10 molar equiv of methyl iodide and a large excess of neat trifluoromethanesulfonic acid (triflic acid), which functioned both as solvent and catalyst. A simple workup of the reaction mixture afforded *closo*-8,9,10,12-Me_4-1,2-$C_2B_{10}H_8$ (**4**) in 65% yield (eq 1). This single-step electrophilic substitution reaction is analogous to the Friedel–Craft alkylation of aromatic hydrocarbons, and indeed, carboranes are known to be susceptible to alkyl substitution *via* Friedel–Craft conditions.[6] However, the result of such reactions, as with conventional aromatic systems, is invariably a mixture of isomers and substitution products with differing numbers of alkyl groups. The four boron vertices selectively attacked during the reaction with methyl iodide and triflic acid are those furthest away from the comparatively positive carbon vertices of the icosahedron, and thus those with the greatest ground state electron density. This reaction provides a route to a useful compound not otherwise easily accessible and has good potential for expansion to a wider range of substituted carboranes. Recently, we have demonstrated that, with the use of the more powerful methylating agent methyl trifluoromethanesulfonate and triflic acid, it is possible to introduce methyl groups at every vertex of 1,12-$C_2B_{10}H_{12}$.[7]



The host–guest complexes resulting from the reaction of the dilithiated salts of **2**, **3**, and **4** with mercuric iodide are soluble not only in the coordinating solvents required for the unsubstituted congener but also in methylene chloride, in toluene, and to a small extent in benzene. The diiodide complexes of octaethyl[12]mercuracarborand-4 (**5**•I_2Li_2) and octamethyl-[12]mercuracarborand-4 (**6**•I_2Li_2) appeared to have similar solubility properties, while the diiodide complex of hexadecamethyl[12]mercuracarborand-4 (**7**•I_2Li_2) was markedly more

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Table 1. Details of Crystallographic Data Collection

	6·I_2(K·[18]dibenzocrown-6)$_2$	**7**·$I_2(NBu_4)_2$	**6**$_3$·I_4Li_4	**5**·$Br_2(NBu_4)_2$
formula[a]				
fw[b]				
crystal size (mm)	0.08 × 0.05 × 0.12	0.32 × 0.43 × 0.43	0.15 × 0.12 × 0.18	0.12 × 0.12 × 0.22
crystal system	monoclinic	monoclinic	tetragonal	triclinic
space group	$C2/m$	$P2_1/c$	$I4/m$	$P\bar{1}$
a (Å)	28.99(2)	12.77(1)	21.589(2)	10.433(1)
b (Å)	18.19(1)	21.12(2)		13.013(1)
c (Å)	13.61(1)	20.96(2)	21.666(2)	15.867(2)
α (deg)				91.638(2)
β (deg)	113.74(2)	97.87(2)		97.186(3)
γ (deg)				114.202(2)
V (Å^3)	6568	5600	10098	1492
Z	4	2	2	1
ρ_{calc} (g/cm^3)[c]				
radiation (γ, Å)	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107
μ (cm^{-1})[d]				
scan rate (deg/min)	4.5	6	6	9
scan width, below Kα_1 (deg)	1.3	1.3	1.3	1.3
above Kα_2 (deg)	1.6	1.6	1.6	1.6
$2\theta_{max}$ (deg)	40	45	45	50
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,+l$	$+h,\pm k,\pm l$
unique reflections	3536	4280	3403	6849
observed reflections/$I > 3\sigma(I)$	1491	2433	1345	3856
parameters refined	174	181 + 94 (2 blocks)	131	225
R (%)[e]	0.060	0.072	0.058	0.078
R_w (%)[f]	0.070	0.082	0.084	0.104
GOF[g]	1.79	2.59	2.25	3.14

[a] The empirical formula could not be stated due to uncertainties in the cell contents. [b] The formula weight could not be calculated due to uncertainties in the cell contents. [c] The density could not be calculated due to uncertainties in the cell contents. [d] The absorption coefficient could not be calculated due to uncertainties in the cell contents. [e] $R = \Sigma||F_o| - |F_c||/|F_o|$. [f] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2]^{1/2}$. [g] GOF $= [\Sigma w(|F_o| - |F_c|)^2/N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

Table 2. Selected Distances (Å) and Angles (deg) in **6**·I_2(K·[18]dibenzo-crown-6)$_2$, **7**·$I_2(NBu_4)_2$, **6**$_3$·I_4Li_4, and **5**·$Br_2(NBu_4)_2$

6·I_2(K·[18]dibenzo-crown-6)$_2$					
HG1−C2	2.05(3)	HG2−C1	2.11(3)	C1−C2	1.68(4)
HG1−HG2	3.935(2)	HG1−HG1′	5.773(2)	HG2−HG2′	5.349(2)
HG1−I1	3.438(4)	HG2−I1	3.335(3)	I1−I1′	3.985(7)
C1−HG2−C1′	152.4(10)	C2−HG1−C2′	158.0(14)	HG2−C1−C2	122(2)
HG1−C2−C1	123(2)	HG1−HG2−HG1′	94.37(4)	HG2−HG1−HG2′	85.63(4)
7·$I_2(NBu_4)_2$					
HG1−C2B	2.12(3)	HG1−C2A	2.11(3)	HG2−C1A	2.14(4)
HG2−C1B	2.17(4)	C1A−C2A	1.67(5)	C1B−C2B	1.59(5)
HG1−HG2	3.956(2)	HG1−HG2′	3.946(2)	HG1−HG1′	5.640(2)
HG2−HG2′	5.534(2)	HG1−I1	3.441(3)	HG1−I1′	3.397(3)
HG2−I1	3.382(3)	HG2−I1′	3.368(3)	I1−I1′	3.866(4)
C2B−HG1−C2A	155.8(11)	C1A−HG2−C1B	155.8(13)	HG2−C1A−C2A	123(2)
HG1−C2A−C1A	121(2)	HG2−C1B−C2B	123(2)	HG1−C2B−C1B	124(2)
HG2−HG1−HG2′	88.9(10)	HG1−HG2−HG1′	91.1(1)		
6$_3$·I_4Li_4					
HG1A−C1A	2.10(5)	HG1A−C2A	2.03(5)	HG2A−C1B	2.09(4)
HG2A−C2B	2.16(4)	C1A−C2A	1.60(7)	C1B−C2B	1.70(5)
HG1A−HG1A′	4.031(5)	HG1A−HG1A″	5.700(5)	HG2A−HG2A′	4.069(3)
HG2A−HG2A″	5.755(3)	HG2A−I2B	3.288(4)	HG1A−I2A	3.350(9)
HG1A−I2C	4.02(2)	HG2A−I2C	3.85(2)	HG2A−I2A	4.63(1)
I2B−I2C	4.15(3)	I2A−I2C	4.59(3)	I2A−I2B	5.22(2)
C1B−HG2A−C2B	158(2)	C2A−HG1A−C1A	162(1)	HG1A−C2A−C1A	125(2)
HG1A−C1A−C2A	127(2)	HG2A−C1B−C2B	126(3)	HG2A−C2B−C1B	122(3)
5·$Br_2(NBu_4)_2$					
HG1−C1A	2.06(2)	HG1−C1B	2.08(2)	HG2−C2A	2.08(2)
HG2−C2B	2.10(2)	C1A−C2A	1.70(3)	C1B−C2B	1.58(3)
HG1−HG2	3.959(1)	HG1−HG2′	3.920(1)	HG1−HG1′	5.431(1)
HG2−HG2′	5.708(1)	HG1−BR1	3.252(3)	HG1−BR1′	3.300(3)
HG2−BR1	3.372(3)	HG2−BR1′	3.411(3)	BR1−BR1′	3.666(5)
C1A−HG1−C1B	154.9(9)	C2A−HG2−C2B	159.7(9)	HG1−C1A−C2A	123.2(13)
HG1−C1B−C2B	126.0(15)	HG2−C2B−C1B	123.2(15)	HG2−C2A−C1A	121.6(13)
HG2−HG1−HG2′	92.84(3)	HG1−HG2−HG1′	87.16(3)		

soluble in benzene. Complex **5**·I_2Li_2 and the empty host **5** have been previously described.[1b,c] However, the poor yields of compound **2**, the precursor to **5**, made the synthesis of **6** and its complexes an attractive alternative to **5**. Metathesis reactions

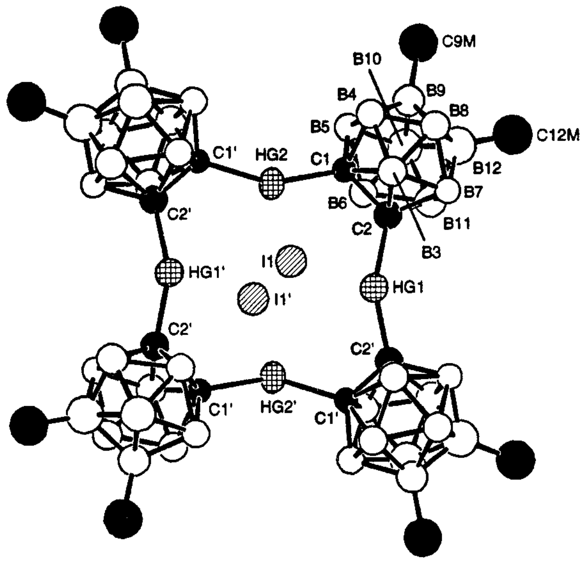


Figure 2. ORTEP representation of the anion $6{\cdot}I_2^{2-}$, which was crystallized as the potassium•dibenzo[18]crown-6 salt, showing the crystallographic numbering scheme. Hydrogen atoms have been removed for clarity.

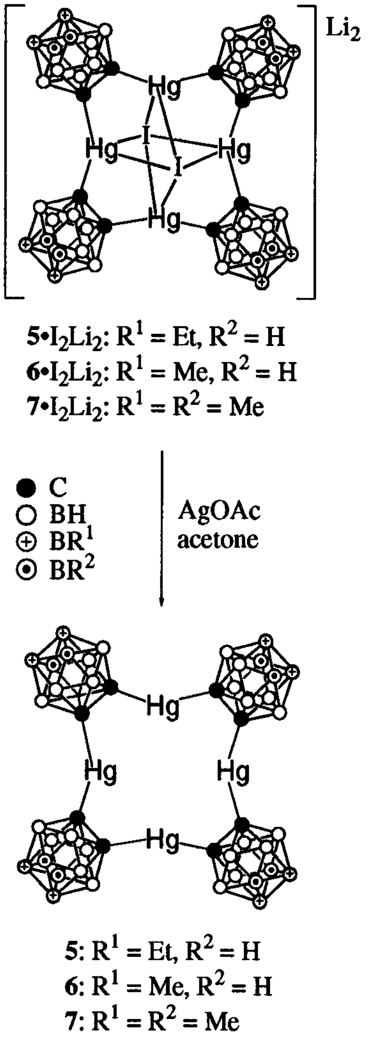
of the host−iodide complexes with salts such as KI or NR_4X (R = alkyl or aryl, X = halide) were facile and quantitative in ethanol solvent, which allowed the lithium counterions to be replaced by a choice of cation.

Crystal Structures of $6{\cdot}I_2$(K•dibenzo[18]crown-6)$_2$ and $7{\cdot}I_2(NBu_4)_2$. X-ray diffraction studies were carried out on both $6{\cdot}I_2$(K•dibenzo[18]crown-6)$_2$ and $7{\cdot}I_2(NBu_4)_2$ in order to have comparative structural data with the diiodide complex of **1**, which was crystallized as its tetraphenylarsonium salt.[1b,f] The nature of the three-center two-electron bonding interactions between filled orbitals of the halide guest and empty mercury p orbitals in the host has been discussed alongside the structural determination of $1{\cdot}I_2(AsPh_4)_2$. The structures of the host−guest complexes are presented in Figures 2 and 3, respectively. Details of data collection and structure determination for all the X-ray structures reported in this article are given in Table 1, and selected bond lengths and angles are given in Table 2. The anion $6{\cdot}I_2^{2-}$ has a mirror plane passing through the mercury atoms HG1 and the iodides I1 and a 2-fold rotational axis through the mercury atoms HG2. Thus, all the carborane icosahedra are related by symmetry, as are the two iodide ions. The mercury atoms are coplanar and lie in a slightly distorted square or rhombus with sides of 3.935(2) Å and internal angles of 94.37(4)° and 85.63(4)°. The carborane carbons C1 and C2 lie slightly above and below the plane of the mercury atoms (0.09 and 0.10 Å, respectively). The coordination around the mercury atoms shows major deviation from linearity, with C1−HG2−C1 and C2−HG1−C2 angles of 152.4(10)° and 158.0(14)°, respectively. The iodide ions lie directly above and below the center of the plane of the mercury atoms at a distance of 1.991 Å. The two Hg−I distances are 3.438(4) and 3.335(4) Å, both shorter than the van der Waals separation of 3.89 Å.[8]

In most respects $7{\cdot}I_2^{2-}$ is very similar to $6{\cdot}I_2^{2-}$. The anion is centrosymmetric, and all the mercury atoms are coplanar, lying in a parallelogram with sides of 3.956(2) and 3.946(2) Å and internal angles of 88.91(5)° and 91.09(5)°. The carborane carbon atoms C1 and C2 are both within 0.06 Å of the plane of the mercury atoms. The C−Hg−C angles are both 156(1)°, and the iodide ions lie above and below the approximate center of the plane of the mercury atoms by 1.933 Å. The Hg−I distances are 3.441(3), 3.397(3), 3.382(3), and 3.368(3) Å.

Comparison of $6{\cdot}I_2^{2-}$ and $7{\cdot}I_2^{2-}$ to $1{\cdot}I_2^{2-}$ reveals an interesting difference in the structures. Whereas the iodides in the former two complexes are approximately equidistant from all four mercury centers, this is not the case for the unsubstituted host complex $1{\cdot}I_2^{2-}$. Instead, each iodide has three short Hg−I distances of 3.277(1), 3.304(1), and 3.306(1) Å and one long distance of 3.774(1) Å. The short distances are markedly shorter than the Hg−I distances seen in $6{\cdot}I_2^{2-}$ and $7{\cdot}I_2^{2-}$, and the slippage presumably reduces iodide−iodide repulsion. All three complexes have approximately equal I−I distances of 3.969(1), 3.985(7), and 3.866(4) Å for $1{\cdot}I_2^{2-}$, $6{\cdot}I_2^{2-}$, and $7{\cdot}I_2^{2-}$, respectively, well within the van der Waals distance of 4.30 Å.[8] This suggests that the iodides in $1{\cdot}I_2^{2-}$ are more tightly bound than those in $6{\cdot}I_2^{2-}$ and $7{\cdot}I_2^{2-}$. The longer Hg−I distances in the alkyl-substituted complexes allow the iodide ions to assume their preferred positions of equal coordination to all the metal atoms without undue repulsion between the iodides.

Decomplexation of Host−Iodide Complexes. Preparation of the free hosts **6** and **7** from their iodide complexes was carried out in a fashion similar to the method reported for **5**.[1c,f] The iodide ions were quantatively removed from the host complex by reaction with ≥2 molar equiv of silver acetate, precipitating silver iodide (eq 2). The acetate ion is bulky and charge-diffuse, and shows no coordination to the host compounds. Removal of the salts by filtration and an aqueous wash allowed the isolation and characterization of compounds **6** and **7**. Progres-



$5{\cdot}I_2Li_2$: R^1 = Et, R^2 = H
$6{\cdot}I_2Li_2$: R^1 = Me, R^2 = H
$7{\cdot}I_2Li_2$: R^1 = R^2 = Me

5: R^1 = Et, R^2 = H
6: R^1 = Me, R^2 = H
7: R^1 = R^2 = Me

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

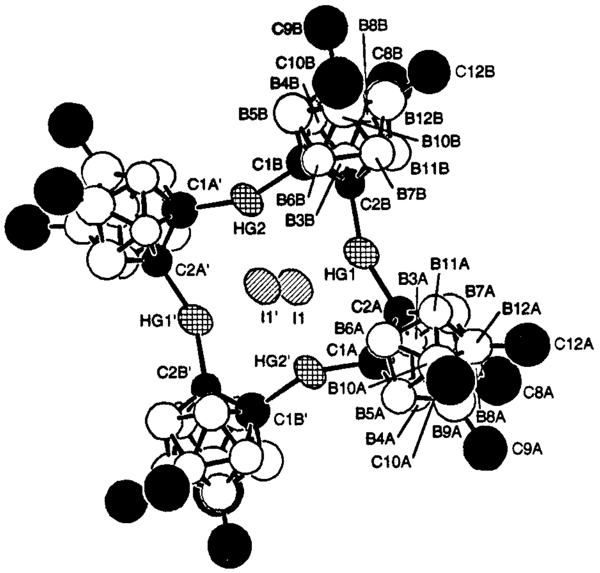

Figure 3. ORTEP representation of the anion $7{\cdot}I_2{}^{2-}$, which was crystallized as the tetrabutylammonium salt, showing the crystallographic numbering scheme. Hydrogen atoms have been removed for clarity.

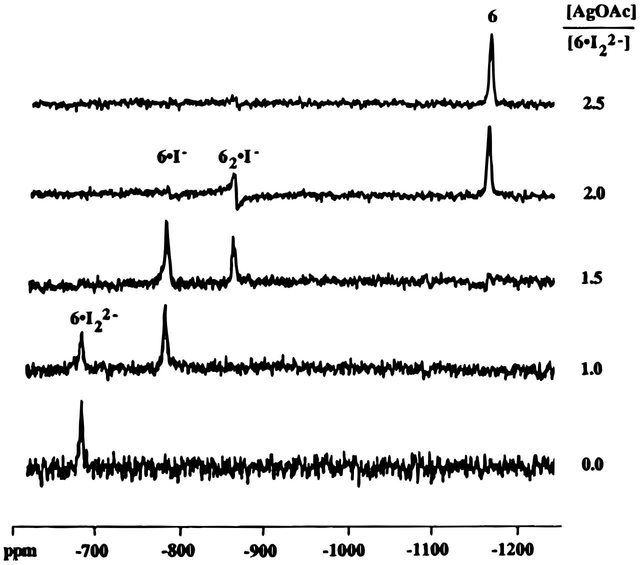

Figure 4. ^{199}Hg NMR spectra showing the effects of incremental addition of silver acetate to $6{\cdot}I_2Li_2$ in acetone solution.

sive removal of the iodide ions from complexes $5{\cdot}I_2Li_2$ and $6{\cdot}I_2Li_2$ by incremental addition of silver acetate, monitored by ^{199}Hg NMR, revealed that intermediate species are formed during this process which are quite distinct in the NMR spectrum, implying that they are stable on the time scale of NMR analysis. The results of the progressive decomplexation of $6{\cdot}I_2Li_2$ by silver acetate are shown in Figure 4. Addition of approximately 1 molar equiv of silver acetate to the diiodide complex (peak at −667 ppm) affords a second species with a resonance at −765 ppm, which we take to be the monoiodo complex **6**·ILi. A significant amount of the diiodide complex still remains, however. We have previously reported X-ray diffraction studies of **1**·ClLi and **1**·BrLi.[1a,f] After further addition of 0.5 molar equiv of silver acetate, the resonance corresponding to the diiodide complex disappears, and a new signal is apparent at −846 ppm. We believe that this resonance arises from a sandwich structure $6_2{\cdot}ILi$, in which a single iodide ion is coordinated simultaneously to two mercuracarborand hosts. After the addition of a total of approximately 2 molar equiv of silver acetate, the majority of the mercuracarborand **6** is decomplexed, as shown by the signal at −1145 ppm in the NMR spectrum. Addition of a final 0.5 molar equiv of silver acetate removes remaining **6**·ILi and $6_2{\cdot}ILi$, leaving only the decomplexed host. The process can be reversed by sequential addition of tetrabutylammonium iodide to regenerate the diiodide complex $6{\cdot}I_2Li_2$. The complex can thus be regarded as an "iodide reservoir" with a maximum capacity of two complexed iodide ions per host molecule.

Table 3. ^{199}Hg NMR Shifts (ppm) of [12]Mercuracarborand-4 Hosts and Host−Guest Complexes[a]

	1	5	6	7
empty host	−1230	−1152	−1145	−1144
$host_2-I^-$	−910	−852	−846	
$host-I^-$	−811	−771	−765	
$host-I_2{}^{2-}$	−713	−672	−667	−676
$host-Br^-$	−1010		−948	
$host-Br_2{}^{2-}$		−805	−797	
$host-B_{10}I_{10}{}^{2-}$		−1006[b]	−1009[b]	
$host-B_{12}I_{12}{}^{2-}$		−1006[b]	−1003[b]	

[a] All measurements in d_6-acetone except when otherwise stated. [b] In DMSO-d_6.

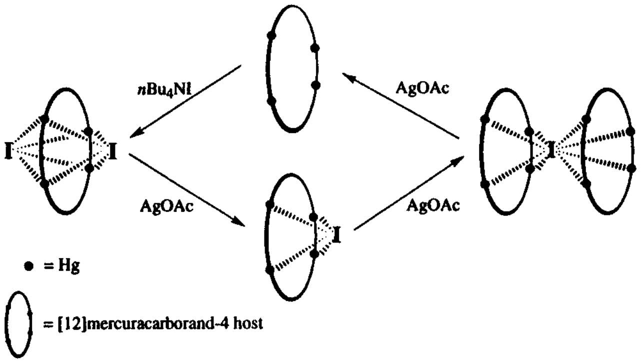

Figure 5. Postulated species present during progressive decomplexation of host−diiodide complexes with silver acetate.

An identical procedure was carried out with both $5{\cdot}I_2Li_2$ and the unsubstituted host compound with similar results. The ^{199}Hg NMR chemical shifts observed for the various hosts studied and their complexes are presented in Table 3, and a schematic diagram of the various iodide complexes and their interconversions is given in Figure 5. It was observed that if partially decomplexed mercuracarborand solutions were allowed to stand for a period of hours, equilibration between the various iodide complexes would occur. This hindered our efforts to obtain crystal structures of the intermediate complexes **5**(**6**)·ILi and **5**(**6**)$_2$·ILi. Several attempts were made to isolate these complexes by progressive decomplexation monitored by ^{199}Hg NMR, but crystallization from the filtered solutions containing the desired intermediates yielded either diiodide complexes or an unusual structure having a surprising stoichiometry of $6_3{\cdot}I_4Li_4$, which is described below.

Crystal Structure of $6_3{\cdot}I_4Li_4$. The structure of the complex anion $6_3{\cdot}I_4{}^{4-}$ is shown in top view in Figure 6 and in side view in Figure 7. It takes the form of a "short stack" of three host molecules alternating with four iodide ions. The molecular aggregate has a 4-fold axis of symmetry running through the iodide atoms and a center of symmetry. The two inner iodide ions are in different positions, one close to the central host molecule and the other approximately halfway between the central host molecule and one of the outer hosts. These positions, however, are disordered with 50% occupancy on each side of the central host. The atoms of the central host molecule which constitute the cycle, C1A, C2A, and HG1A, are rigorously coplanar, and the outer host molecules are very nearly so, with

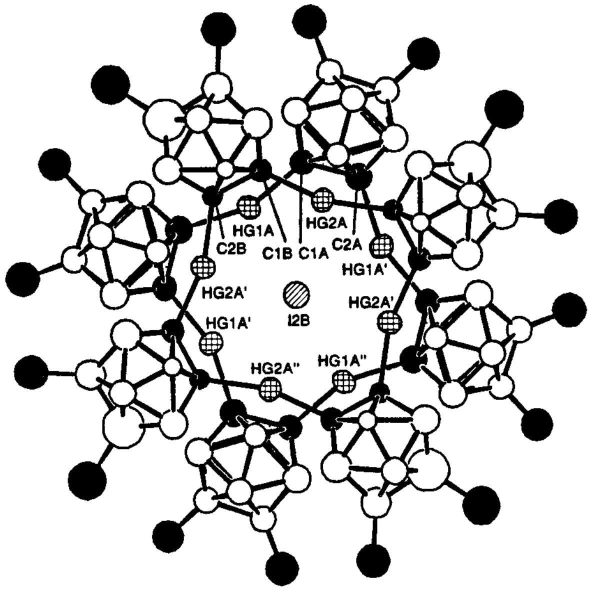

Figure 6. ORTEP representation of the complex anion $\mathbf{6}_3\cdot I_4^-$, which was crystallized as the lithium salt, viewed along the C_4 axis with significant atoms labeled. The full crystallographic numbering scheme is given in the Supporting Information.

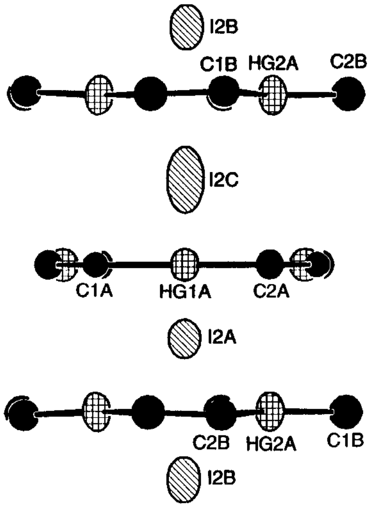

Figure 7. ORTEP representation of the complex anion $\mathbf{6}_3\cdot I_4^-$ viewed perpendicular to the C_4 axis, with boron and hydrogen atoms removed for clarity.

the carbon atoms C1B and C2B not deviating more than 0.05 Å from the plane defined by the mercury atoms. The C−Hg−C angles are 158(2)° for the outer hosts and 162(1)° for the inner host, somewhat larger than those seen in the diiodide complexes discussed above. The separation between the planes of the mercuracarborands in the stack is 5.387 Å. The outer iodide ions I2B are found to be very close to the outer host molecules, with an I2B−HG2A distance of 3.288(4) Å. This is approximately the same as the short Hg−I distances seen in $\mathbf{1}\cdot I_2Li_2$ [3.277(1)−3.306(1) Å]. The distance from the mercury atoms in the outer hosts to the closer of the two inner iodide positions (HG2A−I2C) is considerably longer at 3.85(2) Å, approximately the same as the Hg−I van der Waals distance of 3.89 Å, and the I2B−I2C distance is 4.15(3) Å, much longer than the iodide−iodide separations seen in the diiodide complexes $\mathbf{1}\cdot I_2^{2-}$, $\mathbf{6}\cdot I_2^{2-}$, and $\mathbf{7}\cdot I_2^{2-}$. The distances from the mercury atoms of the central host molecule to the inner iodide ions are 4.02(2) and 3.350(9) Å for HG1A−I2C and HG1A−I2A, respectively. The iodide ions on each side of the central host molecule are therefore separated by 4.59(3) Å, a distance longer than the I−I van der Waals distance of 4.30 Å. Finally, the distance from the mercury atoms of the outer hosts to the further of the two inner iodide ions, HG2A−I2A, is 4.63(1) Å, thus giving an I2B−I2A distance of 5.22(2) Å. None of the iodide ions are “slipped” from the central axis of the molecule, reflecting the fact that they are not forced into sufficiently close proximity for iodide−iodide repulsions to come into play.

While the crystallographic disorder imposes a center of symmetry on the complex ion in the crystal structure, the two outer host molecules are not in the same environment in each individual molecule. Both outer hosts have a strong interaction to the outer iodide ion I2B. However, the interior iodide ion I2C is close to the distance midway between the outer and the central hosts. It is just within the Hg−I van der Waals distance to the outer host, but is a little outside the van der Waals distance from the central host. This iodide ion has been less well-located than the other atoms of the structure, as is reflected by its large thermal ellipsoid, and must have only a weak host−guest interaction. On the other side of the molecule, iodide I2A has a strong interaction to the central host, but lies well-outside the van der Waals distance from the mercury atoms of the outer host.

It seems surprising that there is no evidence of disorder in the outer two host molecules and iodide ions, and yet the two distances between the planes of the host molecules in the stack are identical despite the different environments of the internal iodide ions. It would seem to be incorrect to regard the stack as a single large host−guest complex. It is instead best described as being comprised of three separate monoiodide complexes and a very loosely coordinated iodide. There seems to be no evidence of such a species being present in solution, and it is presumably a crystallographic construct favored for reasons of energetics and solubility relationships. The stacking distance of 5.387 Å is thus not a function of the iodides holding the hosts together and is simply the distance at which they are most “comfortable” in the solid state. The complexes $\mathbf{1}\cdot$ClLi and $\mathbf{1}\cdot$BrLi are observed to form infinite stacks with the halide ions tightly bound to one host in the solid state. The separation between the planes of the host molecules in $\mathbf{1}\cdot$ClLi is 5.63 Å, while in $\mathbf{1}\cdot$BrLi there are two alternating distances between the hosts of 5.57 and 5.74 Å.[1f] While similar to the distance seen in $\mathbf{6}_3\cdot I_4Li_4$, they are slightly longer, suggesting that the larger iodide ions may have at least a small bonding interaction with the hosts to each side. This may explain why we were unable to isolate a true monoiodide complex of **5** or **6** in the solid state, whereas each host will form a monobromide complex (*vide infra*).

^{199}Hg NMR Studies of Host−Guest Interactions. Other than by X-ray crystallography, the most useful way to probe the effects of alkyl substitution of the carboranes upon the coordination properties of the hosts is by NMR spectroscopy. The usual tools of ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy are uninformative about host−guest coordination states, undergoing little change in the host regardless of the presence or absence of a guest. However, ^{199}Hg NMR is very sensitive to changes in the immediate environment around the mercury atom, and we have found it to provide useful information about the extent of interaction between guest and host. It is apparent from the chemical shifts of the resonance observed for the empty hosts (Table 3) that alkyl substitution has an effect on the environment of the mercury atoms, with upfield shifts of 60−70 ppm being observed for **5**, **6**, and **7** compared to that of **1**. The size of the upfield shift is relatively insensitive to the degree of substitution; the peaks for **5**, **6**, and **7** lie within 8 ppm of each other. When the hosts are each coordinated to two iodide ions, significant

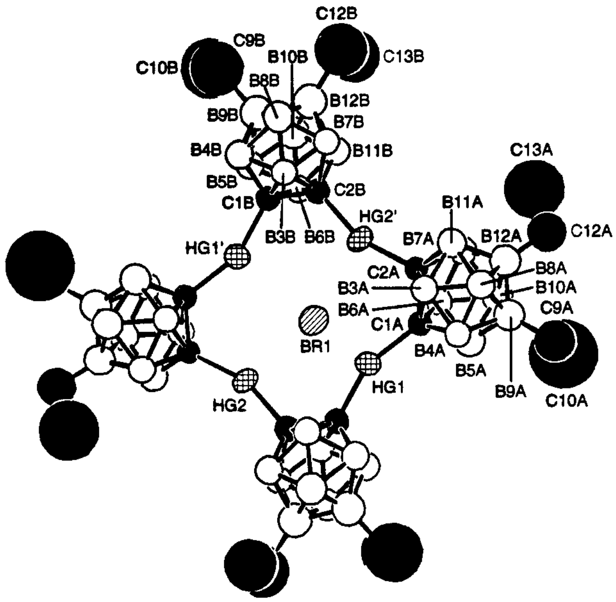

Figure 8. ORTEP representation of $5 \cdot Br_2^{2-}$, which was crystallized as the tetrabutylammonium salt, showing the crystallographic numbering scheme. Hydrogen atoms have been removed for clarity.

shifts are seen in the ^{199}Hg NMR spectra, on the order of 470–500 ppm. The magnitude of the NMR shift upon iodide coordination varies somewhat with the degree of alkyl substitution. The largest upfield shift (498 ppm) is seen for the unsubstituted host. The alkyl-substituted hosts **5**, **6**, and **7** show smaller shifts indicative of a weaker interaction between the host and the iodide guests. The ^{199}Hg NMR signals for hosts **5** and **6** shift 480 and 478 ppm, respectively, or approximately 20 ppm less than that of the unsubstituted host, while the signal for **7**, the most substituted host, shifts only 468 ppm, approximately 30 ppm less than that of the unsubstituted host.

Overall, it appears that introduction of alkyl substituents to the more distant boron vertices of the cage from the mercury atoms has relatively little effect on the coordinating properties of the mercuracarborands, while having significant effects upon the solubilities of the various substituted hosts. However, a definite, if small, trend indicating that the degree of coordination of guests to the mercury atoms decreases with increasing alkyl substitution can be seen by ^{199}Hg NMR.

Crystal Structure of $5 \cdot Br_2(NBu_4)_2$. Reaction of the empty host molecules **5** and **6** with bromide salts allowed isolation of both dibromide complexes $5 \cdot Br_2(NBu_4)_2$ and $6 \cdot Br_2(NBu_4)_2$, as well as the monobromide complex **6**·BrK. As we have not previously determined the structure of a dibromide complex of any host, crystals of $5 \cdot Br_2(NBu_4)_2$ were obtained and an X-ray diffraction study was carried out, the results of which are shown in Figure 8. The anion $5 \cdot Br_2^{2-}$ is centrosymmetric, with the four mercury atoms coplanar and arranged in a parallelogram with sides of 3.959(1) and 3.920(1) Å and internal angles of 92.84(3)° and 87.16(3)°. The carboranyl carbon atoms deviate by a maximum of 0.11 Å from this plane. The mercury atoms are bent in toward the center of the molecule, with C–Hg–C angles of 154.9(9)° and 159.7(9)°, essentially the same as those seen in the diiodide complexes of **1**, **6**, and **7**, but smaller than those found in **1**·BrLi (average 163.0°). The bromide ions lie above and below the plane of the mercury atoms and are approximately equidistant from them, with Hg–Br distances of 3.252(3), 3.300(3), 3.372(3), and 3.411(3) Å. These are considerably longer than the average Hg–Br distance found in **1**·BrLi, which is 3.063(5) Å. The Br–Br distance is 3.666(5) Å, within the van der Waals distance of 3.90 Å.

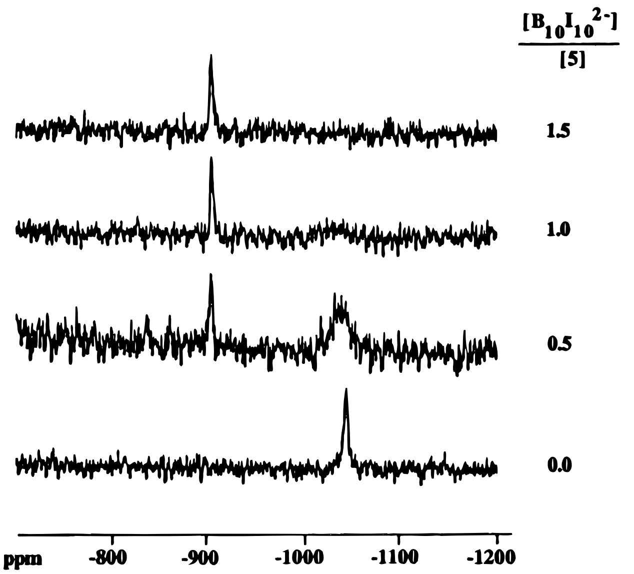

Figure 9. ^{199}Hg NMR spectra showing the effects of incremental addition of $B_{10}I_{10} \cdot (NMe_3H)_2$ to **5** in dimethyl sulfoxide solution.

Comparison of the ^{199}Hg NMR values of **1**, **5**, and **6** and their known bromide complexes (Table 3) reveals trends similar to those seen for the iodide complexes. Coordination of one bromide ion to the empty host **1** results in a downfield shift of 220 ppm in the NMR signal, whereas with the octamethyl host **6** the shift is only 197 ppm, implying weaker coordination. On coordination of two bromide ions, hosts **5** and **6** show essentially identical downfield ^{199}Hg NMR shifts of 347 and 348 ppm, respectively. All of these shifts are much smaller than those observed for the iodide complexes and suggest a significantly weaker interaction between bromide and mercury, which is not immediately apparent from the structural information.

Supramolecular Interactions between Mercuracarborands and Polyhedral Anions. Among the remarkable properties of the mercuracarborands is their ability to coordinate extremely weak neutral nucleophiles such as the carborane derivatives $9,12\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and $9\text{-}I\text{-}12\text{-}Et\text{-}1,2\text{-}C_2B_{10}H_{10}$, Lewis bases such as 1,10-phenanthroline, and polyhedral borane anions such as $B_{10}H_{10}^{2-}$, resulting in the formation of supramolecular arrays.[1] The formation of a supramolecular system relies on complementary bonding between the various components, and the mercuracarborands achieve these in different ways depending on the identity of the guest. For instance, the dianion $B_{10}H_{10}^{2-}$ uses four equatorial BH vertices to form three-center two-electron B–H–Hg bonds to each mercury atom of the host cycle **5** in the solid state. While the matching symmetry of the tetrameric host (C_{4h}) and guest (D_{4d}) allows a significant bonding interaction due to complementary shape (as measured by the *ca.* 260 ppm shift in the ^{199}Hg NMR of **5** upon complexation of guest), the 5-fold symmetric dianion $B_{12}H_{12}^{2-}$ (I_h) shows no propensity to form host–guest complexes with the tetrameric mercuracarborands. A much weaker interaction is seen upon complexation of $9,12\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and $9\text{-}I\text{-}12\text{-}Et\text{-}1,2\text{-}C_2B_{10}H_{10}$ (*ca.* 5 ppm shift in the ^{199}Hg NMR of **5** upon complexation of guest), but the crystal structure of the complex shows that an iodine atom of each guest molecule is located equidistant from the mercury atoms of the host in a manner similar to the halide-complexed mercuracarborands, although the weaker binding is reflected in longer Hg–I distances. The covalent bonding in this case arises through two Hg–I–Hg three-center two-electron bonds, each utilizing a filled p orbital on the iodine atom which interacts simultaneously with a vacant p orbital on each of two opposite mercury atoms of the host. A similar, though stronger, interaction holds together the host−iodide complexes.[1f]

Incremental addition of the polyhedral anions $B_{10}I_{10}^{2-}$ and $B_{12}I_{12}^{2-}$ to dimethyl sulfoxide solutions of the empty hosts **5** and **6** resulted in downfield shifts in the ^{199}Hg NMR spectra of the host molecules on the order of 140 ppm (Table 3). Although >1 molar equiv of the respective anion was added in each case, only evidence for the existence of a monoadduct was seen in solution. Figure 9 shows the results of one such sequential addition. Crystal structures of **5**$\cdot(B_{10}H_{10}^{2-})_2$ and **5**$\cdot$(9,12-I_2-1,2-$C_2B_{10}H_{10})_2$ showed a preference in the solid state for bisadducts, but in solution these guests formed only monoadducts. Attempts to crystallize the host−guest complexes **5**(**6**)$\cdot B_{10}I_{10}^{2-}$ and **5**(**6**)$\cdot B_{12}I_{12}^{2-}$ unfortunately gave only crystals of the guest salts. The strengths of the bonding interaction for both **5**(**6**)$\cdot B_{10}I_{10}^{2-}$ and **5**(**6**)$\cdot B_{12}I_{12}^{2-}$ as estimated from ^{199}Hg NMR are intermediate between the fairly strong interaction seen in **5**$\cdot B_{10}H_{10}^{2-}$ and the extremely weak interaction seen in **5**$\cdot$9,12-I_2-1,2-$C_2B_{10}H_{10}$. No significant difference was seen between the $B_{10}I_{10}^{2-}$ and $B_{12}I_{12}^{2-}$ adducts, suggesting that the symmetry of the anion plays no part in the bonding interaction. We therefore conclude that bonding takes place through a single iodine atom in a manner similar to that for **5**$\cdot$9,12-I_2-1,2-$C_2B_{10}H_{10}$, and that the stronger interaction is a result of the charge carried by the complex anions. As the charge is mostly localized within the polyhedral framework, however, the interaction is much weaker than that seen for the host−halide complexes.

Conclusions

Derivatives of the charge-reversed crown host [12]mercuracarborand-4 with alkyl substituents directed away from the host cavity have a number of desirable features not seen in the unsubstituted parent. The alkyl groups provide no steric interference to guest coordination, and electronic effects, though measurable, are small. At the same time, the presence of substituents improves the solubility properties of the hosts and their complexes, and the high-yield syntheses of alkyl-substituted carborane precursors allow relatively large-scale production of the substituted hosts. The potential for a range of substituents to impart "tailor-made" properties such as water solubility is under active exploration.

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Diethyl ether was distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Deuteriated solvents were obtained from Cambridge Isotope Laboratories. Mercuric iodide (Cerac), *n*-butyllithium (2.5 M solution in hexanes) (Aldrich), silver acetate (Matheson Coleman and Bell), tetrabutylammonium bromide (Aldrich), tetrabutylammonium iodide (Matheson Coleman and Bell), methyl iodide (Aldrich), and trifluoromethanesulfonic acid (Aldrich) were used as received. *o*-Carborane was obtained from Consumer Health Research of Los Angeles and was sublimed before use. The compounds *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$,[5] *closo*-9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$,[3] **5**, and **5**$\cdot I_2Li_2$[1] were prepared according to previously described procedures.

Physical Measurements. All NMR spectra were recorded at room temperature. The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained with a Bruker ARX 400 spectrometer, and the ^{11}B{^{1}H} and ^{199}Hg{^{1}H} NMR spectra were obtained using a Bruker ARX 500 spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual ^{1}H and ^{13}C present in deuteriated solvents. Chemical shift values for ^{11}B{^{1}H} spectra were referenced relative to external $BF_3\cdot Et_2O$ (0.0 ppm with negative value upfield). The ^{199}Hg{^{1}H} NMR spectra were measured in 10 mm sample tubes at 89.4 MHz using broad band decoupling. A 10 μs pulse width, a 3 s relaxation delay, and a 8333 Hz sweep width were used. External 1.0 M PhHgCl/DMSO-d_6 solution was used as the reference at −1187 ppm relative to neat Me_2Hg. All FAB mass spectra were obtained on a VG ZAB spectrometer with an NBA matrix.

Preparation of *closo*-8,9,10,12-Me_4-1,2-$C_2B_{10}H_8$ (4). A mixture of *closo*-1,2-$C_2B_{10}H_{12}$ (0.50 g, 3.5 mmol) and CH_3I (2.2 mL, 35.0 mmol) in neat trifluoromethanesulfonic acid (3.0 mL) was refluxed for 4 days under argon. Water (20 mL) was added, and the mixture was extracted with diethyl ether (3 × 10 mL). The combined organic phase was dried over $MgSO_4$. After removal of the solvent, the solid obtained was subjected to flash silica gel chromatography, yielding *closo*-8,9,10,12-Me_4-1,2-$C_2B_{10}H_8$ (**4**) as a white solid in 65% yield after removal of solvent: ^{1}H NMR ($CDCl_3$) 4.14 (s, 2 H, CH), 1.28−2.74 (br, 6 H, BH), 0.18, 0.07 (s, 6 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-d_6) 47.8 (CH), −2.1 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (acetone) 7.2 (2 B, BCH_3), 0.2 (2 B, BCH_3), −13.0 (4 B), −17.8 (2 B) ppm; HRMS (EI) for $C_6B_{10}H_{20}$ (*m/z*) calcd 202.2496, obs 202.2503 (M^+).

Preparation of 5$\cdot Br_2(NBu_4)_2$. To a solution of **5**$\cdot I_2Li_2$ (0.25 g, 0.13 mmol) in deuterioacetone (2 mL) in a 10 mm NMR tube was added silver acetate (0.06 g, 0.33 mmol), giving a yellow precipitate of silver iodide. The solution was shaken well, and the ^{199}Hg NMR was taken, confirming that the only species present in solution was the free host. The solution was filtered, and the solvent was removed *in vacuo*. The residue was taken up in diethyl ether (20 mL), washed with water (2 × 10 mL), and dried over sodium sulfate. After removal of solvent the residue (**5**) was dissolved in acetone (10 mL), and tetrabutylammonium bromide (0.11 g, 0.33 mmol) was added. After stirring for 1 h at room temperature, the solvent was removed and the residue redissolved in diethyl ether (20 mL). After washing with water (3 × 10 mL) to remove excess tetrabutylammonium bromide and drying over sodium sulfate, solvent was removed to afford a quantitative yield of **5**$\cdot Br_2(NBu_4)_2$ as a white crystalline solid: ^{1}H NMR (acetone-d_6) 3.44 (m, 16 H, NCH_2), 1.82, 1.44 (m, 2 × 16 H, CH_2), 0.99 (t, 24 H, CH_3, J_{HH} = 7 Hz), 0.80 (m, 24 H, BCH_2CH_3), 0.60 (m, 16 H, BCH_2) ppm; ^{13}C{^{1}H} NMR (acetone-d_6) 83.4 (HgC), 58.4 (NCH_2), 23.4, 19.4 (CH_2), 12.9 (BCH_2CH_3), 12.9 (CH_3), 8.6 (vbr, BCH_2) ppm; ^{11}B{^{1}H} NMR ($CHCl_3$) 6.8 (2 B, BCH_2CH_3), −10.8 (2 B), −13.2 (4 B), −16.8 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-d_6) −805 ppm; MS (negative-ion FAB) for $C_{24}H_{72}B_{40}Br_2Hg_4$ (*m/z*) calcd 1756, obs 1754 (M^-, 17), 1677 [$(M - Br)^-$, 100].

Preparation of 6$\cdot I_2Li_2$. To an ethereal solution (20 mL) of *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ (0.50 g, 2.9 mmol) at 0 °C was added *n*-butyllithium (2.4 mL, 6.0 mmol, 2.5 M solution in hexanes), and the slurry was stirred at room temperature under argon. After 4 h, the mixture was cooled to 0 °C and treated with solid mercuric iodide (1.32 g, 2.9 mmol). The stirring was continued overnight as the mixture warmed up to room temperature. The reaction was then quenched with 20 mL of water, and the organic phase was separated. The water layer was extracted with diethyl ether (3 × 5 mL). The combined organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum. The residue was triturated with pentane to give the diiodide complex of octamethyl-[12]mercuracarborand-4 (**6**$\cdot I_2Li_2$) as a white crystalline solid (85%): ^{1}H NMR (acetone-d_6) 0.05 (s, 24 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-d_6) 86.3 (HgC), 0.9 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR ($CHCl_3$) 10.3 (2 B, BCH_3), −3.7 (2 B), −7.2 (4 B), −10.5 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-d_6) −667 ppm; MS (negative-ion FAB) for $C_{16}H_{56}B_{40}Hg_4I_2$ (*m/z*) calcd 1737, obs 1737 (M^-, 11), 1612 [$(M - I)^-$, 100].

Preparation of 6. The complex **6**$\cdot I_2Li_2$ (0.25 g, 0.14 mmol) in 10 mL of acetone was treated with $Ag(OAc)_2$ (0.05 g, 0.30 mmol) at room temperature, and a yellow precipitate immediately formed. After 20 min, the mixture was filtered, the solvent was removed, and the residue was triturated with pentane to give octamethyl[12]mercuracarborand-4 (**6**) in quantitative yield: ^{1}H NMR (acetone-d_6) 0.03 (s, 24 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-d_6) 86.3 (HgC), 0.8 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (acetone-d_6) 9.4 (2 B, BCH_3), −4.5 (2 B), −8.0 (4 B), −10.7 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-d_6) −1145 ppm.

Preparation of 6$\cdot$BrK. To a solution of **6** (0.20 g, 0.13 mmol) in acetone (10 mL) was added potassium bromide (0.02 g, 0.13 mmol), and the solution was stirred for 1 h. Solvent was removed *in vacuo* and the residue taken up in diethyl ether (20 mL). The solution was washed with water (3 × 10 mL) and dried over sodium sulfate. Removal of solvent afforded **6**·BrK as a white crystalline solid in quantitative yield: ^{1}H NMR (acetone-*d*$_6$) 0.06 (s, 24 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-*d*$_6$) 86.1 (HgC), 1.0 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (acetone-*d*$_6$) 10.1 (2 B, BCH_3), −3.8 (2 B), −8.0 (4 B), −11.5 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-*d*$_6$) −948 ppm.

Preparation of 6·$Br_2(NBu_4)_2$. In a manner similar to the preparation of **6**·BrK above, addition of tetrabutylammonium bromide (0.09 g, 0.27 mmol) to an acetone solution of **6** (0.20 g, 0.13 mmol) gave, after workup, **6**·$Br_2(NBu_4)_2$ as a white crystalline solid in quantitative yield: ^{1}H NMR (acetone-*d*$_6$) 3.45 (m, 16 H, NCH_2), 1.81, 1.44 (m, 2 × 16 H, CH_2), 0.99 (t, 24 H, CH_3, $J_{HH} = 7$ Hz), 0.06 (s, 24 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-*d*$_6$) 85.5 (HgC), 59.3 (NCH_2), 24.4, 20.3 (CH_2), 13.9 (BCH_3), 1.2 (vbr, BCH_2) ppm; ^{11}B{^{1}H} NMR ($CHCl_3$) 9.6 (2 B, BCH_3), −4.4 (2 B), −7.7 (4 B), −10.6 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-*d*$_6$) −797 ppm; MS (negative-ion FAB) for $C_{16}H_{56}B_{40}Br_2Hg_4$ (*m/z*) calcd 1643, obs 1559 [(M − Br)$^-$, 100].

Preparation of 7·I_2Li_2. To an ethereal solution (20 mL) of **4** (0.20 g, 1.0 mmol) at 0 °C was added *n*-butyllithium (0.80 mL, 2.0 mmol, 2.5 M solution in hexanes), and the slurry was stirred at room temperature under argon. After 4 h, the mixture was cooled to 0 °C and treated with solid HgI_2 (0.45 g, 1.0 mmol). The stirring was continued overnight as the mixture warmed to room temperature. The reaction was then quenched with 20 mL of H_2O, and the organic phase was separated. The water layer was extracted with diethyl ether (3 × 5 mL). The combined organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was triturated with pentane to give the diiodide complex of hexadecamethyl[12]mercuracarborand-4 (**7**·I_2Li_2) as a white solid in 78% yield: ^{1}H NMR (CD_2Cl_2) 0.15, 0.09 (s, 24 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-*d*$_6$) 85.6 (HgC), −1.8 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR ($CHCl_3$) 9.8 (2 B, BCH_3), 2.9 (2 B, BCH_3), −8.5 (4 B), −13.7 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-*d*$_6$) −676 ppm; MS (negative-ion FAB) for $C_{24}H_{80}B_{40}Hg_4I_2$ (*m/z*) calcd 1858, obs 1860 (M$^-$, 10), 1733 [(M − I)$^-$, 57].

Preparation of 7. The complex **7**·I_2Li_2 (0.20 g, 0.11 mmol) in 10 mL of acetone was treated with $Ag(OAc)_2$ (0.40 g, 0.24 mmol) at room temperature, and a yellow precipitate immediately formed. After 20 min, the mixture was filtered, the solvent was removed, and the residue was triturated with pentane to give hexadecamethyl[12]mercuracarborand-4 (**7**) in quantitative yield: ^{1}H NMR (acetone-*d*$_6$) 0.12, −0.11 (s, 24 H, BCH_3) ppm; ^{13}C{^{1}H} NMR (acetone-*d*$_6$) 82.8 (HgC), −2.0 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (acetone) 10.8 (2 B, BCH_3), 3.8 (2 B, BCH_3), −7.4 (4 B), −13.3 (2 B) ppm; ^{199}Hg{^{1}H} NMR (acetone-*d*$_6$) −1144 ppm.

Stepwise Decomplexation of the Iodide Ion Complexes of 5 and 6. Decomplexation reactions of **5**·I_2Li_2 and **6**·I_2Li_2 were carried out in the same fashion. An accurately weighed amount (*ca*. 0.25 g) of the complex was dissolved in approximately 2 mL of deuteriated acetone in a 10 mm NMR tube. Solid silver acetate was added in increments of 0.5 molar equiv. After each increment of the silver salt was added, the mixture was mixed well and the ^{199}Hg NMR spectrum taken. The procedure was repeated until no further change in the spectrum was observed.

Complexation Chemistry of 5 and 6 with $[NMe_3H]B_{10}I_{10}^{2-}$ and $[NMe_3H]B_{12}I_{12}^{2-}$ Investigated by ^{199}Hg NMR Spectroscopy. The anion complexation properties of the hosts **5** and **6** were studied by first generating the hosts from their iodide complexes in a manner similar to that described above. An accurately weighed amount of the complex was dissolved in approximately 2 mL of deuteriated dimethyl sulfoxide in a 10 mm NMR tube, and sufficient silver acetate was added in increments to ensure complete decomplexation of the host, as monitored by ^{199}Hg NMR spectroscopy. After generation of the free host, the salt of the relevant borane anion was added in increments of 0.5 molar equiv until no further change was observed in the ^{199}Hg NMR spectrum.

Supporting Information Available: For compounds **6**·I_2(K·[18]-dibenzocrown-6)$_2$, **7**·$I_2(NBu_4)_2$, **6**$_3$·I_4Li_4, and **5**·$Br_2(NBu_4)_2$, crystallographic experimental details and tables listing full data collection and processing parameters, full bond lengths and angles, torsion angles, anisotropic displacement parameters, and atom coordinates (31 pages). Ordering information is given on any current masthead page.

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