Crystal data for 1a: [Cu(C$_3$H$_5$N$_2$O$_2$)$_2$]·$\alpha$-HCl·19.67 H$_2$O. $M_r$ = 2001.50, rhombohedral, space group $R_3$ (No. 148), $a = b = 29.1533(10)$, $c = 26.7471(13)$ Å, $V = 19897(10)$ Å$^3$, $Z = 9$, $\rho_{max} = 1.519$ g cm$^{-3}$, $T = 188$ K, Siemens SMART CCD diffractometer, $\mu = 2.42$ cm$^{-1}$. The structure was solved by the Patterson method (SHELXS-86). All non-hydrogen atoms were refined anisotropically (SHELXL-93).

Final block-diagonal matrix least-squares refinement on $R$ group 1a

$R = 0.2737$, and $R_{w} = 0.2745$, $S = 1.068$, Crystal data for 1b: [C$_3$H$_5$N$_2$O$_2$]·$\alpha$-HCl·19.67 H$_2$O. $M_r$ = 1999.64, rhombohedral, space group $R_3$ (No. 148), $a = b = 29.3372(7)$, $c = 26.6945(10)$ Å, $V = 19897(10)$ Å$^3$, $Z = 9$, $\rho_{max} = 1.502$ g cm$^{-3}$, $T = 213$ K, $\mu = 2.38$ cm$^{-1}$, $R$ (1 > 2σ(I)) = 0.118, $R_{w}$ (all data) = 0.2957, and $GOF = 1.088$. Crystal data of 2a: [C$_3$H$_5$N$_2$O$_2$]·[Cu(C$_3$H$_5$N$_2$O)$_2$]·2H$_2$O. $M_r$ = 1995.30, rhombohedral, space group $R_3$ (No. 148), $a = b = 29.8575(3)$, $c = 24.8758(4)$ Å, $V = 19205(4)$ Å$^3$, $Z = 9$, $\rho_{max} = 1.553$ g cm$^{-3}$, $T = 188$ K, $\mu = 3.70$ cm$^{-1}$, $R$ (1 > 2σ(I)) = 0.1015, $R_{w}$ (all data) = 0.3134, and $GOF = 1.063$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156566 (1a), -156567 (1b), and -156568 (2a). Copies of the data can be obtained from charge on application to CCDC. 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[4] meso-Tetra(4-arylpyridyl)phosphinatozinc bound in a cyclic zinc porphyrin macrocycle. The most challenging endeavor in this context, their perfluoroalkylation.[12] Up to 14 perfluoroalkyl addends (R$_f$) (R$_f$ = CF$_3$, C$_2$F$_5$, C$_3$F$_7$, C$_4$F$_9$) can be added to C$_{60}$, about half the number needed to achieve a perfluorinated surface. Solutions of the mixtures of C$_{60}$R$_f$$_2$H$_{60}$ have been shown to be resistant to acids and bases.[13]

The generation of a neutral perfluorinated nanosphere by replacement of all H atoms of per-B-methylated carbanions by fluorine appeared to us to be a feasible goal. Previously, the radical chlorination of 1,12-(H)$_2$-1,12-C$_{2}$B$_{10}$Me$_{10}$ (I), yielding 1,12-(H)$_2$-1,12-C$_{2}$B$_{10}$H$_{10}$ (II) as well, but under basic aqueous conditions.[8]

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A Perfluorinated Nanosphere: Synthesis and Structure of Perfluoro-deca-B-methylpara-carbomane**

Axel Herzog, Ryan P. Callahan, Charles L. B. Macdonald, Vincent M. Lynch, M. Frederick Hawthorne,* and Richard J. Lagow*

In the early stages of the chemistry of polyhedral boranes the direct, exhaustive halogenation of closo-boranes and carboranes was one of the first reactions studied in detail.[3]

While the existence of B$_2$F$_2$$_2$$_2$ was never confirmed,[3] all three carborane fluorides can be isolated and 1,12-(H)$_2$-1,12-C$_{2}$B$_{10}$H$_{10}$ can even be handled in the presence of moist air. In aqueous media however, they hydrolyze to form boric acid as the final product.[3] The recently reported anion 1-HCB$_1$F$_{11}$ has been shown to undergo the nucleophilic substitution at the B—F moieties by OH$^-$ as well, but under basic aqueous conditions.[4]

History repeated itself with the discovery of C$_{60}$.[7] Shortly thereafter its exhaustive fluorination was intensively investigat[ed][8] and it is now widely accepted that C$_{60}$F$_{60}$ is the most fluorine-rich fullerene which can be isolated.[9] However, C$_{60}$F$_{60}$ is metastable in solution, decomposing according to the reaction C$_{60}$F$_{60}$ → C$_{60}$F$_{60}$ + 6F$_2$[10] and hydrolyzing rapidly in aqueous media.[11] The idea of a chemically resistant “fluorinated ball” based on C$_{60}$ was further pursued through its perfluoroalkylation.[12] Up to 14 perfluoroalkyl addends (R$_f$) (R$_f$ = CF$_3$, C$_2$F$_5$, C$_3$F$_7$, C$_4$F$_9$) can be added to C$_{60}$, about half the number needed to achieve a perfluorinated surface. Solutions of the mixtures of C$_{60}$R$_f$$_2$H$_{60}$ have been shown to be resistant to acids and bases.[13]

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the underlying B–B framework intact. In fact, the explosive "inert" anion 1-CB$_{11}$(CF$_3$)$_{12}$ was synthesized starting from the permethylated anion 1-CB$_{11}$(CH$_3$)$_{12}$ by using F$_2$ and K$_3$NiF$_6$ as fluorination reagents.[15] This report cited our preliminary results on the fluorination of 1[16] and its 1,12-dimethyl derivative 1,12-C$_2$B$_{10}$Me$_{10}$ (2).[16a]

Initially, the fluorination of 2 was studied, and it was found that at 25 °C using various F$_2$/N$_2$ (10–100% F$_2$) concentrations only partial fluorination occurred to yield 1,12-C$_2$B$_{10}$C$_6$H$_4$F$_{36}$ (n = 3–6). At a reaction temperature of 60 °C the formation of the desired 1,12-C$_2$B$_{10}$(CF$_3$)$_3$ (3) was observed. However, under these conditions partial disruption of the C–C bonds of 2 also led to the formation of 1,12-C$_2$B$_{10}$(CF$_3$)$_4$ (4) and 1,12-(F)$_2$-1,12-C$_2$B$_{10}$(CF$_3$)$_4$ (5). Under no conditions examined did compound 3 form without the concomitant formation of 4 and 5. All attempts to separate compounds 3–5 were unsuccessful.

Fluorination of 1 was initially conducted at low temperature (<35 °C) using various F$_2$/N$_2$ concentrations with the goal of 1,12 C–H retention. However, under the varied reaction conditions employed only mixtures of 5, 1,12-(H)$_2$-1,12-C$_2$B$_{10}$(CF$_3$)$_4$ (6), and 1-H-12-F-1,12-C$_2$B$_{10}$(CF$_3$)$_4$ (7) were obtained in ratios which depended on the reaction temperature and time. Attempts to separate compounds 5–7 from each other by gradient sublimation[17] or column chromatography were unsuccessful. Single crystals of 1-H-12-X-1,12-C$_2$B$_{10}$(CF$_3$)$_4$ (X = 92% H, 8% F) (8), obtained from sublimation, were suitable for an X-ray diffraction study.[14] The refined structure revealed that all methyl groups were converted into CF$_3$ groups.

Fluorination of 1 at elevated temperatures (>35 °C) using a high F$_2$ to N$_2$ ratio (1:3) for 14 days provided 5 in quantitative yield. Product formation was monitored by both mass spectrometry and $^1$B NMR analysis. Compound 5 is a colorless solid that sublimes at 65°C/0.01 mmHg to give colorless crys- 

tals. It has a melting point of 186 °C (sealed tube) and the molten compound remains colorless and inert up to 300 °C. In contrast to 1-CB$_{11}$(CF$_3$)$_{12}$, 5 does not detonate on percussion.[17] It is sparingly soluble in all common organic solvents, does neither hydrolyze in the presence of H$_2$O and nor oxidize on air. In acidic medium (CH$_2$Cl$_2$/CF$_3$COOH) 5 remains unchanged, whereas under basic conditions (CH$_3$COOH/NEt$_3$) it slowly decomposes. The $^1$B NMR spectrum reveals that deboronation occurs initially to produce nido species which finally decompose to borates. The nature of the decomposition products has not yet been determined. The $^19$F NMR spectrum of 5 shows a signal for the F atoms of its C–F vertices at $\delta = -157.5$ comparable with the shifts of the $^19$F NMR resonance signals observed for BF$_3$·THF[19] ($\delta = -155.7$) or the para-F atom in trans-C$_2$F$_6$-CH=CHCl ($\delta = -155.3$).[20] Single crystals of 5 were obtained by the slow evaporation of a solution of 5 in toluene and Freon 113. The structure of 5 determined by X-ray analysis[21] is shown in Figure 1. It represents the first structurally characterized perfluorinated icosaedral borane derivative.

Compound 5 crystallizes in the triclinic space group PI with one carborane per unit cell. Each molecule of 5 occupies a crystallographic inversion center. There are no unusually short intermolecular contacts. The C$_2$B$_{10}$ core is indistinguishable from those reported for analogous carboranes such as 1[16] and 1,12-(H)$_2$-1,12-C$_2$B$_{10}$(CHCl)$_8$.[13] As predicted by Michl and King for the anion 1-CB$_{11}$(CF$_3$)$_{12}$,[15] the average diameter (as calculated by F–F distances) of the fluorinated sphere is approximately 8.04 Å. All other metrical parameters are typical and do not warrant further comment. Aside from the difference in the crystal packing, these findings account as well for 8.[16]

We are currently exploring the feasibility of performing reactions at the C–H vertices of mixtures such as 8[22] Their 1- and 1,12-functionalization would allow their separation by column chromatography and open an avenue for further chemistry. At the same time we are probing the fluorination of other camouflaged carborane compounds[18] including the possibility of generating fluorinated sticks and ropes from rigid rods consisting of tethered species derived from 1[23]

**Experimental Section**[24]

**Caution:** Fluorine is a powerful oxidizer and should not be handled except in carefully controlled environments.[25, 24]

**Caution:** Compounds such as 5 are potentially explosive.[25] In spite of having not experienced explosions when preparing or handling 5, we advise extreme caution in doing so.

Analytical instruments used: VG Analytical ZAB2-E mass spectrometer (HR-MS); Varian Unity plus-300 ($^1$H NMR); Bruker ARX 400 ($^1$C NMR);
Scratching sublimed crystals with a metal spatula caused the material to detonate.
Modular Self-Assembly of a Microporous Solid Based upon Mercuracarborand-4 and a New Bonding Motif**

Hans Lee, Carolyn B. Knobler, and M. Frederick Hawthorne*

Mercuracarborands[1] comprise a class of novel macrocyclic multidentate Lewis acids[2] and possess useful properties in molecular recognition,[1, 3] optical sensors,[4] and catalysis.[5] Macrocyclic mercuracarborands are composed of alternating ortho-carborane icosahedra and mercury atoms linked by C-Hg-C moieties. The electron-withdrawing character of the o-carborane cage strengthens the Lewis acidity of the mercury centers, thereby enhancing the ability of the mercuracycle to function as a host for electron-rich guests.[6] An added benefit derived from the carborane cage is the fact that the boron vertices can be selectively functionalized to manipulate solubility[6, 7] and/or structural features required for supramolecular self-assembly.[8] The majority of carborane self-assembly chemistry is directed by the acidic C – H vertices of the carborane[9] and examples in which nonacidic B – H vertices direct self-assembly are limited.[10] As part of our ongoing investigation of mercuracarborand chemistry, we now report the synthesis and solid-state structure of Li2[(Hg3C2BìB10H8I2)4 ·I2] (Li2[(Hg3C2BìB10H8I2)4 ·I2]), an example of self-assembly directed by novel B–I···Li···B linkages which form microporous channels subsequently occupied by solvent molecules.

Electrophilic iodination at the electron-rich 9,12-vertices of ortho-carborane[11] followed by lithiation of the C–H vertices[11] provided the corresponding dilithium reagent, Li2C2BìB10H8I2. The reaction of Li2C2BìB10H8I2 with one molar equivalent of HgI2 in dry diethyl ether at room temperature afforded the diiodide ion complex, Li2·[1·1·I], of the bis-iodo-tetrameric cycle, in 78% yield. The resulting Li2·[1·1·I] species is an air- and moisture-stable crystalline solid that is soluble in a variety of organic solvents such as acetone, acetonitrile, diethyl ether, and dichloromethane. The 1H, 13C, and 199Hg NMR spectra of Li2·[1·1·I] revealed a highly symmetrical structure in solution. The 199Hg NMR spectrum of Li2·[1·1·I] in acetone exhibits a sharp singlet at δ = −622 which is essentially independent of concentration at room temperature. The negative-ion fast atom bombardment mass spectrum exhibits a peak centered at m/z 2640, with the isotopic pattern expected for Li2·[1·1·I]−, and an anion envelope at m/z 2505, which corresponds to [1·1·I]−. The species at m/z 2505 is presumed to arise through the elimination of LiI from Li2·[1·1·I]−, since a second resonance signal was not observed in the 199Hg NMR spectrum of the latter.

A single crystal of [Li4(CH3)2CO][1·1·I]·4H2O, grown from an acetone/dichloromethane solution, was selected for an X-ray diffraction study.[12] It crystallized in the monoclinic space group C2/m. The Li2·[1·1·I] structure consists of four divalent 9,12-I2-1,2-C2B10H8 cages linked at carbon by four Hg atoms in a cyclic tetramer with an iodide ion located above and below the tetramer cavity (Figure 1). The four Hg atoms are coplanar and lie in a parallelogram with sides of Hg1···Hg2 3.901(1)Å and internal angles of Hg2Hg1Hg2 87.40(4)° and Hg1Hg2Hg1 92.60(4)°. Iodide ions are located 1.912(1)Å above and below the plane of the four Hg atoms. Each iodide ion is bonded to all four Hg atoms; the Hg···I distances range from 2.315(2) to 2.607(2) Å, that is less than the sum of the van der Waals radii of 3.88 Å (Hg = 1.73[13] and I = 2.15 Å[14]). The Hg···I distances are comparable to those in previously reported mercuracyclic Hg···I complexes (3.249 – 3.487 Å).[15, 16] The Hg···I coordination in [1·1·I]− arises from the interaction of filled iodide ion p orbitals with empty mercury p orbitals that have the proper orientation to form three-center, two-electron bonds.[17]