**Synthetic Methods**

**Innovative Syntheses of Cyano(fluoro)borates: Catalytic Cyanation, Electrochemical and Electrophilic Fluorination**

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**Abstract:** Different types of high-yield, easily scalable syntheses for cyano(fluoro)borates Kt[BF(CN)x]-(n = 0–2) (Kt = cation), which are versatile building blocks for materials applications and chemical synthesis, have been developed. Tetrafluoroborates react with trimethylsilyl cyanide in the presence of metal-free Brønsted or Lewis acid catalysts under unprecedentedly mild conditions to give tricyanofluoroborates or tetracyanoborates. Analogously, pentafluoroethyltricyanoborates were converted into pentafluoroethyltricyanoborates. Boron trifluoride etherate, alkali metal salts, and trimethylsilyl cyanide selectively yield dicyanodifluoroborates or tricyanofluoroborates. Fluorination of cyanohydrideriborates is the third reaction type that includes direct fluorination with, for example, elemental fluorine, stepwise halogenation/fluorination reactions, and electrochemical fluorination (ECF) according to the Simons process. In addition, fluorination of [BH(CN)2(O)(OEt)]– to result in [BF(CN)3(O)(OEt)]– is described.

**Introduction**

Borate anions are important building blocks for a wealth of applications, especially as weakly coordinating anions for the stabilization of reactive cations[14] and for ionic liquids (ILs).[2] The tetrafluoroborate anion [BF4]–, which can be considered as the prototype borate anion, was reported by Berzelius already in 1824.[15] Only in 1991, the [BF4]– anion was used for the synthesis of the first air and water stable room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazoliumtetrafluoroborate ([EMIm][BF4]).[16] Later, RTILs with cyano(fluoro)boronite anions [BF(CN)3]– (n = 1 (MFB), 2 (DBF), 3) and the tetracyanoborate anion [B(CN)4]– (TCB) have been described. These RTILs were found to have superior properties, such as low viscosity, high specific conductivity in conjunction with high electrochemical and thermal stability compared to tetrafluoroborate-based RTILs.[17–19] Therefore, they have been tested in many different applications, especially in electrochemical and optoelectronic devices,[20–22] as well as lanthanide complexes.[23,24] Again, potential applications have been studied, for example, Li[B(CN)4] was tested as...
component of non-aqueous electrolytes used in lithium batteries. The follow-up chemistry of cyano(fluoro)borate anions enables the synthesis of unprecedented otherwise inaccessible boron species. Examples are the homoleptic cyanoborate anions \([\text{B}(_2\text{CN})_4]^{n-}\) and \([\text{B}(\text{CN})_3]^{n-}\) which are accessible for example, from KMFB, and the borate anions \([\text{B}(\text{CF}_3)_2\text{O}]^{n-}\) and \([\text{B}(\text{CO}_2\text{H})_4]^{n-}\) which have been prepared starting from tetracyanoborates.

Because of the fundamental and applied interest in cyano(fluoro)borates, a number of different syntheses have been developed in recent years. Especially, alkali metal salts have been in the focus since they are convenient starting materials for the preparation of salts with organic cations, such as room temperature ionic liquids (RTILs) and metal salts and complexes. The first syntheses for tetracyanoborates have been reported in 2000 independently by two research groups,\([6, 7]\) and the borate anions \([\text{BF}(_2\text{CN})_3]^{n-}\) and \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) have been used as starting compounds for the catalytic conversion of organic tetracyanoborates into cyano- and perfluoroalkyltricyanoborates of sodium, potassium, and lithium.\([25, 37]\) Later, many further syntheses including improved methods have been described.\([38, 39]\) Currently, the best synthetic approach towards tetracyanoborates relies on a sinter process that uses \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) as starting material.\([3, 4, 22]\) The tricyanofluoroborate anion (MFB) was identified by NMR spectroscopy already in 2000\([34]\) and crystal structures of \([\text{M}[\text{BF}(_2\text{CN})_3]^{n-}\) \((\text{M} = \text{Ag, Cu})\) were reported in 2002.\([25]\) In both cases, no syntheses have been described.\([27, 34]\) First reactions yielding tricyanofluoroborates were reported in 2003 using \([\text{Li}[\text{BF}(_2\text{CN})_3]^{n-}\) and \([\text{CH}_3\text{SiCN}\) as starting materials.\([23]\) These procedures suffer from long reaction times and laborious purification steps to obtain pure \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) by procedures that required additional purification steps.\([26, 30, 39]\) Recently, sodium and potassium MFB have become available in high yields and purity starting from \([\text{Na}[\text{BF}(_2\text{CN})_3]^{n-}\). The key idea of this synthesis was the introduction of trimethylsilyl chloride as a Lewis acid catalyst (Scheme 1).\([40, 41]\) Other Lewis acids have been studied for the catalytic conversion of organic tetracyanoborates into cyano- and perfluoroalkyltricyanoborates \([\text{BF}(_2\text{CN})_3]^{n-}\) \((n = 0–2)\).\([42]\)

Both anions, \([\text{BF}(_2\text{CN})_3]^{n-}\) and \([\text{BF}(_2\text{CN})_3]^{n-}\) (DFB) were identified by NMR spectroscopy in 1978.\([43]\) More than 20 years later, first reactions towards \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) and \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) have been reported.\([23, 25]\) Either \([\text{BF}(_2\text{CN})_3]^{n-}\) or \([\text{BF}(_2\text{CN})_3]^{n-}\) react with \([\text{KCN}\) in acetone to give DFB (Scheme 1). The synthesis of \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) was accomplished using \([\text{BF}(_2\text{CN})_3]^{n-}\) and \([\text{KCN}\) as starting materials but at a lower temperature than for the preparation of DFB.\([22]\) Another synthesis for DFB salts that is based on \([\text{CH}_3\text{SiCN}\) as a CN source instead of \([\text{KCN}\) has some drawbacks, especially a very long reaction time.\([23]\)

Here, we report on a set of different, efficient syntheses providing easy access to alkali metal salts of the cyano and fluoroborates \([\text{BF}(_2\text{CN})_3]^{n-}\) \((n = 1 \text{ (MFB), 2 (DFB)})\), the tetracyanoborate anion \([\text{B}(\text{CN})_3]^{n-}\) (TCB), and the pentafluoroethyltricyanoborate anion \([\text{CF}_2\text{F}(\text{CN})_3]^{n-}\). These syntheses include Lewis acid catalyzed cyanation as well as fluorination methods using salts of \([\text{BH}(\text{CN})_3]^{n-}\) and \([\text{BF}(\text{CN})_3]^{n-}\) which have become easily accessible, respectively.\([16, 44]\) The crystal structures of \([\text{[CH}_3\text{NH}]_3[\text{BF}(_2\text{CN})_3]^{n-}\), \([\text{[CH}_3\text{NH}]_3[\text{B}(\text{CN})_3]^{n-}\), \([\text{Na}[\text{BF}(_2\text{CN})_3]^{n-}\) \((\text{CH}_3\text{CO})\) \([\text{H}]\), and \([\text{PPPh}_3]_3[\text{BF}(_2\text{CN})_3\text{OC(O)}\text{Et}]\) are presented.

Results and Discussion

Lewis acid catalyzed synthesis of cyanoborates

Recently, we have found that the commercially available trimethylsilyl triflate (TMSOTf) \([\text{CF}_3\text{SO}_2\text{O}][\text{CF}_3\text{SO}_2\text{O}]_3\) is a convenient starting material for the exchange of fluorine against cyano groups using trialkylsilanes \([\text{R}_3\text{SiCN} (\text{R} = \text{alkyl})]\) to give alkali metal tricyanofluoroborates, tetracyanoborates, and perfluoroalkyltricyanoborates (Table 1).\([45]\) Presumably, the mechanism of the transformations of fluoroborates into cyanoborates catalyzed by these Lewis acids is analogous to the procedure reported for the conversion of \([\text{Na}[\text{BF}(_2\text{CN})_3]^{n-}\) into \([\text{Na}[\text{BF}(_2\text{CN})_3]^{n-}\) in the presence of trimethylsilyl chloride (entry MFB1).\([40, 41]\) However, the triflate-based catalysts allow for the conversion of \([\text{BF}(_2\text{CN})_3]^{n-}\) into \([\text{BF}(_2\text{CN})_3]^{n-}\) under much milder conditions even at room temperature and in almost quantitative yield in 3 h (Table 1, entry MFB1). A reduction of the catalyst loading from 61 mol% (MFB1) to 18 mol% (MFB2a) results in a slightly longer reaction time of 5 h. It is worth mentioning that the catalyst retains its activity after recycling as shown by entry MFB2b. No additional amount of catalyst was required to achieve full conversion of \([\text{Na}[\text{BF}(_2\text{CN})_3]^{n-}\) into MFB (entry MFB2b). Although the reaction is preferably carried out without any additional solvent, it was shown that the synthesis of \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) can be performed in acetone or dichloromethane leading to a similar yield, as well (entry MFB3). Method MFB3 exemplifies the reduction of the amount of \([\text{CH}_3\text{SiCN}\) by dibromides of this procedure. It is to be noted that the yield of \([\text{K}[\text{BF}(_2\text{CN})_3]^{n-}\) has been used as starting compound instead of

![Scheme 1. Literature known syntheses of K[B(N(CN))₃] (KTCB) [5, 13], K[B(CN)₃] (KMB) [46, 47], and K[B(CN)₃] (KDFB) [2, 11].](image)

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Na[BF₄]⁻, a higher reaction temperature and a longer reaction time would have been necessary, which is explained by the low solubility of potassium tetrafluoroborate (entry MFB4). Mixed cyanofluoroborates are potential starting materials, as well, as demonstrated by the conversion of K[BF(CN)]⁻ into K[BF(CN)]⁻ (entry MFB5). Entries MFB7-MFB9 demonstrate that the catalyst (CH₃)₂SiOSO₂CF₃ can be generated in situ by the interaction of trimethylsilyl cyanide (CH₃)₂SiCN with trifluoromethanesulfonic acid (CF₃SO₂OH), trifluoromethanesulfonic acid anhydride (CF₃SO₂O₂, CF₃SO₂O₂), or trifluoromethanesulfonic acid (CF₃SO₂OH). Trifluoromethanesulfonic acid (CF₃SO₂O₂) is a highly efficient catalyst for the conversion of Na[BF₄]⁻ into Na[BF(CN)]⁻. Only 6 mol% of (CF₃SO₂O₂)O with respect to Na[BF₄]⁻ was required to complete the reaction at 40 °C within 4 h (entry MFB7). Trimethylsilyl nonafluorobutanesulfonate (CF₃CF₂FSO₂OSi(CH₃)₃) was successfully introduced as an alternative catalyst for CF₃CF₂FSO₂OSi(CH₃)₃ (entry MFB6).

Surprisingly, the aforementioned trflate-based catalysts allow the synthesis of tetracyanofluoroborates starting from tetracyanofluoroborates even at 100 °C, thus, avoiding any autoclave technique (Table 1). Trimethylsilyl triflate with 61 mol% loading afforded MB[CN]⁺ (M = Na, K) in more than 90% yield at 100 °C and in 6–22 h depending on the amount of (CH₃)₂SiCN (entries TCB1 and TCB2). The more active catalyst triflic anhydride resulted in the formation of 71% of K[B(CN)]⁻ with a loading of 6 mol%, only (entry TCB3).

Triflic acid anhydride (CF₃SO₂)₂O with respect to Na[BF₄]⁻ was used as more reactive alternative to M[BF₄]⁻ (M = Na, K) for the synthesis of MFB salts. The reactions took place within 30 minutes from 0 °C to room temperature in the presence of potassium halides KX (X = Cl, F, Br) or potassium cyanide and resulted in the formation of KMF in up to 73% yield and 99% purity (Scheme 2).[40] The best yield of KMF was achieved with KCl and trimethylsilyl cyanide. KBr and KF are in combination with (CH₃)₂SiCN less reactive with respect to the conversion of BF₃OEtO into K[B(CN)]⁻. If lithium bromide was used instead of a potassium salt, dicyanodifluoroborates were formed almost exclusively (Scheme 2). Thus, the reaction of BF₃OEtO,

\[
\text{(CF₃SO₂)}₂O + \text{Na[BF₄]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
\]

[c] The mixture was stirred for 1 h at 50 °C before heating to 100 °C. The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
\]

[c] The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
\]

[c] The mixture was stirred for 1 h at 50 °C before heating to 100 °C. The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
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\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
\]

[c] The mixture was stirred for 1 h at 50 °C before heating to 100 °C. The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
\]

[c] The mixture was stirred for 1 h at 50 °C before heating to 100 °C. The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

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\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
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[c] The mixture was stirred for 1 h at 50 °C before heating to 100 °C. The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
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[c] The mixture was stirred for 1 h at 50 °C before heating to 100 °C. The mixture was stirred for 5 h at 100 °C before heating to 120 °C.

\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
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\[
\text{BF₃OEtO} + \text{Na[B(CN)]} \rightarrow \text{BF₃OEtO} + \text{Na[B(CN)]} 
\]
Cyanofluoroborates from cyanohydridoborates

An alternative synthetic approach to tricyanofluoroborates is based on the easily accessible potassium tricyanohydridoborate \( \text{K}[\text{BH}(\text{CN})]_3 \) (KMH) as the starting compound. The hydrogen atom in \( \text{[BH(CN)]}^+ \), which is protic in nature, can be replaced either directly by fluorine or by a substituent that is easily exchanged against fluorine in a subsequent second step (Table 2).\(^\text{[20]}\)

The transformation of \( \text{K}[\text{BH}(\text{CN})]_3 \) into \( \text{K}[\text{BF}(\text{CN})]_3 \) can be conveniently carried out in a single step by direct fluorination using elemental fluorine (entry MHB1), F-TEDA (entry MHB2), with \( \text{(CH}_3)_2\text{SiCN} \) can be easily tuned by the selection of the appropriate alkali metal salt.

The reaction of neat trimethylsilyl cyanide with BF\(_3\)OEt\(_2\) described in the literature, resulted in the formation of \( \text{(CH}_3)_2\text{SiCNBF(CN)}_2 \). This silyl derivative reacted even at room temperature with trimethylsilyl cyanide to give \( \text{(CH}_3)_2\text{SiNCBF(CN)}_2 \).\(^\text{[21]}\) The addition of alkali metal halides or potassium cyanide resulted in a reduction of the Lewis acidity of the reaction mixture (Scheme 2). Thus, this new protocol allowed for the fine tuning of the Lewis acidity resulting in the formation of alkali metal tricyanofluoroborates or dicyanofluoroborates in high selectivities.

**Scheme 2.** Preparation of KMF\(_2\) and KDF\(_2\) from BF\(_3\)OEt\(_2\). One formula unit of NaDF\(_2\) \( \text{K}[\text{BH}(\text{CN})]_3 \) in the crystal (displacement ellipsoids at 50% probability; H atoms are shown with arbitrary radii.) Selected bond lengths (\( \text{Å} \)) and angles (\( ^\circ \)) (range of bond lengths and angles where applicable): B-F 1.392(2)-1.396(2), B-C 1.623(2)-1.630(3), C-N 1.414(3)-1.417(2), B-C-N 177.9(2)-178.5(2), C-B-F 109.31(14)-110.28(15), C-B-C 108.15(15), F-B-F 108.89(14), Na-F 2.278(2)-2.296(2), Na-N 2.439(2)-2.741(2), Na-O 2.3956(11).

**Table 2.** Conversion of cyanohydridoborate anions \( \text{[BH}(\text{CN})]^{-} \) (MHB) and \( \text{[BH}_{3}(\text{CN})]^{-} \) (DH9) into cyanofluoroborate anions \( \text{[BF}(\text{CN})]^{-} \) (MFB) and \( \text{[BF}_{3}(\text{CN})]^{-} \) (DFB), respectively.

| Entry | Starting material | Reagent/Solvent | T [°C] | t | Product | Yield [%] |
|-------|------------------|----------------|--------|---|---------|----------|
| MHB1  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | F\(_2\)/aHF\(^{[a]}\) | 78-0 | 14 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 88 |
| MHB2  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | F-TEDA\(^{[b]}\)/CH\(_3\)CN | 52 | 72 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 36 |
| MHB3  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | XeF\(_2\)/CH\(_3\)CN | 52 | 48 h | \( \text{[BF}(\text{CN})]^{-} \) | 74 |
| MHB4  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | K\(_2\)(NF\(_2\))/aHF | r.t. | 14 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 15 |
| MHB5  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | ECF\(^{[c]}\)/aHF | 0-5 | | \( \text{[BF}(\text{CN})]^{-} \) | 45 |
| MHB6  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | 1. Cl\(_2\)/CH\(_3\)CN | 1.78-0 | 1.14 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 80 |
| MHB7  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | 2. (CH\(_3\)O)\(_2\)N/CH\(_3\)CN | 2. r.t. | 2.14 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 39\(^{[e]}\) |
| MHB8  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | 3. Cl\(_2\)/CH\(_3\)CN | 1.78-0 | 1.1 h | \( \text{[BF}(\text{CN})]^{-} \) | 67 |
| MHB9  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | 1. Et\(_2\)N/CH\(_3\)CN | 2.50 | 2.24 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 90 |
| MHB10 | \( \text{K}[\text{BH}(\text{CN})]_3 \) | 2. Et\(_2\)N/CH\(_3\)CN | 2. r.t. | 2.4 d | | 61 |
| MHB11 | \( \text{K}[\text{BH}(\text{CN})]_3 \) | Br\(_2)/\text{Et}_3\text{N}\text{H}_3\text{F} | 50 | 3 d | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 90 |
| MHB12 | \( \text{EMIm}\)[\(\text{BH(CN)}\] | 1. Cl\(_2\)/CH\(_3\)CN\(^{[d]}\) | 1. r.t. | 1.15 h | \( \text{EMIm}\)[\(\text{BF(CN)}\] | 77\(^{[d]}\) |
| MHB13 | \( \text{Na}[\text{BH}(\text{CN})\text{OC(O)Et}] \) | 1. Br\(_2)/\text{Et}_3\text{N}\text{H}_3\text{F} | 1. r.t. | 1.1 min | \( \text{EMIm}\)[\(\text{BF(CN)}\] | 75 |
| DHB1  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | XeF\(_2\)/CH\(_3\)CN | 40-50 | 48 h | \( \text{[BF}_{3}\text{(CN)}]^{-} \) | 28 |
| DHB2  | \( \text{K}[\text{BH}(\text{CN})]_3 \) | 1. Cl\(_2\)/CH\(_3\)CN | 1.78-0 | 1.1 h | \( \text{[BF}(\text{CN})]^{-} \) | 30 |
| DHB3  | \( \text{EMIm}\)[\(\text{BH(CN)}\] | 1. Br\(_2)/\text{Et}_3\text{N}\text{H}_3\text{F} | 2.40 | 2.24 h | \( \text{EMIm}\)[\(\text{BF(CN)}\] | 70\(^{[f]}\) |

\( ^{[a]} \text{aHF = anhydrous HF.} \)
\( ^{[b]} \text{F-TEDA = 1-Chloromethyl-4-fluoro-1,4-diazabicyclo[2.2.2]octane-1,4-dilium bis(tetrafluoroborate), Selectfluor.} \)
\( ^{[c]} \text{ECF = Electrochemical fluorination (Simons process).} \)
\( ^{[d]} \text{Purity: 87%} \)
\( ^{[e]} \text{[EMIm][BF(CN)]}_3 \) was isolated in 84% yield.\(^{[17]}\) The yield of the fluorination was 92%.\(^{[17]}\) [EMIm][BF(CN)]\(_3\) was isolated in 79% yield.\(^{[17]}\) The yield of the fluorination was 89%.
or xenon difluoride (entry MHB3). The reaction of K[BH(CN)]$_2$ with F$_2$ in anhydrous HF is accompanied by partial attack of the cyano groups (Figure 1). After aqueous work-up the acid amide [BF(CN)$_3$][C(O)NH$_3$]$^+$ was identified by NMR spectroscopy and mass spectrometry. A small sample of [nBu$_4$N][BF(CN)$_3$][C(O)NH$_3$]$^+$ was obtained by selective precipitation from an aqueous solution and characterized by multinuclear NMR spectroscopy, in detail (see Supporting Information). Dehydration of oxalyl chloride or phosgene gives [BF(CN)$_3$]$^+$ providing KMF$_2$ in an overall yield of 88%. Most likely, [BF(CN)$_3$][C(O)NH$_3$]$^+$ was formed by hydrolysis of BF(CN)$_3$[CF$_2$=N]$_2$ during aqueous work-up. The iminium derivative BF(CN)$_3$[CF$_2$=N]$_2$ was identified in anhydrous HF (aHF) as component of the reaction mixture by $^{19}$B and $^{19}$F NMR spectroscopy (Figure 1). In addition, the NMR signals of the related diiminium cation [BF(CN)$_2$][C(O)NH$_2$]$^+$ were assigned (Figure 1). The NMR spectroscopic data are listed in detail in the Supporting Information. Since the cyanoborate anions [BH(CN)$_3$]$^-$ and [BF(CN)$_3$]$^-$ are stable against aHF at room temperature for at least one day, the addition of HF to the cyano group(s) has to be promoted by F$_2$. A similar reactivity was found if BF$_3$ was added to aHF, as well.$^{14}$ The reaction of [BF(CN)$_3$]$^-$ with elemental fluorine in aHF to give BF(CN)$_3$[CF$_2$=N]$_2$ is slow, while fluorination of [BF(CN)$_3$]$^-$ with F$_2$ yields significantly more BF(CN)$_3$[CF$_2$N]$_2$. Presumably, the attack at the cyano group occurs before or in parallel to the fluorination of the B–H moiety.

The transformation of cyano into iminium groups at boron is related to the activation of nitriles in aHF. Fluorinated nitriles were found to add two equivalents of HF, for example, trifluoroacetonitrile gave CF$_3$CF$_2$NH$_2$.$^{14}$ In contrast, more electron rich nitriles, which have a CH$_2$ instead of a CF$_3$ group adjacent to CN, yielded a mixture of the protonated nitrile RCH$_2$CNH$^+$, the iminium species RCH$_2$CF$_2$=N$^+$, and the ammonium ion RCH$_2$CF$_2$NH$_3$.$^{14}$ Cyano groups bonded to boron are even more electron rich, which for example is evident from i(CN) that decreases in the order RCF$_2$CN > RCH$_2$CN > [R$_3$BCN]$^-$.$^{15}$

Thus, the low reactivity of cyanoborates against anhydrous HF is presumably related to the comparably high electron density of the cyano group. So, a promoter such as fluorine or bromine is necessary to activate a B–C≡N–H$^-$ unit towards a fluoro-ride anion attack at carbon.

A further example for a direct fluorination of K[BH(CN)$_3$] is the reaction with K$_3$[NiF$_6$] in anhydrous HF (entry MHB4). Although the yield was quite low, this reaction tempted us to perform an electrochemical fluorination (ECF) of K[BH(CN)$_3$] using Ni-anodes in anhydrous HF (Simons process).$^{11}$ K[BH(CN)$_3$]$_2$ was obtained in a moderate yield of 45% (entry MHB5). However, this reaction is remarkable because it is the first example for an electrochemical fluorination of a B-containing species. Furthermore, this procedure might be of interest for large-scale applications since the Simons process is well established on an industrial scale and it has the advantage that only anhydrous HF and electricity are consumed during this process.

The [BH(CN)$_3$]$^-$ anion was chlorinated or brominated to give [BX(CN)$_3$]$^-$ (X = Cl,$^{14}$ Br)[$^{15}$]. These anions were subsequently converted into MFB by fluorination with Et$_3$N·3HF (TREAT-HF), [Me$_3$NF], or KF (entries MHB6-MHB12, Table 2). Similar to K[BH(CN)$_3$]$_2$, the RTIL [EMIm][BH(CN)$_3$]$_2$ was converted into [EMIm][BF(CN)$_3$]$_2$ via [EMIm][BC(CN)$_3$]$^{14}$ with elemental chlorine and Et$_3$N·3HF (MHB12).

The reaction of Na[BH(CN)$_3$][OC(O)Et]$^{14}$ with elemental bromine in Et$_3$N·3HF gave K[BF(CN)$_3$][OC(O)Et]$_2$ that subsequently converted into K[BF(CN)$_3$]$_2$ in 75% yield using (CH$_3$)$_2$SiCN in the presence of the Lewis acid (CH$_3$)$_2$SiCl$_2$ (entry MHB13). The hydrolytically stable intermediate [BF(CN)$_3$][OC(O)Et]$^-$ was isolated as [Ph$_2$P]$^+$ salt in 86% yield and characterized by single-crystal X-ray diffraction (Scheme 3).

Similar to the fluorination of tricyanohydridoborates to give tricyanofluoroborates, dicyanodihydridoborates K[BH(CN)$_3$]$_2$ yielded dicyanodifluoroborates K[BF(CN)$_3$]$_2$ (Table 2). The yields
Scheme 3. Synthesis of [Ph₃P]BF(CN)(OC(O)Et) and one formula unit of the borate anion in the crystal (displacement ellipsoids at 50% probability; H atoms are shown with arbitrary radii.) Selected bond lengths (Å) (range of bond lengths and angles where applicable): B–F 1.394(3), B–O 1.472(3), B–C 1.621(4)–1.630(4), C–N 1.143(4)–1.146(3), C–O 1.335(3), C–C 1.213(3), O(O)–C 1.507(4), C–CH 1.518(4), B–C–N 177.1(3)–177.2(3), F–B–O 107.6(2), C–B–F 109.02(2)–109.2(2), C–B–C 109.8(2), C–B–O 110.5(2)–110.7(2), B–O 119.9(2), C–O–C 123.1(2), O–C–C 112.4(2), O = C–C 124.4(3).

are typically lower, which at least in part is due to the higher reactivity of [BH₃(CN)]⁻ compared to [BH₃]⁻. As a further consequence of this higher reactivity, fluorinations of K[BH₃(CN)] are slightly faster than fluorinations of K[BH(CN)]₂. K[BH₃(CN)] and two equivalents of XeF₂ gave K[BF(CN)]₂ in 28% yield (entry DHB1). Care has to be taken because even solid K[BH₃(CN)]₂ reacts violently with XeF₂, which is in contrast to KMHB. So, K[BH₃(CN)]₂ and XeF₂ were dissolved in acetone-tritile, separately, and these solutions were combined.

The successful chlorination/fluorination of Kt[BH₃(CN)] in Kt[BF(CN)]₂ (Table 2). K[BH₃(CN)]₂ was converted into K[B(CN)]₂ using elemental chlorine that was subsequently reacted with Et₃N·3HF to give Kt[B(CN)]₂ in 30% yield (entry DHB2). The analogous synthesis using [EMIm][BH₃(CN)] and tert-butyl hypochlorite as starting compounds gave [EMIm][BCl(CN)]₂ that was treated with Et₃N·3HF to yield [EMIm][BF₃(CN)] in 70% yield (entry DHB3).

Conclusions

A series of convenient syntheses towards alkali metal cyanofluoroborates was developed. Many of these syntheses provide an easy scalable access to salts that are of interest for the preparation of diverse materials, which are valuable for various applications, especially for electrochemical devices. The methods presented are diverse with respect to the starting materials, reaction conditions, and mechanisms. They include Lewis acid catalyzed transformations providing straight forward access even to tetracyanoborates and perfluoralkylcyanoborates, direct fluorinations using for example, elemental fluorine, combined halogenation–fluorination reactions, as well as electrochemical fluorination (ECF) according to the Simons process. The latter process is well established on an industrial scale and it is the first example for an electrochemical fluorination of a boron species, at all.

Furthermore, the reactivity studies provide valuable insights into the chemistry of cyanoborates and cyano derivatives/nitriles, in general. The results presented show that electron-rich cyano groups are less prone to attack by HF. A promoter is necessary to trigger the conversion of cyano groups into iminium groups. In contrast, electron-poor nitriles such as CF₃CN are easily attacked by HF.

Experimental Section

General

Reactions with air- and moisture-sensitive compounds were performed in round-bottom flasks or glass tubes equipped with valves with PTFE stems (Rettenberg, Göttingen) under Ar using Schlenk techniques. Fluorine and anhydrous hydrogen fluoride (aHF) were manipulated in a stainless-steel apparatus of known volume equipped with capacitance pressure gauges (type 626BX13TBE and 626BX01TBE MKS Instruments and with bellow valves (type BPV2504 Balzers; type SS-4H and SS-8BG Swagelok) and with Cajon® VCR fittings. Fluorination reactions in aHF were performed in 100 or 250 mL reactors consisting of a PFA bulb with a NS29 socket standard taper (Bohlender, Lauda, Germany) in connection with a PFA NS29 core standard taper and a PFA needle valve (type 204-30 Galtek®, Entegris). The parts were held together with a metal compression flange. ¹H, ³¹P and ¹³C NMR spectra were recorded at 25 °C in (CD₂)₂CO or CD₂CN on a Bruker Avance 500 NMR spectrometer. The NMR signals were referenced against TMS (¹H, ¹³C, BF₃-Ofet in CDCI₃ with δ(TMS) = 32.083974 %, CFCI₃ with δ(C) = 94.904011 %, and 85 % aqueous H₂PO₄, δ(P) = 40.480742 % as external standard.

¹H and ¹³C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively (δ(H): (CD₂)₂CO or CD₂CN, 2.05 ppm, CD₂HCO 1.94 ppm; δ(C): (CD₂)₂CO 206.26 and 29.84 ppm, CD₂CN 118.26 and 1.32 ppm). IR spectra were recorded at r.t. on a Bruker Alpha spectrometer with an apodized resolution of 4 cm⁻¹ in the attenuated total reflection (ATR) mode in the region of 4000-500 cm⁻¹ using a setup with a diamond crystal. Raman spectra were recorded at r.t. on a Bruker IFS-120 spectrometer with an apodized resolution of 2 cm⁻¹ using the 1064 nm excitation line of a Nd:YAG laser on crystalline samples contained in melting point capillaries in the region of 3500–100 cm⁻¹. MALDI mass spectra were acquired on an Autoflex II LRF (Bruker). Elemental analysis (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech). All yields are reported with respect to the starting boron compound. If not stated differently, the purity of the borates was 96% or higher as assessed by NMR spectroscopy. The NMR spectroscopic data of the salts are given in the Supporting Information.

Chemicals

All standard chemicals were obtained from commercial sources and used without further purification. Xenon difluoride was purchased from ABCR. F-TEDA (Selectfluor®) and Et₃N·3HF were obtained from Sigma–Aldrich. tert-Butyl hypochlorite was synthesized according to a literature protocol. Anhydrous HF and elemental F₂ were obtained from Solvay Fluor GmbH. Kt[BH₃(CN)] (K, [EMIm]Cl) and K[BH(CN)] (K, [EMIm]Cl) Na[BH(CN)]₂(OC(O)Et) [EMIm][BCl(CN)]₂ and [EMIm][BF₃(CN)] were prepared as described elsewhere. Solvents were dried according to standard protocols and stored in flasks equipped with valves with PTFE stems under an Ar atmosphere.

Caution! Elemental fluorine, anhydrous HF (aHF), and xenon difluoride 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.
Synthesis: Lewis and Brønsted acid catalyzed syntheses (Table 1)

**K[BF(CN)]₃** from Na[BF₄] and TMSOTf (entry MFB1): Na[BF₄] (1.00 g, 9.11 mmol) was suspended in (CH₂)₃SiCN (110.0 mL, 87.7 mmol) and TMSOTf (trimethylsilyl triflate, CF₃SO₂OSi(CH₃)₃) (1.0 mL, 5.5 mmol, 60 mol% calculated for Na[BF₄]) was added. The mixture was stirred for 3 h at r.t. All volatiles were removed under reduced pressure. The dark-brown residue was dried under vacuum, treated with aqueous H₂O₂ (10 mL, 35% v/v), and K₂CO₃ (3 g) was added in portions. This mixture was stirred for 1 h at r.t. All volatiles were removed using a rotary evaporator. The residue was extracted with acetonitrile (3 × 20 mL). The combined acetonitrile phases were dried with KCl, filtered, and the filtrate was concentrated with a rotary evaporator to about 12 mL. The addition of CH₂CN (0.5 mL). After 5 min, water (3 mL) and K₂CO₃ (3 g) was added. The mixture was stirred for 4.5 h at r.t. The dark suspension was filtered and the filtrate was used for the next synthesis (entry MFB2b). The tan solid residue was dissolved in CH₂CN (50 mL) and the solution was treated with iso-propanol (0.5 mL). After 5 min, water (3 mL) and K₂CO₃ (5 g) were added and the suspension was stirred for 30 min at r.t. The upper colorless liquid phase was separated. The remaining acetonitrile phase was decanted from the precipitate, which was extracted with acetonitrile (5 × 20 mL). The combined CH₂CN phases were dried with KCl, filtered, and the filtrate was concentrated with a rotary evaporator to about 12 mL. The addition of CH₂Cl₂ (100 mL) resulted in a colorless K[BF(CN)]₃ that was filtered off and dried under vacuum. Yield: 110.9 g (74.9 mmol, 82%).

**Entry MFB2b:** Na[BF₄] (10.0 g, 91.1 mmol) was suspended in (CH₂)₃SiCN (40.0 mL, 318.7 mmol). The filtrate of entry MFB2a was added and the reaction was performed similar to entry MFB2a. Yield: 13.8 g (93.9 mmol, 103%). The isolated material included Na[BF₄] that had formed during entry MFB2a, which explains the yield of more than 100%. The combined yield of entries MFB2a and MFB2b was 24.8 g (168.8 mmol, 93% calculated for Na[BF₄] of both entries).

**K[BF(CN)]₃** from Na[BF₄] and TMSOTf (entry TCB2): Na[BF₄] (1.00 g, 9.11 mmol) was suspended in TMSCN (15.0 mL, 119.5 mmol) and reacted with TMSOTf (1.0 mL, 5.5 mmol, 60 mol% calculated for Na[BF₄]) for 22 h at 100 °C. All volatiles were removed in a vacuum and the black residue was dried under vacuum. The solid was dissolved in the acetonitrile (15 mL) and treated with iso-propanol (2 mL). Water (4 mL) and K₂CO₃ (5 g) were added, the acetonitrile phase was separated, and the residue was extracted with CH₂CN (4 × 30 mL). The combined organic phases were dried with K₂CO₃ and filtered. The filtrate was concentrated with a rotary evaporator to about 4 mL. The addition of CH₂Cl₂ (75 mL) resulted in a precipitate that was filtered off and dried under vacuum. Yield: 1.31 g (8.50 mmol, 93%).

**Synthesis:** Conversion of BF₃·OEt₂ into cyanofluoroborates (Scheme 2)

K[BF(CN)]₃ from BF₃·OEt₂ and KCl: KCl (1.49 g, 20.0 mmol) was reacted with BF₃·OEt₂ (2.5 mL, 20.3 mmol) and (CH₂)₃SiCN (8.7 mL, 69.3 mmol) at 0 °C. The mixture was stirred for 30 min at 10 °C. Subsequently, all volatiles were removed in a vacuum. The residue was dissolved in acetonitrile (15 mL) and iso-propanol (15 mL) was added. The mixture was stirred for 1 h at r.t., treated with K₂CO₃ (5 g) and stirred for another hour at r.t. The suspension was filtered and CH₂Cl₂ (500 mL) was added. The pale-brown precipitate was filtered off and dried under vacuum. Yield: 2.13 g (14.5 mmol, 73%).

**Synthesis:** Fluorination reactions of cyanohydrinoborates (Table 2)

**[Ph₃P][BF(CN)]₃** from K[BH(CN)]₃ and F₂ (entry MHB1): K[BH(CN)]₃ (280 mg, 2.17 mmol) was dissolved in aHF (10 mL) in a 100 mL PFA flask. The solution was cooled to −78 °C and F₂ (90 mg, 2.4 mmol) was added. The mixture was slowly warmed to r.t. and stirred overnight. All volatiles were removed under reduced pressure, the residue was dissolved in water (10 mL), and an aqueous solution of KF (910 mg, 2.17 mmol, 10 mL) was added. The mixture was extracted with CH₂Cl₂ (3 × 10 mL), the combined organic phases were evaporated, and the colorless residue that consisted of [Ph₃P][BF(CN)]₃ and [Ph₃P][BF(CN)₂Cl](NH₃) was dried under vacuum. The mixture was taken-up into CH₂CN (7 mL) and Et₃N (0.8 mL, 5.74 mmol), and phosgene (103 mg, 1.04 mmol) was added at −78 °C. The mixture was warmed to room temperature and stirred overnight. All volatiles were removed in a vacuum to give solid [Ph₃P][BF(CN)]₃. Yield: 850 mg (1.90 mmol, 88%).

**[K[BH(CN)]₃]** from K[BH(CN)]₃ and XeF₂ (entry MHB3): K[BH(CN)]₃ (110 mg, 0.85 mmol) and XeF₂ (200 mg, 1.18 mmol) were dissolved in CH₂CN (4 mL). The mixture was stirred for 2 d at 50 °C, cooled to r.t., and all volatiles were removed under reduced pressure. The residue was dissolved in THF (3 mL) and CH₂Cl₂ (15 mL) was added. The colorless solid was filtered off and dried under vacuum. Yield: 93.0 mg (0.63 mmol, 74%).

K[BF(CN)]₃ from K[BH(CN)]₃ by ECF (entry MHB5): A stainless steel electrochemical fluorination apparatus equipped with Ni-electrodes (a description was given elsewhere) was charged with aHF (250 mL). The aHF was dried at 5.2 V until the current dropped to less than 0.6 A. A solution of Na[HB(CN)]₃ (5 g, 44.3 mmol) dissolved in aHF (10 mL) was added. The electrolysis (voltage: 5.1–5.4 V; current density: 0.2 A·dm⁻²) was conducted for 7 h with a cell temperature of 0 °C. The temperature of the reflux condenser was maintained at −35 °C. After consumption of 10560 C electricity, the HF solution was removed from the cell. The HF was distilled off and the residue was dried under vacuum. The solid residue was taken up into THF (15 mL) filtered, and the remainder was washed with THF (3 × 5 mL). Water (2 mL) and K₂CO₃ (5 g) were added to the combined THF solutions. The mixture was stirred for 10 min, filtered, and the residual K₂CO₃ was extracted with THF (2 × 5 mL). The volume of the combined THF phases was reduced to 4 mL. The addition of CH₂Cl₂ (100 mL) resulted in a precipitate (3.33 g) that consisted of K[BF(CN)]₃ (86%), K[BF(CN)]₃·2Cl(NH₃) (12%), and K[BH(CN)]₃ (2%). The mixture (3.33 g) was dissolved in THF (10 mL) and Et₃N (4 mL, 28.7 mmol). Oxaly chloride (3 mL, 35.0 mmol) was added and the mixture was stirred for 2 h at r.t. The suspension was filtered and the remainder was washed with THF (20 mL). The combined THF phases were evaporated. The residue was dissolved in water (7 mL), filtered, and all volatiles were removed under reduced pres-
sure. The residue was dissolved in THF (3 mL) and K[BF(CN)]$_4$ was precipitated by the addition of CH$_2$Cl$_2$ (100 mL). The product was filtered off, washed with CH$_2$Cl$_2$ (10 mL), and dried under vacuum. Yield: 2.93 g (20.0 mmol, 45%).

[nBu$_4$N][BF(CN)$_3$] from [KH[B(CN)$_2$]$_n$, Cl$_n$, and [(CH$_3$)$_4$NF (entry MHB6): [KH[B(CN)$_2$]$_n$] (1.0 g, 7.75 mmol) was dissolved in CH$_2$CN (10 mL). Cl$_2$ gas (6.4 g, 90.3 mmol) was added. The mixture was stirred for 1 h at –78 °C and stored overnight at 0 °C. All volatiles were removed in a vacuum and the residue was dissolved in CH$_2$CN (20 mL). Anhydrous [(CH$_3$)$_4$NF (500 mg, 5.37 mmol) and after 2 h 600 mg, 6.44 mmol) was added and the mixture was stirred overnight at rt. After filtration, the filtrate was evaporated with a rotary evaporator. The residue was taken up into water (30 mL), all insolubles were filtered off, and the filtrate was treated with an aqueous solution of [nBu$_4$N]OH (12.0 mL, 20 wt%, 9.2 mmol). The precipitate was filtered off, washed with water, and dried under vacuum. Yield: 2.16 g (6.17 mmol, 80%).

[nBu$_4$N][BF(CN)$_3$] from [KH[B(CN)$_2$]$_n$, BuOCl, and Et$_3$N·3HF (in situ (entry MHB11): [KH[B(CN)$_2$]$_n$] (770 mg, 5.97 mmol) was dissolved in Et$_3$N·3HF (10 mL, 9.9 g, 63.1 mmol) and elemental bromine (2.8 g, 17.6 mmol) was added. The reaction mixture was warmed up to 50 °C and stirred for 3 d. The mixture was poured into water (50 mL) at rt and K$_2$CO$_3$ (ca. 10 g) was added until the mixture was found to be basic. The suspension was filtered and the filtrate was treated with an aqueous solution of [nBu$_4$N]OH (10 mL, 20 wt%, 7.63 mmol). The solid was filtered off and dried under vacuum. Yield: 1.89 g (5.40 mmol, 90%).

[EMIm][BF(CN)$_3$] from [EMIm][BH(CN)$_2$]$_n$, Cl$_n$, and Et$_3$N·3HF (entry MHB12): [EMIm][BH(CN)$_2$]$_n$ was synthesized as described in the literature from [EMIm][BH(CN)$_2$]$_n$ and Cl$_n$ in 84% yield. [EMIm][BH(CN)$_2$]$_n$ (200 mg, 0.85 mmol) was placed into a 100 mL PFA flask and Et$_3$N·3HF (40 mL, 4.0 g, 24.7 mmol) was added. The mixture was stirred at 50 °C for 48 h, cooled to rt., and water (5 mL) and K$_2$CO$_3$ (5 g) were added. All volatiles were removed in a vacuum. The residue was dissolved with CH$_2$Cl$_2$ (5 × 5 mL). The combined organic phases were dried with K$_2$CO$_3$ (5 g), and the solvent was removed under reduced pressure. Yield: 171 mg (0.78 mmol, 92% calculated for [EMIm][BH(CN)$_2$]$_n$); overall yield calculated for [EMIm][BH(CN)$_2$]$_n$: 77%.

Crystallographic data
Deposition numbers 2002467, 2002468, 2002469, and 2002470 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of interest
The authors disclose no conflict of interest.

Keywords: cyanoborates · electrochemical fluorination · fluorination · fluoroborates · ionic liquids

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