

Fluorination of deltahedral *closo*-borane and -carborane anions with *N*-fluoro reagents

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Received 11 July 1996; accepted 23 October 1997

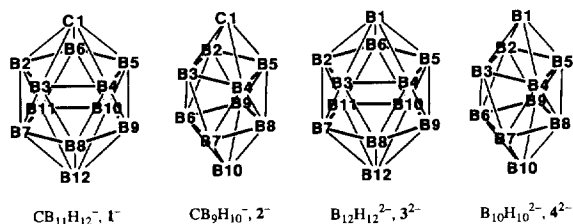
Abstract

The treatment of cesium salts of $\text{CB}_{11}\text{H}_{12}^-$, $\text{CB}_9\text{H}_{10}^-$, $\text{B}_{12}\text{H}_{12}^{2-}$, and $\text{B}_{10}\text{H}_{10}^{2-}$ with the commercially available *N*-fluoro reagent 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA) resulted in the formation of fluorinated derivatives of these 10- and 12-vertex borane and carborane anions. This is the first reported use of an *N*-fluoro reagent to fluorinate B–H bonds of any type. The effects of changing the solvent, temperature, and reagent stoichiometry were studied. The derivatives 1- $\text{B}_{10}\text{H}_9\text{F}_2^-$, 2- $\text{B}_{10}\text{H}_9\text{F}_2^-$, and 1,10- $\text{B}_{10}\text{H}_8\text{F}_2^{2-}$ are the first fluorinated derivatives of the parent $\text{B}_{10}\text{H}_{10}^{2-}$ cluster. For the other three parent anions, reactions with F-TEDA resulted in a higher degree of fluorination than reactions with liquid anhydrous hydrogen fluoride (LAHF) at the same temperature. However, F-TEDA was found to be less regioselective than LAHF for B–H → B–F transformations. © 1998 Elsevier Science S.A. All rights reserved.

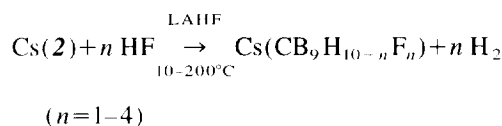
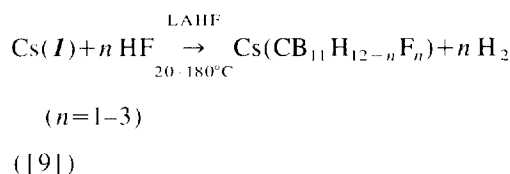
Keywords: Fluorination; *N*-fluoro; Borane; Carborane

1. Introduction

We have started a program to prepare highly fluorinated derivatives of the monocarborane monoanions $\text{CB}_{11}\text{H}_{12}^-$ (**1**[−]) and $\text{CB}_9\text{H}_{10}^-$ (**2**[−]) for use as new, chemically robust, weakly coordinating anions.²



To date, we have used liquid anhydrous hydrogen fluoride (LAHF) as the fluorinating agent (and as the solvent) for the following transformations [9–11].



The products of these reactions 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 isomerically pure **Cs(12-CB₁₁H₁₁F)** [9], while treatment of **Cs(2)** with LAHF at 200°C for 66 h afforded a 89% yield of isomerically pure **Cs(6,7,8,9-CB₉H₆F₄)** [11].

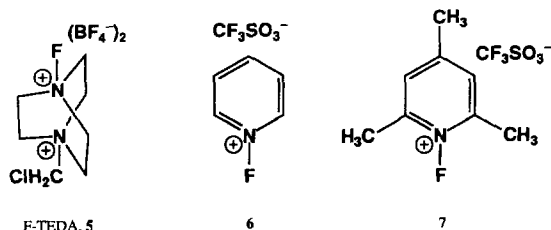
In earlier published reports that inspired our above-mentioned work, the facile polyfluorination of salts of the icosahedral dianion $\text{B}_{12}\text{H}_{12}^{2-}$ (**3**^{2−}) with LAHF was described [12–14]. However, the dianion $\text{B}_{10}\text{H}_{10}^{2-}$ (**4**^{2−}) cannot be fluorinated in this manner, since it is destroyed by LAHF even at temperatures below 0°C (see below). In order to find an alternative to the use of supercritical HF ($T_c \sim 200^\circ\text{C}$ [15]) to more fully fluorinate **1**[−] and **2**[−], and to find a means

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² For a recent review of weakly coordinating anions see Ref. [1]. Leading references for the chlorination, bromination and iodination of **1**[−] and **2**[−] are Refs. [2–8].

of fluorinating 4^{2-} , we are investigating other potential methodologies for the conversion of deltahedral B–H bonds into B–F bonds. We have discovered that one particular *N*-fluoro reagent, F-TEDA (**5**), which is commercially available from Air Products and Chemicals [16],³



will fluorinate all four of the above-mentioned anions under relatively mild conditions, and we herein report our results. As far as we are aware, this is the first reported use of an *N*-fluoro reagent to fluorinate B–H bonds of any type.⁴

2. Experimental details

2.1. Inert atmosphere

None of the borane or carborane anions appeared to be oxygen-sensitive at 25°C. As a precaution, however, preparations at elevated temperatures were carried out with rigorous exclusion of oxygen. Schlenk, glovebox, or high-vacuum techniques were employed, with purified nitrogen or argon used when an inert atmosphere was required [18].

2.2. Reagents and solvents

These were reagent grade or better. The following compounds were used as received: D₂O (Cambridge); CsOH (Aldrich); AgNO₃ (MCB); N(*n*-Bu)₄Cl (Aldrich); PPh₄Cl (Aldrich); (NEt₃H)₂B₁₂H₁₂ (Callery); F-TEDA (**5**, Air Products); 1-fluoropyridinium triflate (**6**, Aldrich); and 1-fluoro-2,4,6-trimethylpyridinium triflate (**7**). Trifluoroacetic acid (Aldrich) was distilled. Distilled water was deionized by passage through a Bardstead Nanopure water treatment system. Decaborane (**14**) (B₁₀H₁₄; Callery) was sublimed at 70°C under vacuum [Caution: B₁₀H₁₄ is toxic and is an explosion hazard if heated in air]. The following compounds were prepared following literature procedures: Cs(CB₉H₁₀) [19]; Cs(CB₁₁H₁₂) [20,21]; Cs₂(B₁₀H₁₀) [22]. The compound Cs₂(B₁₂H₁₂) was prepared from an aqueous mixture of (NEt₃H)₂B₁₂H₁₂, KOH, and CsCl (NEt₃ was extracted with

benzene before the addition of CsCl). The following solvents were purified by distillation: acetone and acetone-*d*₆ (from P₂O₅ or activated 4 Å molecular sieves); acetonitrile (from CaH₂), dimethylformamide (DMF; not dried prior to distillation).

2.3. Fluorination reactions

The compounds Cs(**1**) and Cs(**2**) (acetonitrile) and Cs₂(**3**) and Cs₂(**4**) (water or 4:1 (v:v) DMF:water) were dissolved in the indicated solvents and treated with one or more equivalents of the *N*-fluoro reagents F-TEDA (**5**), **6**, or **7** at various temperatures. At selected time intervals, samples were withdrawn, and treated as follows. For reactions of Cs(**1**) and Cs(**2**), acetonitrile was removed under vacuum and all carborane-containing salts were extracted from the solid residue with acetone. Acetone was removed under vacuum, the solid residues were dissolved in 5% aqueous KOH, and N(*n*-Bu)₄Cl was added to quantitatively precipitate all carborane anions as N(*n*-Bu)₄⁺ salts. For reactions of Cs₂(**3**) and Cs₂(**4**) in water, 5% aqueous KOH was added until the pH was in the range 10–12, and N(*n*-Bu)₄Cl was added to quantitatively precipitate all borane anions as N(*n*-Bu)₄⁺ salts (in the case of Cs₂(**4**), sparingly soluble B₂₀H₁₈²⁻ salts were filtered before the addition of N(*n*-Bu)₄Cl). For reactions of Cs₂(**3**) and Cs₂(**4**) in 4:1 (v:v) DMF:water, the reaction mixtures were diluted with water (final mixtures were 1:4 (v:v) DMF:water). For Cs₂(**3**), addition of N(*n*-Bu)₄Cl quantitatively precipitated all borane anions as N(*n*-Bu)₄⁺ salts. For Cs₂(**4**), addition of N(*n*-Bu)₄Cl precipitated only (N(*n*-Bu)₄)₂(B₂₀H₁₈). The filtrate was treated with PPh₄Cl to quantitatively precipitate all B₁₀-containing anions as PPh₄⁺ salts.

The borane and carborane salts were analyzed spectroscopically to determine: (i) the composition, or relative amounts of anions with different numbers of fluorine atoms (negative ion electrospray mass spectrometry); (ii) the number of isomers present for a given degree of fluorine substitution (¹⁹F NMR spectroscopy); and (iii) where possible, the geometric structure of the various isomers (1D and 2D ¹¹B NMR spectroscopy).

2.4. Spectroscopic measurements

Samples for 1D and 2D COSY ¹¹B and 1D ¹⁹F NMR spectroscopy were acetone-*d*₆ or D₂O solutions in 5-mm glass tubes. Spectra were recorded on a Bruker WP-300 spectrometer. Chemical shifts (δ scale) are relative to external BF₃·OEt₂ (¹¹B) and internal CFC₃ (¹⁹F). Samples for negative ion electrospray mass spectrometry were solutions in either water, acetonitrile, methanol, or a mixture of these three solvents. Spectra were recorded on a Fisons VG Quattro-SQ mass spectrometer. The sample cone voltage was 75 V, high enough to preclude the formation of ion clusters [23]. Control experiments with mixtures of known amounts of Cs(CB₉H₁₀) and Cs(CB₉H₈F₂) [10] demonstrated that

³ F-TEDA (also abbreviated F-TEDA-BF₄)—one of Air Products Select-fluor® reagents, fluorinates organic compounds (i.e., C–H bonds) with good yield and regioselectivity [16]. For information about F-TEDA, contact Mr. Gary T. Saba, Air Products and Chemicals, Specialty/Industrial Gas Department, 7201 Hamilton Blvd., Allentown, PA 18195-1501.

⁴ Some of these results, including the purification and crystal structure of [Ag][Ag(CH₃CN)₃][2-B₁₀H₆F], were briefly reported recently in Ref. [17]. We recently learned of the use of F-TEDA to prepare B₆H₅F²⁻ from B₆H₆³⁻ [Wilhelm Preetz, personal communication].

Table 1
Products of fluorination reactions comments

Reactants	Conditions	Products	Comment
CsCB ₁₁ H ₁₂ + 10 equiv. F-TEDA	CH ₃ CN, 25°C, 90 h	F ₀ (82%), F ₁ (11%), F ₂ (7%), F ₃ (trace)	[F ₁]/[F ₂] = 1.6
CsCB ₁₁ H ₁₂ + 10 equiv. F-TEDA	CH ₃ CN, 40°C, 90 h	F ₀ (35%), F ₁ (52%), F ₂ (10%), F ₃ (3%), F ₄ (trace)	[F ₁]/[F ₂] = 5.2; [12-F ₁]/[7-F ₁] 1.3; major F ₂ isomer = 7,12-F ₂
CsCB ₁₁ H ₁₂ + 10 equiv. F-TEDA	CH ₃ CN, 100°C, 90 h	F ₂ (15%), F ₃ (40%), F ₄ (34%), F ₅ (10%), F ₆ (1%)	major F ₃ isomer = 7,9,12-F ₃ ; major F ₄ isomer = 7,9,10,12-F ₄
CsCB ₉ H ₁₀ + 10 equiv. F-TEDA	CH ₃ CN, 25°C, 90 h	F ₀ (40%), F ₁ (46%), F ₂ (10%), F ₃ (3%), F ₄ (1%), F ₅ (trace)	only F ₁ isomer present was 6-F ₁ ; [6,7-F ₂]/[6,8-F ₂] = 0.9
CsCB ₉ H ₁₀ + 10 equiv. F-TEDA	CH ₃ CN, 40°C, 90 h	F ₁ (20%), F ₂ (37%), F ₃ (23%), F ₄ (16%), F ₅ (4%)	[6,7-F ₂]/[6,8-F ₂] = 0.7; major F ₃ isomer = 6,7,8-F ₃ ; major F ₄ isomer = 6,7,8,9-F ₄
CsCB ₉ H ₁₀ + 10 equiv. F-TEDA	CH ₃ CN, 100°C, 90 h	F ₅ (9%), F ₆ (59%), F ₇ (24%), other anions (8%)	major F ₆ isomer = 5,6,7,8,9,10-F ₆
CsCB ₉ H ₁₀ + 10 equiv. 6	CH ₃ CN, 100°C, 90 h	F ₀ (63%), F ₁ (30%), F ₂ (4%), F ₃ (3%)	only F ₁ isomer present was 6-F ₁ ; [6,7-F ₂]/[6,8-F ₂] ~ 1
CsCB ₉ H ₁₀ + 10 equiv. 7	CH ₃ CN, 100°C, 90 h	F ₀ (97%), F ₁ (3%)	
Cs ₂ B ₁₂ H ₁₂ + 1 equiv. F-TEDA	H ₂ O, 25°C, 24 h	F ₀ (49%), F ₁ (34%), F ₂ (15%), F ₃ (2%)	[F ₁]/[F ₂] = 2.3
Cs ₂ B ₁₂ H ₁₂ + 1 equiv. F-TEDA	DMF/H ₂ O (4/1), 25°C, 24 h	F ₀ (24%), F ₁ (59%), F ₂ (17%)	[F ₁]/[F ₂] = 3.5
Cs ₂ B ₁₂ H ₁₂ + 12 equiv. F-TEDA	DMF/H ₂ O (4/1), 25°C, 24 h	F ₄ (60%), F ₅ (40%)	
Cs ₂ B ₁₂ H ₁₂ + 12 equiv. F-TEDA	DMF/H ₂ O (4/1), 60°C, 24 h	F ₁ (2%), F ₃ (48%), F ₆ (45%), F ₇ (5%), F ₈ (<1%), F ₉ (trace)	total isolated yield of N(<i>n</i> -Bu) ₄ ⁺ salts = 79% based on Cs ₂ B ₁₂ H ₁₂
Cs ₂ B ₁₀ H ₁₀ + 1 equiv. F-TEDA	H ₂ O, 25°C, 24 h	F ₀ (47%), F ₁ (36%), F ₂ (11%), F ₃ (4%), F ₄ (2%)	[1-F ₁]/[2-F ₁] = 0.7
Cs ₂ B ₁₀ H ₁₀ + 1 equiv. F-TEDA	DMF/H ₂ O (4/1), 25°C, 24 h	F ₀ (49%), F ₁ (36%), F ₂ (13%), F ₄ (trace), F ₅ (trace)	[1-F ₁]/[2-F ₁] = 2.0

mass spectral peak intensities, ¹¹B NMR peak integrals, and ¹⁹F NMR peak integrals were all approximately proportional to the concentrations of the anions present.

3. Results and discussion

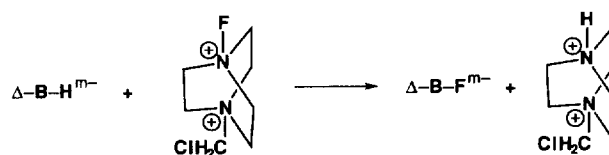
3.1. Attempted fluorination of B₁₀H₁₀[−] with LAHF

Treatment of Cs₂(**4**) with LAHF at various temperatures ranging from −70°C to 25°C did not produce any fluorinated derivatives of **4**^{2−}. Instead, the boron-containing products of the reactions, after workup with water, were BF₄[−], borates including B(OH)₄[−] and its oligomers, and uncharacterized B–H-containing species. ¹⁹F NMR spectra indicated only the presence of BF₄[−]; no other B–F-containing species were present. The decomposition of **4**^{2−} in LAHF stands in sharp contrast to the behavior of **1**[−], **2**[−], and **3**^{2−} in this solvent: the latter three anions are selectively fluorinated in high yield without any changes in the polyhedral skeletal structures of the parent anions.

3.2. Fluorinations with *N*-fluoro reagents

The results of these reactions are listed in Table 1. For each of the four anions studied, the code used to designate the products of the reactions is as follows: F₀ designates the parent anion (**1**[−], **2**[−], **3**[−], or **4**[−]); F_{*n*} designates the sum of

isomers having *n* fluorine atoms (CB₁₁H_{12−*n*}F_{*n*}[−], CB₉H_{10−*n*}F_{*n*}[−], B₁₂H_{12−*n*}F_{*n*}^{2−}, or B₁₀H_{10−*n*}F_{*n*}^{2−}). Numbers preceding the designation F_{*n*} are the boron-atom vertices bearing the fluorine atoms (see numbering schemes above). In each case, the percentages listed in Table 1 were estimated from the relative intensities of peaks in negative ion electrospray mass spectra (NIEMS) of the reaction mixtures. In favorable cases, the concentration ratio of geometric isomers formed for a given value of *n* was determined from the relative intensities of peaks in ¹¹B and ¹⁹F NMR spectra of the reaction mixtures. These reactions represent the first examples of direct B–H → B–F conversion using *N*-fluoro reagents. They consist of a series of sequential steps depicted generically for F-TEDA by the reaction below (Δ = a borane or carborane cluster minus one vertex, *m* = 1 or 2).



3.2.1. Fluorination of CB₁₁H₁₂[−] (I[−])

Treatment of Cs(**1**) with 10 equiv. **5** at 25°C, 40°C, and 100°C resulted in mixtures of fluorinated derivatives of **1**[−], including the following anions recently prepared [9] by treatment of Cs(**1**) with LAHF at various temperatures: 12-F₁, 7,12-F₂, 7,9,12-F₃, and 7,8,10,12-F₄. Experimental and calculated NIEMS are displayed in Fig. 1. The observed iso-

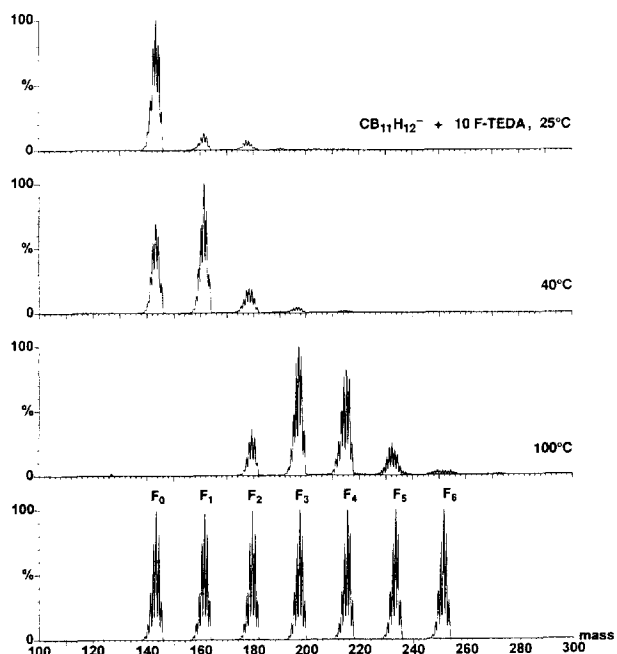


Fig. 1. NIEMS of products of the $\text{Cs}(\text{CB}_{11}\text{H}_{12})/\text{F-TEDA}$ reactions at 25°C, 40°C, and 100°C in acetonitrile (top three spectra). Calculated spectra for $\text{CB}_{11}\text{H}_{12-n}\text{F}_n$ species (abbreviated F_n) are shown at the bottom. The mass scale is Daltons per electron.

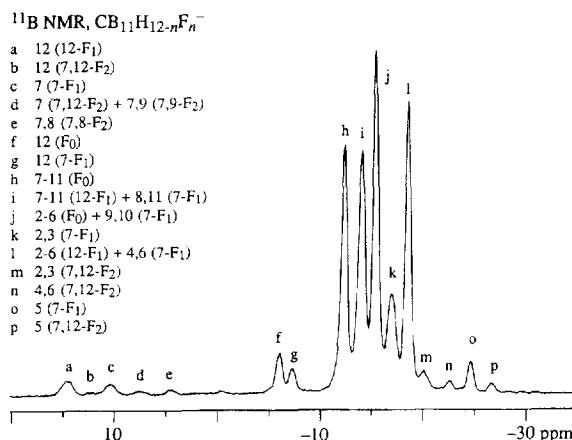
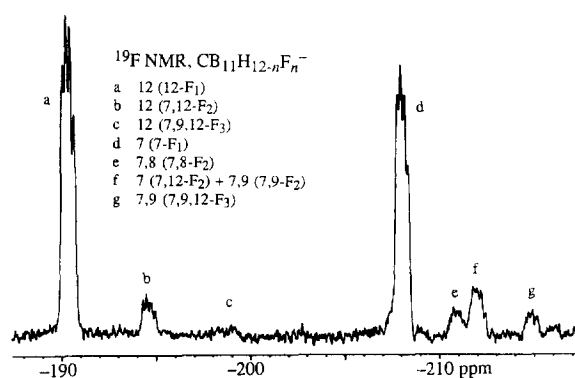


Fig. 2. The 96.3 MHz $^{11}\text{B}\{^1\text{H}\}$ and 282.4 MHz ^{19}F NMR spectra (acetone- d_6) of products of the $\text{Cs}(\text{CB}_{11}\text{H}_{12})/\text{F-TEDA}$ reaction at 40°C in acetonitrile.

tope patterns are those expected for anions with eleven boron atoms having a natural abundance of 20% ^{10}B and 80% ^{11}B . ^{11}B and ^{19}F NMR spectra for the 40°C reaction mixture are displayed in Fig. 2. NMR data are listed in Table 2. Peak assignments for the previously unknown monofluoro isomer 7- F_1 were made using a ^{11}B - ^{11}B 2D COSY NMR spectrum of the 40°C reaction mixture, which is shown in Fig. 3. The 7- F_1 isomer is the third and final B-F isomer in the $\text{CB}_{11}\text{H}_{11}\text{F}^-$ system: in addition to 12- F_1 [9], 2- F_1 had also been previously prepared [24]. Some peaks in Fig. 2 have been tentatively assigned to the previously unknown difluoro isomers 7,8- F_2 , and 7,9- F_2 .

The results clearly indicate that F-TEDA will polyfluorinate $\mathbf{1}^-$, but the compositional and isomeric purity of the products are quite different than LAHF fluorination. For example, it was possible to obtain high yields of pure 12- F_1 and 7,12- F_2 using LAHF at 25°C and 140°C, respectively [9], but it appears doubtful that this will be possible at any temperature using F-TEDA. However, F-TEDA would be the reagent of choice if isomerically pure salts of 7- F_1 were desired (this, of course, will require chromatographic, precipitation, extraction, or ion-exchange methodologies that are better developed than those at present). The results also clearly indicate that fluoro derivatives of $\mathbf{1}^-$ with $n \geq 5$ can be prepared using glass apparatus and a common organic solvent. This represents an important advantage over the use of supercritical HF as the fluorinating agent.

It was not possible to determine whether the C_{5v} isomer 7,8,9,10,11,12- $\text{CB}_{11}\text{H}_6\text{F}_6^-$ ($\mathbf{8}^-$) was present in the small amount of F_6 that was formed at 100°C. In ongoing work, we will attempt to increase the yield of F_6 isomers and to improve ways to separate the products of the reactions. If relatively pure salts of $\mathbf{8}^-$ can be prepared, its stability and coordinating ability can be compared with its hexachloro-, -bromo-, and -iodo weakly coordinating analogues, which have been the focus of an important series of studies by Xie et al. [25].

3.2.2. Fluorination of $\text{CH}_9\text{H}_{10}^-$ ($\mathbf{2}^-$)

Treatment of $\text{Cs}(\mathbf{2})$ with 10 equiv. $\mathbf{5}$ at 25°C, 40°C, and 100°C resulted in mixtures of fluorinated derivatives of $\mathbf{2}^-$, including the following anions [10,11] previously prepared by treatment of $\text{Cs}(\mathbf{2})$ with LAHF at various temperatures: 6- F_1 ; 6,7- F_2 ; 6,8- F_2 ; 6,7,8- F_3 ; and 6,7,8,9- F_4 . Experimental and calculated NIEMS are displayed in Fig. 4. The observed isotope patterns are those expected for anions with nine boron atoms having a natural abundance of 20% ^{10}B and 80% ^{11}B . The NMR data are listed in Table 2 (spectra not shown). As above, some peak assignments were determined from ^{11}B - ^{11}B 2D COSY NMR spectra. The results listed in Table 1 clearly indicate that the 10-vertex deltahedral carborane anion $\mathbf{2}^-$ is more reactive than the 12-vertex anion $\mathbf{1}^-$. Under identical conditions (10 equiv. $\mathbf{5}$, 100°C, 90 h), 59% of all fluorinated CB_9 anions formed were $\text{CB}_9\text{H}_4\text{F}_6^-$ whereas only 1% of all fluorinated CB_{11} anions formed were $\text{CB}_{11}\text{H}_6\text{F}_6^-$. It is also clear that *N*-fluoropyridinium salts [26] are considerably less reactive than F-TEDA for B-H \rightarrow B-F transformations.

Table 2
NMR spectral data for fluorinated *closo*-borane and -carborane anions^a

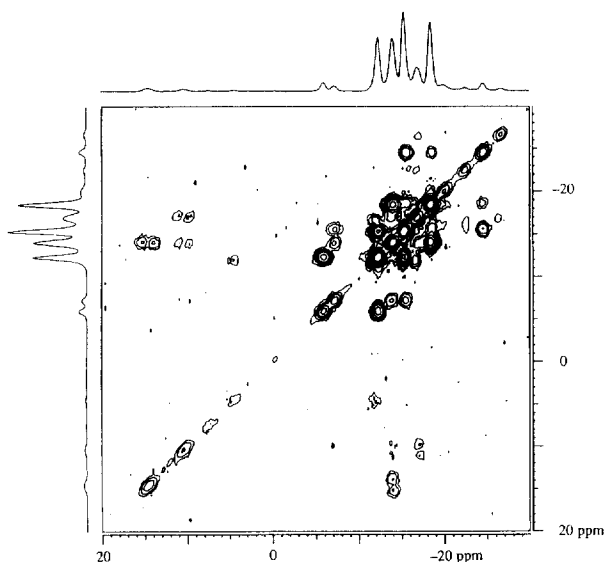
Anion	$\delta(^{11}\text{B})$ (assign.)	$\delta(^{19}\text{F})$
$\text{CB}_{11}\text{H}_{12}^-$ (F_0)	–6.0 (B12) –12.4 (B7–B11) –15.3 (B2–B6)	
12- $\text{CB}_{11}\text{H}_{11}\text{F}$ (12-F_1)	14.3 (B12) –14.4 (B7–B11) –18.8 (B2–B5)	–190.4
7- $\text{CB}_{11}\text{H}_{11}\text{F}$ (7-F_1)	10.2 (B7) –7.4 (B12) –14.2 (B8, B11) –15.5 (B9, B10) –17.4 (B2, B3) –18.8 (B4, B5) –24.8 (B5)	–208.0
7,12- $\text{CB}_{11}\text{H}_{10}\text{F}_2^-$ ($7,12\text{-F}_2$)	12.3 (B12) 7.5 (B7) –15.9 (B8, B11) –16.9 (B9, B10) –19.9 (B2, B3) –22.6 (B4, B6) –26.6 (B5)	–194.4 –212.0
7,9,12- $\text{CB}_{11}\text{H}_9\text{F}_3^-$ ($7,9,12\text{-F}_3$)	9.9 (B12) 5.1 (B7, B9) –17.2 (B8) –18.4 (B10, B11) –23.7 (B3, B4) –26.9 (B6) –28.2 (B2, B5)	–198.1 –216.0
$\text{CB}_9\text{H}_{10}^-$ (F_0)	30.6 (B10) –18.7 (B2–B5) –24.2 (B6–B9)	
6- $\text{CB}_9\text{H}_9\text{F}^-$ (6-F_1)	24.1 (B10) 4.4 (B6) –13.1 (B4, B5) –18.8 (B7, B9) –20.6 (B2, B3) –32.5 (B8)	–231.4
6,7- $\text{CB}_9\text{H}_8\text{F}_2^-$ ($6,7\text{-F}_2$)	16.7 (B10) 6.9 (B6, B7) –7.7 (B5) –14.9 (B2, B4) –22.3 (B3) –27.9 (B8, B9)	–223.9
6,8- $\text{CB}_9\text{H}_8\text{F}_2^-$ ($6,8\text{-F}_2$)	17.8 (B10) –2.5 (B6, B8) –14.3 (B2–B5, B7, B9)	–243.6
6,7,8- $\text{CB}_9\text{H}_7\text{F}_3^-$ ($6,7,8\text{-F}_3$)	10.8 (B10) 8.2 (B7) –0.1 (B6, B8) –9.1 (B2, B5) –16.1 (B3, B4) –24.6 (B9)	–217.5 –238.2

(continued)

Table 2 (continued)

Anion	$\delta(^{11}\text{B})$ (assign.)	$\delta(^{19}\text{F})$
6,7,8,9- $\text{CB}_9\text{H}_6\text{F}_4^-$ ($6,7,8,9\text{-F}_4$)	4.7 (B10) 0.2 (B6–B9) –10.3 (B2–B5)	–234.1
$\text{B}_{12}\text{H}_{12}^{2-}$ (F_0)	–14.4 (B1–B12)	
1- $\text{B}_{12}\text{H}_{11}\text{F}^{2-}$ (1-F_1)	9.8 (B1) –16.0 (B2–B6) –17.6 (B7–B11) –23.3 (B12)	–208.4

^aAll spectra at 25°C in acetone-*d*₆ unless otherwise noted. All CB_{11} and CB_9 samples were Cs^+ salts; all B_{12} and B_{10} samples were $\text{N}(n\text{-Bu})_4^+$ salts; $\delta(^{11}\text{B})$ for $\text{BF}_3(\text{OEt}_2) = 0$; $\delta(^{19}\text{F})$ for $\text{CFCl}_3 = 0$; assign. = assignment. Spectral data for $\text{B}_{10}\text{H}_{10}^{2-}$, 1- $\text{B}_{10}\text{H}_9\text{F}^{2-}$, 2- $\text{B}_{10}\text{H}_9\text{F}^{2-}$, and 1,10- $\text{B}_{10}\text{H}_8\text{F}_2^{2-}$ are available in Ref. [17].

Fig. 3. The 96.3 MHz ^{11}B – ^{19}F COSY spectrum (acetone-*d*₆) of products of the $\text{Cs}(\text{CB}_{11}\text{H}_{12})/\text{F-TEDA}$ reaction at 40°C in acetonitrile.

The greater reactivity of F-TEDA relative to other *N*-fluoro reagents was recently demonstrated for $\text{C-H} \rightarrow \text{C-F}$ transformations [16].

No observable amount of 10- $\text{CB}_9\text{H}_9\text{F}^-$ (10-F_1) was formed in any of the reactions of $\text{Cs}(\mathbf{2})$ with *N*-fluoro reagents: 6- F_1 was the only F_1 isomer present. The same regio-specificity was observed for the reaction of $\text{Cs}(\mathbf{2})$ with LAHF [10]. However, the relative amounts of 6,7- F_2 and 6,8- F_2 isomers are strongly dependent on which fluorinating agent is used. Using F-TEDA, nearly equal amounts of the two difluoro isomers are formed. Using LAHF, the mixture of difluoro products was 3% 6,7- F_2 and 97% 6,8- F_2 . Therefore, F-TEDA would allow a reasonably good yield of 6,7- F_2 to be isolated once separation procedures are improved.

3.2.3. Fluorination of $\text{B}_{12}\text{H}_{12}^{2-}$ (3^-)

The products observed in the fluorination of $\text{Cs}_2(\mathbf{3})$ with $\mathbf{5}$ depended on the solvent, the stoichiometric ratio of the two

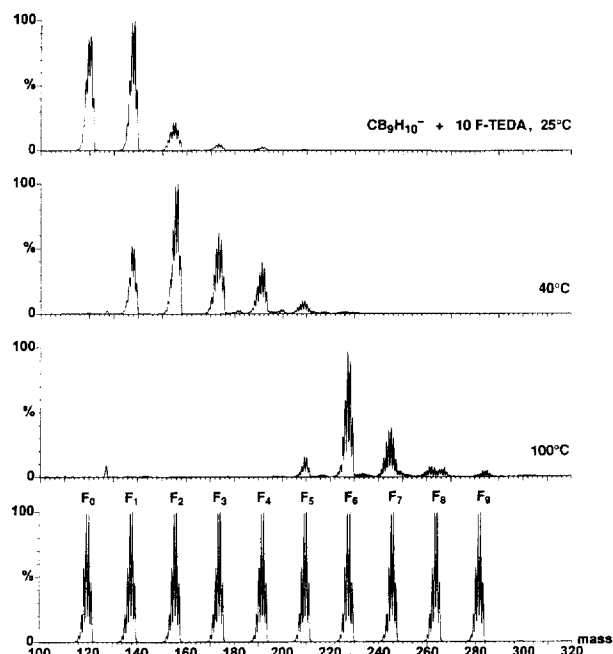


Fig. 4. NIEMS of products of the $\text{Cs}(\text{CB}_9\text{H}_{10})/\text{F-TEDA}$ reactions at 25°C, 40°C, and 100°C in acetonitrile (top three spectra). Calculated spectra for $\text{CB}_9\text{H}_{10-n}\text{F}_n^-$ species (abbreviated F_n) are shown at the bottom. The mass scale is Daltons per electron.

reagents, and the temperature (see Table 1). NMR data for F_0 and F_1 are listed in Table 2 (assignments for more highly fluorinated products were precluded by the apparent presence of multiple geometric isomers). When the solvent was changed from water to DMF/water, the rate of F-TEDA fluorination at 25°C increased for $\text{B}_{12}\text{H}_{12}^{2-}$ (F_0) but decreased for $\text{B}_{12}\text{H}_{11}\text{F}^{2-}$ (F_1) and $\text{B}_{12}\text{H}_{10}\text{F}_2^{2-}$ (F_2). When the stoichiometric ratio of **5** to $\text{Cs}_2(\mathbf{3})$ was increased from 1:1 to 12:1, the fluorinated products formed in DMF/water at 25°C changed from a mixture of F_1 and F_2 to a mixture of F_4 and F_5 . When the temperature was changed from 25°C to 60°C for the 12:1 ratio of **5** to $\text{Cs}_2(\mathbf{3})$ in DMF/water, a mixture of predominantly F_5 and F_6 was formed, which also contained small amounts of F_7 , F_8 , and F_9 . With a large enough excess of F-TEDA, it might be possible to prepare the perfluorinated anion $\text{B}_{12}\text{F}_{12}^{2-}$ (F_{12}) in DMF/water at temperatures $\leq 100^\circ\text{C}$. Note that the preparation of F_{12} using LAHF required temperatures in excess of 500°C [14].

The NIEMS of the product mixture from the 60°C DMF/water reaction is shown in Fig. 5. There are two sets of isotope patterns, both of which are consistent with anions having twelve natural abundance boron atoms. The sets of peaks between 100 and 160 mass units (Daltons per electron) correspond to the parent dinegative ions $\text{B}_{12}\text{H}_{12-n}\text{F}_n^{2-}$ ($n=4-9$). The much less intense sets of peaks between 200 and 260 mass units correspond to uninegative ions $\text{B}_{12}\text{H}_{11-n}\text{F}_n^-$ ($n=4-6$) having *one fewer hydrogen atom* than the parent species. Hop et al. [23] recently observed a small amount of $\text{B}_{12}\text{H}_{11}^-$ in electrospray mass spectra of $\text{Na}_2(\text{B}_{12}\text{H}_{12})$. The uninegative ions probably result from one-electron oxidation

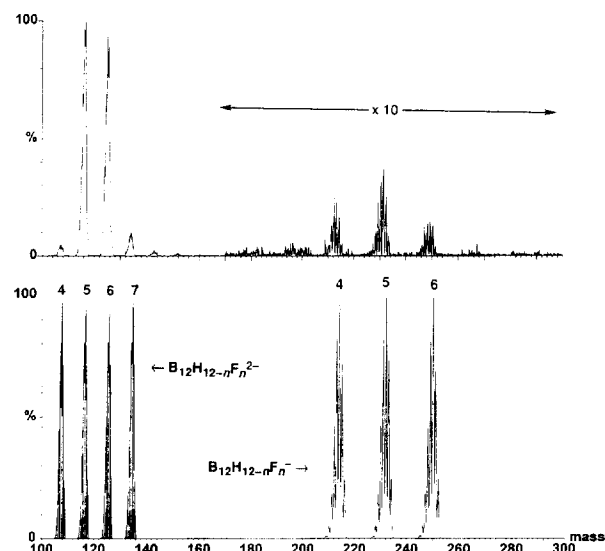


Fig. 5. NIEMS of products of the $\text{Cs}_2(\text{B}_{12}\text{H}_{12})/\text{F-TEDA}$ reactions of 60°C in DMF:water (top). The intensity of the indicated region has been multiplied by a factor of 10. Calculated spectra for $\text{B}_{12}\text{H}_{12-n}\text{F}_n^{2-}$ and $\text{B}_{12}\text{H}_{11-n}\text{F}_n^-$ species (abbreviated n) are shown at the bottom. The mass scale is Daltons per electron.

of the parent dinegative ions (in the mass spectrometer spray chamber) followed by hydrogen atom loss.



Wiersema and Middaugh [27] proposed the transient existence of the unsubstituted $\Delta\text{-B}^-$ species, $\text{B}_{12}\text{H}_{11}^-$, to account for the formation of $\text{B}_{24}\text{H}_{23}^{3-}$ during the one-electron electrochemical oxidation of $\text{B}_{12}\text{H}_{12}^{2-}$ in acetonitrile. Note that the relative intensities of the mass spectral peaks for the uninegative anions $\text{B}_{12}\text{H}_{11-n}\text{F}_n^-$ ($n=4-6$) suggest that one-electron oxidation of the dinegative anions $\text{B}_{12}\text{H}_{12-n}\text{F}_n^{2-}$ becomes progressively more difficult as the number of fluorine atoms increases (i.e., as n increases). This conclusion is in harmony with the known anodic-wave $E_{p/2}$ values for $\text{B}_{12}\text{H}_{12}^{2-}$ [27] and $\text{B}_{12}\text{Cl}_{12}^{2-}$ [28] in acetonitrile, which are 1.4 and > 2.1 V vs. SCE, respectively.

3.2.4. Fluorination of $\text{B}_{10}\text{H}_{10}^{2-}$ (**4**⁻)

The bicapped square-antiprismatic cluster $\text{B}_{10}\text{H}_{10}^{2-}$ is 1 V easier to oxidize than $\text{B}_{12}\text{H}_{12}^{2-}$ [27]. Accordingly, the reaction of $\text{Cs}_2(\mathbf{4})$ with F-TEDA at temperatures above 25°C or with more than 1 equiv. F-TEDA per equiv. $\text{Cs}_2(\mathbf{4})$ resulted in the formation of $\text{B}_{20}\text{H}_{18}^{2-}$ (identified by its ^{11}B NMR spectroscopy and NIEMS) instead of fluorine-substituted anions $\text{B}_{10}\text{H}_{10-n}\text{F}_n^{2-}$. Nevertheless, the reaction of $\text{Cs}_2(\mathbf{4})$ with 1 equiv. F-TEDA at 25°C in either water or DMF/water produced the first examples of fluorinated derivatives of **4**⁻: $\text{B}_{10}\text{H}_{10-n}\text{F}_n^{2-}$ ($n=1-4$). The results are listed in Table 1. The NIEMS for the DMF/water reaction mixture is shown in Fig. 6. Peaks for the dinegative anions $\text{B}_{10}\text{H}_{10-n}\text{F}_n^{2-}$ were not observed, presumably because of the ease with which these ions are oxidized within the mass

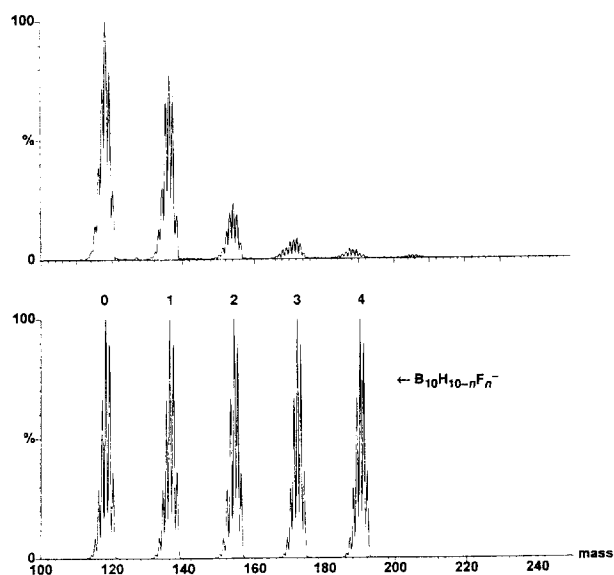


Fig. 6. NIEMS of products of the $\text{Cs}_2(\text{B}_{10}\text{H}_{10})/\text{F-TEDA}$ reaction at 25°C in water (top). Calculated spectra for $\text{B}_{10}\text{H}_{10-n}\text{F}_n^-$ species (abbreviated n) are shown at the bottom. The mass scale is Daltons per electron.

spectrometer spray chamber. Instead, the observed spectrum consists of B_{10} patterns corresponding to a set of uninegative ions $\text{B}_{10}\text{H}_{10-n}\text{F}_n^-$. Unlike the mass spectral results for the B_{12} system, the uninegative B_{10} ions have their original complement of hydrogen atoms. This may be because $\text{B}_{10}\text{H}_{10-n}\text{F}_n^-$ radicals are more stable than their $\text{B}_{12}\text{H}_{12-n}\text{F}_n^-$ counterparts: cyclic voltammetric experiments indicated that the electrochemical one-electron oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ is quasi-reversible [29], whereas the one-electron electrochemical oxidation of $\text{B}_{12}\text{H}_{12}^{2-}$ is irreversible [27].

The solvent effect on the ratio of 1- F_1 to 2- F_1 isomers is readily apparent from ^{19}F NMR spectra of the water-only and DMF/water reaction mixtures (not shown). It is also apparent that a number of F_2 isomers are present, although the predominant isomer is 1,10- F_2 . The two equivalent apical positions of 4^- (B_1 and B_{10}) are expected to undergo much more rapid electrophilic substitution than the eight equivalent equatorial positions [30]. In practice, however, the relative rates of electrophilic substitution for the two types of positions of 4^- depend on the nature of the electrophilic reagent [31,32].

In spite of the facile oxidation of 4^{2-} and its fluorinated derivatives, moderate yields of mixtures of salts of the new anions 1- $\text{B}_{10}\text{H}_9\text{F}^{2-}$, 2- $\text{B}_{10}\text{H}_8\text{F}_2^{2-}$, and 1,10- $\text{B}_{10}\text{H}_8\text{F}_2^{2-}$ can be obtained. When the water-only reaction mixture was filtered (to remove $\text{B}_{20}\text{H}_{18}^{2-}$ salts) and treated with $\text{N}(n\text{-Bu})_4\text{Cl}$, all B_{10} -containing anions precipitated to give a mixture of $[\text{N}(n\text{-Bu})_4][\text{B}_{10}\text{H}_{10-n}\text{F}_n]$ salts ($n=0-4$) that corresponded to 67% recovery of B_{10} clusters based on $\text{Cs}_2(4)$. Thus, the isolated yield of $[\text{N}(n\text{-Bu})_4]_2[\text{B}_{10}\text{H}_{10-n}\text{F}_n]$ salts with $n \geq 1$ was 36% based on $\text{Cs}_2(4)$. The isolated yield of $[\text{N}(n\text{-Bu})_4]_2[\text{B}_{10}\text{H}_{10-n}\text{F}_n]$ salts with $n \geq 1$ was 17% for the DMF/water reaction mixture. The mixtures of products have now been separated using column

chromatography, and ^{11}B and ^{19}F NMR spectral data for F_0 , 1- F_1 , 2- F_1 , and 1,10- F_2 have been communicated earlier [17].

4. Abbreviations

- 1⁻, $\text{CB}_{11}\text{H}_{12}^-$ dodecahydro-1-cabra-*closo*-dodecaborate(1⁻)
 - 2⁻, $\text{CB}_9\text{H}_{10}^-$ decahydro-1-carba-*closo*-deca-borate(1⁻)
 - 3⁻, $\text{B}_{12}\text{H}_{12}^{2-}$ dodecahydro-*closo*-dodecaborate(2⁻)
 - 4⁻, $\text{B}_{10}\text{H}_{10}^{2-}$, decahydro-*closo*-decaborate(1⁻)
 - 5, F-TEDA 1-chloromethyl-4-fluoro-1,4-diazoniabi-cyclo[2.2.2]octane bis(tetrafluoroborate)
 - 6, 1-fluoropyridinium triflate
 - 7, 1-fluoro-2,4,6-trimethylpyridinium triflate
- NIEMS, negative ion electrospray mass spectrum or spectra

Acknowledgements

This research was supported by grants from the National Science Foundation (CHE-9628769 and CHE-9308583). We also thank Akzo Nobel for financial support, Callery Chemical for a gift of $(\text{NEt}_3\text{H})_2\text{B}_{12}\text{H}_{12}$ and $\text{B}_{10}\text{H}_{14}$, Air Products and Chemicals for a gift of F-TEDA, Mr. D.L. Dick for invaluable assistance with mass spectrometry, and Dr. G. Pez for his advice about the use of F-TEDA and for suggesting that F-TEDA might fluorinate B-H bonds under mild conditions.

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