Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

Mechanistic Study on the Fluorination of $K[B(CN)_4]$ with ClF Enabling the High Yield and Large Scale Synthesis of $K[B(CF_3)_4]$ and $K[(CF_3)_3BCN]$

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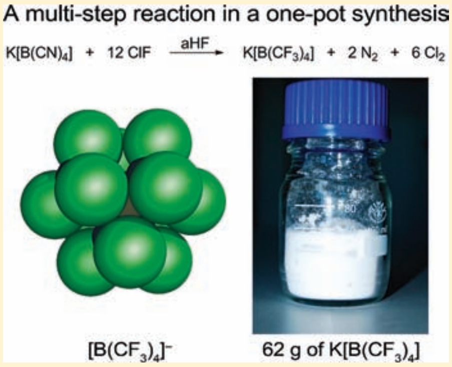
Supporting Information

ABSTRACT: The fluorination of $K[B(CN)_4]$ with ClF is studied by millimolar test reactions in aHF and CH_2Cl_2 solution and by subsequent identification of intermediates such as $B{-}CF{=}NCl$, $B{-}CF_2{-}NCl_2$, and $B{-}CF_3$ species as well as NCl_3 by ^{19}F, ^{11}B NMR, and Raman spectroscopy, respectively. At first one cyano group of $K[B(CN)_4]$ is converted fast into a CF_3 group, and with increasing fluorination the reaction becomes slower and several intermediates could be observed. On the basis of these results, a synthesis was developed for $K[B(CF_3)_4]$ on a 0.2 molar scale by treatment of $K[B(CN)_4]$ diluted in aHF with ClF. The course of the reactions was followed by (i) monitoring the vapor pressure inside the reactor, (ii) observing the heat dissipation during ClF uptake, and (iii) measuring the volume of the released nitrogen gas. Since the fluorination of the last cyano group proceeds very slowly, the selective synthesis of $K[(CF_3)_3BCN]$ on a 0.2 molar scale is possible, as well. The analysis of the mechanisms, thermodynamics, and kinetics of the fluorination reactions is supported by density functional theory (DFT) calculations.



INTRODUCTION

Since decades the development of weakly coordinating anions remains a very important topic in inorganic and applied chemical research.[1] The title compound $K[B(CF_3)_4]$ contains the very promising weakly coordinating anion that can be used in electrolytes, in dye-sensitized solar cells, in Li-ion batteries, in ionic liquids, as counteranion for the stabilization of novel highly electrophilic cations, with possible applications, for example, in cationic catalysis. Simple $M[B(CF_3)_4]$ salts with the single-charged cations $M^+ = Li^+, K^+, Cs^+, Ag^+$ have been synthesized and fully characterized structurally and spectroscopically for the first time only 10 years ago.[2,3] It turned out that the highly symmetric $[B(CF_3)_4]^-$ anion is most weakly coordinating, since so far it is the only anion that stabilizes the $[Ag(CO)_4]^+$ cation[2] and it exhibits the highest $\nu(N{-}H)$ vibrational frequency for the ion pair $[(nC_8H_{17})_3NH]^+\cdots[B(CF_3)_4]^-$ observed in CCl_4 solution, indicating its extremely low basicity.[4] The $[B(CF_3)_4]^-$ anion is very redox stable,[5] and it is stable against many highly reactive cations,[3,6] for example, NO^+,[7] N_5^+,[8] $[H(OEt_2)_2]^+$,[9] $[Ph_3C]^+$,[9] $[Cp_2ZrMe]^+$,[9] $[Co(CO)_5]^+$,[10] $[Co(CO)_2(NO)_2]^+$,[10] and $[C_6F_5Xe]^+$.[11] In the presence of strong Lewis and Brønsted acids the stability of the $[B(CF_3)_4]^-$ anion is limited.[12] However, this reactivity makes the $[B(CF_3)_4]^-$ anion a valuable starting material for the preparation of a broad variety of derivatives of the elusive free Lewis acid $(CF_3)_3B$[3,12] since in concentrated sulfuric acid the reactive boron carbonyl $(CF_3)_3BCO$ is formed.[13,14] This boron carbonyl can be used as starting material for the synthesis of many $(CF_3)_3B$ derivatives,[3,6] for example, $[(CF_3)_3BCPnic]^-$ (Pnic = N, P, As)[15,16] and $[(CF_3)_3BC(O)Hal]^-$ (Hal = F, Cl, Br, I).[17]

Out of these derivatives the $[(CF_3)_3BCN]^-$ anion is of special interest since its potential as building block, for example, in ionic liquids $[EMIM][(CF_3)_3BCN]$,[18,19] as starting material for the synthesis of novel weakly coordinating anions $[(CF_3)_3BCNB(CF_3)_3]^-$,[6] as part of Brønsted acids $(CF_3)_3BCNH$ or $(CF_3)_3BCNH\cdots OEt_2$,[6,18,20] and as ligand in transition metal chemistry $[Cp_2ZrMe\{NCB(CF_3)_3\}]$ as well as $[(PPh_3)_3RhNCB(CF_3)_3]$[6,18,21] has been demonstrated.[3]

The $[B(CF_3)_4]^-$ anion is accessible by fluorination of the tetracyanoborate anion,[22] $[B(CN)_4]^-$, with either ClF or ClF_3.[2] In contrast, related reactions of nitriles with chlorine fluorides result in most cases in simple addition reactions to the $R{-}C{\equiv}N$ triple bond yielding $R{-}CF_2{-}NCl_2$ or $R{-}CF_2{-}NFCl$ compounds.[23−26] So far, the formation of $CH_3{-}CF_3$ as a side product[24] and in 45% yield[25] has only been observed for the fluorination of acetonitrile with ClF_5 and ClF/F_2, respectively. There is only one further example known in which the fluorination with ClF results in the partial cleavage of $CF_2{-}NCl_2$ bonds.[26] In contrast, reactions with bromine trifluoride proceed under complete cleavage of $C{\equiv}N$ triple bonds resulting in trifluoromethyl compounds,[27,28] and iodine pentafluoride does not react

Received: June 20, 2011
Published: September 22, 2011

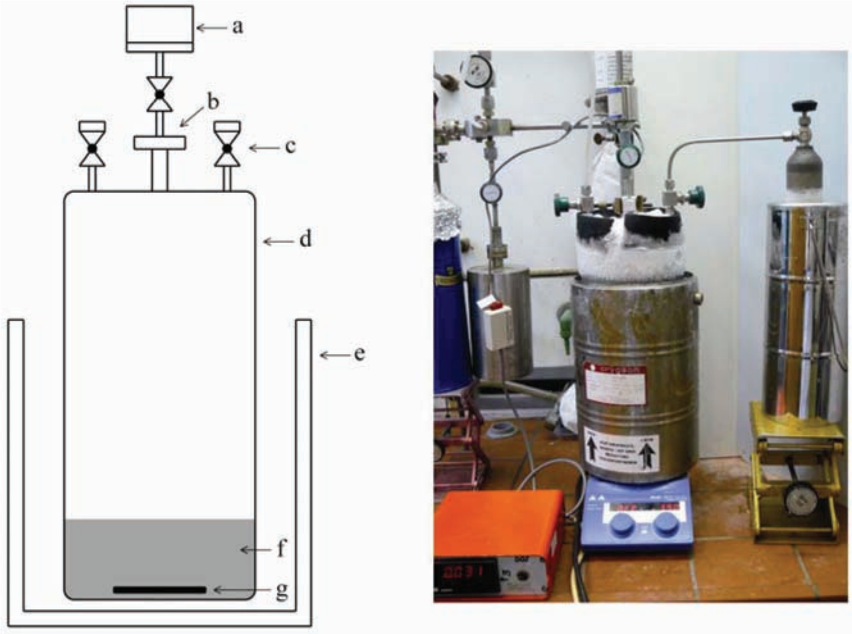


Figure 1. Stainless steel apparatus for the synthesis of K[B(CF_3)$_4$]: (a) capacitance manometer, (b) 16 mm flange with Cu gasket, (c) bellow valve with 6 mm fitting, (d) 5.6 L reactor, (e) Dewar vessel, (f) reaction mixture, and (g) stir bar. The photo shows the cooled reactor (middle) connected to the cooled ClF cylinder (right).

with nitriles at all.[28] Transition metal cyano complexes have been converted into the corresponding trifluoromethyl complexes by the reaction with ClF,[29] similar to the synthesis of the [B(CF_3)$_4$]$^-$ anion.

The main obstacle for the further development of the chemistry of the [B(CF_3)$_4$]$^-$ anion is its availability in millimolar quantities only.[2] For this reason we have studied the course and mechanism of the fluorination of K[B(CN)$_4$] in detail and then developed an improved and safe synthesis for K[B(CF_3)$_4$] in high purity on a 0.2 molar scale, which is presented in this contribution. Furthermore, it turned out that under controlled conditions K[(CF_3)$_3$BCN] can be obtained in high yield, which was previously only accessible in a multistep synthesis via (CF_3)$_3$BCO.[16,30]

RESULTS AND DISCUSSION

According to the original report,[2] salts of the [B(CN)$_4$]$^-$ anion can be fluorinated in aHF with either ClF or ClF_3 in millimolar quantities. Attempts to scale up the reaction with ClF_3 were found to be dangerous, because the highly exothermic reaction is very difficult to control. The use of ClF in place of ClF_3 has the advantage that ClF is a gas under the reaction conditions and, hence, the exothermic reaction in diluted aHF solution is easier to control. The reaction setup is depicted in Figure 1.

The reaction was found to proceed via 3 equiv of ClF per cyano group according to eq 1.

$$\mathrm{K[B(CN)_4] + 12ClF \rightarrow K[B(CF_3)_4] + 2N_2 + 6Cl_2} \tag{1}$$

The release of nitrogen was verified by cooling the reaction mixture to −78 °C and pumping Cl_2 and N_2 gas through a cold trap held at −196 °C. Only N_2 leaves the exhaust tube of the vacuum pump and is collected in a measuring glass filled with water. The reaction enthalpy for the fluorination of the tetracyanoborate anion was estimated by the hypothetical model reaction of HCN with ClF to result in HCF_3, nitrogen, and chlorine (eq 2) using experimental enthalpies of formation.[31]

$$\begin{array}{llllll} \mathrm{4\,HCN + 12\,ClF} \longrightarrow & \mathrm{4\,HCF_3} & + \mathrm{2\,N_2} & + \mathrm{6\,Cl_2} & \Delta H^\circ_{298\,\mathrm{K}} = -2654.4\ \mathrm{kJ\,mol^{-1}} & \\ 4\cdot 135.1 \quad 12\cdot(-55.6) & 4\cdot(-695.3) & 0 & 0 & [\mathrm{kJ\,mol^{-1}}] & (2) \end{array}$$

The reaction enthalpy of −2654.4 kJ mol^{-1} is in very good agreement to the value derived for this model reaction from density functional theory (DFT) calculations of −2613.2 kJ mol^{-1}. The synthesis of the [B(CF_3)$_4$]$^-$ anion is predicted to be a little less exothermic: −2390.4 kJ mol^{-1} (eq 1). This high reaction enthalpy shows the importance of controlling the reaction conditions, which is easily accomplished with gaseous ClF, to avoid overheating and, hence, B−C bond cleavage that results in the formation of fluoroborate anions as side products.

Even at −78 °C the partially dissolved K[B(CN)$_4$] in aHF (vapor pressure <1 mbar) reacts with ClF very fast as monitored by the pressure increase in the reactor (Figure 1). ClF at a pressure of 10 to 20 mbar in the cold reactor is completely consumed in large amount of aHF solution within a few seconds. At the same time the dry ice in the cold bath evaporates faster because of the exothermic reaction. After about 30 min one-third of the required ClF is consumed, and the pressure increases to approximately 20 mbar. During the addition of the second third of ClF, heat release is still observed, and the pressure inside the reactor increases to about 800 mbar within 1 h. To complete the reaction, the reactor is warmed to room temperature overnight. Subsequently the reactor is cooled to −78 °C again, all volatile products (Cl_2 and N_2) are pumped off through a cold trap held at −196 °C, and the N_2 gas is collected at the exhaust of the pump. The last third of ClF (in total ca. 15 equiv) is added to the reaction mixture at −78 °C and subsequently the reactor is

Table 1. NMR Data of Borates Containing B−F, B−CN, B−CFNCl, B−CF_2NCl_2, B−CF_3, B−CF_2Cl, and B−CF_2NClF Groups Observed in Different Stages of the Reaction of K[$B(CN)_4$] with ClF

anion	$\delta(^{11}B)$ [ppm]	$\delta(^{19}F)$ [ppm]	$^2J(^{19}F,^{11}B)$ [Hz]	$^4J(^{19}F,^{19}F)$ [Hz]
$[B(CN)_4]^-$	−38.6			
$[B(CF_3)(CN)_3]^-$	−32.1	−67.0[a]	36.5	
$[B(CF_3)_2(CN)_2]^-$	−26.6	−65.3[a]	32.5	
$[B(CF_3)_3(CN)]^{-g}$	−22.3	−63.9[a]	28.9	6.6
$[B(CF_3)_4]^{-h}$	−19.0	−63.3[a]	25.9	5.8
$[B(CF_2NCl_2)(CN)_3]^-$	−31.0	n.o.	29.7	
$[B(CF_2NCl_2)_2(CN)_2]^-$	−24.8	−86.4[b]	26.1	
$[B(CF_2NCl_2)_3(CN)]^-$	−20.3	−84.0[b]	22.9	
$[B(CFNCl)(CN)_3]^-$	−33.1	n.o.	41.7	
$[B(CFNCl)_2(CN)_2]^-$	−29.2	n.o.	30.0	
$[B(CF_3)_3(CF_2NCl_2)]^-$	−17.4	−60.7[a], −81.5[b]	25.3, 21.2	6.9
$[B(CF_3)_3(CFNCl)]^-$	−18.5	−62.6[a], −5.2[c]	27.0, 28.8	6.3
$[B(CF_2NCl_2)_2(CF_2NClF)_2]^-$	−13.7	−84.6[b], −92.9[d]	23.3, 18.0	6.9
$[B(CF_3)_2(CN)(CFNCl)]^-$	−21.9	−64.1[a], −7.1[c]	30.4, 33.5	5.6
$[B(CF_3)(CN)_2(CF_2NCl_2)]^-$	−25.7	−64.9[a], −87.2[b]	32, 27	7.5
$[B(CF_3)_3(CF_2Cl)]^-$	−17.1	−62.7[a], −53.9[e]	25.2, 20.7	6.6
$[B(CF_3)_2(CF_2Cl)CN]^-$	−20.0	−63.1[a], −55.0[e]	28.3, 23.4	6.8
$[BF(CF_3)_3]^-$	−7.0	−70.8[a], −232.1[f]	28.9, 58.4(^{1}J)	5.1(^{3}J)

[a] CF_3. [b] CF_2NCl_2. [c] CFNCl. [d] CF_2NClF. [e] CF_2Cl. [f] BF. [g] $[B(CF_3)_3(CN)]^-$: $\delta(^{13}C, CF_3) = 132.4$ ppm, $\delta(^{13}C, CN) = 127.5$ ppm, $^1J(^{11}B,^{13}C, CF_3) = 76.3$ Hz, $^1J(^{11}B,^{13}C, CN) = 63.4$ Hz, $^1J(^{19}F,^{13}C) = 303.8$ Hz, $^1\Delta^{19}F(^{12/13}C) = 0.1305$ ppm, $^2\Delta^{19}F(^{10/11}B) = 0.009$ ppm. [h] $[B(CF_3)_4]^-$: $\delta(^{13}C) = 133.0$ ppm, $^1J(^{11}B,^{13}C) = 73.4$ Hz, $^1J(^{19}F,^{13}C) = 304.4$ Hz, $^2J(^{19}F,^{10}B) = 8.7$ Hz, $^3J(^{19}F,^{13}C) = 3.9$ Hz, $^1\Delta^{19}F(^{12/13}C) = 0.1314$ ppm, $^1\Delta^{11}B(^{12/13}C) = 0.0035$ ppm, $^2\Delta^{19}F(^{10/11}B) = 0.0111$ ppm, $^3\Delta^{19}F(^{12/13}C) = 0.0011$ ppm.

warmed to 30 °C for 15 h. Then the product is worked up and isolated.

To gain a deeper insight into the course and the mechanism of the reaction, fluorination experiments were conducted with (i) a stoichiometrically deficient proportion of ClF at −78 °C with the potassium salt in neat aHF and with (ii) an excess of ClF with the tetrabutylammonium salt in dichloromethane in the presence of potassium fluoride. From the NMR spectroscopic analyses (see Table 1) it is evident that the transformation of the cyano groups to trifluoromethyl groups proceeds in three steps: (i) the addition of ClF results in B−CF═NCl species, (ii) the further addition of ClF gives B−CF_2−NCl_2 derivatives, and (iii) the cleavage of the C−N bond with ClF results in B−CF_3 species and NCl_3. The formation of NCl_3 was unambiguously proven by Raman spectroscopy. NCl_3 is unstable in the later stage of the reaction and decomposes to elemental nitrogen and chlorine even at −78 °C.

Calculations of transition states for the reaction of ClF with CF_2−NCl_2 groups resulting in CF_3 groups and NCl_3 ruled out a concerted mechanism for the addition to and the cleavage of the C−N single bond. On the basis of the calculations, an ionic transition state according to eq 3 is involved in the C−N bond cleavage.[‡]

$$[R_3B{-}CF_2{-}NCl_2]^- + ClF \rightarrow \{[R_3B{-}CF_2{-}N^+Cl_3\cdots F^-]^-\}^\ddagger \rightarrow [R_3B{-}CF_3]^- + NCl_3 \qquad (3)$$

The calculated activation barrier for this process of approximately 200 kJ mol^{-1} is too high for the observed reaction. However, solvation of F^- in the ionic transition state by at least 2 molecules of either HF or ClF lowers the barrier to less than 50 kJ mol^{-1}. In dichloromethane the transition state needs to be stabilized via solvation with ClF. Since (i) ClF is a less effective solvating agent than HF and (ii) the concentration of ClF in dichloromethane is much lower compared to that of HF in aHF solution, the reaction proceeds much slower in dichloromethane.

A strong solvent effect was found for the CF_2−NCl_2 bond cleavage. In all reactions performed at −78 °C in aHF only small amounts of BCF_2−NCl_2 species were detected whereas in the dichloromethane/KF system the main component is the $[B(CF_2{-}NCl_2)_3(CN)]^-$ anion. This observation indirectly supports the results of the DFT calculations that predict a participation of HF and/or further ClF in the reaction.

Three of the cyano groups of the $[B(CN)_4]^-$ anion undergo fast addition of ClF in aHF and dichloromethane. The transformation of the fourth group is much slower and prolonged reaction times and reaction temperatures of up to 30 °C are necessary for a complete conversion of all four CN to CF_3 groups. In aHF it was possible to selectively synthesize the potassium salt of the $[B(CF_3)_3(CN)]^-$ anion that was previously accessible via multistep protocols from $(CF_3)_3BCO$, only.[16,30] Furthermore, it is possible to selectively prepare salts of the new, unusual anion $[B(CF_2{-}NCl_2)_3(CN)]^-$ in CH_2Cl_2.

It was found that all borates carrying −CF_2−NCl_2 or −CF═NCl groups are quite stable in neutral aqueous solution. However, the −CF_2−NCl_2 group decomposes under basic or acidic conditions, but −CF═NCl is only acid sensitive. More work is needed to isolate the new borates with −CF_2−NCl_2 or −CF═NCl groups in pure form and to explore their chemistry in detail.

■ CONCLUSION

Transformations of cyano groups into trifluoromethyl groups with halogen fluorides, for example, ClF, ClF_3, or BrF_3, are of broad interest in inorganic and organic chemistry. However, only little is known on the mechanism of this reaction and, hence, the insights into the addition reactions of chlorine monofluoride to the $[B(CN)_4]^-$ anion to result in $-CF{=}NCl$ and $-CF_2-NCl_2$ boron species and the subsequent cleavage of the C−N single bond by ClF provide valuable information for the further development of such reactions.

With the new synthesis of the $K[B(CF_3)_4]$ and $K[(CF_3)_3BCN]$ on a 0.2 molar scale using the readily available $K[B(CN)_4]$ and chlorine monofluoride the borate anions are available in larger quantities for the first time.[2] This will enable the further development of their chemistry and their use in various applications, for example, in coordination chemistry, for the stabilization of highly reactive cations, and in ionic liquids.

■ EXPERIMENTAL SECTION

Caution! *ClF_3, ClF, and aHF are highly toxic and can cause severe injuries via skin and eye contact or inhalation. Therefore all manipulations of these chemicals have to be performed under a well-ventilated fume hood, and wearing of protective gloves, an apron, and a head screen is strongly recommended. Before starting the transfer of ClF_3, ClF, or aHF, the apparatus must be checked carefully for any leaks.*

Materials and Apparatus. ^1H, ^{11}B, and ^{19}F NMR spectra were recorded at 25 °C in D_2O or CD_3CN solution on a Bruker DRX 400 spectrometer operating at 400.17 (^1H), 128.39 (^{11}B), 100.61 (^{13}C), and 376.45 (^{19}F) MHz. The NMR signals were referenced against Me_4Si (^1H, ^{13}C), $BF_3\cdot OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F) as external standards. For the determination of the relative amounts of borate anions that had formed in the reactions only the ^{19}F NMR data were used for the integration, because the intensities of the ^{11}B NMR signals in many cases do not display the correct relative intensities. This effect in the ^{11}B NMR spectra is due to very long relaxation times of the $[B(CF_3)_4]^-$ and $[B(CN)_4]^-$ anions.[14,16] In Table 1 the NMR spectroscopic data of all anions that could be assigned in the spectra of the test reaction mixtures and in the large scale syntheses are summarized. The assignments were supported by calculated chemical shifts, which are listed in Table S1 in the Supporting Information. Raman spectra were recorded at room temperature on a Bruker EQUINOX 55 FT Raman spectrometer (Bruker, Karlsruhe, Germany) using the 9394.8 cm^{-1} excitation line (100 mW) of an Nd/YAG laser. In the region of 3000−50 cm^{-1} spectra were recorded with a resolution of 2 cm^{-1} by addition of 64 scans.

The syntheses were performed in a stainless steel reactor as depicted in Figure 1. It consisted of a cylinder (o.d. 15 cm, height 32 cm, wall thickness 4 mm, volume 5.6 L) equipped with 3 bellow valves (Swagelok SS-4H), and a capacitance manometer (Setra 205−2, 0−3.5 bar) connected via a 16 mm flange with a Cu gasket. The starting materials $K[B(CN)_4]$[22] (donated by Merck KGaA, Darmstadt, Germany) and ClF[32] (commercially available from Ozark, U.S.A.) was synthesized according to a literature procedure. aHF was donated by Solvay (Bad Wimpfen) and ClF_3 by Urenco (Gronau).

Preparation of $K[B(CF_3)_4]$. In a typical run the reactor was charged via the CF 16 flange with $K[B(CN)_4]$ (30.8 g, 0.20 mol) and a big magnetic stir bar and then evacuated via a 6 × 1 mm PFA tube for several hours. The lower part of the reactor was cooled with an ethanol bath at −20 °C, and liquid aHF (about 800 g) was introduced into the reactor. While the suspension of $K[B(CN)_4]$ in aHF was stirred the upper part of the reactor was cooled with dry ice to result in the condensation of the refluxing aHF and to wash down the $K[B(CN)_4]$, which possibly stuck at the upper part of the reactor. Subsequently, the ethanol bath was cooled to −78 °C with dry ice and when the vapor pressure of HF dropped below 2 mbar 54 g, 1 mol of ClF (the container cooled to −78 °C) was introduced into the reactor within half an hour. During the addition the pressure inside the reactor was checked and did not exceed 20 mbar. All ClF was consumed with release of heat, as evident from a faster evaporation of the dry ice in the cold bath. Another portion of ClF (1 mol; in total 10 equiv) was added to the reaction mixture within 1 h. During this time the pressure inside the reactor increased to about 800 mbar, and there was only little heat release. The reactor was warmed overnight to room temperature and then cooled to −78 °C again. Volatile Cl_2 and N_2 were slowly pumped off through a cold trap held at −196 °C and at the end of the exhaust tube of the vacuum pump 7.0 L of N_2 were collected at room temperature in a measuring glass (2 L, in 4 portions) filled with water. Subsequently the cold reactor was filled with ClF (1 mol; in total 15 equivalents) within 1 h while the pressure increased to 900 mbar. The reactor was kept at 30 °C for 15 h and then cooled to −78 °C again. Volatile Cl_2 and N_2 were slowly pumped off through the cold trap held at −196 °C and at the exhaust of the vacuum pump 3.5 L of N_2 were collected. In total 10.5 L of N_2 (~0.4 mol) had formed, which is in agreement to the stoichiometry given in eq 1. All aHF was recovered in a 1.5 L steel storage vessel held at −78 °C while stirring the solution under heating the reactor with warm water to room temperature. After all aHF was transferred, the reactor was evacuated for 20 min, the CF flange was opened, and the content was worked up.

The raw product was washed out of the reactor using an aqueous K_2CO_3 solution (50 g dissolved in 200 mL of H_2O) and two portions of water (100 mL). The collected aqueous washings were combined and extracted with 3 portions of diethyl ether (200 + 100 + 100 mL). The collected ethereal extracts were treated with K_2CO_3 to remove most of the water. The ether solution was evaporated, and the solid residue was treated at 80 °C with ultrasonic sound in a vacuum. The dry solid product was crushed in a mortar, washed with CH_2Cl_2 and dried in a vacuum. Yield: 62.3 g (96%, purity 99.0%; traces of $K[(CF_3)_3BF]$ (0.59%), $K[(CF_3)_3BCN]$ (0.31%), $K[(CF_3)_2BF_2]$ (0.06%), and $K[(CF_3)_2B(CN)_2]$ (0.01%)).

Preparation of $K[(CF_3)_3BCN]$. The procedure used for the preparation of $K[(CF_3)_3BCN]$ was similar to that described for the synthesis of $K[B(CF_3)_4]$. In a typical run the reactor was charged with $K[B(CN)_4]$ (30.8 g, 0.20 mol) and treated with ClF at −78 °C until 2 mol ClF were consumed. Subsequently the reaction mixture was stirred for further 4 h at −78 °C to complete the reaction. Then all volatile products (excess of ClF, Cl_2 and N_2) were pumped off through a trap held at −196 °C. At the exhaust tube of the pump 5.8 L of N_2 were collected. To decompose all residual NCl_3, the reaction mixture was warmed to room temperature overnight. As expected, the volatile products contained an additional amount of 1.5 L of N_2 (in sum ~0.3 mol). The isolation of the product was performed in analogy to that of $K[B(CF_3)_4]$. Yield: 47.3 g (83%; composition: 76% $K[(CF_3)_3BCN]$, 10% $K[(CF_3)_2B(CN)_2]$, 6% $K[(CF_3)_3BCFNCl]$, 0.9% $K[B(CF_3)_4]$, 0.3% $[B(CF_3)_3(CF_2Cl)]^-$, 0.1% $K[(CF_3)B(CN)_3]$ and 6.7% other complexes).

A portion of the raw product (2.18 g, containing 76% of $K[B(CF_3)_3CN]$) was dissolved in water (10 mL) and conc. HCl (10 mL), and the solution was stirred for 5 min. Subsequently, a solution of $[Me_3NH]Cl$ (1.66 g, 17.4 mmol) in water (10 mL) was added to the solution of the raw product. After 5 min of stirring, the suspension was filtered off and washed with water (20 mL). The product was dissolved in acetonitrile and transferred into a bulb. After evaporation of the acetonitrile at the rotary evaporator and drying of the product in a vacuum 1.91 g containing 89% of $[Me_3NH][B(CF_3)_3CN]$ and 9% of $K[(CF_3)_2B(CN)_2]$ were obtained. The $[Me_3NH]^+$ salt can be converted with KOH solution into the potassium salt, and the purification process can be repeated.

NMR Spectroscopic Study of the Reaction of $K[B(CN)_4]$ with ClF in aHF. A 100 mL PFA reactor equipped with a magnetic stirring bar was charged with $K[B(CN)_4]$ (160 mg, 1.0 mmol) and anhydrous HF (10 mL). The reaction mixture was cooled to −78 °C and ClF was added until its consumption declined. All highly volatile materials (Cl_2, N_2, and ClF) were removed at −78 °C.

A sample of the yellow suspension was cannula transferred at low temperature into a PFA inliner and studied at −70 and −60 °C by NMR spectroscopy. Only very broad signals were observed in the ^{11}B and ^{19}F NMR spectra. However, the formation of trifluoromethylborates was evident from these spectra. Upon warming of the suspension inside the PFA inliner the yellow solid liquefied at approximately −40 °C and separated as a yellow phase at the bottom of the inliner (NCl_3).

All volatiles of the reaction mixture in the PFA flask were removed in a vacuum while warming up to room temperature. The solid yellow residue was studied by NMR spectroscopy in CD_3CN and by Raman spectroscopy at room temperature. The Raman spectrum was dominated by strong bands at 540, 351, and 260 cm^{-1} that were assigned to NCl_3,[33] adsorbed on the borate salts. A mixture of borate anions with CN, CF_3, $CF_2{-}NCl_2$, and CF=NCl groups was observed by ^{11}B and ^{19}F NMR spectroscopy. The main components of the mixture are the anions $[(CF_3)_3BCN]^-$, $[(CF_3)_2B(CN)_2]^-$, and $[B(CF_2NCl_2)_2(CN)_2]^-$.

NMR Spectroscopic Study of the Reaction of K[B(CN)$_4$] with ClF in CH$_2$Cl$_2$. A 100 mL PFA reactor equipped with a magnetic stirring bar was charged with [*n*Bu$_4$N][B(CN)$_4$] (300 mg, 0.8 mmol), spray-dried KF (1.75 g, 30 mmol), and dichloromethane (20 mL). At −78 °C ClF was added (12 g, 220 mmol) over 4 h. Then all volatiles were removed under reduced pressure at low temperature. The remaining white solid residue was studied by ^{11}B and ^{19}F NMR spectroscopy at room temperature, and the data of the anions that could be assigned are collected in Table 1. [*n*Bu$_4$N][B(CF$_2$NCl$_2$)$_3$CN] is the main product of the fluorination experiment (70%) followed by [*n*Bu$_4$N][B(CF$_3$)$_4$] (15%), [*n*Bu$_4$N][B(CF$_2$NCl$_2$)$_2$(CF$_2$X)$_2$] (X probably NClF) (5%), and [*n*Bu$_4$N][B(CF$_3$)$_3$(CF$_2$NCl$_2$)] (4%).

DFT Calculations. DFT calculations[34] were carried out using the B3LYP method[35] with the basis sets 6-311++G(d,p) as implemented in the Gaussian 03 program suite.[36] Diffuse functions were incorporated because improved energies are obtained for anions.[37] Frequency calculations were performed for all species, and all structures represent true minima without imaginary frequencies on the respective hypersurface. Transition states exhibit one imaginary frequency and IRC calculations were performed to verify that the transition states connect the products and reactants, respectively.[38] All energies presented herein are zero point corrected. For enthalpies and free energies the thermal contributions are included for 298 K. DFT-GIAO[39] NMR shielding constants $\sigma(^{11}B)$ and $\sigma(^{19}F)$ were calculated at the B3LYP/6-311++G(d,p) level of theory.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** A table containing calculated ^{19}F and ^{11}B NMR chemical shifts of borate anions containing B−CN, B−CFNCl, B−CF$_2$NCl$_2$, B−CF$_3$, B−CF$_2$Cl, and B−CF$_2$NClF groups as well as ^{19}F and ^{11}B NMR spectra of selected borate anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was financial supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We appreciate Dr. J. Eicher (Solvay Fluor GmbH) for donating aHF to us and Dr. N. Ignatiev (Merck KGaA) for donating K[B(CN)$_4$] to us.

■ DEDICATION

Dedicated to Prof. Dr. Felix Aubke on the occasion of his 80th birthday.

■ REFERENCES

(1) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405–1421. Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927–942. Krossing, I.; Raabe, I. *Angew. Chem.* **2004**, *116*, 2116–2142. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066–2090. Reed, C. A. *Acc. Chem. Res.* **2010**, *43*, 121–128.

(2) Bernhardt, E.; Henkel, G.; Willner, H.; Pawelke, G.; Bürger, H. *Chem.—Eur. J.* **2001**, *7*, 4696–4705.

(3) Finze, M.; Bernhardt, E.; Willner, H. *Angew. Chem.* **2007**, *119*, 9340–9357. *Angew. Chem., Int. Ed.* **2007**, *46*, 9180–9196.

(4) Bernhardt, E.; Berkei, M.; Willner, H. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2009–2015.

(5) Schmidt, M.; Kühner, A.; Willner, H.; Bernhardt, E. Merck Patent GmbH EP1205480(A2), 2002.

(6) Finze, M. Ph.D. Thesis, University of Hannover, Hannover, Germany, 2004.

(7) Bernhardt, E.; Finze, M.; Willner, H. *Z. Anorg. Allg. Chem.* **2006**, *632*, 248–250.

(8) Wilson, W. W.; Vij, A.; Vij, V.; Bernhardt, E.; Christe, K. O. *Chem.—Eur. J.* **2003**, *9*, 2840–2844.

(9) Finze, M.; Bernhardt, E.; Berkei, M.; Willner, H.; Hung, J.; Waymouth, R. M. *Organometallics* **2005**, *24*, 5103–5109.

(10) Bernhardt, E.; Finze, M.; Willner, H.; Lehmann, C. W.; Aubke, F. *Chem.—Eur. J.* **2006**, *12*, 8276–8283.

(11) Koppe, K.; Bilir, V.; Frohn, H.-J.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **2007**, *46*, 9425–9437. Koppe, K.; Frohn, H.-J.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **2008**, *47*, 3205–3217.

(12) Finze, M.; Bernhardt, E.; Zähres, M.; Willner, H. *Inorg. Chem.* **2004**, *43*, 490–505.

(13) Terheiden, A.; Bernhardt, E.; Willner, H.; Aubke, F. *Angew. Chem.* **2002**, *114*, 823–825. *Angew. Chem., Int. Ed.* **2002**, *41*, 799–801.

(14) Finze, M.; Bernhardt, E.; Terheiden, A.; Berkei, M.; Willner, H.; Christen, D.; Oberhammer, H.; Aubke, F. *J. Am. Chem. Soc.* **2002**, *124*, 15385–15398.

(15) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Angew. Chem.* **2004**, *116*, 4253. *Angew. Chem., Int. Ed.* **2004**, *43*, 4160.

(16) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 10712–10722.

(17) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Angew. Chem.* **2003**, *115*, 1082. *Angew. Chem., Int. Ed.* **2003**, *42*, 1052. Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Chem.—Eur. J.* **2005**, *11*, 6653–6665.

(18) Finze, M.; Bernhardt, E.; Willner, H.; Ignatiev, N. V.; Welz-Biermann, U. Merck Patent GmbH WO2006045405A1, 2006.

(19) Bernhardt, E.; Willner, H., unpublished results.

(20) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391–395.

(21) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Organometallics* **2006**, *25*, 3070–3075.

(22) Bernhardt, E.; Finze, M.; Willner, H. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1229–1234.

(23) Boguslavskaya, L. S. *Usp. Khim.* **1984**, *53*, 2024–2055. *Russ. Chem. Rev.* **1984**, *53*, 1178–1194. Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488–489. Young, D. E.; Anderson, L. R.; Fox, W. B. *Chem. Commun.* **1970**, 395.Young, D. E.; Anderson, L. R.; Fox, W. B.; 1972; Sekiya, A.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1979**, *101*, 7640–7641. Thrasher, J. S.; Bauknight, C. W.; DesMarteau, D. D. *Inorg. Chem.* **1985**, *24*, 1598–1599. Marsden, H. M.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 169–172. Bauknight, C. W.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1990**, *112*, 728–733. Zheng, Y. Y.; Patel, N. R.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1992**, *31*, 488–491.

(24) Lustig, M. *Inorg. Chem.* **1967**, *6*, 1064–1065.

(25) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1981**, *20*, 1–3.

(26) Foropoulos, J.; Shreeve, J. M. *Inorg. Chem.* **1991**, *30*, 2699–2701.

(27) Rozen, S. *Acc. Chem. Res.* **2005**, *38*, 803–812.Baker, M. T.; Ruzicka, J. A.; 1997; Baker, M. T.; Ruzicka, J. A.; Tinker, J. H. *J. Fluorine Chem.* **1999**, *94*, 123–126. Rozen, S.; Rechavi, D.; Hagooly, A. *J. Fluorine Chem.* **2001**, *111*, 161–165.

(28) Stevens, T. E. *J. Org. Chem.* **1961**, *26*, 1627–1630.

(29) Bernhardt, E.; Finze, M.; Willner, H. *J. Fluorine Chem.* **2004**, *125*, 967–973. Balters, S.; Bernhardt, E.; Willner, H.; Berends, T. *Z. Anorg. Allg. Chem.* **2004**, *630*, 257–267.

(30) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Inorg. Chem.* **2006**, *45*, 669–678.

(31) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; American Chemical Society and American Institute of Physics for the National Bureau of Standards: Washington, DC, 1986; Law, C.-K.; Chien, S.-H.; Li, W.-K.; Cheung, Y.-S. *J. Phys. Chem. A* **2000**, *106*, 11271–11276. Csontos, J.; Rolik, Z.; Das, S.; Kallay, M. *J. Phys. Chem. A* **2010**, *114*, 13093–13103.

(32) *Handbuch der Präparativen Anorganischen Chemie*, Erster Band, 3rd ed.; Brauer, G., Ed.; Ferdinand Enke Verlag: Stuttgart, Germany, 1975. Schack, C. J.; Wilson, R. D. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 393–396.

(33) Schneider, S.; Gerken, M.; Haiges, R.; Schroer, T.; Boatz, J. A.; Dixon, D. A.; Grant, D. J.; Christe, K. O. *Inorg. Chem.* **2007**, *46*, 93–102.

(34) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(35) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Kudin, T. V. K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; ; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(37) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231.

(38) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. Gonzales, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(39) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.