5320 *J. Am. Chem. Soc.* **1993,** *115,* 5320–5321

An Iodide Ion Complex of a Hydrophobic Tetraphenyl [12]Mercuracarborand-4 Having a Sterically Encumbered Cavity

Zhiping Zheng, Xiaoguang Yang, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, California 90024

Received April 5, 1993

Anion complexation by multidentate Lewis acid hosts has attracted increasing attention due to their ability to recognize, bind, transport, and chemically activate stereochemically complementary electron-rich guests.[1] In this vein, we have recently reported a novel class of electrophilic metallacyclic mercuracarborand hosts[2] supported by carborane cages, as well as their halide complexes[3a,b] and a supramolecular complex with *closo*-$B_{10}H_{10}^{2-}$.[3] These mercuracarborand species are quite soluble in most organic solvents with the exception of hydrocarbons, and the empty hosts bind electron-donor solvents, thereby mitigating their potential usefulness in the homogeneous catalysis of organic reactions. In order to eliminate this competitive binding of solvent molecules and at the same time test the effect of steric encumbrance of the host cavity, we have synthesized the hydrophobic tetraphenyl derivatives reported here. The ring-closure reaction using 3-phenyl-1,2-$C_2B_{10}H_{11}$[4] instead of 1,2-$C_2B_{10}H_{12}$[2,3] should, in principle, produce four isomers of the corresponding mercuracarborand having phenyl substituents arrayed about the periphery of the host cavity. We describe here the synthesis and the crystallographic characterization of the single stereoisomer formed in the synthesis of the cyclic tetrameric iodide ion complex $[(C_6H_5C_2B_{10}H_9Hg)_4]\cdot ILi$ (**1**·Li).

The reaction of HgI_2 with 3-phenyl-1,2-Li_2-1,2-$C_2B_{10}H_9$ in diethyl ether at room temperature results in the formation of the corresponding iodide ion complex of the cyclic tetramer with a phenyl substituent on each of the four component carborane cages, as shown in Scheme I.

The product, **1**·Li, is a colorless, air-stable, crystalline solid isolated in 85% yield. It was characterized by multinuclear NMR spectroscopy,[5] and its negative-ion FAB mass spectrum[6] exhibited an anion with *m*/*z* 1803, which corresponds to **1**. It is, in contrast with the species described previously,[3] soluble in dichloromethane and somewhat soluble in chloroform.

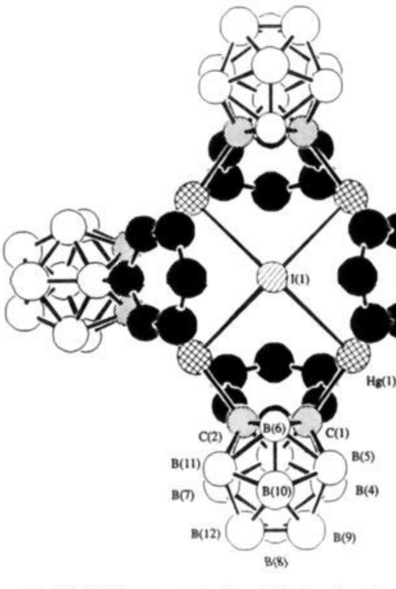
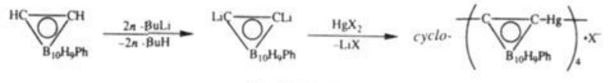


Figure 1. ORTEP representation of **1** showing the anion moiety with the labeling scheme. Hydrogen atoms are removed for clarity. Selected values of bond distances (Å) and angles (deg) are as follows: C1-Hg1 = 2.10(4), C2-Hg1 = 2.10(4), C1-C2 = 1.64(5), Hg1-I1 = 3.125(5); C1-Hg1-C2 = 162(2), C2-C1-Hg1 = 125(2).

Scheme I



Remarkably, the synthesis affords only one of four possible stereoisomers of **1**, as shown by HPLC[7] and NMR analyses of the reaction mixtures.

A single crystal of **1**·Li grown from diethyl ether/pentane was selected for an X-ray diffraction study.[8] The molecular structure of **1**, illustrated in Figure 1, shows four divalent 3-phenyl-1,2-$C_2B_{10}H_9$ cages linked by four Hg atoms in a cyclic tetramer and an iodide ion located in the center of the array 3.125(5) Å from each Hg. The four Hg atoms are coplanar and arranged in a perfect square with a Hg–Hg distance of 4.052(2) Å. The iodide ion is displaced 1.25 Å above or below the plane of the four mercury atoms with half occupancy in each of these two positions. The Hg-I distance of 3.125(5) Å is significantly shorter than the van der Waals distance between Hg and I (3.89 Å).[9,10] The Hg-C distance is 2.10(4) Å, which is essentially the same as that found for the monoclinic crystals of the cyclic trimer of 1,2-phenylenemercury, $(1,2\text{-}C_6H_4Hg)_3$.[11] An interesting feature of the structure of **1**·Li is the saddle-shaped twelve-membered ring whose distortion from planarity is obviously due to the steric interaction between opposite pairs of phenyl substituents. As a result, the interplanar angle is 14.8° between the plane of the four Hg atoms and the plane formed by the two carbon atoms of a carborane and the two Hg atoms they link. (Figure 2).

---

[1] For references to recent work on multidentate Lewis acids, see: (a) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410. (b) Beauchamp, A. L.; Oliver, M. J.; Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73. (c) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1987**, *109*, 4714. (d) Fackler, J. P., Jr.; Kresinski, R. A. *Organometallics* **1991**, *10*, 3392. (e) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294. (f) Newcomb, M.; Blanda, M. T. *Tetrahedron Lett.* **1988**, 29, 4261. (g) Newcomb, M.; Madonik, A. M.; Blanda, M. T.; Judice, J. K. *Organometallics* **1987**, *6*, 145. (h) Katz, H. E. *Organometallics* **1987**, *6*, 1134. (i) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640. (j) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420. (k) Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179. (l) Reetz, M. T.; Niemeyer, C. M.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1472. (m) Phan Viet, M. T.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026. (n) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931.

[2] (a) Yang, X.; Johnson, S. E.; Khan, S. I.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 893. (b) Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 193.

[3] (a) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1507. (b) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 380. (c) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.*, in press.

[4] Wegner, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 896.

[5] Spectroscopic data for **1**·Li: ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 1.0–3.6 (carborane), 7.3–7.8 (m, C_6H_5); ^{13}C NMR (90 MHz, $(CD_3)_2CO$) δ 100.1 (carborane); ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3\cdot Et_2O$ external, decoupled) δ 1.0, –3.5, –8.1; IR (Nujol) ν 2562, 725, 700.

[6] Negative-ion FAB: *m*/*z* 1803 (100), 2221 (pentamer·I^-, 40).

[7] HPLC analysis of the reaction mixtures for **1**·Li was performed at 25 °C using a phenyl column (reversed-phase packing) with MeOH:H_2O (85:15) as eluent. Four peaks were identified, and only one corresponds to **1** (negative-ion FAB: *m*/*z* 1803, 100).

[8] Crystallographic data for **1**·Li: tetragonal, space group $I4_1/amd$, a = 17.520(2) Å, c = 35.432(5) Å, V = 10876 Å^3, Z = 4, ρ_{calcd} = 1.23 g cm^{-3}, t = 25 °C. Data were collected on a Huber diffractometer, using Mo Kα radiation, to a maximum $2\theta = 44°$, giving 4222 unique reflections, and structure was solved by heavy atom methods. The final discrepancy index was R = 0.069, R_w = 0.095 for 733 independent reflections with $I > 3\sigma(I)$.

[9] Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225.

[10] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry Comprehensive Text*, 4th ed.; Wiley Interscience: New York, 1980; p 543.

[11] Brown, D. S.; Massey, A. G.; Wickens, D. A. *Inorg. Chim. Acta* **1980**, *44*, L193.

0002-7863/93/1515-5320$04.00/0

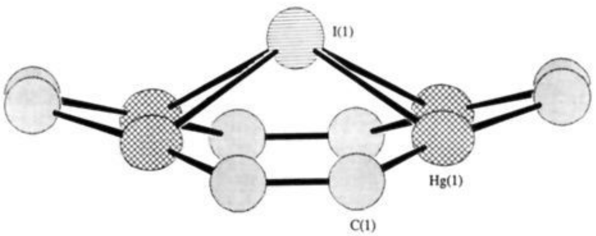


Figure 2. Side view of **1** showing only the twelve-membered ring and the complexed iodide ion (one of the two possible locations) for clarity.

The synthesis of **1**·Li is significant since it demonstrates the facile structural modification of the cavity of conformationally immobile mercuracarborand species and portends the creation of chiral complexes and hosts having special structural features. We have previously postulated that the efficient assembly of halide ion complexes of tetrameric [12]mercuracarborand-4, $[(C_2B_{10}H_{10}Hg)_4\cdot X_n]Li_n$ ($X = Cl^-$, Br^-, $n = 1$; $X = I^-$, $n = 1, 2$), must be due to a template effect with halide ion serving in that role,[3a,b] since the trimeric [9]mercuracarborand-3[2b] structure is stereochemically more favorable than the tetramer actually obtained in such cases. In the case of the system described here, this anion effect becomes even more obvious, because preliminary work[12] indicates that three isomeric chloride ion complexes are formed, although the 1,3-alternate isomer found in **1**·Li is sterically favored.

It has been demonstrated that the halide ions can be removed from their mercuracarborand complexes with Ag^+.[3] We are now studying the complexation of the free host derived from **1**·Li with a variety of inorganic anions and organic substrates as well as its potential as a homogeneous catalyst. In addition, the characterization of the isomeric tetrameric chloride complexes is also in progress.

Acknowledgment is made to the NSF (Grant No. CHE-91-11437) for support of this work. We are also grateful to Dr. Robert R. Kane for assistance with the HPLC.

Supplementary Material Available: Experimental details, tables of position and thermal parameters, bond lengths and angles, and crystallographic data (6 pages); listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

---

[12] HPLC analysis of the product mixtures obtained with $HgCl_2$ indicates the presence of three peaks which have the same negative-ion FAB mass spectrum with *m*/*z* 1711 (100). This value corresponds to the tetramer·Cl^- complex.