A Hexamethyl Derivative of [9]Mercuracarborand-3: Synthesis, Characterization, and Host−Guest Chemistry

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Abstract: Hexamethyl[9]mercuracarborand-3, $[(CH_3)_2C_2B_{10}H_8Hg]_3$ (**3**), was isolated in 60% yield from the reaction of *closo*-1,2-Li_2-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_8$ with mercuric acetate. The title compound was characterized by multinuclear NMR spectroscopy and its halide ion complexes by negative ion FAB mass spectrometry. Both **3** and its complexes are air-stable and soluble in poorly or noncoordinating solvents such as CH_2Cl_2 and toluene. Compound **3** crystallized from acetonitrile in the triclinic space group $P\bar{1}$ with $a = 13.362(6)$ Å, $b = 14.071(6)$ Å, and $c = 14.303(6)$ Å, $\alpha = 105.15(1)°$, $\beta = 95.77(1)°$, and $\gamma = 110.14(1)°$, $V = 2383$ Å^3, and $Z = 2$. The final discrepancy indexes were $R = 0.059$, $R_w = 0.064$ for 5987 independent reflections with ($I > 3\sigma(I)$). Halide ion complexes of **3** were formed upon treatment of **3** with salts of the corresponding halide ions. The complexation behavior of **3** in acetone was studied by ^{199}Hg NMR spectroscopy, and the guest/host ratio of the resulting complexes has been established to be 1, 2, and 2 for chloride, bromide, and iodide, respectively.

Introduction

The coordination of a guest to a host molecule resulting in selective activation for a subsequent reaction is a common motif in both biological and chemical processes. In current organic synthesis, Lewis acid-promoted reactions are growing in importance.[1] In general, the initial activation of the substrate by a Lewis acid through coordination is followed by trapping of the activated species by a nucleophile and formation of the product with accompanying regeneration of the Lewis acid catalyst.[2] While simple monodentate Lewis acids have been employed to mediate a wide variety of C−C bond-forming reactions,[3] multidentate Lewis acids, *i.e.*, those with several electrophilic centers, provide the possibility of specific substrate binding accompanied by catalysis with high chemo- and stereoselectivity.[4] The key concept is to exploit simultaneous and cooperative interaction of the Lewis acidic sites with basic atoms in the guest molecules; the multiple interactions between the host and the guest stabilize the host−guest complex and activate the substrate in a way not possible with a monodentate Lewis acid. With catalysis of this type as a goal, we have recently reported a novel class of macrocyclic multidentate Lewis acid hosts in which three or four carbonate cages are interlinked by an equal number of mercury atoms (Figure 1).[5]

Initial studies have been focused primarily upon the halide ion complexes of the neutral tetrameric host molecule **1**,[5] which

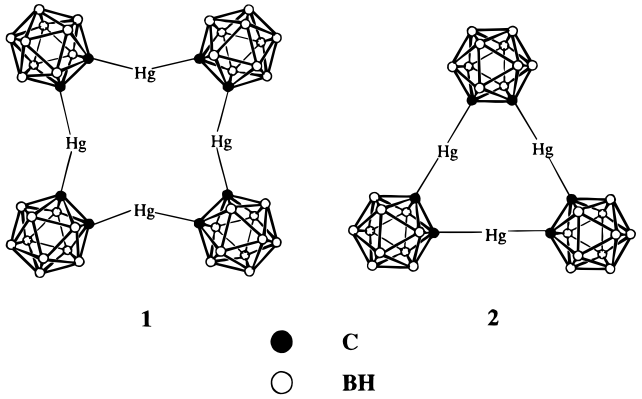

Figure 1. Representations of [12]mercuracarborand-4, **1**, and [9]-mercuracarborand-3, **2**.

are prepared through the reaction of *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{10}$[6] with the mercuric ion salts of the corresponding halide ion. The formation of the anion-free trimeric [9]mercuracarborand-3 host, **2**,[7] has also been achieved by the reaction of *closo*-1,2-Li_2-1,2-$C_2B_{10}H_{10}$ with mercuric acetate. The acetonitrile complexes of **2** have been structurally characterized by X-ray crystallography, and the chloride ion complex of the same host has been detected by mercury-199 NMR and negative ion FAB spectroscopy.

During the investigation of mercuracarborand chemistry,[5] it has become obvious that the parent unsubstituted host molecules are only soluble in electron-donor solvents, and solvent molecules are invariably found to be coordinated to the Lewis acidic mercury atoms upon attempted isolation of the free host. Such solvent complexation mitigates the potential usefulness of mercuracarborands as Lewis acid catalysts. A possible approach to correct this problem is to modify the supporting carborane cages with lipophilic substituents.[8] In this article, we report

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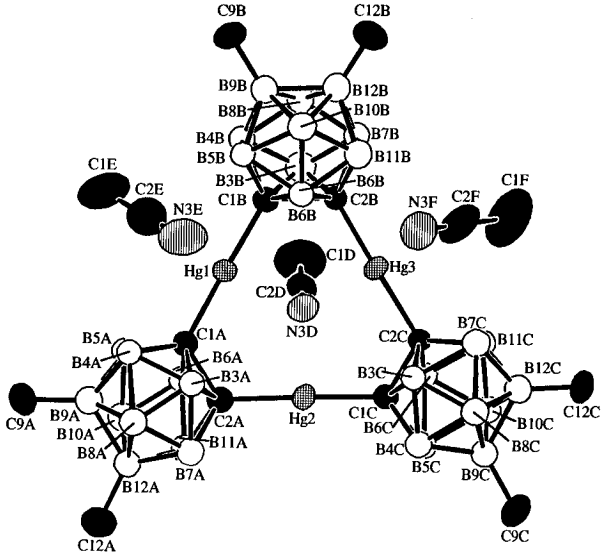

Figure 2. ORTEP plot of $[(CH_3)_2C_2B_{10}H_8Hg]_3(CH_3CN)_3$, **3**·$(CH_3CN)_3$, with the labeling scheme. Hydrogen atoms are omitted for clarity.

the synthesis and characterization of the hexamethyl derivative of [9]mercuracarborand-3, **3**, which is soluble in noncoordinating solvents. Complexation of halide ions by **3** will also be described.

Results and Discussion

Synthesis of Hexamethyl [9]Mercuracarborand-3 (3). Reaction of *closo*-9,12-$(CH_3)_2$-1,2-Li_2-$C_2B_{10}H_8$[8] with mercuric acetate in diethyl ether at room temperature afforded *cyclo*-$[(CH_3)_2C_2B_{10}H_8Hg]_3$ (**3**) in 60% yield. Both the anion-free host **3** and its halide ion complexes have been characterized by multinuclear NMR spectra, and the trimeric nature of **3** was confirmed by the negative FAB mass spectra of its halide ion complexes discussed below. The host and its halide ion complexes are air- and moisture-stable crystalline solids and are readily soluble in common electron-donor solvents. They also exhibit, as expected, enhanced solubilities in poorly or noncoordinating solvents such as benzene, toluene, chloroform, and methylene chloride. Their unsubstituted counterparts are essentially insoluble in any of these solvents.

Molecular Structure of $[(CH_3)_2C_2B_{10}H_8Hg]_3(CH_3CN)_3$. The trimeric structure of **3** in its CH_3CN complex was confirmed by X-ray crystallography and is shown in Figure 2. A summary of the crystallographic data is presented in Table 1, and selected bond distances and angles for **3**·$(CH_3CN)_3$ are given in Table 2.

In comparison with the acetonitrile complexes of the unsubstituted host,[7] the structure of **3**·$(CH_3CN)_3$ shows a number of notably different features. The crystal of **3**·$(CH_3CN)_3$ contains three molecules of acetonitrile per trimer moiety. In contrast, the crystal of $[(C_2B_{10}H_{10}Hg)_3]_2(CH_3CN)_8$ contains two different acetonitrile adducts in equal amounts in the solid state with three (**2A**) and five (**2B**) coordinated acetonitrile molecules, respectively (Figure 3).[7] Another distinct difference between these complexes of hosts **2** and **3** is the organization of the acetonitrile molecules with respect to the host. Thus, in **3**, all of the CH_3CN molecules are located on one side of the plane formed by the three Hg atoms, whereas in **2A**/**B** acetonitrile molecules are found on both sides of the Hg plane (Figure 3).[9] One of the three acetonitrile molecules in **3**·$(CH_3CN)_3$, identified by N(3D), is located an almost equal distance from each of the three Hg atoms (N(3D)−Hg(1) separations 2.916(15)−3.031(16) Å). The other two coordinated acetonitrile molecules are each near only one Hg atom, at distances of N(3F)−Hg(3) 2.90(2) and N(3E)−Hg(1) 3.03(2) Å, respectively. All of these separations are smaller than the sum of the van der Waals radii of nitrogen (1.5 Å)[10] and mercury (1.73 Å),[11] indicating moderately strong interactions between nitrogen atoms and mercury atoms. The lengths of the Hg−C bonds in **3** are conventional and vary from 2.07(15) to 2.11(13) Å with an average value of 2.08(15) Å. This distance is similar to the lengths of the Hg−C bonds observed in **2A**/**B** (2.06(2)−2.15(3) Å). Thus, the substitution of electron-donating methyl groups in **3** does not lead to any significant lengthening of the Hg−C bonds.

The three Hg atoms in **3**·$(CH_3CN)_3$ are arranged in an equilateral triangle with Hg−Hg distances ranging from 3.703(1) to 3.761(1) Å and Hg−Hg−Hg angles ranging from 59.2(2) to 60.7(2)°. The corresponding distances and angles in the structures of **2A**/**B** are 3.732 Å and 60.0° (average values), respectively, implying an almost identical cavity size for these two trimeric host molecules. Although the C−Hg−C angles, ranging from 172.7(6)° to 174.9(6)°, are smaller than those in

Table 1. Crystal Data and Data Collection Parameters for **3**·$(CH_3CN)_3$

formula	$C_{18}B_{30}H_{51}N_3Hg_3$
crystal system	triclinic
crystal dimens, mm	0.4 × 0.2 × 0.5
appearance	colorless parallelepiped
space group	$P\bar{1}$
a, Å	13.362 (6)
b, Å	14.071 (6)
c, Å	14.303 (6)
α, deg	105.15 (1)
β, deg	95.77 (1)
γ, deg	110.14 (1)
V, Å^3	2383
Z	2
density (calcd), gcm^{-3}	1.78
T, K	298
radiation, *λ* (Å)	Mo Kα (0.7107)
μ cm^{-1}	96.6
scan width	
below Kα$_1$	1.3
above Kα$_2$	1.6
no. unique reflcns	13892
no. observed reflcns ($I > 3\sigma(I)$)	5987
no. parameters refined	365
2*θ* max (deg)	60
R, R_w, GOF[a]	0.059, 0.064, 1.74

[a] $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

Table 2. Selected Distances (Å) and Angles (deg) for **3**·$(CH_3CN)_3$

Lengths (Å)			
Hg1−C1A	2.077 (15)	C1B−C2B	1.72 (2)
Hg1−C1B	2.066 (15)	C1C−C2C	1.64 (2)
Hg2−C1C	2.065 (15)	Hg1−N3E	3.03 (2)
Hg2−C2A	2.069 (15)	Hg1−N3D	3.031 (16)
Hg3−C2B	2.067 (14)	Hg2−N3D	2.916 (15)
Hg3−C2C	2.114 (13)	Hg3−N3D	2.954 (16)
C1A−C2A	1.65 (2)	Hg3−N3F	2.90 (2)
Angles (deg)			
C1A−Hg1−C1B	172.7 (6)	C2B−Hg3−C2C	173.3 (5)
C2A−Hg2−C1C	174.9 (6)	Hg1−Hg2−Hg3	60.73 (2)
Hg2−Hg3−Hg1	60.08 (2)	Hg3−Hg1−Hg2	59.19 (2)

(9) We recently determined the structure of **2** crystallized from an acetone solution. Three molecules of acetone were found in the structure, each coordinated to one Hg atom. All the acetone molecules were organized on one side of the plane through the three Hg atoms.

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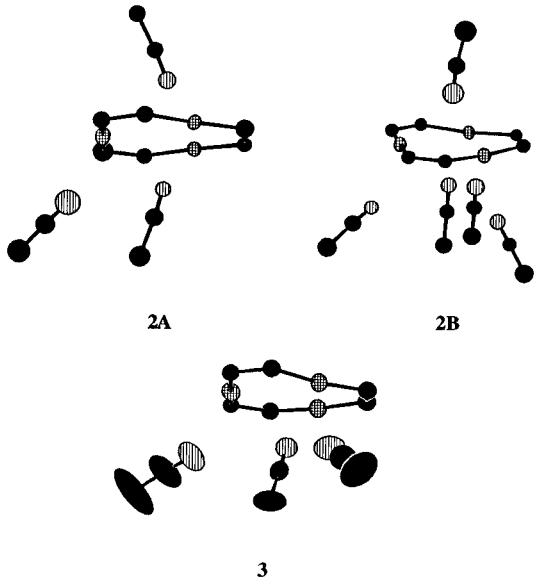

Figure 3. Side views of the coordination of acetonitrile molecules to the Hg_3C_6 rings of **2** and **3**. Boron and hydrogen atoms are removed for clarity.

the unsubstituted trimer hosts **2A** (176.1(8)−178.2(9)°) and **2B** (174.1(8)−177.8°(8)), they do not differ significantly from the 180° expected for the *sp* hybridization of the Hg orbitals.

Mercury-199 NMR Spectroscopic Investigation of Halide Ion Complexation of $[(CH_3)_2C_2B_{10}H_8Hg]_3$. Although the 1:1 chloride ion complex (**3**·Cl^-) was obtained when dilute HCl was used for workup of the reaction mixture, very little is known of the complexation behavior of **3** with respect to other halide ions. Mercury-199 NMR[12] spectroscopy has been employed for this purpose. The ^{199}Hg nucleus has a spin quantum number of $I = 1/2$ and a moderately large natural abundance (16.9%).[13] The extreme sensitivity of ^{199}Hg chemical shifts to their immediate environment makes ^{199}Hg NMR spectroscopy very useful in the study of the systems we have described here and elsewhere,[5a,b] especially so since mercuracarborands and their corresponding anion complexes have very similar ^{13}C and ^{11}B NMR spectra.

Interestingly, stepwise addition of halide ion salts to an acetone solution of **3** does not result in the formation of discrete sets of signals as observed in ^{199}Hg NMR studies of the tetrameric mercuracarborands.[5] Instead, only a single resonance is observed after each addition of the halide salt even though more than one species is believed to be present in the solution (*vide infra*). This suggests that at room temperature the observed ^{199}Hg resonances are time-averaged and result from ion exchange processes which are faster than the NMR time scale both between the individual halide ion and its complexes and between the complexes themselves.

The ^{199}Hg resonance of **3** was observed at −1158 ppm in acetone-d_6. The incremental addition of solid Ph_4AsCl to an acetone-d_6 solution of **3** results in the downfield chemical shift of the complex as shown in Figure 4.

The ^{199}Hg resonances are very solvent dependent. Acetone-d_6 was chosen for these measurements because all of the [9]mercuracarborand-3 studies could be carried out in this solvent, and the relative positions of the signals could then be solely attributed to differences in hosts or in complexes. The titration curve clearly demonstrates complexation of the chloride

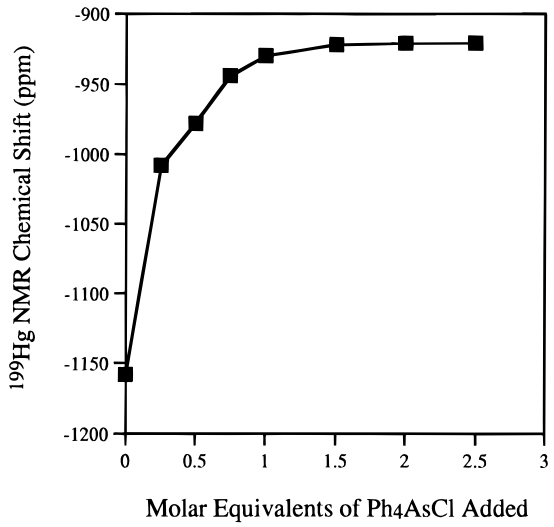

Figure 4. Plot of the ^{199}Hg chemical shift of $[(CH_3)_2C_2B_{10}H_8Hg]_3$ (**3**; 0.10 M solution in acetone-d_6) versus the molar equiv of Ph_4AsCl added.

ion by Lewis acidic host **3**. When more than 1 equiv of Ph_4AsCl was added to the acetone solution described above, no further change in the spectrum was observed, indicating that **3** is incapable of hosting more than one chloride ion. This suggests that a 1:1 complex is formed in solution with the chloride guest ion coordinated simultaneously to the three Hg atoms, as proposed for the unsubstituted trimeric host **2**.

We have previously reported the molecular structure of **1**·ClLi in which the chloride ion is bound to the four Hg atoms while exhibiting nearly perfect square planar coordination. Although the chloride ion in **1**·ClLi is located in the center of the tetrameric array, it is displaced 0.383 Å above or below the plane formed by the four Hg atoms. Considering the significantly smaller size of **3** (average adjacent Hg−Hg distance of 3.732 Å in **3** vs 4.129 Å for **1**·ClLi), the chloride ion in **3**·ClLi is probably located above or below the plane formed by the three Hg atoms.

The ^{199}Hg NMR chemical shift of **3** at −1158 ppm is 206 ppm from that of the unsubstituted host trimer (−1364 ppm),[7] and the resonance for **3**·Cl^- (−930 ppm) is shifted downfield only 91 ppm from that of the unsubstituted host (−1021 ppm). In other words, the complexation of chloride ion to host **3** causes a 228 ppm downfield shift as opposed to 343 ppm for **2**. This is presumably due to the methyl substituents present on the supporting carborane cages; the accumulation of methyl groups decreases the electron deficiency of the Hg atoms. Therefore complexation of an anionic guest does not produce such a large perturbation of the chemical shifts as that found for the unsubstituted host. Similar results were obtained for the alkyl (methyl or ethyl) substituted tetrameric mercuracarborands.[14]

Complexation studies of **3** with bromide and iodide ions have been carried out in a similar fashion. The incremental addition of solid $n$$Bu_4NBr$ to an acetone-d_6 solution of **3** results in the formation of **3**·Br^- (−915 ppm). When more than 1 equiv of $n$$Bu_4NBr$ was added to the mixture, the ^{199}Hg resonance shifted further downfield, and one new signal at −868 ppm was observed when 2 equiv of bromide ion were added. Figure 5 shows in detail the two-stage complexation of the bromide ion by host **3**. The initial downfield shift increase of 243 ppm is large for **3**·Br^-. In contrast, in progressing from **3**·Br^- to **3**·Br_2^{2-}, the difference is only 47 ppm, implying a dramatically reduced interaction between the second bromide ion with the

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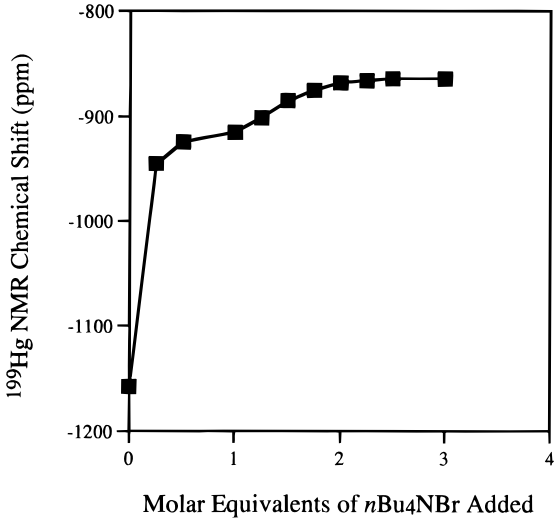

Figure 5. Plot of the ^{199}Hg chemical shift of $[(CH_3)_2C_2B_{10}H_8Hg]_3$ (**3**; 0.10 M solution in acetone-d_6) versus the molar equiv of nBu$_4$NBr added.

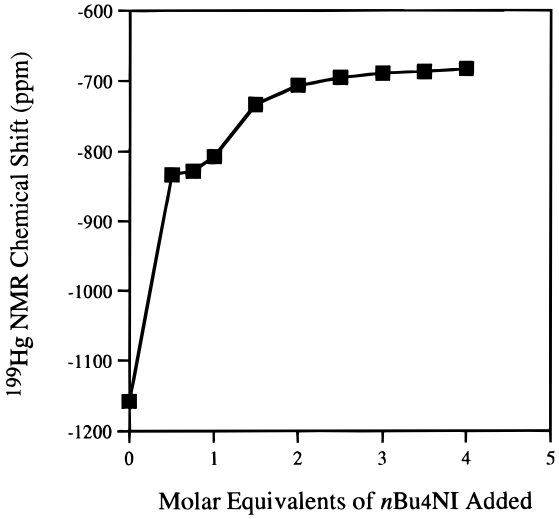

Figure 6. Plot of the ^{199}Hg chemical shift of $[(CH_3)_2C_2B_{10}H_8Hg]_3$ (**3**; 0.10 M solution in acetone-d_6) versus the molar equiv of nBu$_4$NI added.

monobromide complex. Subsequent changes at higher Br^- concentrations are negligible, indicating that **3** is incapable of hosting more than two bromide ions.

The complexation of I^- by **3** in acetone resembles that of Br^- as can be seen from the ^{199}Hg NMR titration curve shown in Figure 6. Again, host **3** is not capable of binding more than two iodide ions. The ^{199}Hg resonance shifts downfield by 351 ppm in progressing from the empty host to **3**·I^- (−807 ppm) and by an additional 101 ppm in proceeding from **3**·I^- to **3**·I_2^{2-} (−706 ppm). Table 3 summarizes the ^{199}Hg chemical shift of **3** and its different halide ion complexes which clearly demonstrate that the interactions between different halide ions and **3** increase in the order of $Cl^- < Br^- < I^-$. Relevant resonances of **2** and **2**·Cl^- are also included for comparison.

It is noteworthy that the structurally related trimeric perfluoro-1,2-phenylenemercury (o-$C_6F_4Hg)_3$[15] forms complexes with halide ions of the composition $[(o\text{-}C_6F_4Hg)_3X]^-$ (X = Br or I) or $\{[(o\text{-}C_6F_4Hg)_3]Cl_2\}^{2-}$, whereas in the present study, each molecule of **3** binds one chloride, two bromide, or two iodide ions, respectively. Yet the structural similarity between (o-$C_6F_4Hg)_3$ and **3** suggests the extrapolation that complex **3**·Cl^-, in the solid state would exhibit a polydecker sandwich structure similar to that of $[(o\text{-}C_6F_4Hg)_3Br][PPh_4]$.[15]

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

^{199}Hg containing species	chemical Shift δ (ppm)	ref
2	−1364	7
2·ClLi	−1021	7
3	−1158	this work
3·Cl($AsPh_4$)	−930	this work
3·Br[N(nBu)$_4$]	−915	this work
3·Br_2[N(nBu)$_4$]$_2$	−868	this work
3·I[N(nBu)$_4$]	−807	this work
3·I_2[N(nBu)$_4$]$_2$	−706	this work

[a] See Experimental Section for the experimental conditions employed. Acetone-d_6 solution was used and all spectra were proton decoupled.

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. Hg(OAc)$_2$ (Mallinckrodt), Ph_4AsCl (Aldrich), nBu$_4$NBr (Aldrich), nBu$_4$NI (Matheson Coleman and Bell), and n-BuLi (2.5 M solution in hexanes) (Aldrich) were used as received. *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ was prepared according to the previously described procedure.[8]

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 an 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·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 by using broad band decoupling. External 1.0 M PhHgCl/DMSO-d_6 solution was used as the reference at −1187 ppm relative to neat Me_2Hg. All FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer.

Synthesis of 3. To an ethereal solution (20 mL) of *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ (2.9 mmol, 0.50 g) at 0 °C was added n-butyllithium (6.0 mmol, 2.4 mL, 2.5 M solution in hexanes), and the slurry was stirred at room temperature under argon. After 4 h, the mixture was brought back to 0 °C and treated with solid mercuric acetate (2.9 mmol, 0.92 g). Stirring was continued overnight, while the mixture warmed to room temperature. The reaction was then quenched with 20 mL of water, and the organic phase 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 **3** as a white crystalline solid in 60% yield: ^{1}H NMR (200 MHz, $(CD_3)_2CO$) δ 0.09 (BCH_3), 1.2−3.0 (carborane BH); ^{13}C{^{1}H} NMR (90 MHz, $(CD_3)_2CO$) δ 86.7 (carborane), 1.3 (broad, BCH_3); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$) δ 10.2, −4.2, −8.9 (2:2:6); ^{199}Hg{^{1}H} NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C) δ −1158; IR (Nujol) ν [cm^{-1}] 2578; elemental analyses were unreliable due to the presence of solvent in the product.

Synthesis of the Halide Complexes of 3. The synthesis of the halide ion complexes of **3** has been achieved by mixing **3** (typically a 0.10 M solution in acetone) with 1 equiv (for chloride ion) or 2 equiv (for bromide or iodide ion) of the corresponding halide salt in acetone solution. The host/guest ratio has been determined by ^{199}Hg NMR titration of individual halide ion with anion-free host **3** in an acetone solution. The spectroscopic data are as summarized below.

3·Cl($AsPh_4$). ^{1}H NMR (200 MHz, $(CD_3)_2CO$) δ 7.8 (m, C_6H_5), 0.8−3.5 (carborane BH), 0.12 (BCH_3); ^{13}C{^{1}H} NMR (90 MHz, $(CD_3)_2$-

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CO) δ 135.4, 134.2, 131.9, 126.0 (C_6H_5), 86.9 (carborane), 1.3 (broad, BCH_3); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$) δ 10.6, −3.3, −8.1 (2:2:6); $^{199}Hg\{^1H\}$ NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C): δ −930; negative-ion FAB *m/z* 1148 (**3**·Cl^-, 100%).

3·Br$_2$(*n*Bu$_4$N)$_2$. ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 3.4, 1.8, 1.4, 1.0 (*n*Bu), 1.0−3.0 (carborane BH), 0.08 (CH_3); $^{13}C\{^1H\}$ NMR (90 MHz, $(CD_3)_2CO$): δ: 86.8 (carborane), 59.3, 24.3, 20.3, 13.8 (*n*Bu), 1.3 (broad, BCH_3); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$) δ 10.4, −3.3, −8.0, −10.3 (2:2:4:2); $^{199}Hg\{^1H\}$ NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C) δ −868; negative-ion FAB: *m/z* 1192 (**3**·Br^-, 100%), 1274 (**3**·Br^{2-}, 5%).

3·I$_2$(*n*Bu$_4$N)$_2$. ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 3.4, 1.8, 1.4, 1.0 (*n*Bu), 1.0−3.0 (carborane BH), 0.05 (CH_3); $^{13}C\{^1H\}$ NMR (90 MHz, $(CD_3)_2CO$) δ 85.2 (carborane), 59.2, 24.2, 20.2, 13.8 (*n*Bu), 0.83 (broad, BCH_3); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$) δ 10.5, −3.7, −9.0 (2:2:6); $^{199}Hg\{^1H\}$ NMR (89.4 MHz, $(CD_3)_2CO$, 25 °C) δ −706; negative-ion FAB: *m/z* 1239 (**3**·I^-, 100%), 1367 (**3**·I^{2-}, 7%).

X-ray Crystallography. A colorless crystal of **3**, obtained from an acetone/acetonitrile solution, was mounted in a capillary and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 30 accurately centered reflections (8.1° < 2θ < 19.4°). Data were collected at 25° in the θ−2θ scan mode. Three intense reflections (5 2 −2, 2 −4 1, 2 1 4) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 4% during the course of the experiment (96.5 h). Of the 13 892 unique reflections measured, 5987 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and absorption. Programs used in this work include locally modified versions of the crystallographic programs listed in ref 16.

Atoms were located by use of heavy atom methods. All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. The crystal contains four molecules of acetonitrile per trimer. With the exception of carboranyl C and B atoms, all non-hydrogen atoms were refined with anisotropic parameters. Methyl H atoms were refined as members of rigid CH_3 groups, C−H = 1.0 Å, H−C−H angles = 109.5°. Isotropic displacement parameters for H (u) were assigned based on the atom attached to H. H atoms on the carborane cage were included in located positions and were not refined. Scattering factors for H were obtained from ref 17 and for other atoms were taken from ref 18. The largest peak on a final difference electron density map, near Hg(3) was 0.93 e·Å^{-3}.

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Supporting Information Available: Tables of position and thermal parameters, bond lengths and angles, and crystallographic data, and an ORTEP view of $[(CH_3)_2C_2B_{10}H_8Hg]_3$-$(CH_3CN)_3$, (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) CARESS (Broach, Coppens, Becker and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin and Levy), structure factor calculation and full-matrix least-squares refinement, ORTEP (Johnson) figure plotting, SHELX76 (Sheldrick) crystal structure package and SHELX86 (Sheldrick) crystal structure solution package.

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