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Synthesis of Boron-Iodinated *o*-Carborane Derivatives. Water Stability of the Periodinated Monoprotic Salt

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Boron periodination of *o*-carborane has been achieved by taking account of the fact that B atoms in the cluster are of two types, i.e., those adjacent to both C atoms and the remainder. The high number of nonequivalent leaving groups opens the possibility through B–C coupling to materials with novel possibilities and to self-assembling due to the enhanced polarizability of the C–H bond. Periodination has accentuated the acidity of the carborane, and monoprotic salts are stable in water.

Highly iodinated molecular species are of great interest in medical applications[1] as well as in materials science, as demonstrated by the many studies on C_6I_6 for which even superconductivity was found.[2] Boron cluster compounds would be ideal for incorporating a large number of I atoms. However, whereas substitutions have been achieved with good success with the cluster anions, this was not the case in 1,2-dicarba-*closo*-dodecaborane (*o*-carborane or 1,2-*closo*-$C_2B_{10}H_{12}$; Figure 1). The latter are, nevertheless, the most intensively investigated of the borane and heteroborane clusters.[3]

The paucity of reported examples is in agreement with the relative rates of halogenation, which decrease in the order $[B_{12}H_{12}]^{2-} > [CB_{11}H_{12}]^{-} > C_2B_{10}H_{12}$.[4] While perfluorination[5] and perchlorination[6] of dicarbaboranes have been obtained, perbromination and periodination of *o*-carborane have never been achieved. Although reference to tetrasubstitution at the 8, 9, 10, and 12 positions had been made on *o*-carboranes,[7] well-defined synthetic procedures existed only for 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$.[8] A major progress was achieved upon the synthesis of 4,5,7,8,9,10,11,12-I_8-1,2-*closo*-$C_2B_{10}H_4$.[9]

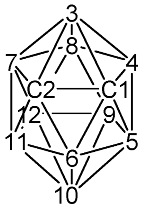

Figure 1. Vertex numbering in 1,2-*closo*-$C_2B_{10}H_{12}$, *o*-carborane.

The C's adjacent positions B(3,6) did not iodinate because these are the most electron-deficient sites in the molecule. Calculations on 1,2-*closo*-$C_2B_{10}H_{12}$, at the B3LYP/6-31G* level,[10] have shown that Mulliken charges are considerably more positive at B(3,6) than at B(8,9,10,12) (+0.017 vs −0.061).[11] Therefore, the strongest halogenating agents F^+ and Cl^+ are capable of substituting all B atoms, but the weakest, Br^+ and I^+, do not.[12] This led us to consider the positive B(3,6) atoms separately from the rest, and in this way, 3,4,5,7,8,9,10,11,12-I_9-1,2-*closo*-$C_2B_{10}H_3$,[13] along with 3,6,9-I_3-1,2-*closo*-$C_2B_{10}H_9$, 3,9,12-I_3-1,2-*closo*-$C_2B_{10}H_9$, and 3,6,9,12-I_4-1,2-*closo*-$C_2B_{10}H_8$, B-substituted species were synthesized.[14] There remained the periodinated 1,2-

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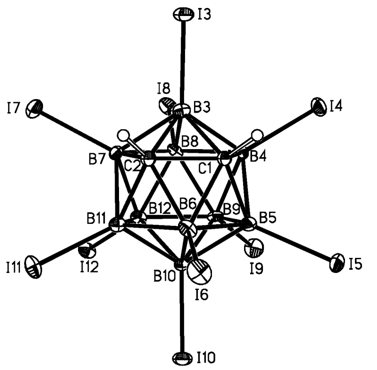
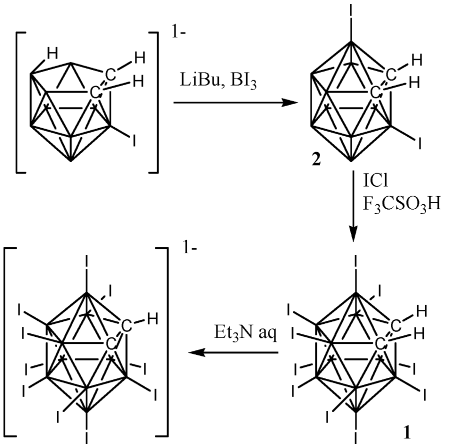


Figure 2. Perspective view of **1** with 30% ellipsoids. Selected bond lengths (Å): C1−C2, 1.640(9); B−I, 2.126(8)−2.158(8).

Scheme 1. Synthesis of the Periodinated Carboranes



H_2-1,2-*closo*-$C_2B_{10}I_{10}$ (**1**) to be made. In this paper, we report on this first all iodinated B-substituted *o*-carborane, its unprecedented acid properties, and the stability of the monoanionic species in water. Starting from $[3\text{-I-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{11}]^-$,[15] the first step consists of producing 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (**2**).[14,16] The first total boron periodination was achieved by reacting **2** with triflic acid and ICl to yield **1** (Scheme 1). In a typical experiment, **2** (1.00 g, 2.50 mmol) was dissolved in triflic acid (10 g) and ICl (6 mL) and refluxed at 90 °C for 5 days. After workup, a 73% yield of **1** was obtained. The $^{11}B\{^1H\}$ NMR shows a pattern 2:2:4:2 in which no boron resonance splits in ^{11}B NMR, confirming that all B atoms have one *exocluster* I. The structure of **1** was confirmed by X-ray diffraction analysis as the **1**·1.350DMSO·0.650acetone adduct (DMSO = dimethyl sulfoxide).[17] (Figure 2) In the adduct, weak C−H···O interactions, with C···O distances of 2.92−3.01 Å, between the cluster C−H and the disordered solvent molecules are found.

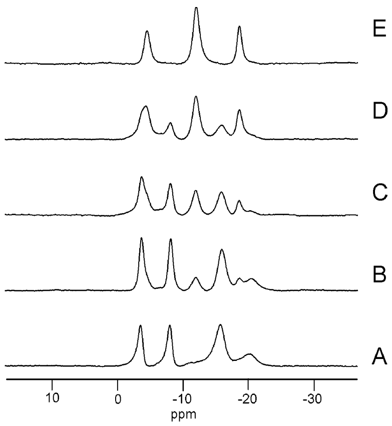


Figure 3. ^{11}B NMR spectra of **1** (A) in DMSO-d_6 and after additions of *t*-BuOK in ratios 1:0.2 (B), 1:0.4 (C), 1:0.8 (D), and 1:1 (E).

This implies that the C−H bond is polarized, a fact that is corroborated by the C−*H* resonance shifts in the ^1H NMR of **2** (4.1 ppm) and **1** (7.4 ppm). A continuous C−*H* downfield chemical shift is observed paralleling an increasing number of I atoms, 1,2-*closo*-$C_2B_{10}H_{12}$ (3.6 ppm), 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ (3.8 ppm), 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (4.1 ppm), and **1** (7.4 ppm), and an increasing acidity. The C−*H* shift of 1,2-*closo*-$C_2B_{10}H_{12}$ is slightly acid, $pK_a = 22$ but requires strong bases to be removed.[18] Would it then be possible to remove the C−H protons in highly iodinated carborane derivatives with relatively weak bases? Would their conjugate acids not be regenerated in water? In 1963, Schroeder et al. reported[6b] the preparation of $[HNEt_3]_2$[1,2-*closo*-$C_2B_{10}Cl_{10}$], which is stable in aqueous media. They reacted NEt_3 and 1,2-H_2-1,2-*closo*-$C_2B_{10}Cl_{10}$ in benzene or ethanol. The existence of this salt was later put in doubt by Zakharkin and Ogorodnikova, who proved that in aqueous ethanol 1,2-H_2-1,2-*closo*-$C_2B_{10}Cl_{10}$ behaved as a monoprotic acid and not as a diprotic acid.[18] The ^1H NMR spectrum of 1,2-H_2-1,2-*closo*-$C_2B_{10}Cl_{10}$ indicating that CH's at 5.9 ppm was given. Additionally, the value of the experimental pK_a was 6.98.[18] According to the ^1H NMR data, the pK_a of 1,2-H_2-1,2-*closo*-$C_2B_{10}Cl_{10}$ should be more positive than that of **1**, and possibly a water-stable salt of a carborane derivative could be produced. Upon dissolution of **1** in CD_3OD and the addition of 1 equiv of *t*-BuOK, the ^1H NMR C−*H* resonance originally present at 7.4 ppm was eliminated. The ^{11}B NMR spectrum presented an abrupt change, now showing three peaks at −7.7, −14.9, and −21.1 ppm. A further addition of *t*-BuOK did not produce any change in the spectrum. The same experiment was run again in DMSO-d_6 with different ratios of **1** to *t*-BuOK, 1:0, 1:0.2, 1:0.4, 1:0.8, and 1:1. The results are presented in Figure 3. Labels A−E refer to the different spectra from 1,2-H_2-1,2-*closo*-$C_2B_{10}I_{10}$ (A) to $[1,2\text{-}C_2B_{10}I_{10}H]^-$ (E). When water was added to the methanolic or DMSO solution of $[1,2\text{-}C_2B_{10}I_{10}H]^-$, the spectrum remained unaltered and protonation did not occur. Subsequent tests were directly performed in water, in which **1** is insoluble, but the addition of $HNEt_2$ ($pK_a = 10.9$) leads

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(17) Crystals were obtained from a DMSO/acetone (1:5) mixture. Crystal data: $C_{6.650}H_{14}B_{10}I_{10}O_2S_{1.350}$ or $C_2H_2B_{10}I_{10}$·1.350DMSO·0.650acetone; orthorhombic; *Pbca* (No. 61); colorless; $a = 17.0878(2)$ Å; $b = 19.0063(2)$ Å; $c = 19.9227(2)$ Å; $V = 6470.41(12)$ Å^3; $Z = 8$; $D_{calcd} = 3.175$ g cm^{-3}; μ(Mo Kα) = 9.673 mm^{-1}; data collection temperature 173 K; R1 = 0.0318; wR2 = 0.0535 [$I > 2\sigma(I)$]; GOF on $F^2 = 1.023$. Full details are described in the Supporting Information.

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to gradual dissolution. After total dissolution, the ^{11}B NMR spectrum is identical with that obtained after the addition of 1 equiv of *t*-BuOK in either DMSO or methanol.

The addition of acids with strength higher than or equal to pK_a = 2.9, i.e., HCl (pK_a = −7), CCl_3COOH (pK_a = 0.6), and $CH_2ClCOOH$ (pK_a = 2.9), led to insoluble **1**. This is not the case for CH_3COOH (pK_a = 4.7), which is unable to protonate the species existing in E. Therefore, the pK_a of **1** must lie between 2.9 and 4.7, being a stronger acid than 1,2-H_2-1,2-*closo*-$C_2B_{10}Cl_{10}$, in agreement with the ^{1}H NMR C−*H* resonance. Can the fully deprotonated species be generated? Our experiments show that the addition of more than 1 equiv of a strong base gradually leads to degradation of the cluster. We have tested this with *n*-BuLi in dimethyl ether and *t*-BuOK in ethanol. As a last test, $[N(PPh_3)_2]Cl$ was added to the aqueous solution of [1,2-*closo*-$C_2B_{10}I_{10}H]^-$, and $[N(PPh_3)_2]$[1,2-*closo*-$C_2B_{10}I_{10}H$] was precipitated. Similarly, $[N(PPh_3)_2]Cl$ in methanol was added to the methanolic solution of [1,2-*closo*-$C_2B_{10}I_{10}H]^-$ to produce the same salt. The MALDI-TOF-MS spectrum showed a peak at *m*/*z* 1402.4 ($C_2B_{10}I_{10}H^-$), which demonstrates the monoanionic character of the cluster. This work has permitted isolation for the first time of a water-stable salt of the 1,2-*closo*-$C_2B_{10}H_{12}$ derivative, through the synthesis of the boron-periodinated *o*-carborane **1**. This is more acidic than its chlorinated homologues and permits the isolation of $[N(PPh_3)_2]$[1,2-*closo*- $C_2B_{10}I_{10}H$]. Our interpretation of Schroeder's salt[9] is that an adduct C−H···N is generated. It was already treated as an adduct by Zakharkin and Ogoronikova.[18]

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Supporting Information Available: Experimental data for **1** and **2** and crystallographic data (CIF) for **1**·1.350DMSO·0.650acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

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