Fluorination of $B_{10}H_{10}^{2-}$ with an *N*-Fluoro Reagent. A New Way To Transform B−H Bonds into B−F Bonds

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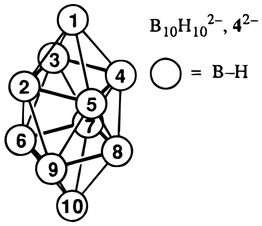
The anions $CB_{11}H_{12}^-$ ($\mathbf{1}^-$), $CB_9H_{10}^-$ ($\mathbf{2}^-$), and $B_{12}H_{12}^{2-}$ ($\mathbf{3}^{2-}$) have been successfully fluorinated using liquid anhydrous hydrogen fluoride (LAHF).[2−5] A typical series of reactions ($n = 1-3$) is the following:[2]

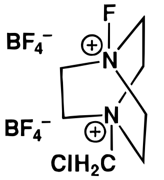
$$\mathrm{Cs}(\mathbf{1}) + n\mathrm{HF} \xrightarrow[20-188\ ^\circ\mathrm{C}]{\mathrm{LAHF}} \mathrm{Cs}(\mathrm{CB}_{11}\mathrm{H}_{12-n}\mathrm{F}_n) + n\mathrm{H}_2$$

The products were obtained in good yields and in high compositional and isomeric purity. For example, treatment of Cs(**1**) with LAHF at 23 °C for 20 h afforded a 96% yield of $Cs(12\text{-}CB_{11}H_{11}F)$,[2] while treatment of Cs(**2**) with LAHF at 200 °C (the critical temperature of HF) for 66 h afforded a 89% yield of $Cs(6,7,8,9\text{-}CB_9H_6F_4)$.[4]

We now report that the dianion $B_{10}H_{10}^{2-}$ ($\mathbf{4}^{2-}$) cannot be fluorinated in this manner. Treatment of $Cs_2(\mathbf{4})$ with LAHF at various temperatures ranging from −70 to +25 °C did not produce any fluorinated derivatives of $\mathbf{4}^{2-}$. Instead, the boron-containing products of the reactions, after workup with water, were BF_4^-, borates including $B(OH)_4^-$ and its oligomers, and uncharacterized species containing B−H bonds. The decomposition of $\mathbf{4}^{2-}$ in LAHF stands in sharp contrast to the behavior of $\mathbf{1}^-$, $\mathbf{2}^-$, and $\mathbf{3}^{2-}$ when dissolved in this solvent. The acid lability of $B_{10}H_{10}^{2-}$ (*closo* → *nido* cage rearrangement) was recently reported by Hawthorne and co-workers.[6]

$B_{10}H_{10}^{2-}$, $\mathbf{4}^{2-}$





F-TEDA

In order to find an alternative means of fluorinating $\mathbf{4}^{2-}$, we are investigating other potential methodologies for B−H → B−F transformations. We have discovered that the *N*-fluoro reagent F-TEDA[7,8] will fluorinate $B_{10}H_{10}^{2-}$ under relatively mild conditions. This is the first reported use of an *N*-fluoro reagent to fluorinate B−H bonds of any type, as well as the first reported fluorine-substituted derivatives of $B_{10}H_{10}^{2-}$.

The reaction of $Cs_2(\mathbf{4})$ with 1 equiv of F-TEDA for 24 h at 25 °C in either water or DMF/water produced the first examples of fluorinated derivatives of $\mathbf{4}^{2-}$:[9]

$$\mathrm{B}_{10}\mathrm{H}_{10}{}^{2-} + \text{F-TEDA} \rightarrow \mathrm{B}_{10}\mathrm{H}_{10-n}\mathrm{F}_n{}^{2-} + \text{H-TEDA}$$

When the solvent was water, the reaction mixture contained the following $B_{10}H_{10-n}F_n^{2-}$ species (note that $n = 0$ is the starting material; relative percentages determined by negative ion electrospray mass spectrometry (NIEMS)):[10] $n = 0$, 47%; $n = 1$, 36%; $n = 2$, 11%; $n = 3$, 4%; $n = 4$, 2%. When the solvent was 4/1 (v/v) DMF/water, the following species were present: $n = 0$, 49%; $n = 1$, 36%; $n = 2$, 13%; $n = 3$, ~1%; $n = 4$, ~1%. All B_{10}-containing anions were isolated as a mixture of $[N(n\text{-}Bu)_4]_2[B_{10}H_{10-n}F_n]$ salts (67% based on $Cs_2(\mathbf{4})$, $n = 0-4$). Therefore, using the NIEMS percentages, the yield of fluorinated $[N(n\text{-}Bu)_4]_2[B_{10}H_{10-n}F_n]$ salts (i.e., $n \geq 1$) was 36% based on $Cs_2(\mathbf{4})$ for the reaction in water (the yield of fluorinated salts was 17% for the DMF/water reaction mixture).[10] Other species present in the reaction mixture included oxidation products of $B_{10}H_{10}^{2-}$ such as $B_{20}H_{18}^{2-}$ and its derivatives as well as $B(OH)_4^-$ and its oligomers. Interestingly, when the solvent was anhydrous DMF or anhydrous acetonitrile, only $B_{20}H_{18}^{2-}$ was observed. Water is apparently a necessary component to achieve fluorination, as opposed to oxidation, of $B_{10}H_{10}^{2-}$ with F-TEDA. In spite of the facile oxidation of $\mathbf{4}^{2-}$, mixtures of salts of the new anions $1\text{-}B_{10}H_9F^{2-}$, $2\text{-}B_{10}H_9F^{2-}$, $1,10\text{-}B_{10}H_8F_2^{2-}$, and $1,2,10\text{-}B_{10}H_7F_3^{2-}$ were obtained.

The $Cs_2B_{10}H_{10-n}F_n$ salts were separated on a 5 mm × 700 mm column of Sephadex G-15 (40−120 μm): mobile phase = 20 mM NaCl in 0.04 M phosphate buffer (pH 7.5); flow rate = 8 mL/h, 25 °C.[9] Boron-11 NMR peak assignments were made using ^{11}B-^{11}B 2D NMR spectra when necessary.[11,12] The ^{11}B NMR spectrum of purified $[PPh_4]_2[1,10\text{-}B_{10}H_8F_2]$ is consistent with the proposed C_{4v} symmetry of the anion (see synopsis on Table of Contents). The ^{11}B NMR and NIEMS spectra of purified $Cs_2(2\text{-}B_{10}H_9F)$ are shown in Figure 1.

The structure of $Ag_2(CH_3CN)_3(2\text{-}B_{10}H_9F)$ consists of dimeric $[Ag_2(2\text{-}B_{10}H_9F)_2]^{2-}$ units weakly interacting with two $[Ag(CH_3CN)_3]^+$ cations.[13] Four hydrogen atoms from three different cluster anions form a distorted tetrahedron around Ag1.

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(1) (a) Colorado State University. (b) Russian Academy of Sciences.

(2) Ivanov, S. V.; Lupinetti, A. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 6419.

(3) Ivanov, S. V.; Rockwell, J. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. submitted for publication.

(4) Ivanov, S. V.; Rockwell, J. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Manuscript in preparation.

(5) (a) Knoth, W. H.; Miller, H. C.; Sauer, J. C.; Balthis, J. H.; Chia, Y. T.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 159. (b) Miller, H. C.; Muetterties, E. L. U. S. Patent 3,551,120 (assigned to DuPont), 1970. (c) Solntsev, K. A.; Mebel', A. M.; Votinova, N. A.; Kuznetsov, N. T.; Charkin, O. P. *Koord. Khim.* **1992**, *18*, 340.

(6) Hawthorne, M. F.; Mavunkal, I. J.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 4427.

(7) F-TEDA (also abbreviated F-TEDA-BF_4) is one of Air Products Selectfluor reagents.[8] Its chemical name is 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate).

(8) F-TEDA fluorinates organic compounds (i.e., C−H bonds) with good yields and regioselectivity: Lal, G. S. *J. Org. Chem.* **1993**, *58*, 2791.

(9) See Supporting Information for details of the synthesis and purification.

(10) Negative ion electrospray mass spectra consisted of B_{10} patterns corresponding to a set of uninegative ions $B_{10}H_{10-n}F_n^-$. Peaks for the parent ions $B_{10}H_{10-n}F_n^{2-}$ were not observed, presumably because of the ease with which these ions are oxidized within the mass spectrometer spray chamber. Note that the electrochemical one-electron oxidation of $B_{10}H_{10}^{2-}$ is quasi-reversible, implying that the radical species $B_{10}H_{10}^-$ is stable to some extent with respect to chemical fragmentation: Middaugh, R. L.; Farha, F., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4147.

S0020-1669(96)01043-9 CCC: $12.00

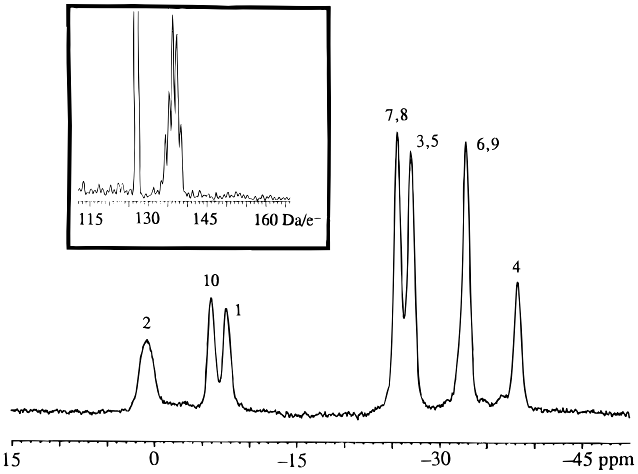

Figure 1. 96.3 MHz $^{11}B\{^1H\}$ NMR spectrum and (inset) negative ion electrospray mass spectrum of $Cs_2(2\text{-}B_{10}H_9F)$. Peak numbers in the NMR spectrum (D_2O solvent) correspond to the numbering scheme given in the text. The large peak at 126.9 Da/e$^-$ in the mass spectrum is from added I^- ion. Note that M_r = 118.2, 136.2, and 154.2 g mol^{-1} for $B_{10}H_{10}^{2-}$, $B_{10}H_9F^{2-}$, and $B_{10}H_8F_2^{2-}$, respectively.

The Ag1−H bond distances range from 2.02(5) to 2.25(5) Å and the H−Ag1−H bond angles range from 87(1)° (H3−Ag1−H10′) to 133(1)° (H3−Ag1−H7′). Significantly, there is no interaction between the fluorine atom and either Ag^+ ion. Three nitrogen atoms and two hydrogen atoms form a slightly distorted trigonal bipyramid around Ag2 (the H6−Ag2−H5′ angle is 164°). The AgN_3 unit is nearly trigonal planar. The Ag2−N distances range from 2.2 to 2.3 Å and the Ag2−H6 and Ag2−H5′ distances are 2.16(4) and 2.36(5) Å, respectively.

In summary, the *N*-fluoro reagent F-TEDA can fluorinate a relatively reactive (i.e., acid labile,[6] readily oxidized[10]) boron cluster anion under very mild conditions (25 °C, aqueous solution). The first fluorinated derivatives of $B_{10}H_{10}^{2-}$ have been generated, and several of them have been separated by fractional crystallization and column chromatography. These new anions complete the corresponding series of chloro, bromo, and iodo derivatives of $B_{10}H_{10}$[5a,14] some of which were reported as long ago as 1962.

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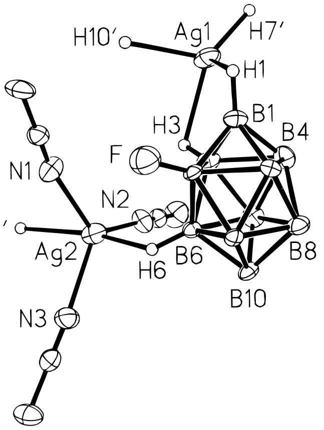

Figure 2. Structure of a portion of the centrosymmetric dimer $[Ag(CH_3CN)_3]_2[Ag_2(2\text{-}B_{10}H_9F)_2]$ (50% probability ellipsoids except for hydrogen atoms). Only one of the two disordered fluorine half-atoms is shown. Some hydrogen atoms (H4, H5, H7, H8, H9, H10) have been omitted for clarity. Hydrogen atoms H5′, H7′, and H10′ are connected to other $2\text{-}B_{10}H_9F^{2-}$ clusters. Selected interatomic distances (Å): Ag1−H1, 2.14(5); Ag1−H3, 2.25(5); Ag1−H7′, 2.02(5); Ag1−H10′, 2.11(5); Ag2−H6, 2.16(4); Ag2−H5′, 2.36(5); Ag2−N1, 2.267(5); Ag2−N2, 2.219(5); Ag2−N3, 2.289(5); B2−F, 1.346(8).

Supporting Information Available: Text giving synthetic details, figures showing ^{11}B NMR and NIEMS spectra of salts of a number of $B_{10}H_{10-n}F_n^{2-}$ ions, and tables listing details of the X-ray diffraction study, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom parameters (11 pages). See any current masthead page for ordering information and Internet access instructions.

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(11) ^{11}B NMR (25 °C, acetone-d_6, PPh_4^+ salts, δ ($BF_3(OEt_2)$) = 0, J_{BH} = 115−138 Hz): $B_{10}H_{10}^{2-}$, δ 0.0 (B1, B10), δ −27.9 (B2−B9); $1\text{-}B_{10}H_9F^{2-}$, δ 27.4 (B1), δ −13.4 (B10), δ −31.1 (B2−B5), δ −32.7 (B6−B9); $2\text{-}B_{10}H_9F^{2-}$, δ 3.6 (B2), δ −2.7 (B10), δ −4.8 (B1), δ −22.2 (B7, B8), δ −23.4 (B3, B5), δ −29.2 (B6, B9), δ −34.4 (B4); $1,10\text{-}B_{10}H_8F_2^{2-}$, δ 21.8 (B1, B10), δ −34.6 (B2−B9); $1,2,10\text{-}B_{10}H_7F_3^{2-}$, δ 21.8 (B10), δ 15.0 (B1), δ −4.1 (B2), δ −29.4 (B7, B8), δ −30.6 (B3, B5), δ −34.7 (B6, B9), δ −40.4 (B4). ^{19}F NMR (25 °C, acetone-d_6, PPh_4^+ salts, δ $CFCl_3$ = 0): $1\text{-}B_{10}H_9F^{2-}$, δ −225.7; $2\text{-}B_{10}H_9F^{2-}$, δ −236.4; $1,10\text{-}B_{10}H_8F_2^{2-}$, δ −257.8; $1,2,10\text{-}B_{10}H_7F_3^{2-}$, δ −242.9, −257.7, −260.3.

(12) ^{11}B NMR (25 °C, D_2O, Cs^+ salt, δ ($BF_3(OEt_2)$) = 0, J_{BH} = 123−144 Hz): $2\text{-}B_{10}H_9F^{2-}$, δ 0.8 (B2), δ −6.0 (B10), δ −7.6 (B1), δ −25.7 (B7, B8), δ −27.1 (B3, B5), δ −32.9 (B6, B9), δ −38.3 (B4).

(13) A solution of $[PPh_4]_2[2\text{-}B_{10}H_9F]$ in 9:1 dichloromethane−toluene was treated with $Ag(CF_3CO_2)$, which caused the precipitation of $Ag_2(2\text{-}B_{10}H_9F)$. Crystals of $[Ag][Ag(CH_3CN)_3][2\text{-}B_{10}H_9F]$ were grown from a saturated acetonitrile solution: $C_6H_{18}Ag_2B_{10}FN_3$, M_r = 475.1, monoclinic, space group $P2_1/n$, a = 7.3918(2) Å, b = 25.3378(1) Å, c = 9.0839(2) Å, β = 99.64(1)°, V = 1677.33(6) Å^3, Z = 4, ρ_{calc} = 1.88 g cm^{-3}, $F(000)$ = 912, λ(Mo Kα) = 0.710 73 Å, μ = 23.3 cm^{-1}, T = −115 °C, crystal dimensions 0.02 × 0.08 × 0.02 mm; Siemens Smart CCD diffractometer, 7252 reflections collected, 2397 independent reflections after merging, SADABS (G. M. Sheldrick) program used for empirical absorption correction, Siemens SHELXTL software (G. M. Sheldrick, v. 5.03, 1994) used for all calculations; anisotropic refinement (full-matrix least-squares on F^2) for all nonhydrogen atoms, hydrogen atoms on boron refined isotropically, on carbon in idealized positions, 50/50 disorder in fluorine (and related hydrogen) positions (one-half of each atom on B2 and B9); R_1(on F) = 0.045, wR_2(on F^2) = 0.070 for all data, 241 refined parameters.

(14) (a) Knoth, W. H.; Miller, H. C.; England, D. C.; Parshall, G. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1962**, *84*, 1056. (b) Knoth, W. H.; Sauer, J. C.; England, D. C.; Hertler, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 3973. (c) Bührens, K.-G.; Preetz, W. *J. Chromatogr.* **1977**, *139*, 291 and references therein. (d) Preetz, W.; Nachtigal, C. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1632, and references therein.