SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, AND STRUCTURE OF *closo*-1,10-B$_{10}$H$_8$F$_2^{2-}$ AND RELATED FLUORINATED DERIVATIVES OF B$_{10}$H$_{10}^{2-}$

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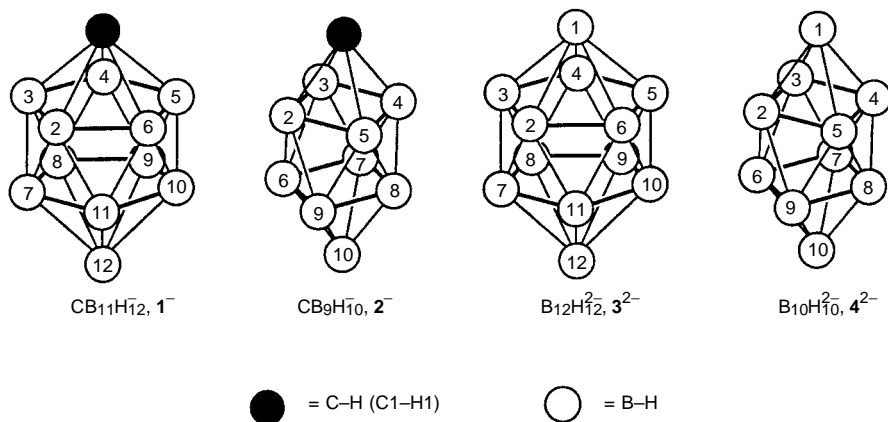
Dedicated to Professor Jaromir Plesek, a valued friend, inspirational colleague, and extraordinary boron chemist, on the occasion of his 70th birthday.

The treatment of salts of the B$_{10}$H$_{10}^{2-}$ anion 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 this ten-vertex borane dianion. The effects of changing the solvent, temperature, and reagent stoichiometry were studied. The derivatives 1-B$_{10}$H$_9$F^{2-}, 2-B$_{10}$H$_9$F^{2-}, 1,2-B$_{10}$H$_8$F$_2^{2-}$, 1,6-B$_{10}$H$_8$F$_2^{2-}$, 1,10-B$_{10}$H$_8$F$_2^{2-}$, and 1,2,10-B$_{10}$H$_7$F$_3^{2-}$ were examined by a combination of ^{11}B and ^{19}F NMR spectroscopy and by IR spectroscopy. The salt [Ph$_4$P]$_2$[1,10-B$_{10}$H$_8$F$_2$] . 3 CH$_2$Cl$_2$ was structurally characterized by single-crystal X-ray crystallography: C$_{51}$H$_{48}$B$_{10}$Cl$_6$F$_2$P$_2$, monoclinic, *C2/c*, *a* = 13.8134(9), *b* = 19.141(1), *c* = 21.136(1) Å, β = 91.546(1)°, *Z* = 4, *T* = –100 °C, *R* = 0.077.
**Key words:** Decaborane; Fluorination; *N*-Fluoro reagents.

We are preparing and studying highly fluorinated derivatives of the carborane and borane anions CB$_{11}$H$_{12}^-$ (**1**$^-$), CB$_9$H$_{10}^-$ (**2**$^-$), B$_{12}$H$_{12}^{2-}$ (**3**$^{2-}$), and B$_{10}$H$_{10}^{2-}$ (**4**$^{2-}$) for use as chemically robust, weakly coordinating anions[1–8]. Our studies were inspired by the work of other boron chemists[9–24], especially the elegant work of Professor Jaromir Plesek and his collaborators[9–17] on the chlorination, bromination, and iodination of **1**$^-$, **2**$^-$, **3**$^{2-}$, and **4**$^{2-}$, and other borane and heteroborane clusters. As far as fluorinated derivatives of **1**$^-$, **2**$^-$, **3**$^{2-}$, and **4**$^{2-}$ are concerned, only 2-CB$_{11}$H$_{11}$F$^-$ (ref.[25]) and several fluorinated derivatives of **3**$^-$ (refs[1,26,27]) were known before 1995. Since then, several fluorinated derivatives of **1**$^-$, **2**$^-$, and **4**$^{2-}$ have been reported[2,4–7]. The fluorinating agents used were liquid anhydrous hydrogen fluoride[2,5,7] and, more recently, *N*-fluoro reagents including 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)[4,6,7] (F-TEDA, **5**). This *N*-fluoro reagent has also been used by Preetz and co-workers to selectively fluori-

nate $B_6H_6^{2-}$ (ref.[28]). Except for $B_6H_6^{2-}$ and $B_{10}H_{10}^{2-}$, F-TEDA has not been reported to effect E–H $\rightarrow$ E–F transformations generally (E = a p-block element other than carbon). In contrast, F-TEDA has been extensively studied as a reagent for effecting C–H $\rightarrow$ C–F

CB$_{11}$H$_{12}^-$, **1$^-$**   CB$_9$H$_{10}^-$, **2$^-$**   B$_{12}$H$_{12}^{2-}$, **3^{2-}**   B$_{10}$H$_{10}^{2-}$, **4^{2-}**

● = C–H (C1–H1)   ○ = B–H

transformations regioselectively[29–31]. In this paper, we report further details about the reaction of F-TEDA with $B_{10}H_{10}^{2-}$, including some observations about how to control the regioselectivity of hydrogen–fluorine exchange. We also report the spectroscopic characterization of the anionic fluorinated products, $B_{10}H_{10-n}F_n^{2-}$ and the structure of one of them, $1,10\text{-}B_{10}H_8F_2^{2-}$.

F-TEDA, **5**   **6**   **7**
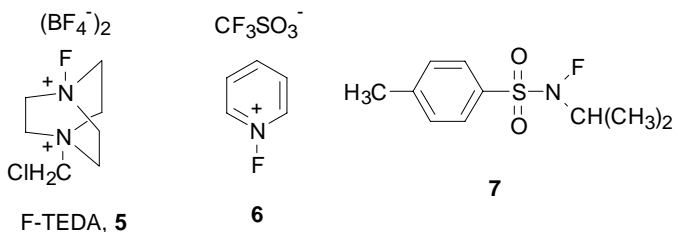
EXPERIMENTAL

General

Schlenk, glovebox, or high-vacuum techniques were employed, with purified nitrogen or argon used when an inert atmosphere was required[32]. All reagents and solvents were reagent grade or better. The following compounds were used as received: D$_2$O (Cambridge), CsOH (Aldrich), AgNO$_3$ (MCB), N(n-Bu)$_4$Cl (Aldrich), Ph$_4$PCl (Aldrich), K$_2$B$_{10}$H$_{10}$ (Callery), F-TEDA (**5**, Air Products), *N*-fluoro-pyridinium triflate (**6**, Aldrich), *N*-fluoro-*N*-propyl-*p*-toluenesulfonamide (**7**, Aldrich). Trifluoroacetic acid (Aldrich) was distilled. Distilled water was deionized by passage through a Barnsted Nanopure water treatment system. The following solvents were purified by distillation from the indicated

drying agent: acetone and hexadeuterioacetone (from P_2O_5 or activated 4Å molecular sieves); aceto-nitrile (from CaH_2), dimethylformamide (DMF; not dried prior to distillation).

Reaction of $B_{10}H_{10}^{2-}$ with F-TEDA in CH_3CN

A stirred, –20 °C solution of $[N(n\text{-Bu})_4]_2[\mathbf{4}]$ (0.20 g, 0.33 mmol) in CH_3CN (15 ml) was treated with a solution of F-TEDA (0.12 g, 0.33 mmol) in CH_3CN (10 ml) under aerobic conditions. A white precipitate and a colorless supernatant formed almost immediately. The mixture was slowly (*ca* 1 h) warmed to room temperature, at which point the supernatant was blue. After 3 h of additional stirring at room temperature, the mixture was filtered. The crude solid product was dried in vacuum. The dried solid (86 mg) was only slightly soluble in H_2O or DMF, but dissolved completely in 0.5 M aqueous NaOH (10 ml). Addition of $N(n\text{-Bu})_4Cl$ (1.2 equivalent based on $B_{10}H_{10}^{2-}$) to the basic solu-tion caused the precipitation of $[N(n\text{-Bu})_4]_2[B_{10}H_{10-n}F_n]$ (0.12 g, 56% yield based on mass spectral evaluation of the average value of n; $n = 0$–3). A control experiment demonstrated that the yield was essentially the same (58%) when the reaction (but not the workup) was performed under strict an-aerobic conditions.

Reaction of $B_{10}H_{10}^{2-}$ with F-TEDA in H_2O

A solution of $K_2[\mathbf{4}]$ (0.74 g, 3.8 mmol) in H_2O (150 ml) was treated with a solution of F-TEDA (1.8 g, 5.1 mmol) in H_2O (50 ml) for 20 h under aerobic conditions. A large amount of precipitate formed almost immediately, most of which dissolved during the course of the reaction. The reaction mixture was filtered, yielding 0.4 g of a slightly yellow solid which proved to be a salt of $B_{20}H_{18}^{2-}$ by ^{11}B NMR spectroscopy. The colorless filtrate was treated with $N(n\text{-Bu})_4Cl$ (1.2 equivalent based on $B_{10}H_{10}^{2-}$), which caused the precipitation of a mixture of salts of the general formula $[N(n\text{-Bu})_4]_2[B_{10}H_{10-n}F_n]$ (1.59 g, 70% yield based on mass spectral evaluation of the average value of n; $n = 0$–5). A nega-tive-ion electrospray mass spectrum of this mixture indicated the presence of the following species (approximate relative abundances in parentheses): $n = 0$ (47%); $n = 1$ (32%); $n = 2$ (12%); $n = 3$ (6%); $n = 4$ (2%), $n = 5$(1%).

Reaction of $B_{10}H_{10}^{2-}$ with F-TEDA in DMF or DMF–H_2O

A solution of $Cs_2[\mathbf{4}]$ (0.10 g, 0.26 mmol) in 4 : 1 (v/v) DMF–H_2O (10 ml) was treated with a solu-tion of F-TEDA (0.092 g, 0.26 mmol) in 4 : 1 (v/v) DMF–H_2O (5 ml) under aerobic conditions. A dark blue solution formed immediately. The color disappeared within 5 min. After 20 h, 30 ml of H_2O was added, and the resulting solution was treated with $N(n\text{-Bu})_4Cl$ (1.2 equivalent based on $B_{10}H_{10}^{2-}$), which caused the precipitation of 15 mg of a light-yellow mixture of $[N(n\text{-Bu})_4]_2[B_{20}H_{18}]$ and $[N(n\text{-Bu})_4]_2[B_{20}H_{17}F]$ (based on a ^{11}B NMR spectrum). The colorless filtrate was treated with Ph_4PCl (1.2 equivalent based on $B_{10}H_{10}^{2-}$), which caused the precipitation of $[Ph_4P][BF_4]$ and a mixture of salts of the general formula $[Ph_4P]_2[B_{10}H_{10-n}F_n]$. The solids were redissolved in CH_3CN (5 ml) and treated with $Cs(CF_3CO_2)$ (0.2 g, 0.8 mmol). The precipitated cesium salts were redissolved in H_2O (20 ml) and treated with $N(n\text{-Bu})_4Cl$ (0.20 g, 0.72 mmol), which caused the precipitation of a mixture of salts having the general formula $[N(n\text{-Bu})_4]_2[B_{10}H_{10-n}F_n]$ (0.055 g, 34% yield based on mass spectral evaluation of the average value of n). When the reaction was performed using neat DMF, only very small amounts (<5%) of fluorinated derivatives of $\mathbf{4}^{2-}$ were observed.

Chromatographic Separation of $B_{10}H_{10-n}F_n^{2-}$ Anions

The mixture of $N(n-Bu)_4^+$ salts from the reaction of $\mathbf{4}^{2-}$ with F-TEDA in H_2O was dissolved in acetone and treated with an excess of $Cs(CF_3CO_2)$. The precipitated $Cs_2B_{10}H_{10-n}F_n$ salts (0.9 g) were collected by filtration and redissolved in H_2O (100 ml) and treated with $AgNO_3$ (0.35 g, 2.0 mmol). This procedure led to the quantitative precipitation of $Ag_2B_{10}H_{10}$ together with small amount of $Ag_2(1-B_{10}H_9F)$ and $Ag_2(2-B_{10}H_9F)$. After filtration, the filtrate was reduced in volume to 20 ml and eluted through a 20×400 mm column of Bio-Gel P-2 (45–90 µm particle size; mobile phase 20 mM aqueous NaCl in 0.04 M phosphate buffer, pH 7.5; flow rate 50 ml/h; temperature 25 °C). Two fractions were collected for further treatment. The first fraction, from eluent volume 200 to 220 ml, contained $2-B_{10}H_9F^{2-}$, $1,2-B_{10}H_8F_2^{2-}$, $1,6-B_{10}H_8F_2^{2-}$, $2,X-B_{10}H_8F_2^{2-}$ (an unidentified equatorial–equatorial isomer of $B_{10}H_8F_2^{2-}$), and $1,2,10-B_{10}H_7F_3^{2-}$. The second fraction, from eluent volume 221 to 250 ml, contained mostly $1-B_{10}H_9F^{2-}$ and $1,10-B_{10}H_8F_2^{2-}$. These fractions were separated on a 5×700 mm column of Sephadex G-15 (40–120 µm particle size; mobile phase 20 mM aqueous NaCl in 0.04 M phosphate buffer, pH 7.5; flow rate 8 ml/h; temperature 25 °C). The order of retention times was $2-B_{10}H_9F^{2-}$ < $1-B_{10}H_9F^{2-}$ ≈ $2,X-B_{10}H_8F_2^{2-}$ < $1,2-B_{10}H_8F_2^{2-}$ ≈ $1,6-B_{10}H_8F_2^{2-}$ < $1,10-B_{10}H_8F_2^{2-}$ < $1,2,10-B_{10}H_7F_3^{2-}$. The fractions containing the separated isomers were treated with $N(n-Bu)_4Cl$, which resulted in the precipitation of the following purified salts: $[N(n-Bu)_4]_2[2-B_{10}H_9F]$ (52 mg, 7% yield based on $B_{10}H_{10}^{2-}$), $[N(n-Bu)_4]_2[1-B_{10}H_9F]$ (20 mg, 3%), $[N(n-Bu)_4]_2[1,10-B_{10}H_8F_2]$ (25 mg, 3%). A mixture of $[N(n-Bu)_4]_2[1,2-B_{10}H_8F_2]$ and $[N(n-Bu)_4]_2[1,6-B_{10}H_8F_2]$ was isolated from the fraction containing the two inseparable difluoro isomers. In a separate experiment, the anions were precipitated from the eluent fractions as Ph_4P^+ salts using Ph_4PCl.

Spectroscopy

Samples for ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy were hexadeuterioacetone solutions in sealed 5-mm glass tubes. Spectra were recorded on a Bruker WP-300 spectrometer. Chemical shifts (δ-scale) are relative to external BF_3 . OEt_2 (^{11}B), internal Me_4Si (^{13}C), and internal $CFCl_3$ (^{19}F). Samples for negative-ion electrospray mass spectrometry (NIEMS) 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 varied from 10–120 V to preclude the formation of ion clusters[33].

Crystallographic Study

Crystals of $[Ph_4P]_2[1,10-B_{10}H_8F_2]$. $3 CH_2Cl_2$ were grown by slow evaporation of solvent from a saturated dichloromethane solution. A suitable crystal was placed in the cold nitrogen stream of the low temperature unit of the Siemens SMART CCD diffractometer system. The diffraction data collection and subsequent structural computations were performed by using the crystallographic software supplied by Siemens[34] and by Prof. G. M. Sheldrick[35]. Lorentz, polarization, and empirical absorption corrections were applied to the data. Details of the crystallographic experiment and subsequent computations are as follows: $C_{51}H_{48}B_{10}Cl_6F_2P$ (1 050.7), monoclinic, $C2/c, a = 13.8134(9)$, $b = 19.141(1)$, $c = 21.136(1)$ Å, $\beta = 91.546(1)°$, $Z = 4$, $T = -100$ °C, $\rho(calc) = 1.29$ g/cm^3, dimensions $0.08 \times 0.28 \times 0.40$ mm, $\mu = 0.406$ mm^{-1}, θ range = 1.82–23.27°, $-15 \leq h \leq 15$, $-21 \leq k \leq 10$, $-23 \leq l \leq 23$, 12 292 reflections collected (4 020 independent reflections for 351 parameters).

The structure was solved by direct methods and refined by using full-matrix least-squares procedures on F^2 for all data. All non-hydrogen atoms were refined anisotropically with the exception of the disordered atoms of the occluded dichloromethane solvent molecules. Hydrogen atoms on the borane anion were located in the difference density map and refined with isotropic thermal parameters

20% larger than the equivalent U value of the boron atoms to which they were attached. Hydrogen atoms on the cation were placed in idealized calculated positions ($U(H) = 1.2U(C)$). Hydrogen atoms were not included on the disordered dichloromethane molecules. The highest peak and deepest hole in the final ΔF map were 0.66 e/Å³ and –0.52 e/Å³, respectively. The final values of R_1 ($I > 2\sigma(I)$) and wR_2 (all data) were 0.077 and 0.177, respectively. Selected interatomic distances and angles are listed in Table I*.

RESULTS AND DISCUSSION

Synthesis

Although $B_{12}H_{12}^{2-}$ can be fluorinated using liquid anhydrous HF (LAHF), the ten-vertex analog $B_{10}H_{10}^{2-}$ (**4**$^{2-}$) cannot. This is because **4**$^{2-}$ is acid labile[36] and is completely destroyed by LAHF (ref.[2]). Three different *N*-fluoro fluorinating reagents, **5**, **6**, and **7**,

TABLE I
Selected interatomic distances (Å) and angles (°) for $[N(n\text{-}Bu)_4][1,10\text{-}B_{10}H_8F_2] \cdot 3\ CH_2Cl_2{}^a$

Atoms	Distances	Atoms	Distances
B1–F1	1.412(6)	B1–B2	1.690(8)
B1–B3	1.686(8)	B1–B4′	1.677(8)
B1–B5′	1.696(8)	B2–B3	1.836(8)
B2–B5′	1.854(8)	B3–B4′	1.847(8)
B4′–B5′	1.836(8)	B2–B4	1.811(8)
B2–B5	1.813(8)	B3–B4′	1.847(8)
B3–B3′	1.826(11)	B3–B4	1.817(8)
B5–B5′	1.802(11)		

Atoms	Angles
B_{eq}–B1–B_{eq}	65.9(3)–66.7(3), 101.1(4), and 101.2(4)
B_{eq}–B_{eq}–B_{eq}	89.7(3)–90.3(4) within squares, 58.9(3)–61.7(3) within triangles

^{a} eq = Equatorial boron atom (B2–B9).

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* Complete tables of atomic positional parameters and equivalent isotropic thermal parameters, distances, angles, anisotropical thermal parameters, and observed and calculated structure factors can be obtained from the authors upon request.

were therefore tested for their ability to fluorinate 4^{2-}. The least powerful reagent, **7**, reacted only very slowly with $[N(n\text{-Bu})_4]_2[4]$ in CH_3CN at 25 °C. The reaction was monitored for 20 days by ^{11}B NMR spectroscopy and NIEMS. The only fluorinated product was the BF_4^- anion: no $B_{10}H_{10-n}F_n^{2-}$ anions were observed.

The reaction of **6** with $[N(n\text{-Bu})_4]_2[4]$ in CH_3CN at 25 °C resulted in the formation of a white precipitate which completely redissolved during 20 h. Spectroscopic analysis of the reaction mixture indicated that the major product was $2\text{-}B_{10}H_9(NCCH_3)^-$ (>60%), an anion previously prepared by Hawthorne and co-workers[37]. The anions $B_{20}H_{18}^{2-}$ and BF_4^- were also observed, but only a few percent of a mixture of $B_{10}H_{10-n}F_n^{2-}$ ions were evident in the NMR and mass spectra. When the solvent was water instead of CH_3CN, no reaction was observed: 100% of the starting material 4^{2-} was recovered unchanged from the reaction mixture.

Successful B–H → B–F transformations occurred in reactions of F-TEDA with 4^{2-} salts: mixtures of $B_{10}H_{10-n}F_n^{2-}$ anions ($n = 0$–5) were observed for reactions in H_2O, DMF–H_2O, DMF, or CH_3CN, as listed in Table II. The addition of F-TEDA to an aqueous solution containing 4^{2-} resulted in the immediate formation of a white precipitate, most of which disappeared with stirring. The supernatant was colorless throughout

TABLE II
Relative percentages of isomeric $B_{10}H_{10-n}F_n^{2-}$ products of reactions of salts of $B_{10}H_{10}^{2-}$ with F-TEDA in different solvents[a]
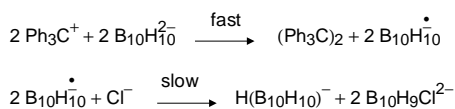
Isomer	H_2O	DMF–H_2O 4:1	CH_3CN anaerobic	CH_3CN aerobic
$1\text{-}B_{10}H_9F^{2-}$	30	48	66	66
$2\text{-}B_{10}H_9F^{2-}$	46	21	21	20
$1,2\text{-}B_{10}H_8F_2^{2-}$	4	4	2	1
$1,6\text{-}B_{10}H_8F_2^{2-}$	5	5	4	3
$1,10\text{-}B_{10}H_8F_2^{2-}$	7	17	4	8
$2\text{-}X\text{-}B_{10}H_8F_2^{2-,b}$	4	2	3	1
$1,2,10\text{-}B_{10}H_7F_3^{2-}$	4	3	0	1
$1\text{-}F_1/2\text{-}F_1$ ratio	0.6	2.6	3.1	3.3
Total F_1/F_2 ratio	3.8(3.3^c)	2.5(2.7^c)	6.3(6.7^c)	6.6(5.5^c)
Yield of $B_{10}H_{10-n}F_n^{2-}$ ($n = 0$–3)	67	33	58	56
Yield of $B_{10}H_{10-n}F_n^{2-}$ ($n = 1$–3)	36	17	15	16

[a] Determined by integration of ^{19}F NMR spectra of $[N(n\text{-Bu})_4]_2B_{10}H_{10-n}F_n$ reaction products prior to purification. [b] An unidentified isomer with fluorine atoms bonded to two equatorial boron atoms. [c] Determined from relative intensities in negative-ion electrospray mass spectra.

the reaction. In the case of DMF or DMF–H_2O solutions, a dark blue solution was formed and no precipitate was observed. The blue color disappeared within 5 min. In the case of CH_3CN solutions, a white precipitate and colorless solution formed immediately, but the supernatant became blue within several minutes. The blue color disappeared, but a white precipitate remained after 8 h.
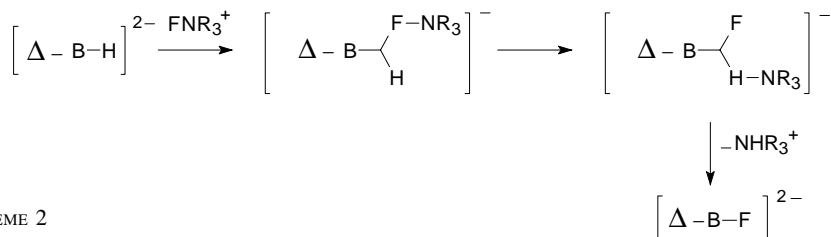
A blue free radical, presumed to be $B_{10}H_{10}^{\cdot -}$, was observed when $B_{10}H_{10}^{2-}$ was oxidized by anhydrous $CuCl_2$ (ref.[38]). However, the following results suggest that the radical is *not* an intermediate in the formation of $B_{10}H_{10-n}F_n^{2-}$ anions. When $[N(n\text{-}Bu)_4]_2[B_{10}H_{10}]$ and Ph_3CCl were mixed in CH_2Cl_2, a blue color formed that disappeared over time. The NIEMS and NMR spectra of the reaction products showed a 50 : 50 mixture of $B_{10}H_{10}^{2-}$ and $2\text{-}B_{10}H_9Cl^{2-}$ (the latter anion has been reported by Preetz and co-workers[39]), which implies the reaction scheme (Scheme 1).

$$2\,Ph_3C^+ + 2\,B_{10}H_{10}^{2-} \xrightarrow{\text{fast}} (Ph_3C)_2 + 2\,B_{10}H_{10}^{\cdot -}$$

$$2\,B_{10}H_{10}^{\cdot -} + Cl^- \xrightarrow{\text{slow}} H(B_{10}H_{10})^- + 2\,B_{10}H_9Cl^{2-}$$

SCHEME 1

When $N(n\text{-}Bu)_4)F \cdot 3\,H_2O$ was added immediately after addition of $[N(n\text{-}Bu)_4]_2[B_{10}H_{10}]$ and Ph_3CCl, only BF_4^- and unsubstituted $B_{10}H_{10}^{2-}$ were observed. Furthermore, when the one-electron oxidant $Ce(NH_4)_2(NO_3)_6$ was mixed with $[N(n\text{-}Bu)_4]_2[B_{10}H_{10}]$ and CsF in DMF, a blue color developed but the only boron-containing products were BF_4^- and $B_{20}H_{18}^{2-}$.

If the radical species $B_{10}H_{10}^{\cdot -}$ is not an intermediate in the B–H $\rightarrow$ B–F transformations, it is possible, although by no means demonstrated, that a complex of $B_{10}H_{10}^{2-}$ and the *N*-fluoro cation of F-TEDA is formed during the H/F metathesis, as depicted in the following speculative reaction scheme (Scheme 2) (Δ = the boron cluster minus one B–H vertex).

$$\left[\Delta - B{-}H\right]^{2-} \xrightarrow{FNR_3^+} \left[\Delta - B\left\langle{}^{F-NR_3}_{H}\right.\right]^- \longrightarrow \left[\Delta - B\left\langle{}^{F}_{H-NR_3}\right.\right]^-$$

$$\downarrow{}_{-NHR_3^+}$$

$$\left[\Delta - B{-}F\right]^{2-}$$

SCHEME 2

Clearly more data will be needed to completely understand the mechanism or mechanisms of this interesting reaction. We note that the mechanisms by which F-TEDA and

other *N*-fluoro reagents transform C–H into C–F bonds are by no means completely understood at the present time[30,31].

The distribution of *n* values for the reaction products $B_{10}H_{10-n}F_n^{2-}$ was different as the solvent was changed, as shown in Table II. In all of the reactions the ratio of $1\text{-}B_{10}H_9F^{2-}$ to $2\text{-}B_{10}H_9F^{2-}$ was greater than 0.25, the ratio expected due to the statistical factor of eight equatorial B–H bonds *versus* two apical B–H bonds. This result is in harmony with the greater propensity of electrophilic attack of aqueous DCl on the apical B–H bonds relative to the equatorial B–H bonds of $B_{10}H_{10}^{2-}$ (ref.[40]).

The smallest ratio of $1\text{-}B_{10}H_9F^{2-}$ to $2\text{-}B_{10}H_9F^{2-}$ was found when the solvent was H_2O. This could be due to stronger B–H...H–O hydrogen bonding for apical B–H bonds relative to equatorial B–H bonds: the stronger hydrogen bonding might render the apical B–H bonds less prone to electrophilic attack by F-TEDA. In the aprotic solvents DMF and CH_3CN there can be no hydrogen bonding and hence the apical B–H bonds should fluorinate faster – the observed $1\text{-}B_{10}H_9F^{2-}/2\text{-}B_{10}H_9F^{2-}$ ratio was 3.3 for CH_3CN and 3.6 for anhydrous DMF.

Structure of $1,10\text{-}B_{10}H_8F_2^{2-}$

The structure of $[Ph_4P]_2[1,10\text{-}B_{10}H_8F_2]$. 3 CH_2Cl_2 consists of distinct Ph_4P^+ cations, $1,10\text{-}B_{10}H_8F_2^{2-}$ anions, and CH_2Cl_2 molecules with no significant intermolecular interactions. The distances and angles within the Ph_4P^+ cations are normal. The CH_2Cl_2 molecules are disordered by rotation, one pair about the crystallographic 2-fold axis and the other about a general position.

The $1,10\text{-}B_{10}H_8F_2^{2-}$ anion, shown in Fig. 1, has crystallographic 2-fold symmetry. The crystallographic 2-fold axis bisects the B3–B3′ and B5–B5′ bonds. The two symmetry-related fluorine atoms are bonded to the two apical boron atoms. The two square-planes of
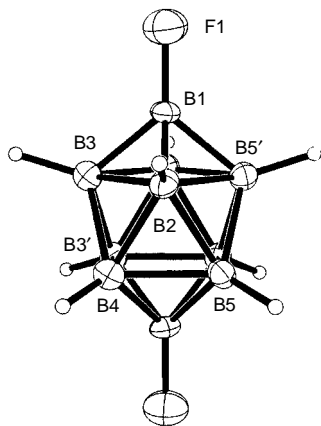

FIG. 1

Structure of the $1,10\text{-}B_{10}H_8F_2^{2-}$ anion in $[Ph_4P]_2[1,10\text{-}B_{10}H_8F_2]$. 3 CH_2Cl_2 (50% probability ellipsoids except for hydrogen atoms, which are shown as spheres of arbitrary size)

equatorial boron atoms (B(eq)) are each planar to within ±0.03 Å. These two planes are virtually parallel, making an interplanar angle of only 0.5°.

The anion has idealized D_{4d} symmetry: the four B1–B(eq) bond distances, which range from 1.677(8) to 1.696(8) Å, are the same within experimental error. The B(eq)–B(eq) distances within the square planes range from 1.836(8) to 1.854(8) Å, and the B(eq)–B(eq) distances between the two square planes range from 1.802(11) to 1.826(11) Å. These ranges are not significantly different than the corresponding ranges in $B_{10}H_{10}^{2-}$ (refs[41,42]) or in other derivatives with idealized four-fold symmetry, including 1-$B_{10}H_9I^{2-}$ (ref.[43]), 1-$B_{10}H_9(NO_2)^{2-}$ (ref.[44]), or 1,10-$B_{10}H_8(N_2)_2$ (ref.[45]).

The B1–F1 distance is 1.412(6) Å. This is significantly longer than the B–F distance reported by us in 2-$B_{10}H_9F^{2-}$, 1.346(8) Å (ref.[4]), which is contrary to the expectation that B–X bonds to *ipso*-boron atoms bonded to four other boron atoms (B_{4k}–X) should be stronger and perhaps slightly shorter than B–X bonds to *ipso*-boron atoms bonded to five other atoms (B_{5k}–X). For example, the B–I distances in 1-$B_{10}H_9I^{2-}$ and 2-$B_{10}H_9I^{2-}$, at 2.209(6) and 2.230(2) Å, respectively, are marginally different[39,43]. However, the fluorine atom in 2-$B_{10}H_9F^{2-}$ is disordered over two sites (B2 and B9). Accordingly, the derived B–F distance in 2-$B_{10}H_9F^{2-}$ may be affected by the disorder and should not be used for a direct comparison with the B–F distance in 1,10-$B_{10}H_9F^{2-}$.

Other reported B_{5k}–F distances are 1.38(2) and 1.42(2) Å in 6,8-$CB_9H_8F_2^-$ (ref.[5]) and 1.37(1) Å in 12-$CB_{11}H_{11}F^-$ (ref.[2]). The B_{5k}–F distance in the four-fold symmetric 6,7,8,9-$CB_9H_6F_4^-$ ion is 1.389(2) Å, and the B_{5k}–F and B_{4k}–F distances in four-fold symmetric 6,7,8,9,10-$CB_9H_5F_5^-$ are 1.386(4) and 1.378(8) Å, respectively[46]. Thus, it appears that there is no clear evidence yet that B_{4k}–F distances are shorter than B_{5k}–F distances. Nevertheless, it is possible that the two B–F bonds in 1,10-$B_{10}H_8F_2^{2-}$ will be found to be longer and weaker than the single B–F bond in 1-$B_{10}H_9F^{2-}$, which has not yet been structurally characterized, because of a strong antipodal effect[47–49] that each B–F moiety in 1,10-$B_{10}H_8F_2^{2-}$ exerts on the other. However, note that the B–I distances in $B_6H_5I^{2-}$ and $B_6I_6^{2-}$, which are 2.174(3) (ref.[50]) and 2.18 (av)[51], respectively, are essentially the same.

Spectroscopic Study of $B_{10}H_{10-n}F_n^{2-}$ Anions

The new fluorinated derivatives of 4^{2-} were studied by negative-ion electrospray mass spectrometry (NIEMS), ^{11}B, ^{11}B-^{11}B 2D-COSY, and ^{19}F NMR spectroscopy, and by IR spectroscopy. The NIEMS spectrum of [N(n-Bu)$_4$]$_2$[1,10-$B_{10}H_8F_2$] (CH$_3$CN solution) is shown in Fig. 2. There is a good correlation between the observed spectrum and the isotope pattern calculated for the one-electron-oxidized mononegative ion $B_{10}H_8F_2^-$. Similar behavior was found for all of $B_{10}H_{10-n}F_n^{2-}$ anions studied (n = 0–3). Presumably these ions oxidize within the mass spectrometer spray chamber to form relatively stable mononegative radical ions (note that the $B_{10}H_{10}^-$ radical anion was proposed as an intermediate in the chemical[38] and electrochemical[52] one-electron oxidation of $B_{10}H_{10}^{2-}$).

The slightly higher intensities on the low mass side of the observed spectrum in Fig. 2 could be due to presence of signals from a small concentration of $B_{10}H_7F_2^-$ (*i.e.*, $B_{10}H_8F_2^{2-} - H^-$). Note that the NIEMS spectrum of salts of $B_{12}H_{12-n}F_n^{2-}$ anions ($n = 0$–6) consisted of signals from $B_{12}H_{11-n}F_n^-$ ions and not from the simple one electron-oxidized parent anions $B_{12}H_{12-n}F_n^-$ (refs[6,33]). Although signals from the parent ion 1,10-$B_{10}H_8F_2^{2-}$ were not observed at high sample cone voltages, signals due to the mononegative ion-cluster $\{[N(n\text{-}Bu)_4][1,10\text{-}B_{10}H_8F_2]\}^-$ were observed at low sample cone voltages (the intensities of these signals were approximately 3% of the intensities of the signals due to the 1,10-$B_{10}H_8F_2^-$ ion).

Boron-11 and ^{19}F NMR data for salts of the $B_{10}H_{10-n}F_n^{2-}$ anions ($n = 0$–3) are listed in Table III. The ^{11}B NMR spectrum of 1-$B_{10}H_9F^{2-}$, shown in Fig. 3, is consistent with the presumed C_{4v} symmetry of this anion. The substitution of a fluorine atom for one of the apical hydrogen atoms in $B_{10}H_{10}^{2-}$ causes shielding of the ^{11}B resonances for the unsubstituted boron atoms. The shielding of the B10 resonance, 13 ppm, is much larger than the shielding of the B2-B5 and B6-B9 resonances, 3.0 and 4.5 ppm, respectively,
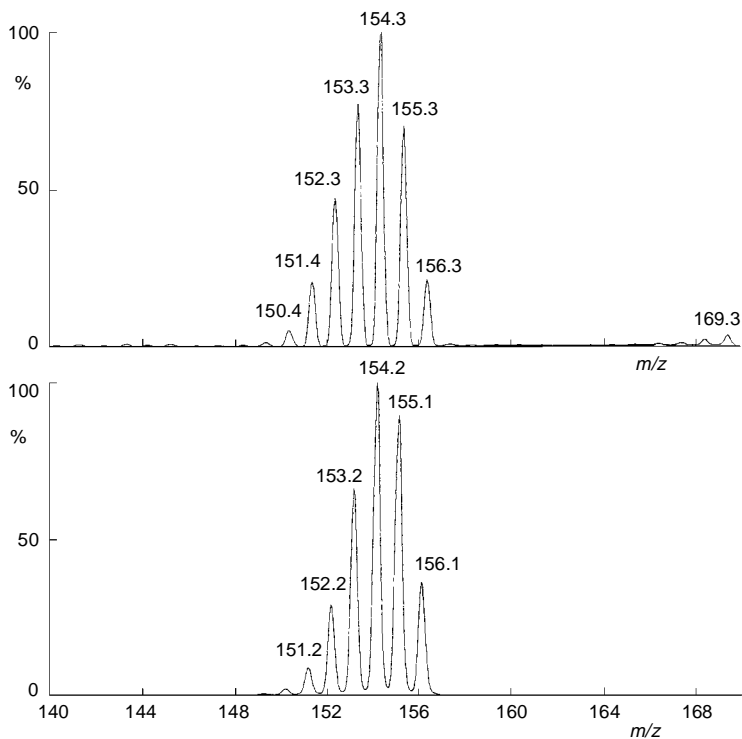

FIG. 2

Negative-ion electrospray mass spectra. The top spectrum is the experimental spectrum for Cs_2(1,10-$B_{10}H_8F_2$). The bottom spectrum is a calculated spectrum for the monoanion $B_{10}H_8F_2^-$

NMR spectral data for $B_{10}H_{10-n}F_n^{2-}$ anions[a]

Anion	$\delta(^{19}F)$	$\delta(^{11}B)$, int., pattern (assign.)[b]	$J(^{11}B,^1H)$, Hz[c]
$B_{10}H_{10}^{2-}$		0.0, 2, d (B1,B10)	140
		–27.9, 8, d (B2–B9)	125
1-$B_{10}H_9F^{2-}$	–225.7	27.5, 1, bd s (B1)	
		–13.3, 1, d (B10)	148
		–30.9, 4, d (B2–B5)	128
		–32.4, 4, d (B6–B9)	123
2-$B_{10}H_9F^{2-}$	–236.4	3.1, 1, bd s (B2)	
		–2.7, 1, d (B10)	144
		–4.8, 1, d (B1)	143
		–22.0, 2, d (B7,B8)	120
		–23.2, 2, d (B3,B5)	122
		–28.8, 2, d (B6,B9)	129
		–34.2, 1, d (B4)	124
1,2-$B_{10}H_8F_2^{2-}$	–229.7	20.8, 1, bd s (B1)	
	–240.6	–0.1, 1, bd s (B2)	
		–15.1, 1, d (B10)	143
		–27.4, 4, d (B3,B5,B7[d],B8[d])	125
		–32.6, 2, d (B6[d], B9[d])	120
		–36.8, 1, d (B4)	n.o.
1,6-$B_{10}H_8F_2^{2-}$	–226.2	25.7, 1, bd s (B1)	
	–239.0	–0.1, 1, bd s (B6)	
		–17.9, 1, d (B10)	149
		–24.8, 2, d (B4[d],B5[d])	134
		–27.4, 2, d (B7,B9)	125
		–31.8, 2, d (B2[d],B3[d])	n.o.
		–38.4, 1, d (B8)	n.o.
1,10-$B_{10}H_8F_2^{2-}$	–257.8	21.8, 2, bd s (B1,B10)	
		–34.6, 8, d (B2–B9)	125
1,2,10-$B_{10}H_7F_3^{2-}$	–257.8	20.3, 1, bd s (B10)	
	–260.3	15.0, 1, bd s (B1)	
	–242.9	–4.1, 1, bd s (B2)	
		–29.4, 2, d (B7,B8)	123
		–30.6, 2, d (B3,B5)	120
		–34.7, 2, d (B6,B9)	n.o.
		–40.4, 1, d (B4)	126

[a] All spectra recorded at 25 °C for $N(n\text{-}Bu)_4^+$ salts dissolved in hexadeuterio acetone; $\delta(^{11}B)$ for $BF_3(OEt_2)$ = 0; $\delta(^{19}F)$ for $CFCl_3$ = 0; ^{19}F NMR resonances were broad doublets with unequal intensities. [b] int. integrated intensity; assign. assignment; d doublet, bd s broad singlet (unresolved multiplet). [c] n.o. Not observable due to poor signal/noise or overlapping resonances. [d] These assignments are uncertain due to weak ^{11}B-^{11}B coupling in 2D NMR spectra.

and is expected manifestation of the antipodal effect[47–49,53,54]. Interestingly, no corresponding antipodal effect was observed for the $1-B_{10}H_9I^{2-}$ anion[55].

Substitution of an equatorial hydrogen atom for a fluorine atom, producing $2-B_{10}H_9F^{2-}$, has an opposite effect on the resonances for B3, B5 and for B4, in harmony with well-established trends for ^{11}B NMR spectra of *closo*-boranes and -heteroboranes[53,54]. Note that the B2–F moiety has a larger influence (relative to $B_{10}H_{10}^{2-}$) on the B1 resonance ($\Delta\delta = -4.8$) than on the B10 resonance ($\Delta\delta = -2.7$). This result was unexpected because the two apical boron atoms in $2-B_{10}H_9Cl^{2-}$, $2-B_{10}H_9Br^{2-}$, and $2-B_{10}H_9I^{2-}$ (X = Cl, Br, I) have the same ^{11}B chemical shift[55].

Although ^{11}B NMR chemical shift trends, and their underlying causes, are believed to be well understood[47–49,53,54], chemical shift trends for substituent atoms are less well understood because fewer data are available. The ^{19}F NMR results for the $B_{10}H_{10-n}F_n^{2-}$ anions ($n = 0$–3) could allow us to begin to study such trends if unambiguous assignments could be made. Such definite assignments must await the collection of ^{11}B-^{19}F 2D NMR spectra. In the interim, our assignments, shown in Fig. 4, have been tentatively made based on the relative separations of the ^{19}F resonances. This is possible because the peak-to-peak separation for the expected four-line pattern due to ^{11}B-^{19}F coupling is frequently smaller than $J(^{11}B,^{19}F)$: broadened and partially or fully collapsed multiplets due to quadrupolar relaxation have been observed when a ^{19}F atom ($I = 1/2$) is bonded to a quadrupolar ^{11}B atom ($I = 3/2$) (ref.[56]). We have found that the envelope of resonances for $2-B_{10}H_9F^{2-}$ is significantly wider (due to a relatively longer relaxation time) than the envelopes of resonances for $1-B_{10}H_9F^{2-}$ and $1,10-B_{10}H_8F_2^{2-}$. On this
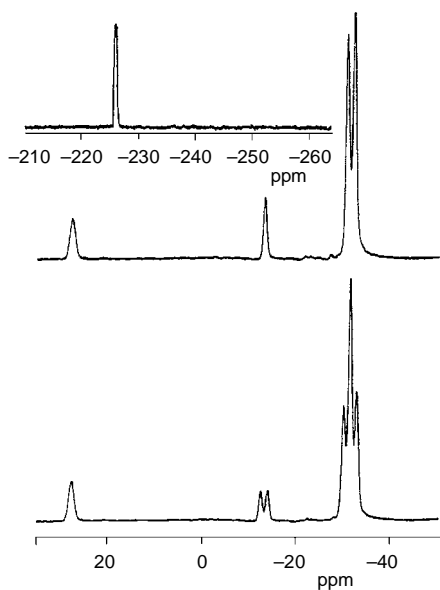
FIG. 3

96.3 MHz $^{11}B\{^1H\}$ (top) and ^{11}B (bottom) spectra (35 to –50 ppm) of $[N(n-Bu)_4]_2[1,10-B_{10}H_8F_2]$ dissolved in hexadeuterioacetone. The 282.4 MHz ^{19}F NMR spectrum (–210 to –265 ppm) is also shown

basis, tentative assignments for $1,2\text{-}B_{10}H_8F_2^{2-}$, $1,6\text{-}B_{10}H_8F_2^{2-}$, and $1,2,10\text{-}B_{10}H_7F_3^{2-}$ were made.

The ^{19}F nucleus in $2\text{-}B_{10}H_9F^{2-}$, bonded to a $5k$ boron atom, is more shielded than the ^{19}F nucleus in $1\text{-}B_{10}H_9F^{2-}$, which is bonded to a $4k$ boron atom (δ –236.4 *vs* δ –225.7, respectively). Adding a second fluorine atom to $1\text{-}B_{10}H_9F^{2-}$ can result in three isomers, $1,2\text{-}B_{10}H_8F_2^{2-}$, $1,6\text{-}B_{10}H_8F_2^{2-}$, and $1,10\text{-}B_{10}H_8F_2^{2-}$. The largest effect on the $^{19}F(B1)$ chemical shift was observed for $1,10\text{-}B_{10}H_8F_2^{2-}$ ($\Delta\delta = -32.1$), a substantial antipodal effect. The corresponding $\Delta\delta$ value for $1,2\text{-}B_{10}H_8F_2^{2-}$ is only –4.0, and δ $^{19}F(B1)$ is nearly the same for $1,6\text{-}B_{10}H_8F_2^{2-}1,6\text{-}B_{10}H_8F_2^{2-}$ ($\Delta\delta = -0.5$). These data as well as ^{19}F NMR data for fluorinated derivatives of 1^-, 2^-, and 3^- will be more completely discussed in a forthcoming paper from our laboratory.

IR spectra of $N(n\text{-}Bu)_4^+$ salts of the new $B_{10}H_{10-n}F_n^{2-}$ anions were recorded as Nujol mulls of CH_2Cl_2 solutions. No significant differences were observed in the $\nu(BH)$ region except that the IR band due to stretching of the apical B–H bonds in $B_{10}H_{10}^{2-}$ (ref.[57]) were absent from spectra of $[N(n\text{-}Bu)_4][1,10\text{-}B_{10}H_8F_2]$ (only one intense band at 2 460 cm^{-1} was observed). Substitution of hydrogen atoms for fluorine atoms resulted in the appearance of intense bands in the 1 200 cm^{-1} region: 1 212 cm^{-1} for $1\text{-}B_{10}H_9F^{2-}$, 1 126 cm^{-1} for $1,10\text{-}B_{10}H_8F_2^{2-}$. It is tempting to conclude that the B1–F bond in $1\text{-}B_{10}H_9F^{2-}$
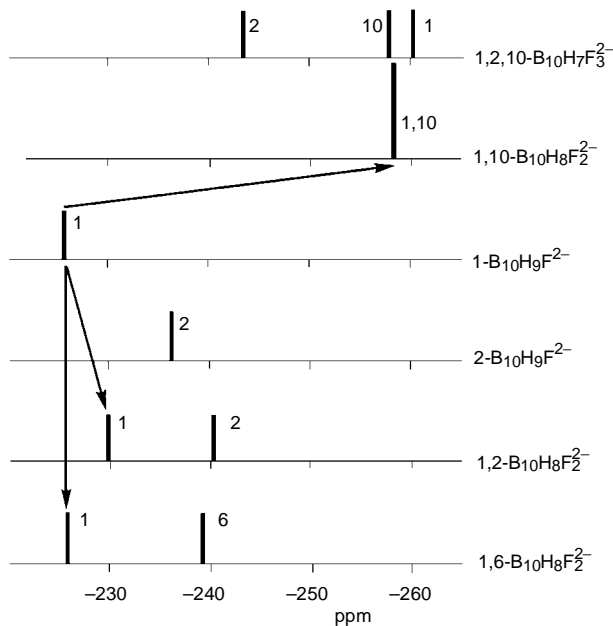

Fig. 4
Fluorine-19 chemical shifts for hexadeuterioacetone solutions of salts of $B_{10}H_{10-n}F_n^{2-}$ anions

is stronger than the B1–F bond in $2\text{-}B_{10}H_9F^{2-}$ ($\Delta\nu = 86$ cm^{-1}), but the observed resonances are probably due to mixtures of B–F and B–B stretching normal modes[58] and not simply due to a single B–F stretching normal mode. As with the ^{19}F NMR data, a more complete analysis of these and related IR data will be forthcoming after more data for a larger number of fluorinated *closo*-boranes and -heteroboranes have been acquired.

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