A Mercuracarborand Characterized by B−Hg−B Bonds: Synthesis and Structure of *cyclo*-[(*t*-BuMe$_2$Si)$_2$C$_2$B$_{10}$H$_8$Hg]$_3$

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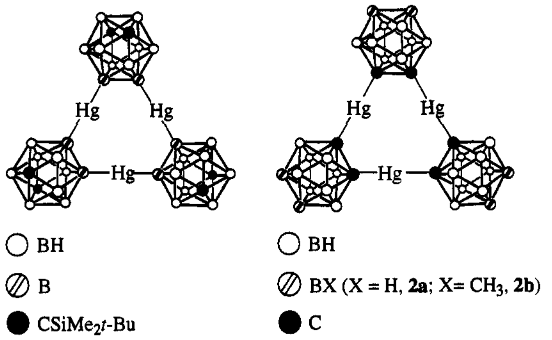
The acidic character of the hydrogen atoms bonded to the positively charged cage carbon atoms of the *ortho* (1,2), *meta* (1,7) and *para* (1,12) isomers of the icosahedral carboranes (*closo*-$C_2B_{10}H_{12}$) allows the facile introduction of functional groups at these positions.[1,2] Studies of electrophilic substitution reactions which occur at the boron vertices of these species are less well developed, except at the electron-rich boron atoms farthest removed from the carbon vertices.[2−4]

We have recently synthesized a new class of electrophilic macrocyclic "mercuracarborands" which serve as hosts to anionic and neutral electron-rich guests.[5] These compounds comprise a ring of carborane cages alternating with mercury atoms through Hg−C bonds at the relatively positive C-vertices of *o*-carborane. Clearly, a powerful method to reverse the electronic demand upon the mercury centers and thus reduce the coordinating properties of the host is to simply shift the mode of mercury-cage bonding from C−Hg−C to B−Hg−B. Here we describe the synthesis and structure of a soluble trimeric macrocycle, *cyclo*-[(*t*-BuMe$_2$Si)$_2$C$_2$B$_{10}$H$_8$Hg]$_3$ (**1**), in which the *m*-carborane cages are directly linked by mercury atoms *via* B−Hg−B bonds. Compound **1** is structurally related to the previously reported [9]mercuracarborand-3 (**2**) (Figure 1).[6] As noted above, the C-carboranyl vertices in *m*-carborane have a strong electron-withdrawing effect, while the equivalent 9- and 10-B-carborane vertices are actually electron-donating to substituents.[2,4] Therefore, we expect profoundly different chemical properties to be associated with the presence of B−Hg−B bonds in **1**.

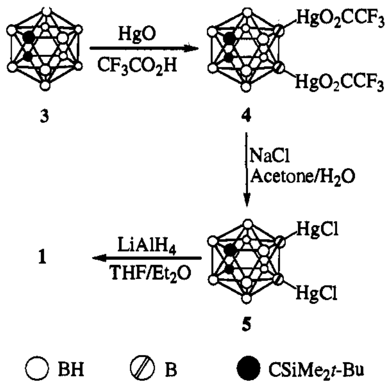
As shown in Scheme 1, *closo*-1,7-(*t*-BuMe$_2$Si)$_2$-1,7-$C_2B_{10}H_{10}$ (**3**)[7] was reacted with 2 molar equiv of mercury oxide in excess trifluoroacetic acid to produce the disubstituted carboranylmercuric trifluoroacetate, *closo*-1,7-(*t*-BuMe$_2$Si)$_2$-9,10-(HgO$_2$CCF$_3$)$_2$-1,7-$C_2B_{10}H_8$ (**4**), in 80% yield,[8a] which was quantitatively converted to *closo*-1,7-(*t*-BuMe$_2$Si)$_2$-9,10-(HgCl)$_2$-1,7-$C_2B_{10}H_8$ (**5**) *via* treatment with sodium chloride in water/acetone solution.[8b] Reaction of **5** with LiAlH$_4$ in THF/ether afforded the trimeric cycle **1** in 70% yield,[8c] which was purified *via* recrystallization from THF/acetone and characterized by its ^{1}H, ^{13}C, ^{11}B, and ^{199}Hg NMR spectra, mass spectrum, and an X-ray diffraction study.[9]



1 **2**

Figure 1. Representations of *cyclo*-[(*t*-BuMe$_2$Si)$_2$C$_2$B$_{10}$H$_8$Hg]$_3$ (**1**) and [9]mercuracarborand-3 (**2**).

Scheme 1. Synthesis of *cyclo*-[(*t*-BuMe$_2$Si)$_2$C$_2$B$_{10}$H$_8$Hg]$_3$ (**1**)



The ^{1}H NMR spectrum of **1** exhibits the two singlets expected for a TBDMS moiety. A singlet at 75.9 ppm in the ^{13}C NMR spectrum was identified as arising from the carborane carbon atoms. The FAB mass spectrum is in agreement with the cyclic trimer structure. In the ^{11}B NMR spectrum, the Hg-substituted B atoms in **1** exhibit a resonance at 41.7 ppm compared to those of **4** and **5** at −4.6 and 0.0 ppm, respectively, giving a notably low-field ^{11}B NMR resonance for a carborane derivative.[10]

The ^{199}Hg NMR resonance arising from **1** (Figure 2) is unusual in several respects. A very broad heptet with relative line intensities of 1:2:3:4:3:2:1 is observed, consistent with each mercury atom being coupled to two boron atoms. By contrast, the ^{199}Hg NMR spectra of **4** and **5** show quartets overlapped with heptets[6] (spin-coupling of the ^{199}Hg nucleus with both the ^{11}B (80.4%, $I = {}^3/_2$) and ^{10}B (19.6%, $I = 3$) nuclei).[11] In this study, the relaxation of the two quadrupolar boron nuclei gives rise to extremely broad lines in the ^{199}Hg NMR spectrum of the bonded mercury atom ($I = {}^1/_2$), and the fine structure of the coupling between ^{199}Hg and ^{10}B ($2nI + 1 = 13$ lines) is not observed. Chemical shifts of the ^{199}Hg nucleus span a range greater than 5000 ppm.[12,13] However, the range of chemical shifts within homologous groups is typically smaller; *i.e.*, the chemical shift of the mercury nucleus is strongly dependent upon

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(9) Characterization data for compounds **3−5**, together with X-ray diffraction details for **1** are provided in the supporting information. Spectroscopic data for **1**: ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ 0.5−0.3 (vbr, BH), 0.99 (s, 9 H, CCH$_3$), 0.13 (s, 6 H, SiCH$_3$); ^{13}C{^{1}H} NMR (90 MHz, CD$_2$Cl$_2$) δ 75.9 (CSi), 27.3 (*C*CH$_3$), 19.6 (C*C*H$_3$), −3.6 (SiCH$_3$); ^{11}B{^{1}H} NMR (160 MHz, CH$_2$Cl$_2$) δ 41.7 (2 B, BHg), 2.1 (2 B), −5.5 (4 B), −8.7 (2 B); ^{199}Hg{^{1}H} NMR (89.4 MHz, CH$_2$Cl$_2$, 25 °C) δ 354.4 [heptet, $J(^{11}B-^{199}Hg) = 1037$ Hz]; FAB-MS for $C_{42}H_{114}B_{30}Hg_3$ calcd 1714, found 1713 (M$^+$). Crystallographic data for **1**: orthorhombic space group *Pnma* with $a = 11.134(9)$ Å, $b = 23.81(2)$ Å, and $c = 31.63(2)$ Å, $V = 8384$ Å^3, and $Z = 4$. The final discrepancy indexes were $R = 0.078$, $R_w = 0.091$ for 3277 independent reflections with ($I > 3\sigma(I)$).

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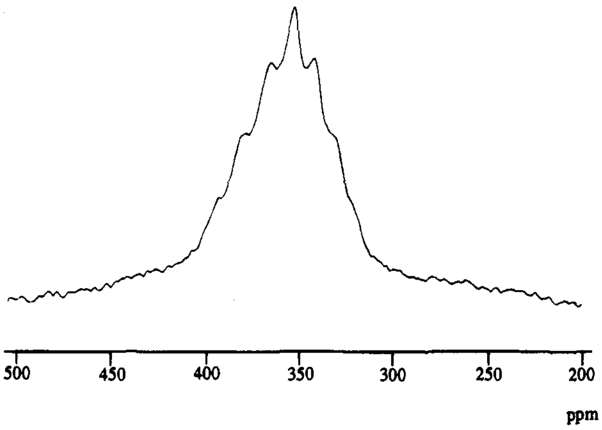

Figure 2. ^{199}Hg NMR spectrum of **1**.

the nature of the group attached. Chemical shift data for ^{199}Hg bonded to boron are rare, and the most comprehensive survey[13] mentions no data of this type. Data accumulated in this laboratory show that most ^{199}Hg chemical shifts of B−Hg moieties appear in the range −800 to −1200 ppm, similar to mercury alkyl species. However, the signal arising from **1** is markedly shifted downfield to 354 ppm, implying a potentially very wide range of ^{199}Hg chemical shifts associated with boron−mercury bonds. Compound **1** is also unusual in that the ^{11}B−^{199}Hg coupling constant is only 1037 Hz, compared to ~3000 Hz in all other surveyed compounds containing a B−Hg bond. The characteristic resonance thus provides a unique confirmation of the existence of a B−Hg−B linkage.

The trimeric structure of **1** was confirmed by a single crystal X-ray diffraction study. The structure was solved by heavy atom methods in space group *Pnma* and refined *via* standard least-squares and Fourier techniques. An ORTEP drawing is shown in Figure 3. The molecule consists of three *closo*-$C_2B_{10}H_8$ cages linked by the same numbers of Hg atoms through B−Hg−B structural motifs in a cyclic trimer. In the Hg "triangle", the sides are 4.076(2), 4.074(2), and 4.102(2) Å. The corresponding distances in [9]mercuracarborand-3[7] range from 3.703(1) to 3.761(1) Å, indicating a larger cavity for **1**. The Hg−Hg−Hg angles are 59.80(3), 59.80(3), and 60.41(3)°. The B−Hg−B angles are 173(1), 174(1), and 174(1)°. All these values, as well as other distances and angles, are similar to those found in related compounds.[6] The boron atoms connecting the mercury atoms are all within 0.10 Å of the plane through the three Hg atoms. Unlike the [9]mercuracarborand-3 series, which contain *o*-carborane icosahedra, the *exo*-cyclic TBDMS substituents do not lie in the plane of the Hg atoms but are directed both above and below the cycle.

Attempts to induce complexation of various guest species to compound **1**, including chloride, iodide, and thiophenolate ions, were unsuccessful. Presumably, the strong electron-donating effect of the 9- and 10-B-vertices deactivates the mercury centers toward Lewis bases. By contrast, addition of a halide ion to **2b**, a C-carboranyl analog of **1**, causes a significant downfield shift of ^{199}Hg resonance (up to 452 ppm) due to the formation of the corresponding halide ion complex.[6b] These results dramatically demonstrate the range of electronic properties available through selective carborane substitution.

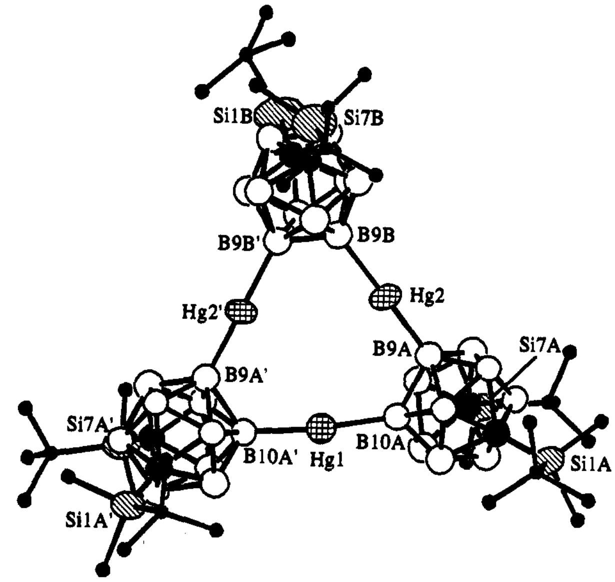

Figure 3. ORTEP plot of **1** with hydrogen atoms omitted and alkyl groups in TBDMS substituents reduced for clarity. The full crystallographic numbering scheme given in the supporting information.

It is now quite possible to make rigid structures using mercury atoms as linkers to construct both B−Hg−B and C−Hg−C mercuracarborand cycles. Using the boron vertices as skeletal connectors frees the easily functionalized carbon vertices open for further chemistry. In a *m*-carborane cage, the 9- and 10-positions are the farthest removed from the carbon vertices and bear the greatest negative charge in the ground state.[14] Electrophilic mercuration preferentially occurs at these vertices,[4] allowing predictable regioselectivity upon formation of the trimeric array. Despite showing no coordinating properties toward electron-rich species, the B−Hg−B motif appears to be more chemically robust toward nucleophilic attack than its C−Hg−C counterpart. In the presence of thiophenolate ion, compounds containing carbon−mercury bonds are eventually decomposed, whereas compound **1** is stable under these conditions. We believe that the ability to construct a series of carborane arrays having a variety of unusual properties will be significantly enhanced by the controlled use of boron−mercury bonds between icosahedra.

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Supporting Information Available: Spectroscopic data for compounds **3**−**5**, tables of position and thermal parameters, bond lengths and angles, and crystallographic data (9 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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