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Direct Perfluorination of $K_2B_{12}H_{12}$ in Acetonitrile Occurs at the Gas Bubble−Solution Interface and Is Inhibited by HF. Experimental and DFT Study of Inhibition by Protic Acids and Soft, Polarizable Anions

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Abstract: During the optimization of the F_2 perfluorination of $K_2B_{12}H_{12}$ in acetonitrile with continuous bubbling of 20/80 F_2/N_2, it was discovered that (i) HF and other protic acids inhibit each of the 12 fluorination steps (in contradiction to recently published findings) and (ii) the fluorinations appear to take place at the gas bubble−solution interface. Experimental results and DFT calculations suggest that these two phenomena are related by the relative propensities of the various $B_{12}H_{12-x}F_x^{2-}$ anions to partition from bulk solution to the interface (i.e., their relative polarizabilities or softness; $0 \le x \le 12$). Relative to the previously reported syntheses of $K_2B_{12}F_{12}$ or $Cs_2B_{12}F_{12}$, the new optimized procedure has the following advantages: (i) the scale was increased 10-fold without sacrificing yield (74% for $K_2B_{12}F_{12}$, 76% for $Cs_2B_{12}F_{12}$) or purity (99.5+%); (ii) the reaction/purification time was decreased from ca. 1 week to 2 days; and (iii) the solvent was changed from anhydrous HF to acetonitrile, allowing ordinary glassware to be used. The anhydrous salt $Cs_2B_{12}F_{12}$ was found to be thermally stable up to 600 °C.

Introduction

The icosahedral $B_{12}H_{12}^{2-}$ anion, the IUPAC-approved numbering for which is shown in Figure 1,[1] was first prepared in 1960.[2] It is the prototype deltahedral *closo*-borane[3,4] as well as the synthetic precursor for a wide variety of $B_{12}X_{12}^{2-}$ anions with X = D,[5] OCOR,[6,7] Me,[8,9] OR,[10,11] OH,[12−14] I,[15] Br,[15,16] Cl,[15−20] and F.[21−25] A species reported in 1962[26] to be $B_{12}F_{12}^{2-}$ was later shown to be the undecafluoromonohydroxy species $B_{12}(OH)F_{11}^{2-}$.[15] The first successful synthesis of $B_{12}F_{12}^{2-}$ was

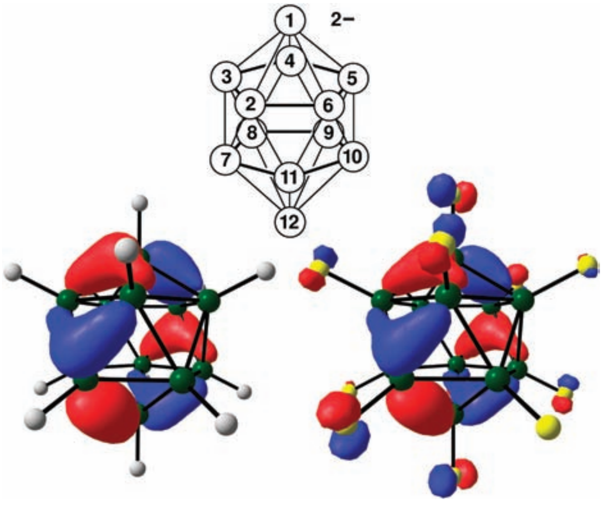

Figure 1. IUPAC-approved numbering of the B_{12} icosahedron in species such as $B_{12}H_{12}^{2-}$ and $B_{12}F_{12}^{2-}$ (top) and one of the DFT-predicted quadruply degenerate HOMOs of $B_{12}H_{12}^{2-}$ (bottom left) and $B_{12}F_{12}^{2-}$ (bottom right).

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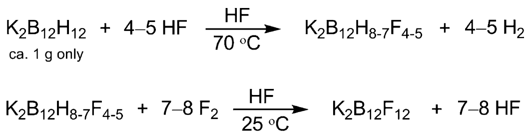
Scheme 1



$$\underset{\text{ca. 1 g only}}{K_2B_{12}H_{12}} + \text{4–5 HF} \xrightarrow[70\ °C]{HF} K_2B_{12}H_{8\text{-}7}F_{4\text{-}5} + \text{4–5 } H_2$$

$$K_2B_{12}H_{8\text{-}7}F_{4\text{-}5} + \text{7–8 } F_2 \xrightarrow[25\ °C]{HF} K_2B_{12}F_{12} + \text{7–8 HF}$$

achieved in 1992, when Solntsev and co-workers reported that the cesium salt could be prepared in 38% yield by heating $Cs_2B_{12}H_{12}$ in supercritical HF to 550 °C for 5 h.[21] The structure of $Cs_2(H_2O)B_{12}F_{12}$ was also reported at that time.[21]

In 2003 we, in collaboration with Solntsev, reported an improved synthesis of $K_2B_{12}F_{12}$ (72% recrystallized yield) in a one-pot reaction that required first heating $K_2B_{12}H_{12}$ in anhydrous HF to only 70 °C and then treating the reaction mixture with 20/80 F_2/N_2 at 25 °C (see Scheme 1).[23,24] However, the scale of the reaction was limited to ca. 1 g of $K_2B_{12}H_{12}$ starting material in order to obtain the highest yield with the fewest byproducts. In addition, a Monel reaction vessel was required because the pressure of F_2/N_2 typically used was 50 psi or higher, too high for routine use of large-volume fluoropolymer reaction vessels. Furthermore, the fluorination took nearly a week to complete (nominally 5−6 days, plus an additional day for workup and recrystallization of the product). In 2004, Casteel and Ivanov reported in a patent that $B_{12}H_{12}^{2-}$ salts could be polyfluorinated with F_2 not only in anhydrous HF but also in aqueous HF, formic acid, and acetic acid.[25] However, complete conversion of $B_{12}H_{12}^{2-}$ to $B_{12}F_{12}^{2-}$ was not reported for any solvent other than anhydrous HF, and neither reaction times nor isolated yields of purified $B_{12}F_{12}^{2-}$ salts were reported. Note that all previous preparations of $K_2B_{12}F_{12}$ or attempts to prepare $B_{12}F_{12}^{2-}$ salts were performed in acidic media.

We now report a procedure for preparing 99.5+ mol % $K_2B_{12}F_{12}$ in 74% recrystallized yield or 99.5+ mol % $Cs_2B_{12}F_{12}$ in 76% recrystallized yield using up to 10 g of $K_2B_{12}H_{12}$ as the starting material, acetonitrile as the solvent, and an ordinary Pyrex flask with standard-taper joints as the reaction vessel. When a mixture of the partially fluorinated salts $K_2B_{12}H_8F_4$ and $K_2B_{12}H_7F_5$ was used instead of $K_2B_{12}H_{12}$ as the starting material, the yield of $K_2B_{12}F_{12}$ was 92%. The development of this procedure was carried out in parallel with DFT calculations, which helped to explain why rigorous *exclusion* of any protic acid was the key to an efficient F_2 perfluorination of $K_2B_{12}H_{12}$. We also report that the anhydrous salt $Cs_2B_{12}F_{12}$ is stable to 600 °C under a helium atmosphere.

Results and Discussion

General Comments about $B_{12}H_{12}^{2-}$ Fluorination and the Determination of $B_{12}H_{12-x}F_x^{2-}$ Mol % Values. Whether the fluorinating agent is anhydrous HF,[21,23] F-TEDA$(BF_4)_2$,[27] or F_2,[23−25] the fluorination of $B_{12}H_{12}^{2-}$ almost certainly involves electrophilic attack on the icosahedral borane dianion.[28] The DFT-predicted highest occupied molecular orbital (HOMO) of $B_{12}H_{12}^{2-}$ is shown in Figure 1. The electrophile probably forms a Lewis acid−base complex with one of the triangular B_3 faces of the $B_{12}H_{12-x}F_x^{2-}$ icosahedron, in much the same way that the 11th H atom (i.e., H^+) in $B_{10}H_{11}^-$ caps a triangular B_3 face of the $B_{10}H_{10}^{2-}$ anion[29] or the 13th H atom (i.e., H^+) in $B_{12}H_{13}^-$ is predicted to cap a triangular face of the $B_{12}H_{12}^{2-}$ anion.[30]

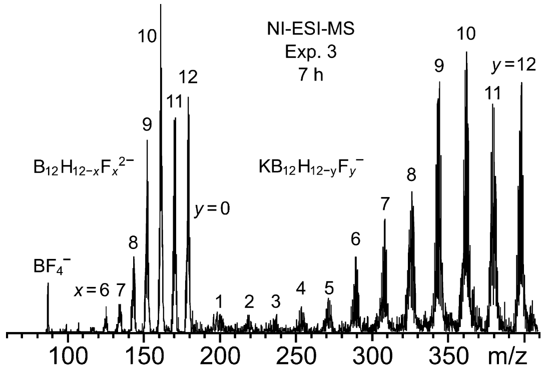


Figure 2. Full-scale negative-ion electrospray-ionization mass spectrum of a sample of the reaction mixture in Expt 3 taken after 7 h of fluorination.

In order to optimize the conditions for F_2 fluorination, we needed a way to reliably measure the mol % of each $B_{12}H_{12-x}F_x^{2-}$ anion in the reaction mixture over time. As in the past,[31−35] we used negative-ion electrospray-ionization mass spectrometry (NI-ESI-MS) for this purpose. [The virtues of NI-ESI-MS for analyzing borane and carborane cluster anions in general have been discussed by Hop et al.[36,37]] A typical intermediate-fluorination-stage NI-ESI mass spectrum is shown in Figure 2. A control experiment using a 50:50 mol % mixture of $K_2B_{12}H_{12}$ and $K_2B_{12}F_{12}$ as the sample revealed that the sensitivity coefficient of $B_{12}F_{12}^{2-}$ is 3.1 times as large as that of $B_{12}H_{12}^{2-}$. Therefore, all mass-spectral intensities were scaled according to their relative sensitivity coefficients, assuming that the relative change in sensitivity coefficient per unit increment in x is constant. For simplicity, we used the sum of the scaled intensities of the most abundant isotopomers for a given $B_{12}H_{12-x}F_x^{2-}/KB_{12}H_{12-x}F_x^-$ pair as an index of the relative amount of $B_{12}H_{12-x}F_x^{2-}$ present for each observed value of x

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(only occasionally were peaks due to $NaB_{12}H_{12-x}F_x^-$ present, usually when the sample inlet system was not rinsed sufficiently before use).

It was not possible to measure the relative concentrations of $B_{12}H_{12-x}F_x^{2-}$ anions in complex mixtures by $^{19}F\{^{11}B\}$ NMR spectroscopy because multiple isomers with overlapping resonances were present for $4 \le x \le 10$ (see, for example, Figure S-1 in Supporting Information). However, only one isomer is possible for $x = 11$ and 12. For a sample containing $B_{12}HF_{11}^{2-}$ and $B_{12}F_{12}^{2-}$, the NI-ESI-MS $B_{12}F_{12}^{2-}/B_{12}HF_{11}^{2-}$ mole ratio was 7.3 and the $^{19}F\{^{11}B\}$ NMR mole ratio was 6.9, a relative error of ca. 6% (see Figure S-2). In another sample containing these two anions, the NI-ESI-MS $B_{12}F_{12}^{2-}/B_{12}HF_{11}^{2-}$ mole ratio was 1.47 and the $^{19}F\{^{11}B\}$ NMR mole ratio was 1.43, a relative error of ca. 3%. Although we cannot rule out larger errors in mole ratios or mol % values determined by the NI-ESI-MS procedure for other mixtures of $B_{12}H_{12-x}F_x^{2-}$ anions, that was not an important issue in this study because, for two reasons, we did not intend to determine rate constants from the changes in mol % values over time (i.e., only qualitative estimations of mol % values were needed). The first reason is that the 20/80 F_2/N_2 flow rate was not kept constant from experiment to experiment or even during a given experiment (see below). The second reason is that no attempt was made to keep the size of the bubbles of F_2/N_2 gas or the size and shape of the reaction vessel constant from experiment to experiment (the scale of the syntheses discussed below varied by a factor of 10; however, the same reaction vessel *was* used for reactions with the same amount of $K_2B_{12}H_{12}$ starting material). The solubility of F_2 in HF and organic solvents is very low,[38,39] and most F_2 fluorinations in organic solvents are believed to occur at the gas bubble–solution interface.[39,40] Therefore, we expected our fluorination reactions to be heterogeneous in nature, and for this reason only qualitative estimations of relative rates of reaction were determined.

The F_2/N_2 flow rate was not kept constant because we were less interested in *minimizing* the reaction time (although *shortening* the reaction time was one of our goals) than in minimizing the $F_2/K_2B_{12}H_{12}$ mole ratio necessary for efficient perfluorination. In general, the flow rate was set at a level that resulted in only a small amount of unreacted F_2 leaving the reaction vessel over time (this was monitored by bubbling the gas leaving the reaction vessel through a solution of KI in H_2O, which was changed periodically). In many experiments it was necessary to decrease the flow rate as the reaction progressed because the uptake of F_2 by the reaction mixture decreased over time. For the most efficient reactions we report below, the flow rates used resulted in negligible amounts of unreacted F_2 leaving the reaction vessel until a short time before the perfluorinations were complete.

Optimization of Fluorination Reaction Conditions. The initial goal of this work was to significantly improve the synthesis of $B_{12}F_{12}^{2-}$ salts relative to our 2003 procedure that is depicted in Scheme 1.[23,24] We wanted to develop an alternative procedure that would allow us to (i) scale-up the reaction so that at least 10 g of $K_2B_{12}H_{12}$ starting material could be used without sacrificing the purity or yield of the final product (the benchmark for the recrystallized yield of 99.5+% pure $K_2B_{12}F_{12}$ was 72%[23]); (ii) shorten the reaction time, including recrystallization of the final product, from ca. 1 week to no more than 2 days; (iii) use as little excess F_2 as possible; and (iv) replace anhydrous HF (a-HF) with a less-reactive and less-volatile solvent so that a fluoropolymer or possibly a Pyrex reaction vessel could be used and so that the F_2/N_2 mixture could be continuously bubbled through the reaction mixture until the reaction was complete.

Acetonitrile has been used for F_2 fluorinations of organic substrates[41−43] because it is fluorinated very slowly at 0 °C.[44,45] It is also a polar solvent in which $K_2B_{12}H_{12}$ is soluble. [We determined the solubility of $K_2B_{12}H_{12}$ to be 0.035 M in "wet" acetonitrile (i.e., ACS-grade acetonitrile as received, containing less than 0.3% water according to the manufacturer's analysis; hereinafter abbreviated as w-CH_3CN); we also determined the solubility to be only 0.008 M in anhydrous acetonitrile (a-CH_3CN).] Therefore, we chose acetonitrile as the most suitable replacement for a-HF in the F_2 fluorination of $K_2B_{12}H_{12}$. The balanced net reaction we were attempting to optimize is given by eq 1:

$$K_2B_{12}H_{12} + 12F_2 \rightarrow K_2B_{12}F_{12} + 12HF \qquad (1)$$

Reaction mixtures consisting of $K_2B_{12}H_{12}$ vigorously stirred in w-CH_3CN at 0 °C were treated with a continuous flow of atmospheric-pressure 20/80 F_2/N_2 that was slowly bubbled through the stirred mixtures (note: atmospheric pressure in Fort Collins is ca. 0.8 atm). The nominal initial concentrations of $K_2B_{12}H_{12}$ anions that were used for the reactions varied from 0.05 to 0.5 M (these are "nominal" concentrations because all of the starting material did not dissolve until several boron vertexes had been fluorinated). The results for two typical reactions under these conditions are listed in Table 1 as Expts 1 and 2. The mol % values listed were determined by NI-ESI-MS. It can be seen that these reaction conditions are not suitable for an efficient large-scale synthesis. For example, consider Expt 2. A significant excess of F_2 was required, and even then the fluoroborane product contained 6% $B_{12}HF_{11}^{2-}$. In addition, the reaction took 52 h to reach only 94% perfluorination, far longer than our goal of less than 24 h for the fluorination phase of the targeted 2-day synthesis. Furthermore, the limited solubility of $K_2B_{12}H_{12}$ and $K_2B_{12}H_{12-x}F_x$ with $x \le 3$ in w-CH_3CN resulted in significant amounts of undissolved solid remaining in the reaction mixture for the first 7 h of F_2 bubbling, and this is certainly one of the causes of the long reaction time.

Nevertheless, the results of Expts 1 and 2 were encouraging: $B_{12}H_{12}^{2-}$ *can* be perfluorinated with F_2 in acetonitrile *without* the formation of byproducts that are difficult to remove from $K_2B_{12}F_{12}$. For example, the potential byproducts KF, KHF_2, and KBF_4 have extremely low solubilities in CH_3CN and therefore are easy to remove from $K_2B_{12}F_{12}$. Furthermore, although it has proven difficult to separate the byproduct $K_2B_{12}HF_{11}$ from $K_2B_{12}F_{12}$ by fractional recrystallization, the presence of 6% $B_{12}HF_{11}^{2-}$ was not considered a problem in the long run because a more efficient set of reaction conditions would transform it

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Table 1. Fluorination of $K_2B_{12}H_{12}$ by 20/80 F_2/N_2 in Acetonitrile and Formic Acid[a]

Expt	scale, mmol $K_2B_{12}H_{12}$	concn, M[b]	solvent	additive (v/v)	F_2/B_{12} mol ratio	time, h	mol % major anionic product(s) [isolated yield of all B_{12} products][c]
1	5.0[d]	0.10	w-CH_3CN	H_2O (<0.3%)	>12	12.0	80% $B_{12}F_{12}^{2-}$, 20% $B_{12}HF_{11}^{2-}$ [54%]
2	23[e]	0.50	w-CH_3CN	H_2O (<0.3%)	27	52.0	94% $B_{12}F_{12}^{2-}$, 6% $B_{12}HF_{11}^{2-}$
3	23	0.046	w-CH_3CN	H_2O (1.0%)	22	12.0	72% $Cs_2B_{12}F_{12}$, 18% $Cs_2B_{12}HF_{11}$, 7% $Cs_2B_{12}H_2F_{10}$ 3% $Cs_2B_{12}H_3F_9$ [39%]
4	5.2	0.052	w-CH_3CN	H_2O (2.0%), a-HF (2.0%)	29	9.5	25% $Cs_2B_{12}F_{12}$, 31% $Cs_2B_{12}HF_{11}$, 23% $Cs_2B_{12}H_2F_{10}$ 12% $Cs_2B_{12}H_3F_9$ 5% $Cs_2B_{12}H_4F_8$ [43%]
5	23	0.046	w-CH_3CN	H_2O (1.0%), KF (400 mmol)	17	11.8	$Cs_2B_{12}F_{12}$ [68%]
6	18	0.038	(1) w-CH_3CN (2) a-CH_3CN	(1) H_2O (1.7%), KF (180 mmol) (2) KF (74 mmol)	(1) 8.9 (2) 5.2	(1) 6.5 (2) 4.5	(1) 12% $B_{12}F_{12}^{2-}$ (2) $K_2B_{12}F_{12}$ [68%]
7	18	0.030	(1) w-CH_3CN (2) a-CH_3CN	(1) H_2O (1.3%), KF (130 mmol) (2) KF (93 mmol)	(1) 8.7 (2) 4.4	(1) 8.3 (2) 3.5	(1) 14% $B_{12}F_{12}^{2-}$ (2) $K_2B_{12}F_{12}$ [71%]
8	23	0.046	(1) w-CH_3CN (2) a-CH_3CN	(1) H_2O (2.4%), KF (220 mmol) (2) KF (100 mmol)	(1) 6.4 (2) 6.4	(1) 6.0 (2) 6.0	(1) 10% $B_{12}F_{12}^{2-}$ (2) $K_2B_{12}F_{12}$ [70%]
9	47	0.094	(1) w-CH_3CN (2) a-CH_3CN	(1) H_2O (2.5%), KF (450 mmol) (2) KF (240 mmol)	(1) 11 (2) 4.2	(1) 22 (2) 8.0	(1) 26% $B_{12}F_{12}^{2-}$ (2) $K_2B_{12}F_{12}$ [72%]
10	46	0.092	(1) w-CH_3CN (2) a-CH_3CN	(1) H_2O (2.4%), KF (390 mmol) (2) KF (470 mmol)	(1) 6.8 (2) 7.2	(1) 6.0 (2) 7.5	(1) 7% $B_{12}F_{12}^{2-}$ (2) $K_2B_{12}F_{12}$ [74%]
11	46	0.092	(1) w-CH_3CN (2) a-CH_3CN	(1) H_2O (2.4%), KF (390 mmol) (2) KF (470 mmol)	(1) 6.8 (2) 7.2	(1) 6.0 (2) 7.5	(1) 6% $B_{12}F_{12}^{2-}$ (2) $Cs_2B_{12}F_{12}$ [76%]
12	4.5[f]	0.25	w-CH_3CN	HCO_2H (50%)	—	12.0	29% $B_{12}F_{12}^{2-}$, 41% $B_{12}HF_{11}^{2-}$, 30% $B_{12}H_2F_{10}^{2-}$
13	5.5	0.55	HCO_2H	H_2O (12%)	28	14.0	39% $B_{12}F_{12}^{2-}$, 44% $B_{12}HF_{11}^{2-}$, 17% $B_{12}H_2F_{10}^{2-}$

[a] All results from this work. [b] The nominal initial concentration of $K_2B_{12}H_{12}$. [c] Isolated recrystallized yield. [d] The amount of time necessary for all solids to dissolve in the reaction mixture was not recorded for this experiment. [e] All solids dissolved in the reaction mixture only after 7 h. [f] All solids dissolved in the reaction mixture after 20 min.

Scheme 2

$$\text{Exp. 3:}\quad K_2B_{12}H_{12} + 22\,F_2 \xrightarrow[0\,^{\circ}\mathrm{C},\ 12\ \mathrm{h}]{\substack{CH_3CN\\ 1\%H_2O}} 72\%\ K_2B_{12}F_{12} + 28\%\ K_2B_{12}H_{12\text{-}x}F_x$$

39% combined isolated yield

$$\text{Exp. 4:}\quad K_2B_{12}H_{12} + 29\,F_2 \xrightarrow[0\,^{\circ}\mathrm{C},\ 9.5\ \mathrm{h}]{\substack{CH_3CN\\ 2\%H_2O\\ 2\%HF}} 25\%\ K_2B_{12}F_{12} + 75\%\ K_2B_{12}H_{12\text{-}x}F_x$$

43% combined isolated yield

$$\text{Exp. 10:}\quad K_2B_{12}H_{12} + 14.0\,F_2 \xrightarrow[0\,^{\circ}\mathrm{C},\ 6\ \mathrm{h}]{\substack{CH_3CN\\ 2.4\%H_2O\\ \text{xs KF}}} \xrightarrow[0\,^{\circ}\mathrm{C},\ 7.5\ \mathrm{h}]{\substack{\text{a-}CH_3CN\\ \text{xs KF}}} 99.5{+}\%\ K_2B_{12}F_{12}$$

74% isolated yield

into $B_{12}F_{12}^{2-}$ (just like the other 94% of $B_{12}HF_{11}^{2-}$ had been transformed into $B_{12}F_{12}^{2-}$). The problem was that, under these conditions, the final fluorination of $B_{12}HF_{11}^{2-}$ was apparently very slow.

To mitigate the problem of undissolved solids at early stages of fluorination, a series of experiments exemplified by Expt 3 in Table 1 were performed (see Scheme 2). The same amount of $K_2B_{12}H_{12}$ was used for Expts 2 and 3, but the solvent for Expt 3 was w-CH_3CN to which 1% H_2O had been added and the concentration of $K_2B_{12}H_{12}$ was reduced by a factor of 10. These changes resulted in a homogeneous solution of $K_2B_{12}H_{12}$ at the start of fluorination. At various intervals, the reaction solution was purged with N_2, and small samples were withdrawn, worked up, and analyzed by NI-ESI-MS. The results are displayed as the blue curves in the panels shown in Figure 3. The x axis in each plot is the $n(F_2)/n(K_2B_{12}H_{12})$ mole ratio (i.e., the ratio of the molar amount of F_2 added at that point in time to the molar amount of $K_2B_{12}H_{12}$ *starting material* (i.e., $n(K_2B_{12}H_{12})$ is *not* the number of moles of $B_{12}H_{12}^{2-}$ remaining at that time; it is constant for a given synthesis)). The y axes are, from top to bottom, the average x value ($\bar{x}$) for all $B_{12}H_{12-x}F_x^{2-}$ anions in the reaction mixture, the mol % $B_{12}H_{12}^{2-}$ remaining in the reaction mixture, and the mol % $B_{12}F_{12}^{2-}$ in the reaction mixture at that point in time.

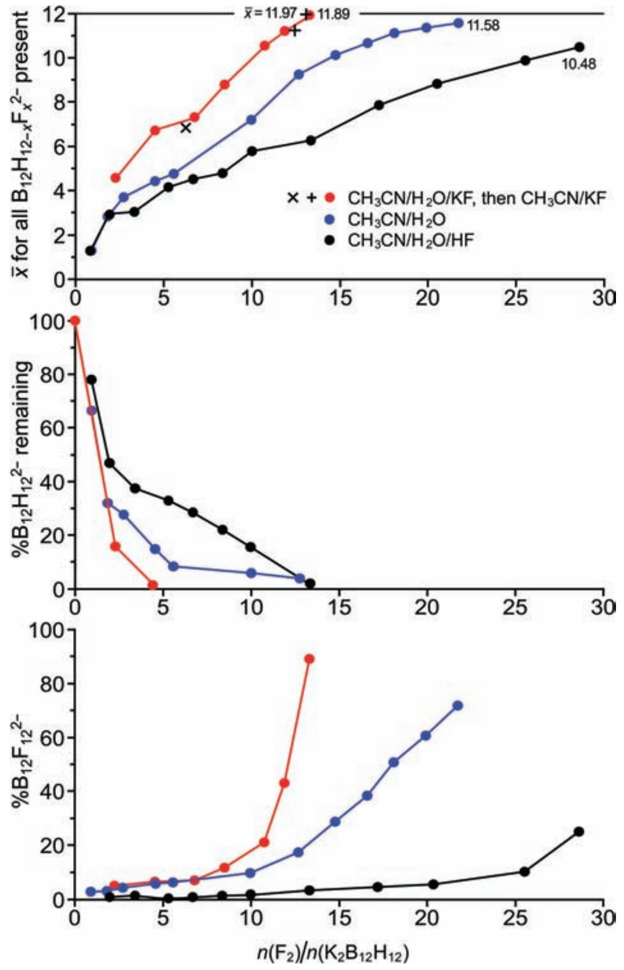

Figure 3. Plots of average *x* values for all $B_{12}H_{12-x}F_x^{2-}$ anions present, % $B_{12}H_{12}^{2-}$ remaining, and $B_{12}F_{12}^{2-}$ formed during fluorination Expts 3, 4, and 11 vs the number of equivalents of F_2 bubbled through the solution per mole of $K_2B_{12}F_{12}$.

At first glance, the blue curves for Expt 3 appear unremarkable: they show an increase in $\bar{x}$, an increase in the mol % $B_{12}F_{12}^{2-}$, and a decrease in the mol % $B_{12}H_{12}^{2-}$ over time. However, mass spectra of samples withdrawn after 30 min and after 7 h, which are shown in Figure 4, revealed a critical detail that cannot be discerned from the plots in Figure 3. [The peaks due to $KB_{12}H_{12-x}F_x^{-}$ monoanions other than $KB_{12}H_{12}^{-}$ are not shown in the spectra in Figure 4, but that does not affect the conclusions that follow because their intensities are roughly proportional to the intensities of the peaks of the corresponding $B_{12}H_{12-x}F_x^{2-}$ anions; the full spectra are shown in Figures 2 and S-3.] Consider the 30 min spectrum in Figure 4. The most abundant $B_{12}H_{12-x}F_x^{2-}$ anion is the starting material, $B_{12}H_{12}^{2-}$. Also present are small amounts of anions with $x = 1-7$ and a significantly larger amount of the final product, $B_{12}F_{12}^{2-}$ (the amount of $B_{12}F_{12}^{2-}$ present is ca. 4% of the amount of $B_{12}H_{12}^{2-}$ present; for comparison, the amount of $B_{12}H_5F_7^{2-}$ present is ca. 2% of the amount of $B_{12}H_{12}^{2-}$). Conspicuously absent ($\ll 1\%$) are anions with $x = 8-11$, which means that *they were converted to $B_{12}F_{12}^{2-}$ faster than they were formed*. Now consider the 7 h spectrum in Figure 4. Along with $B_{12}F_{12}^{2-}$, anions with $x = 9-11$ are the dominant species. In fact, the anions with $x = 9-11$ are collectively ca. 3 times as abundant as $B_{12}F_{12}^{2-}$. The value for Expt 3 was 9.3 after 12.7 equiv of F_2 had been passed through the solution, but only increased to 11.6 after another 9.1 equiv of F_2 had been added (see Figure 3). Thirty minutes into the F_2 fluorination, a significant amount of $B_{12}F_{12}^{2-}$ had been formed, and the concentration of $B_{12}HF_{11}^{2-}$ was so low it could not be detected by NI-ESI-MS. However, after 21.8 equiv of F_2 had been added, the ratio mol($B_{12}F_{12}^{2-}$)/mol($B_{12}HF_{11}^{2-}$) was only 4 (see Table 1). How could this be possible? How could $B_{12}F_{12}^{2-}$ be formed rapidly from $B_{12}HF_{11}^{2-}$ at the beginning of the reaction but formed only slowly in the middle of the reaction and even more slowly at the time that the reaction was stopped?

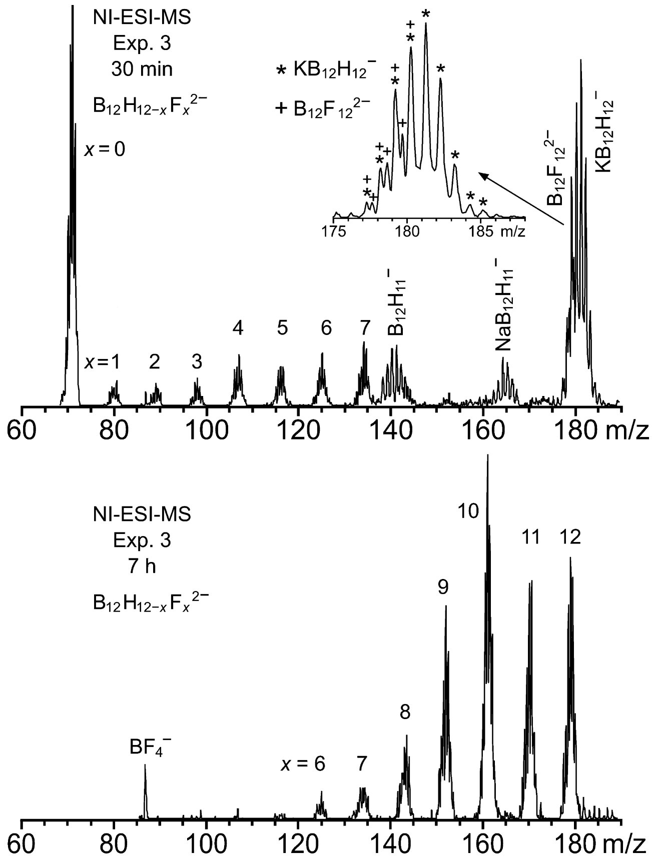

Figure 4. Abbreviated-scale negative-ion electrospray-ionization mass spectrum of samples of the reaction mixture in Expt 3 taken after 30 min (top) and 7 h (bottom) of fluorination.

Several factors were considered. To a first approximation, the total concentration of all B_{12} species, and hence the ionic strength, remained constant throughout the reaction, so that was probably not an issue (control experiments showed that only a few percent of the solvent CH_3CN evaporated during 18 h of F_2/N_2 bubbling at 0 °C). Later experiments (e.g., Expts 7−11) proved that CH_3CN is not fluorinated fast enough under the conditions of our reactions to account for final $n(F_2)/n(K_2B_{12}H_{12})$ ratios much greater than 12. Some B_{12} clusters were destroyed during the fluorinations, producing KBF_4, which is only sparingly soluble in acetonitrile, but the formation of a modest amount of fine precipitate during the reaction did not seem like a plausible explanation for the increasing inhibition of the F_2 fluorination of $B_{12}HF_{11}^{2-}$ over time.

The only possible explanation that remained was that the buildup of HF in the reaction mixture was slowing down the F_2 fluorination, especially for the $x = 9-11$ anions. At first we doubted this possibility, because the Casteel and Ivanov patent contains the statement, "The improvement in the liquid phases process resides in effecting the [F_2] fluorination of said borohydride salts [including $K_2B_{12}H_{12}$] in the presence of a reaction medium having an acidity between that of water and anhydrous HF. More specifically, the reaction medium should have a Hammett acidity, H_0, between $0 > H_0 > -11$." [25] In Example 20 of the patent, the solvent was aqueous $NaHCO_3$. This is the only example with a reaction medium that was not acidic, and the poor results caused the inventors to include the statement "The results show that reaction media which remain below the desired level [of acidity] throughout the reaction give very inefficient fluorination." [25]

Using the final mol % values for the $x = 9-12$ anions in Expt 3 and assuming that no HF was swept out of the reaction vessel by the F_2/N_2 gas, the final concentration of HF would be 0.53 M. After the Expt 3 reaction mixture was filtered, it was neutralized with aqueous KOH. From the amount of KOH used, the concentration of HF (i.e., active H^+) in the final reaction mixture was determined to be 0.49 M, more than 90% of the theoretical amount. To demonstrate more conclusively that the presence of HF inhibited the F_2 fluorination of $B_{12}H_{12}^{2-}$ in w-CH_3CN, we performed several syntheses such as Expt 4, which was similar to Expt 3 except that the solvent consisted of w-CH_3CN to which 2% H_2O *and* 2% anhydrous HF had been added, as shown in Scheme 2. This reaction was also monitored by NI-ESI-MS over time (see the black curves in Figure 3) but was stopped after only 9.5 h because the $n(F_2)/n(K_2B_{12}H_{12})$ ratio had already reached 29 (see Table 1). At that point, $\bar{x}$ was only 10.5. In addition, very little $B_{12}F_{12}^{2-}$ was formed during the first 30 min. The Air Products patent[25] notwithstanding, it was now clear to us that HF *inhibits* the F_2 perfluorination of $K_2B_{12}H_{12}$, and the buildup of HF in the reaction mixture over time had to be avoided to achieve our goal of a rapid and efficient large-scale synthesis of $K_2B_{12}F_{12}$. It is ironic that HF inhibits F_2 fluorination in our reactions because it can slowly fluorinate $B_{12}H_{12}^{2-}$ by itself in w-CH_3CN at 0 °C (as well as in a-HF at higher temperatures[21,23]). We prepared a solution identical to the one used for Expt 4 but did not treat it with F_2/N_2 gas. Within 35 min, 6% of the first fluorination intermediate, $B_{12}H_{11}F^{2-}$, was detected by NI-ESI-MS.

The discovery that HF inhibits the F_2 fluorination of $B_{12}H_{12}^{2-}$ in acetonitrile led to Expts 5−11 in Table 1. The addition of insoluble KF to sequester HF in the form of insoluble KHF_2 proved to be the key to the development of a rapid and efficient F_2 fluorination of $K_2B_{12}H_{12}$. The red curves in Figure 3 correspond to Expt 11. To demonstrate reproducibility, two data points from Expt 9 ("+") and one data point from Expt 8 ("×") are superimposed on the red curve in the top panel of the figure. The curves in the top panel, which are graphs of $\bar{x}$ as a function of the $n(F_2)/n(K_2B_{12}H_{12})$ mole ratio, clearly show that F_2 fluorination is faster as well as more efficient in the absence of the protic acid HF, especially in the later stages of the reaction. For example, for $\bar{x} \approx 7.3$, the $n(F_2)/n(K_2B_{12}H_{12})$ values for the red (KF added), blue (neither KF nor HF added), and black (HF added) curves are ca. 7, 10, and 16, respectively; for $\bar{x} \approx 11.5$, the $n(F_2)/n(K_2B_{12}H_{12})$ values are 12, 20, and >30, respectively. The difference between the red and blue curves for $\bar{x} \approx 7.3$ is only 3 equiv of F_2, but adding the next four F atoms to the B_{12} cages required only an additional 5 equiv of F_2 when KF was present in the reaction mixture but an additional 10 equiv of F_2 when neither KF nor HF was present at the start of F_2 fluorination. The differences between the red and black curves are even larger.

The middle and bottom panels of Figure 3 show that both the disappearance of $B_{12}H_{12}^{2-}$ at the beginning of the reaction and the appearance of $B_{12}F_{12}^{2-}$ toward the end of the reaction are faster in the absence of acid than in the presence of acid. For example, at $n(F_2)/n(K_2B_{12}H_{12}) \approx 5$, $B_{12}H_{12}^{2-}$ had virtually disappeared when KF was present in the reaction mixture (red curve) but was still at one-third of its original concentration when HF had been added to the reaction mixture at the start of F_2 fluorination (black curve). Furthermore, when neither KF or HF had been added (blue curve), the disappearance of $B_{12}H_{12}^{2-}$ became slower and slower as the reaction progressed.

The experiments described above eventually led to a set of conditions that, in our hands, produced either 15 g of 99.5+% pure $K_2B_{12}F_{12}$ (74% yield based on $K_2B_{12}H_{12}$) or 22 g of 99.5% pure $Cs_2B_{12}F_{12}$ (76% yield) in less than 2 days using ordinary Pyrex reaction vessels and acetonitrile containing an excess of KF, as shown in Scheme 2. These optimized syntheses correspond to Expts 10 and 11 in Table 1, respectively. We found that, in order to use as little F_2 as possible, it was necessary to add ca. half the F atoms using w-CH_3CN to which 2.4% H_2O had been added as the solvent, after which the reaction mixture was filtered (to remove KF, KHF_2, and KBF_4) and the solvent was stripped by rotary evaporation. The residue was redissolved in a-CH_3CN containing an excess of KF, and the remaining F atoms were added. This two-step procedure used 14.0 equiv of F_2, which is only a 16.7% excess based on the amount of $K_2B_{12}H_{12}$ starting material. The new procedure is compared with other literature $B_{12}H_{12}^{2-}$ fluorination procedures in Table S-1. It represents a 10-fold increase in the scale of the reaction over our previous procedure without sacrificing yield or purity. In addition, it can be performed in an ordinary Pyrex reaction vessel, and it is very efficient in terms of the amount of excess F_2 that is required. Finally, the 10-fold increase in scale was achieved in one-third of the time necessary for our previous procedure.

It is not absolutely necessary to use the two-step procedure for the perfluorination of $K_2B_{12}H_{12}$. However, when a one-step procedure was used (Expt 5), water was presumably present throughout the reaction, and this both increased the amount of F_2 required from 14 equiv to 17 equiv and lowered the yield of $Cs_2B_{12}F_{12}$ from 76% to 68%. Since the time required to filter the reaction mixture after Step 1 in Expts 6−11, remove the water/acetonitrile solvent by rotary evaporation, and begin the Step 2 fluorination was only ca. 60 min, we believe that the modest amount of extra time and effort is worth the more efficient use of F_2 and the higher yield of the final product.

Does F_2 Fluorination of $B_{12}H_{12-x}F_x^{2-}$ Ions in Acetonitrile Occur at the Gas Bubble−Solution Interface? As stated earlier, it is generally assumed that F_2 fluorinations in organic solvents occur at the interface of bubbles of F_2/N_2 gas and the solution.[39,40] Figure 5 shows a reaction scheme consistent with this hypothesis. It also shows F_2 acting as an electrophile and forming a Lewis acid−base complex with one of the 20 triangular faces of the $B_{12}H_{12}^{2-}$ anion prior to the B−H → B−F transformation, which occurs with the concomitant formation of a molecule of HF. Note that the $B_{12}H_{12}^{2-}$ and $B_{12}H_{11}F^{2-}$ anions depicted at the gas bubble−solution interface are shown, *for simplicity*, half in solution and half in the gas phase (it is *not* known if this is a valid depiction). Although we did not intend to investigate the interfacial nature of this reaction at the beginning of our study, we made several observations that strongly suggest that the F_2 fluorination of $B_{12}H_{12}^{2-}$ did not occur in a homogeneous phase, and we then carried out experiments designed to verify this hypothesis.

If the fluorination of $B_{12}H_{12-x}F_x^{2-}$ anions occurred in homogeneous solution, where all 20 triangular faces were simulta-

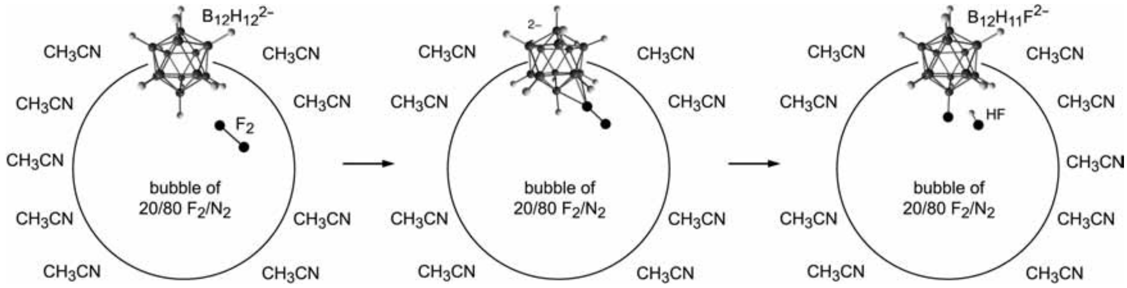

Figure 5. Proposed reaction scheme for the fluorination of $B_{12}H_{12}^{2-}$ on the surface of a bubble of F_2/N_2 gas in acetonitrile. The size of the bubble is not to scale. The fraction of the anion that extends into the bubble is arbitrary.

neously exposed to dissolved F_2 with equal probability, and if the equilibrium binding of F_2 to an anion and the rate of fluorination of an individual B−H vertex were both independent of the value of x, then a statistical factor would cause the first fluorination step, $B_{12}H_{12}^{2-} \rightarrow B_{12}H_{11}F^{2-}$, to be 12 times faster than the last fluorination step, $B_{12}HF_{11}^{2-} \rightarrow B_{12}F_{12}^{2-}$. Given that $B_{12}H_{12-x}F_x^{2-}$ anions become weaker Lewis bases as x increases, and given that the remaining B−H bonds in a $B_{12}H_{12-x}F_x^{2-}$ anion become shorter, and presumably stronger, as x increases (see the DFT-predicted B−H distances in Table S-2 and the FTIR spectra of $K_2B_{12}H_{12}$ and a mixture of $K_2B_{12}HF_{11}$ and $K_2B_{12}F_{12}$ in Figure S-4), one might expect the difference in rates for the first and last steps to be greater than a factor of 12. However, the red curve in the top panel in Figure 3 shows that this is definitely not the case: the slopes of all of the lines connecting two consecutive data points do not differ by more than a factor of 2. This means that *the substitution of H atoms by F atoms occurs at approximately the same rate for all values of x*. [See Supporting Information for possible reasons why the first two red points on this curve have $n(F_2)/n(K_2B_{12}H_{12})$ values $< \bar{x}$.] This is further demonstrated by comparing the average rate of disappearance of $B_{12}H_{12}^{2-}$ at the beginning of the reaction (see the red curve in the middle panel of Figure 3) with the average rate of disappearance of $B_{12}HF_{11}^{2-}$ at the end of the reaction, which is equal in magnitude and opposite in sign to the rate of appearance of $B_{12}F_{12}^{2-}$ at the end of the reaction (see the red curve in the bottom panel of Figure 3). The absolute value of the slope of the first red line in the middle panel is 38% per equiv F_2; the slope of the last red line in the bottom panel is 30% per equiv F_2, only one-fifth smaller.

Roughly equal rates of fluorination for all values of x strongly suggest a heterogeneous reaction involving the gas bubble−solution interface. Let us refine the model shown in Figure 5 in the following ways. We will assume that only *one* triangular face of the anion (i.e., three B-X vertexes) penetrates the gas bubble *and* that the anions are preferentially oriented so that the triangular face that penetrates has the maximum number of B−H vertexes that remain on the anion. In that case, at least one B−H bond would penetrate into the F_2/N_2 bubble for $x < 12$, and an F_2 molecule would bind to and react with the triangular face in the bubble, regardless of how many other faces have B−H vertexes (i.e., in this model, every anion that penetrated the bubble with $x < 12$ would have at least one B−H vertex that can react with F_2).

If these assumptions are valid, there would be essentially no statistical factor that favors the fluorination of anions with low values of x. On the basis of the extensive literature on the partitioning of inorganic anions at the air−water interface[46−50] (and a less extensive but still significant literature on anion partitioning at gas−nonaqueous solution interfaces[51,52]), we propose that the aforementioned assumptions are reasonable and therefore provide an explanation for the qualitatively similar relative rates of F_2 fluorination of $B_{12}H_{12}^{2-}$ and $B_{12}HF_{11}^{2-}$. For example, it is well known that soft, polarizable anions, which generally have large ionic radii, are present, and their concentrations are even enhanced, at the surface of polar liquids, including air bubbles in polar liquids.[46–53] It has been shown that BH_4^- is a softer Lewis base than BF_4^-.[54] Is it possible that $B_{12}H_{12}^{2-}$ is also softer (i.e., more polarizable) than $B_{12}F_{12}^{2-}$? To determine the relative polarizabilities, α, of $B_{12}H_{12}^{2-}$ and $B_{12}F_{12}^{2-}$, we calculated them using DFT methods in a dielectric-continuum model for acetonitrile. For comparison, we also calculated the polarizabilities of Br^-, BH_4^-, and BF_4^- under the same conditions. [The literature values for Br^- (computational)[55] and BH_4^- (experimental, in KBH_4)[56] are 4.5 and 4.0 Å^3, respectively.] Our results are $\alpha(B_{12}H_{12}^{2-}) = 36.5$ Å^3; $\alpha(B_{12}F_{12}^{2-}) = 26.4$ Å^3; $\alpha(Br^-) = 3.6$ Å^3; $\alpha(BH_4^-) = 5.9$ Å^3; $\alpha(BF_4^-) = 3.4$ Å^3. Thus, $B_{12}H_{12}^{2-}$ is significantly more polarizable, and therefore softer, than $B_{12}F_{12}^{2-}$. According to reported second-harmonic-generation and sum-frequency-generation experiments and molecular dynamics calculations on other inorganic anions at the surface of polar liquids,[46–53] the softer $B_{12}H_{12}^{2-}$ anion should have a greater propensity than $B_{12}F_{12}^{2-}$ or $B_{12}HF_{11}^{2-}$ to partition to the gas bubble−solution interface. It is even possible that $B_{12}H_{12}^{2-}$ and $B_{12}H_{12-x}F_x^{2-}$ anions with low values of x could exclude $B_{12}HF_{11}^{2-}$ from the gas bubble/solution interface and, therefore, exclude it from access to F_2.

To test this possibility, we performed the following experiments. A solution of $B_{12}HF_{11}^{2-}$ and $B_{12}F_{12}^{2-}$ was prepared in w-CH_3CN containing 2.4% added H_2O. The mole ratio $[B_{12}HF_{11}^{2-}]/[B_{12}F_{12}^{2-}]$ was determined by ^{19}F NMR integration to be 1.43. The solution was divided into two equal parts, to which either $K_2B_{12}H_{12}$ or $K_{12}B_{12}F_{12}$ was added. The ratios $[B_{12}HF_{11}^{2-}]/[B_{12}H_{12}^{2-}]$ and $[B_{12}HF_{11}^{2-}]$/(added $[B_{12}F_{12}^{2-}]$) were both 1.53.

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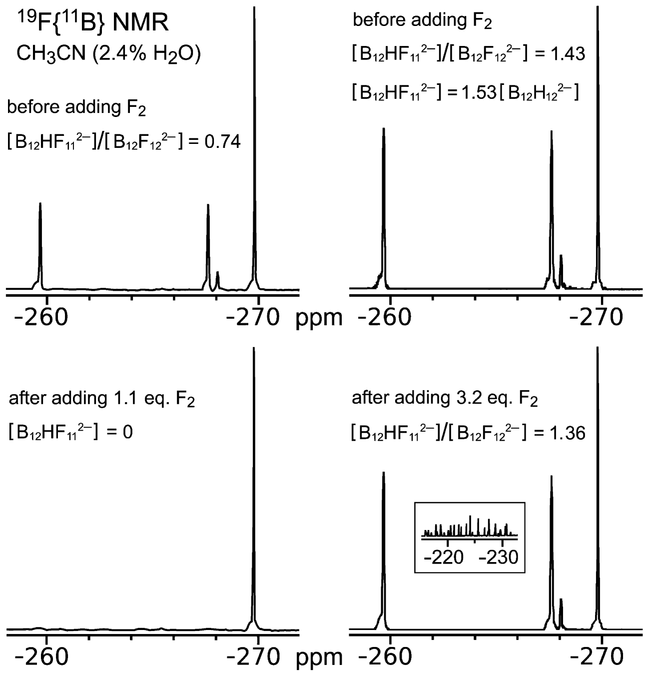

Figure 6. Boron-11 decoupled ^{19}F NMR spectra of mixtures of $K_2B_{12}H_{12}$, $K_2B_{12}HF_{11}$, and $K_2B_{12}F_{12}$ in CD_3CN containing 2.4% H_2O before and after fluorination with 20/80 F_2/N_2 gas.

The total concentration of B_{12} clusters and the concentration of K^+ was therefore the same in the two solutions. Each solution was bubbled with 20/80 F_2/N_2 at the same rate used for Expts 10 and 11 for a given period of time. The results are shown in Figure 6. In the absence of $B_{12}H_{12}^{2-}$, $B_{12}HF_{11}^{2-}$ was converted to $B_{12}F_{12}^{2-}$ with only 1.1 equiv of F_2 (based on $B_{12}HF_{11}^{2-}$), similar to the final red-curve line segment in Figure 3. However, in the presence of $B_{12}H_{12}^{2-}$, only 2% of the $B_{12}HF_{11}^{2-}$ present was converted to $B_{12}F_{12}^{2-}$, even after 3.2 equiv of F_2 had been bubbled through the solution (again based on $B_{12}HF_{11}^{2-}$; this amount of F_2 is 4.0 equiv based on added $B_{12}H_{12}^{2-}$). During the addition of F_2/N_2 to the sample containing $B_{12}H_{12}^{2-}$, that anion was converted to a mixture of $B_{12}H_{12-x}F_x^{2-}$ anions with $x = 0$ (0.24%), 1 (2.08%), 2 (3.61%), 3 (5.58%), 4 (15.01%), 5 (3.24%), and 6 (1.18)%; no $B_{12}HF_{11}^{2-}$ was produced from the added $B_{12}H_{12}^{2-}$. Therefore, $B_{12}H_{12}^{2-}$ and $B_{12}H_{12-x}F_x^{2-}$ anions with low values of x significantly inhibited the fluorination of $B_{12}HF_{11}^{2-}$, which is consistent with the hypothesis that the harder anion $B_{12}HF_{11}^{2-}$ is excluded from the gas bubble−solution interface when the softer anions $B_{12}H_{12}^{2-}$, $B_{12}H_{11}F^{2-}$, $B_{12}H_{10}F_2^{2-}$, etc. are present. When only $B_{12}HF_{11}^{2-}$ and $B_{12}F_{12}^{2-}$ are present, such as during the final stage of Expts 10 and 11, $B_{12}HF_{11}^{2-}$ is *not* excluded from the bubble surface and therefore *is* fluorinated quickly.

The $B_{12}H_{12-x}F_x^{2-}$ series may be an ideal set of anions for air−water interface experimental studies, because the anions have very different polarizabilities but very similar ionic radii (unlike the ionic radii of F^- vs I^-, for example). Furthermore, $B_{12}H_{12-x}F_x^{2-}$ anions with $x < 12$ exhibit ν(BH) infrared/Raman bands in a conveniently transparent spectral region (2400−2600 cm^{-1}). Experiments are in progress to examine this possible use of $B_{12}H_{12-x}F_x^{2-}$ anions.

Why Do Protic Acids Inhibit the F_2 Fluorination of $B_{12}H_{12-x}F_x^{2-}$ Anions? In order to investigate whether the inhibition of F_2 fluorination of $B_{12}H_{12-x}F_x^{2-}$ anions by HF is due to the unique properties of HF dissolved in acetonitrile or to general-acid inhibition, Expts 12 and 13 listed in Table 1 were performed. The solvents were 50/50 (v/v) w-CH_3CN/HCO_2H and 88/12 (v/v) HCO_2H/H_2O, respectively. No KF was added, so HF accumulated in the reaction mixtures over time. In both cases, the presence of a significant amount of formic acid inhibited F_2 fluorination even more than in Expt 1, in which the only acid present was the ever-increasing amount of HF. These results imply that there is general-acid inhibition of F_2 fluorination.

The experiments discussed in the previous section not only support the hypotheses that $B_{12}H_{12-x}F_x^{2-}$ anions with low values of x are more likely to be present at the gas bubble−solution interface than anions with high values of x, but they also suggest that the B−H vertexes of $B_{12}H_{12-x}F_x^{2-}$ anions at the interface are more likely to extend into the bubble of F_2/N_2 than the B−F vertexes of these anions (this is because excess $B_{12}F_{12}^{2-}$ did not prevent the rapid fluorination of $B_{12}HF_{11}^{2-}$ even as the concentration of the latter anion approached zero). When HF is present during the fluorination, it almost certainly solvates $B_{12}H_{12-x}F_x^{2-}$ anions more strongly than does CH_3CN. Even though the dipole moments of gas-phase HF and CH_3CN are 1.80 and 3.92 D, respectively, the H−F bond is considerably more polar than the C−H bonds of CH_3CN. Furthermore, the dielectric constants of neat HF and CH_3CN are 83.6 (0 °C) and 37.6 (15 °C), respectively. We propose that HF preferentially solvates $B_{12}H_{12-x}F_x^{2-}$ anions at triangular B_3 faces with B−H vertexes. If this is true, it would explain the inhibition of F_2 fluorination by the steadily increasing amount of HF byproduct as $B_{12}H_{12}^{2-}$ is converted to $B_{12}F_{12}^{2-}$. For one thing, HF solvation (i.e., formation of an acid−base complex between the anion and HF) would affect the equilibrium binding of F_2 to the anion. For another thing, it would make the portions of the $B_{12}H_{12-x}F_x^{2-}$ anions with soft B−H vertexes less soft, which would affect the extent to which the B−H vertexes extend into the F_2/N_2 bubble (note that the polarizability of HF, 0.83 Å^3,[57] is exceptionally low).

We decided to use DFT calculations to test this proposal. Because DFT is not very reliable for describing weak intermolecular interactions, we calculated the relative energies of monoprotonated adducts of the hypothetical intermediate anion 1,2,3,4,5,6-$B_{12}H_6F_6^{2-}$ and the known intermediate $B_{12}HF_{11}^{2-}$. For each anion, a single H^+ ion was added to different triangular faces, and the resulting monoanions were optimized in a dielectric continuum that is a model for an acetonitrile solution. The DFT-predicted relative energies, which are shown next to each DFT-optimized structure in Figure 7, demonstrate that protonation of 1,2,3,4,5,6-$B_{12}H_6F_6^{2-}$ *on a triangular face that includes B12* is favored relative to that a triangular face that includes B1 by 47.0 kJ mol^{-1}. This is in spite of the dipolar charge distribution that results in negative charge density accumulating at the "F_6" end of the 1,2,3,4,5,6-$B_{12}H_6F_6^{2-}$ anion (see below). The differences for the four types of triangular faces of the last fluorination intermediate, $B_{12}HF_{11}^{2-}$, are smaller but still favor a triangular face that includes the last remaining B−H vertex (i.e., the B12−H12 vertex). On the basis of these results, we conclude that HF and other protic acids inhibit the F_2 fluorination of $B_{12}H_{12-x}F_x^{2-}$ anions by competing with the Lewis acid F_2 for the most basic triangular faces, namely those with the remaining B−H vertexes. The rate of F_2 fluorination becomes slower as HF is formed in the reaction because the concentration of vacant triangular faces with B−H vertexes

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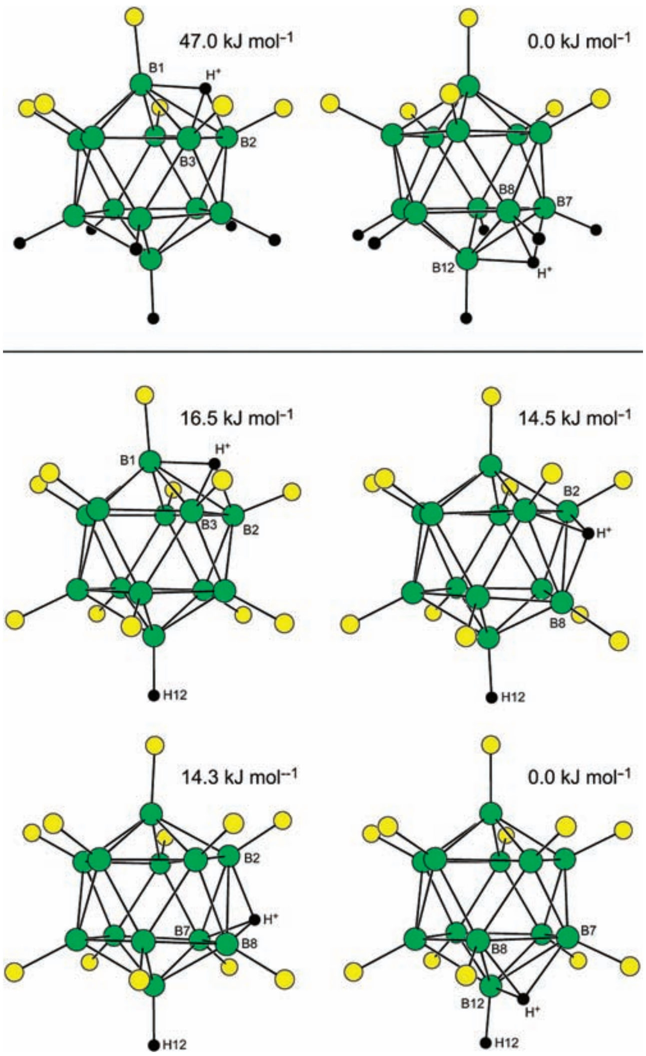

Figure 7. DFT-optimized structures and relative energies for isomers of $HB_{12}H_6F_6^-$ (above the line) and $HB_{12}HF_{11}^-$ (below the line).

becomes lower. As more HF accumulates in solution, the five triangular faces of $B_{12}HF_{11}^{2-}$ that include B12−H12 are, at least in principle, all solvated by HF molecules, significantly decreasing the rate of the final fluorination step: $B_{12}HF_{11}^{2-} + F_2 \rightarrow B_{12}F_{12}^{2-} + HF$.

The isomer 1,2,3,4,5,6-$B_{12}H_6F_6^{2-}$ was chosen for the DFT study described above because of its high symmetry and because the computational results would be easier to interpret than those of a lower-symmetry species. We are not proposing that it is an actual intermediate. In fact, it probably is not an intermediate, because it was not one of the $B_{12}H_6F_6^{2-}$ intermediates observed during the high-temperature HF fluorination of $B_{12}H_{12}^{2-}$.[21,22] It is just a convenient, axially symmetric model anion to simplify the proton affinity DFT calculations.

Solvation of $B_{12}H_{12-x}F_x^{2-}$ Anions. Interestingly, the difference in DFT-predicted energies for the B1,B2,B3 and B7,B8,B12 isomers of $H(B_{12}H_6F_6)^-$ in Figure 7 in the absence of a dielectric continuum (i.e., in vacuum), 36.3 kJ mol^{-1}, is *smaller* than the difference in the dielectric continuum, 47.0 kJ mol^{-1}. This is because the charge asymmetry in $H(B_{12}H_6F_6)^-$ is larger when the added proton is on the B7−B8−B12 face than when it is on the B1−B2−B3 face, and a higher dielectric medium will stabilize a more polar species relative to a less polar one. This explanation can also be used to understand the energy differences for two $K(B_{12}H_6F_6)^-$ ion pairs that were also calculated (see Figure S-5). The DFT-predicted energies were lower, both in vacuo and in the dielectric medium, when the K^+ ion was closest to F1, F2, and F3 rather than when it was closest to H7, H8, and H12, and the difference between them in the dielectric medium, 17.8 kJ mol^{-1}, was *much* smaller than the 70.0 kJ mol^{-1} difference in vacuo. In this case, the more stable ion pair has a lower charge asymmetry than the less stable ion pair.

The greater stability of the F1,F2,F3 isomer of $K(B_{12}H_6F_6)^-$ relative to the H7,H8,H12 isomer does not mean that K^+ should form a stronger ion pair with $B_{12}F_{12}^{2-}$ than with $B_{12}H_{12}^{2-}$. In fact, just the opposite must be true. The NI-ESI mass spectrum of a 50/50 mixture of $K_2B_{12}H_{12}$ and $K_2B_{12}F_{12}$ displayed peaks for the $B_{12}H_{12}^{2-}$ and $KB_{12}H_{12}^-$ ions with an intensity ratio $I(B_{12}H_{12}^{2-})/I(KB_{12}H_{12}^-)$ of ca. 1 (see Figure S-4). In contrast, the ratio $I(B_{12}F_{12}^{2-})/I(KB_{12}F_{12}^-)$ was ca. 15. This is consistent with the observation that ion-pairing for $NaBH_4$ dissolved in poly(ethylene oxide) is more extensive than for $NaBF_4$ dissolved in the same polymer.[58] Furthermore, we measured the conductivities, σ, of 0.092 M solutions of $K_2B_{12}H_{12}$ and $K_2B_{12}F_{12}$ in w-CH_3CN containing 2.4% H_2O (these conditions correspond to Expts 10 and 11). The results are $\sigma(K_2B_{12}H_{12}) = 9.95(5)$ mS cm^{-1} and $\sigma(K_2B_{12}F_{12}) = 13.02(4)$ mS cm^{-1}. Based on all of these results, it is almost certain that ion-pairing between K^+ and $B_{12}H_{12}^{2-}$ is more extensive than between K^+ and $B_{12}F_{12}^{2-}$. It therefore follows that the $K_2B_{12}H_{12}$ lattice energy should be significantly larger than the $K_2B_{12}F_{12}$ lattice energy.

The electrostatic contribution to the acetonitrile solvation energy difference between $B_{12}H_{12}^{2-}$ and $B_{12}F_{12}^{2-}$ can be determined by comparing the difference in DFT-predicted total energies of $B_{12}H_{12}^{2-}$ in vacuum and in the dielectric continuum with the corresponding difference in total energies of $B_{12}F_{12}^{2-}$. The net result is that the electrostatic contribution to the acetonitrile solvation energy is 115 kJ mol^{-1} larger for $B_{12}H_{12}^{2-}$. Since $K_2B_{12}H_{12}$ is much less soluble in anhydrous acetonitrile than $K_2B_{12}F_{12}$, the difference in lattice energies must be greater than the difference in anion solvation energies.

Minimizing the Formation of BF_4^- during $B_{12}H_{12}^{2-}$ Fluorination. One way to further improve the yield of salts of $B_{12}F_{12}^{2-}$ would be to reduce the amount of BF_4^- formed by F_2-induced degradation of $B_{12}H_{12-x}F_x^{2-}$ ions. In our previous work, we demonstrated that most BF_4^- formation occurred when $x = 0-3$.[23] To further test the efficiency of our new F_2 fluorination procedure, we used a ca. 80:20 mixture of $K_2B_{12}H_8F_4$ and $K_2B_{12}H_7F_5$ as the starting material instead of $K_2B_{12}H_{12}$ (this recrystallized and NI-ESI-MS-analyzed mixture was prepared as previously described[23]). The reaction conditions were 0 °C; $[B_{12}H_{8/7}F_{4/5}^{2-}] = 0.045$ M; solvent = a-CH_3CN (the anhydrous solvent was used because these partially fluorinated compounds were soluble without added water); 113 mmol KF; 3.5 h; and F_2/B_{12} mole ratio = 8.3 (6% excess). The yield of 99.5+% $K_2B_{12}F_{12}$ was 92% based on the amount of B_{12} starting material (cf. 74% for Expt 10). Since the yield of the recrystallized sample of $K_2B_{12}H_8F_4$ and $K_2B_{12}H_7F_5$ was ca. 80% based on $K_2B_{12}H_{12}$, the overall yield of $K_2B_{12}F_{12}$ prepared this way was only 74% based on the original starting material, $K_2B_{12}H_{12}$. However, the overall yield can almost certainly be higher, because it is probably not necessary to recrystallize the partially fluorinated mixture.

Two additional pairs of experiments were performed to test the stability of $B_{12}H_{12-x}F_x^{2-}$ anions in the presence of F_2. A

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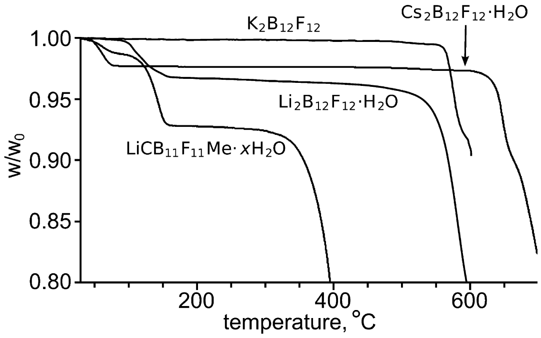

Figure 8. Thermogravimetric curves for $Cs_2(H_2O)B_{12}F_{12}$, $K_2B_{12}F_{12}$, $Li_2(H_2O)B_{12}F_{12}$, and $Li(H_2O)_x(1\text{-}Me\text{-}CB_{11}F_{11})$. The heating rate was 3 °C min^{-1}.

sample of anhydrous $K_2B_{12}H_{12}$ powder was treated with 0.68 atm of dry F_2 (50 psia of 20/80 F_2/N_2) for 10 h at 23 ± 1 °C. The resulting solid did not all dissolve in water, indicating that some oligomeric B_{12}-containing species may have formed. The soluble species were unreacted $B_{12}H_{12}^{2-}$ (51 mol %), BF_4^- (5 mol %), and $B_{12}F_{12}^{2-}$ (44 mol %), indicating that at least 6.2% of the original $B_{12}H_{12}^{2-}$ had been degraded to BF_4^-. Interestingly, anions with $x = 1-11$ were not observed. When a sample of anhydrous $K_2B_{12}F_{12}$ powder was treated with F_2 in the same way, no insoluble products were produced, and the mole ratio of $B_{12}F_{12}^{2-}$ to BF_4^- observed by $^{19}F\{^{11}B\}$ NMR indicated that only 1.8% of the original amount of $B_{12}F_{12}^{2-}$ had been degraded to BF_4^-.

The second additional pair of experiments consisted of treating 0.046 M $K_2B_{12}F_{12}$ in w-CH_3CN with 5.0 equiv of F_2 (as 20/80 F_2/N_2) bubbled through the solution during 2 hours, with and without 2% added HF. There was no precipitate in either case. In the solution without added HF, only $B_{12}F_{12}^{2-}$ and a barely detectable amount of BF_4^- was observed by ^{19}F NMR (the amount of BF_4^- corresponded to $\ll$0.1% cluster degradation). In contrast, when the solution contained 2% HF, 0.5% of the original amount of $B_{12}F_{12}^{2-}$ was converted to BF_4^-. Therefore, not only does HF slow-down the F_2 fluorination of $B_{12}H_{12}^{2-}$ to $B_{12}F_{12}^{2-}$, but it also promotes the degradation of the perfluorinated anion by F_2. The slow degradation of $B_{12}F_{12}^{2-}$ by F_2 in acetonitrile is another reason why the faster two-step synthesis is preferable to the slower one-step synthesis. The less time the perfluorinated anion is in contact with F_2, the better.

Thermal Stability of $B_{12}F_{12}^{2-}$. Figure 8 shows thermogravimetric analysis (TGA) results for $Cs_2(H_2O)B_{12}F_{12}$, $K_2B_{12}F_{12}$, $Li_2(H_2O)B_{12}F_{12}$, and $Li(H_2O)_n(1\text{-}Me\text{-}CB_{11}F_{11})$. The data for the cesium salt show that, after the loss of the water molecule at 30−60 °C, the anhydrous compound $Cs_2B_{12}F_{12}$ was stable until 600 °C (the heating rate was 3 °C/min; recall that the $B_{12}F_{12}^{2-}$ anion is also reasonably stable in anhydrous HF at 550 °C[21]). The compounds $Cs_2B_{12}X_{12}$ (X = Cl, Br, I) are also very stable at high temperature. The chloro compound does not undergo mass loss until ca. 600 °C, and the bromo and iodo compounds do not undergo mass loss until ca. 800 °C.[17] As expected, $K_2B_{12}F_{12}$ and $Li_2B_{12}F_{12}$ underwent decomposition at lower temperatures than $Cs_2B_{12}F_{12}$. In addition, it was found that $Li(1\text{-}Me\text{-}CB_{11}F_{11})$ decomposed at a much lower temperature than $Li_2B_{12}F_{12}$. This could be because the C−CH_3 bond in the former anion is weaker than the B−F bonds in the latter anion, but this has not yet been studied in detail.

Experimental Section

Reagents and Solvents. The salt $K_2B_{12}H_{12}$ (KatChem) was used as received. Potassium fluoride (Mallinckrodt) was ground to a fine powder in a mortar and pestle and dried at 250 °C. The mixture of gaseous fluorine (20%) and nitrogen (80%) was obtained from Air Products and Chemicals, Inc. and used as received. Anhydrous $AlCl_3$ (Mallinckrodt) was sublimed under vacuum. The compounds KI, $KHSO_4$, $KHCO_3$, K_2CO_3, and CaH_2 (Mallinckrodt) were reagent grade or better and were used as received. Acetonitrile (Aldrich; ACS grade) was purified as follows:[59] (i) the as-received solvent was refluxed over anhydrous $AlCl_3$ for 1 h and then distilled; (ii) the distillate was refluxed over $KMnO_4$ and K_2CO_3 for 15 min and then distilled again; (iii) the second distillate was refluxed over $KHSO_4$ for 1 h and then distilled a third time; (iv) the third distillate was refluxed over CaH_2 for 4−6 h, was then distilled for the fourth and last time, and was stored under nitrogen.

Large-Scale Preparation of $K_2B_{12}F_{12}$ and $Cs_2B_{12}F_{12}$: Experiments 10 and 11. The compound $K_2B_{12}H_{12}$ (10.1 g, 45.9 mmol) was dissolved in a mixture of w-CH_3CN (490 mL) and H_2O (12 mL) in a three-neck 1-L Pyrex round-bottom flask to give a colorless solution. Finely ground KF (22.7 g, 390 mmol) was added, most of which did not dissolve. A 20/80 F_2/N_2 mixture was bubbled through the reaction mixture at the rate of 115−125 mL min^{-1} for 6 h with vigorous stirring (this procedure constitutes Step 1 of the fluorination). **CAUTION:** *F_2/N_2 mixtures are extremely hazardous and should only be handled by trained personnel.* The reaction mixture became pale yellow after 3 h of fluorination. The gas flow was stopped after 6 h, and the reaction mixture was bubbled with N_2 for 30 min to remove traces of F_2. The mixture was filtered and the filtrate evaporated to dryness under vacuum. The solid residue was redissolved in 500 mL of a-CH_3CN and filtered. Finely ground KF (27.3 g, 470 mmol) was added to the filtrate. The 20/80 F_2/N_2 mixture was bubbled through the reaction mixture with vigorous stirring for 7 h but at a slightly lower rate, 100−110 mL min^{-1}, than in Step 1. The reaction was judged to be complete when an aqueous KI solution in a trap connected to the outlet of the reaction flask changed from colorless or light yellow to brown. At that time, the reaction mixture was purged with N_2 and filtered. The filtrate was neutralized to pH 7 with aqueous $KHCO_3$. All volatiles were removed under vacuum. The pale-yellow solid residue was mixed with 100 mL of w-CH_3CN and filtered. The filtrate was evaporated to dryness under vacuum. The resulting pale-yellow solid was dissolved in 6% hydrogen peroxide (50 mL) and heated to 80 °C for 2 h, during which the solution became colorless. In order to isolate $K_2B_{12}F_{12}$, the colorless solution was evaporated to dryness, and the white solid residue was recrystallized from acetonitrile and dried at 60 °C under vacuum. Yield: 14.84 g (34.04 mmol $K_2B_{12}F_{12}$, 74.2% based on $K_2B_{12}H_{12}$). In order to isolate $Cs_2B_{12}F_{12}$, the colorless solution was treated with aqueous CsCl (18.1 g, 106 mmol) and cooled to 0 °C. The colorless needle-shaped crystals of $Cs_2B_{12}F_{12}\cdot H_2O$ were isolated by filtration, washed twice with of ice-cold water (2 × 10 mL), and dried in air. Yield: 22.42 g (34.95 mmol $Cs_2B_{12}F_{12}\cdot H_2O$, 76.1% yield based on $K_2B_{12}H_{12}$). The purity of isolated $K_2B_{12}F_{12}$ and $Cs_2B_{12}F_{12}\cdot H_2O$ was judged to be 99.5+% on the basis of their NMR and NI-ESI mass spectra, respesentative examples of which are shown in Figure S-7.

Spectroscopic Measurements. Samples for ^{11}B and $^{19}F\{^{11}B\}$ NMR spectroscopy were acetonitrile-d_3 solutions in 5-mm glass tubes, and the spectra were recorded on a Varian Inova 300 spectrometer operating at 96.2 and 282.2 MHz, respectively. Chemical shifts (δ scale) are relative to external $BF_3(OEt_2)$ for ^{11}B (δ 0.0) and external C_6F_6 for ^{19}F (δ −164.9). Samples for negative-ion electrospray-ionization mass spectrometry (NI-ESI-MS) were

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solutions in w-CH_3CN or w-CH_3CN containing 2.4% H_2O and were recorded on a Fisons VG Quattro-SQ mass spectrometer. Samples for TGA were analyzed using a TA Instruments TGA-2950 instrument (platinum sample pans; *ca.* 10 mg sample size; 25−650 °C temperature range; heating rate 3 °C min^{-1}). Samples for infrared spectroscopy were Nujol mulls between KBr windows. Spectra were recorded on a Nicolet FTIR spectrometer at 2 cm^{-1} resolution. Solution conductivities of $K_2B_{12}H_{12}$ and $K_2B_{12}F_{12}$ were measured in w-CH_3CN containing 2.4% H_2O using a YSI model 32 conductivity bridge operated at 1 kHz with a YSI model 3403 conductivity cell ($k = 0.9964$ cm^{-1}).

DFT Calculations. All DFT calculations were performed using the ORCA code.[60] The PBE0 functional[61,62] and def2-TZVP(-f) basis set[63] with {311/1} contraction scheme for H and {62111/411/11} for B and F atoms was employed throughout calculations. Electrostatic contributions to solvation energies were computed using the conductor-like screening model (COSMO) approach as implemented in ORCA.[64] Symmetry restrictions were not used in the course of optimization.

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Supporting Information Available: Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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