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Crystallographic Characterizations and New High-Yield Synthetic Routes for the Complete Series of 6-X-$B_{10}H_{13}$ Halodecaboranes (X = F, Cl, Br, I) via Superacid-Induced Cage-Opening Reactions of *closo*-$B_{10}H_{10}^{2-}$

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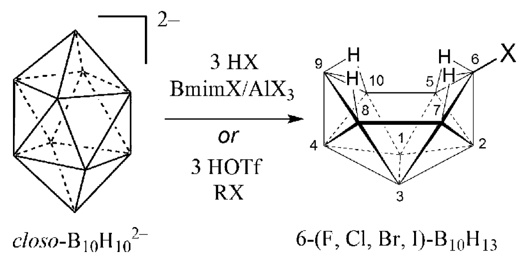
The high-yield syntheses of 6-X-$B_{10}H_{13}$ [X = Cl (88%), Br (96%), I (84%)] resulted from the cage-opening reactions of the $(NH_4^+)_2B_{10}H_{10}^{2-}$ salt with ionic-liquid-based superacidic hydrogen halides, while both the previously unknown 6-F-$B_{10}H_{13}$ (77%) derivative and 6-Cl-$B_{10}H_{13}$ (90%) were synthesized in high yields via the reactions of $(NH_4^+)_2B_{10}H_{10}^{2-}$ with triflic acid in the presence of 1-fluoropentane and dichloromethane, respectively. Structural characterizations of **1**−**4** confirm the predicted structures and indicate strong halogen back-bonding interactions with the B6 boron. The reaction of 6-Br-$B_{10}H_{13}$ with Bu_3SnH produced the parent $B_{10}H_{14}$ in 70% yield, and thus, this reaction, in conjunction with the haloacid-induced *closo*-$B_{10}H_{10}^{2-}$ cage-opening reactions, has the potential to provide an alternative to the traditional diborane pyrolysis route to decaborane.

Halodecaborane derivatives are potentially important synthons in polyborane, organopolyborane, and/or carborane syntheses, but their utilizations have been limited owing to the absence of efficient methods for their selective syntheses. Herein, we report crystallographic structural characterizations of the complete series of 6-X-$B_{10}H_{13}$ [X = F (**1**), Cl (**2**), Br (**3**), I (**4**)] compounds, along with new methods for their convenient, high-yield syntheses by the reactions of $(NH_4^+)_2B_{10}H_{10}^{2-}$ with ionic-liquid-based superacidic hydrogen halides (for **2**−**4**) and/or by the reactions (for **1** and **2**) of $(NH_4^+)_2B_{10}H_{10}^{2-}$ with triflic acid in the presence of alkyl halides (Scheme 1).

The Friedel−Crafts[1] or direct halogenation[2] reactions of decaborane generally produce mixtures of halo derivatives substituted at the 1 and/or 2 borons off the open face. On the other hand, the reactions of anhydrous HX (X = F, Cl, Br, I) with 6,9-$(R_2S)_2$-$B_{10}H_{12}$, or $B_{10}H_{14}$ in the presence of R_2S (R = Me, Et), have been shown to yield mixtures from which the 5-X-$B_{10}H_{13}$ and/or 6-X-$B_{10}H_{13}$ isomers can be isolated in fair to good yields.[3−5]

Scheme 1. Methods for the conversion of *closo*-$B_{10}H_{10}^{2-}$ to 6-X-$B_{10}H_{13}$



The above syntheses all require $B_{10}H_{14}$, a compound most commonly produced by a hazardous diborane pyrolysis reaction.[6] However, **2**−**4** have also been obtained in moderate yields (Cl, 45%; Br, 45%; I, 30%) via the hydrolysis of $(AlX_3)_n$-$B_{10}H_{10}^{2-}$ adducts.[7,8] Because *closo*-$B_{10}H_{10}^{2-}$ can be synthesized from the thermolysis of borohydrides instead of diborane,[9,10] synthetic routes based on the use of *closo*-

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$B_{10}H_{10}^{2-}$ as a starting point could have significant advantages over $B_{10}H_{14}$-based schemes, and this possibility stimulated our interest in *closo*-$B_{10}H_{10}^{2-}$ cage-opening reactions.

Acid-induced opening of *closo*-$B_{10}H_{10}^{2-}$ was first achieved by the reaction of $(NH_4^+)_2B_{10}H_{10}^{2-}$ with HCl in the presence of Et_2S to produce 6,9-$(Et_2S)_2$-$B_{10}H_{12}$.[11] Of most interest to us was Hawthorne's report that *closo*-$B_{10}H_{10}^{2-}$ could be opened to selectively form 6-R-$B_{10}H_{13}$ (R = triflate, phenyl, cyclohexyl) compounds if treated with triflic acid (eqs 1 and 2) in corresponding solvents.[12] More recently, 6-(HO)-$B_{10}H_{13}$ was similarly synthesized from $(NH_4^+)_2B_{10}H_{10}^{2-}$ by treatment with sulfuric acid in hexanes.[13]

$$Cs^+{}_2B_{10}H_{10}{}^{2-} + 3HOTf \rightarrow 6\text{-TfO-}B_{10}H_{13} + 2CsOTf \quad (1)$$

$$Cs^+{}_2B_{10}H_{10}{}^{2-} + 3HOTf + RH \rightarrow 6\text{-R-}B_{10}H_{13} + 2CsOTf + HOTf \quad (2)$$

We found that $(NH_4^+)_2B_{10}H_{10}^{2-}$ was unreactive with anhydrous haloacids (HCl and HBr) in noncoordinating solvents such as CH_2Cl_2 or in ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BmimCl), thus indicating that a higher reactivity is required to induce cage opening. It has been previously shown that an ionic liquid formed by the addition of 55 mol % $AlCl_3$ to BmimCl greatly enhances the acidity and reactivity of dissolved HCl.[14] As described by eq 3, we have now employed these superacidic systems to provide convenient high-yield routes to the 6-(Cl,Br,I)-$B_{10}H_{13}$ derivatives.

$$(NH_4{}^+)_2B_{10}H_{10}{}^{2-} + 3HX \xrightarrow{\text{BmimX/AlX}_3} 6\text{-X-}B_{10}H_{13} + 2NH_4X \quad (3)$$

In a typical reaction, 0.20 g (1.30 mmol) of $(NH_4^+)_2$-$B_{10}H_{10}^{2-}$ was added to an ionic liquid comprised of 6.00 g (34.4 mmol) of BmimCl and 6.00 g (45.0 mmol) of $AlCl_3$. After the mixture was stirred at 75 °C for 2 h under flowing HCl, the reaction was stopped and any remaining HCl removed in vacuo. The ionic liquid was extracted with hexanes until no product was observed in the extract by ^{11}B NMR. Following filtration to remove any solids and solvent evaporation at −20 °C, the remaining residue was sublimed onto a −78 °C coldfinger to give 0.18 g (1.14 mmol, 88%) of **2**. An analogous 2 h reaction and workup of 0.75 g (4.87 mmol) of $(NH_4^+)_2B_{10}H_{10}^{2-}$ in an $AlBr_3$ (15.0 g, 56.2 mmol)/BmimBr (10.0 g, 45.6 mmol)/HBr (flowing) system produced 0.93 g (4.63 mmol, 96%) of **3**.

Compound **4** was likewise initially synthesized using an AlI_3/BmimI/HI system, but it was found that substantially improved yields were obtained when HCl was utilized in place of HI. Thus, the 2 h reaction of 0.20 g (1.30 mmol) of $(NH_4^+)_2B_{10}H_{10}^{2-}$ in AlI_3 (6.10 g, 15.0 mmol)/BmimI (3.00 g, 11.3 mmol)/HCl (flowing) at 70 °C produced 0.27 g (1.10 mmol, 84%) of **4**. The reaction of HCl with AlI_3 should produce H^+ and strongly nucleophilic complex anions, e.g., $Al_2I_6Cl^-$.[14,15] Owing to the stronger Al−Cl versus Al−I bonds in these anions, cage iodation should be favored and, indeed, no formation of 6-Cl-$B_{10}H_{13}$ was experimentally observed in this reaction.

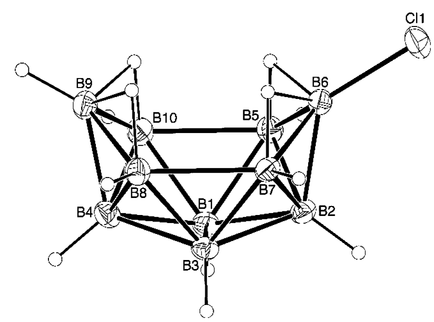

Figure 1. Crystallographically determined structure of 6-Cl-$B_{10}H_{13}$ (**2**). Selected bond lengths (Å) and bond angles (deg): B6−Cl, 1.7644(16); B5−B6, 1.797(2); B6−B7, 1.786(2); B7−B8, 1.992(2); B8−B9, 1.792(2); B9−B10, 1.794(2); B10−B5, 1.987(2); B6−B2, 1.723(2); B9−B4, 1.729(2); Cl−B6−B2, 130.81(11); B7−B6−B5, 105.80(11); B8−B9−B10, 104.94(11).

The spectral data of the final isolated **2**−**4** products match the literature values.[5] As shown in the ORTEP drawing in Figure 1 for **2** (and Figures S1 and S2 in the Supporting Information for **3** and **4**, respectively), crystallographic determinations of **2**−**4** confirm their previously proposed structures, where the halogens are bonded at the terminal position on the B6 boron on the decaborane open face. The observed B−X bond lengths in **2** [B−Cl, 1.764(2) Å], **3** [B−Br, 1.929(4) Å], and **4** [B−I, 2.143(3) Å] are consistent with those found in other halopolyboranes and indicate significant multiple bond character (e.g., for comparison, BCl_3, 1.75(2) Å;[16] BBr_3, 1.8985(5) Å;[17] BI_3, 2.1251(3) Å[17]) resulting from donation of a halogen lone pair to an orbital on the B6 boron.

Synthesis of the final compound of the series, the previously unknown 6-F-$B_{10}H_{13}$ (**1**) derivative, was achieved by the dropwise addition of 0.57 mL (6.27 mmol) of triflic acid to a rapidly stirred suspension of 0.30 g (1.94 mmol) of $(NH_4^+)_2B_{10}H_{10}^{2-}$ and 1-fluoropentane (0.44 mL, 3.85 mmol) in 10 mL of pentane, followed by a 3 h reaction at room temperature. After dilution of the reaction mixture with 20.0 mL of pentane and filtration, followed by solvent evaporation at −20 °C and sublimation of the remaining residue onto a −78 °C coldfinger, 0.21 g (1.50 mmol, 77% yield) of **1** was isolated.

The ^{19}F NMR spectrum of **1** exhibits a single multiplet resonance at −141 ppm. The ^{11}B (Figure 2) and ^{1}H NMR spectra have the characteristic patterns observed for **2**−**4**, with one of the intensity 2 bridge hydrogen resonances appearing as a doublet in the $^{1}H\{^{11}B\}$ spectrum owing to coupling to fluorine (J_{HF} = 21 Hz). The ^{11}B NMR chemical

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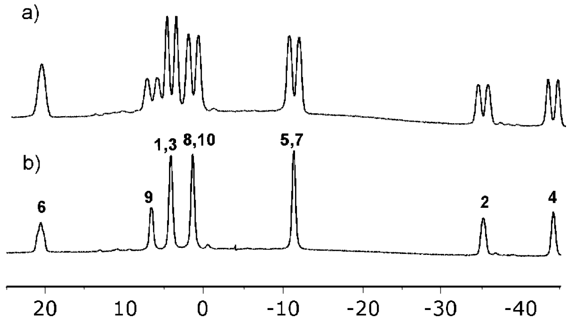

Figure 2. ^{11}B NMR spectra (128.4 MHz, $CDCl_3$) of 6-F-$B_{10}H_{13}$: (a) ^{1}H-coupled; (b) ^{1}H-decoupled. Assignments and chemical shifts (exptl/calcd, ppm): B6 (20.7/18.7), B9 (6.7/3.5), B1,3 (4.2/6.2), B8,10 (1.5/2.1), B5,7 (−11.3/−11.7), B2 (−35.3/−37.1), B4 (−44.2/−45.7). DFT/GIAO calculations were performed at the B3LYP/6-311G* level.

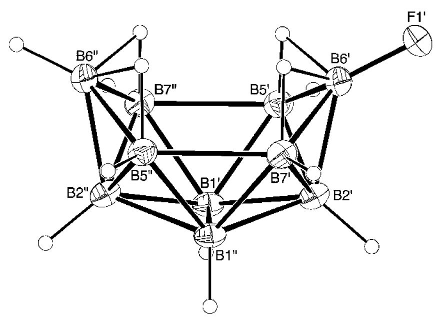

Figure 3. ORTEP drawing showing one of the two independent molecules in the crystallographically determined structure of **1**.

shifts for **1** are also in excellent agreement with the density functional theory (DFT)/gauge-invariant atomic orbital (GIAO)-calculated values (Figure 2, caption). The low-field shift (20.7 ppm) of the singlet resonance of the fluoride-substituted B6 boron is consistent with the trend observed in **2**−**4**, where the B6 resonance shifts to a progressively lower field as the electronegativity of the halogen increases (**2**, 18.4 ppm; **3**, 11.0 ppm; **4**, −5.4 ppm).[5]

A single-crystal X-ray determination of a twinned crystal of **1** confirmed the structure shown in Figure 3, but because of a C_2 rotation disorder that interchanges B6 and B9, the bond distances are averaged and cannot be used for comparisons. Nevertheless, the calculated value for the B−F bond length (1.337 Å) in the DFT-optimized geometry (Figure S3 in the Supporting Information) is closer to that of BF_3 [1.313(1) Å][18] than to that of BF_4^- [1.386(2) and 1.392(2) Å],[19] again suggesting multiple bond character.

Hawthorne postulated[12] that the reaction in eq 2 goes through a pathway where *closo*-$B_{10}H_{10}^{2-}$ becomes triply protonated to form the transient, highly electrophilic $B_{10}H_{13}^+$ cation, which can then abstract an R^- from hydrocarbons or induce electrophilic substitution on aromatics, with the resulting two-electron addition completing the closo to nido structural transformation. As shown in eq 4, a similar pathway can be envisioned for the formation of **1**, with the difference that, owing to the stronger B−F versus B−C bond, F^- abstraction is favored.

$$(NH_4^+)_2B_{10}H_{10}^{2-} + 3HOTf + RF \rightarrow 6\text{-F-}B_{10}H_{13} + ROTf + 2NH_4OTf \quad (4)$$

An analogous 2 h reaction of 0.50 g (3.25 mmol) of $(NH_4^+)_2B_{10}H_{10}^{2-}$ with triflic acid (1.15 mL, 12.9 mmol) in 30.0 mL of CH_2Cl_2 also gave an excellent yield of 0.46 g (2.94 mmol, 90%) of **2**. Reactions with CH_2Br_2 and CH_2I_2 likewise produced **3** and **4**, but owing to the low volatility of CH_2Br_2 and CH_2I_2 and the corresponding ROTf byproducts, product isolation was difficult, making these reactions less synthetically useful than their ionic-liquid-based syntheses discussed earlier.

The efficient high-yield syntheses of **1**−**4** should now allow for extensive investigations of their chemistry and possible applications in polyborane and carborane transformations. In this regard, initial studies have shown that 6-Br-$B_{10}H_{13}$ can be converted in 70% isolated yield to the parent $B_{10}H_{14}$ upon reaction with Bu_3SnH. Thus, 6-X-$B_{10}H_{13}$ reduction reactions, in conjunction with the haloacid-induced *closo*-$B_{10}H_{10}^{2-}$ cage-opening reactions, have the potential to provide an alternative to the traditional diborane pyrolysis route to decaborane.

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Supporting Information Available: Experimental details for all syntheses, X-ray crystallographic data for the structure determinations of **1**−**4** (CIF), ORTEP drawings of the structures of **3** and **4**, a drawing and Cartesian coordinates for the DFT-optimized (B3LYP/6-311G*) geometry of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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