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1. Introduction

In 1992 the first air and water stable room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF₄]), was described by Wilkes *et al.*¹ This finding triggered intensive research in the field of ionic liquids, the study of their physicochemical properties, and investigation of possible practical applications in the fields of materials science, electrochemistry, and chemical engineering.^{2,3} Very soon it turned out that tetrafluoroborate-ILs are not fully hydrolytically stable⁴ and possess relatively high viscosity.⁵ These non-optimal properties of tetrafluoroborate-ILs have limited their practical applications, in particular, in electrochemical devices. Thus, the demand for RTILs with improved properties

Alkoxycyanoborates: metal salts and low-viscosity ionic liquids †‡

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Syntheses of alkoxytricyanoborates and dialkoxydicyanoborates are described using different readily available boron-based starting compounds such as tetrahydrido-, tetrafluoro-, and tetraalkoxyborates, as well as trimethoxyborane and trimethylsilylcyanide as cyano sources. The salts obtained have been characterized by NMR and vibrational spectroscopy, elemental analysis, and DSC and DTA measurements. In addition to alkali metal salts, room temperature ionic liquids $[EMIm][ROB(CN)_3]$ (R = CH₃, C₂H₅, CH₂CF₃) have been prepared. These ionic liquids exhibit very low melting points or glass transition temperatures, low viscosities, and high chemical, thermal, and electrochemical stabilities. The influence of alkyl chain length and the effect of partial fluorination of the alkoxy group on these properties have been elucidated. The advantageous physicochemical properties, in general, and in conjunction with the easy accessibility make alkoxytricyanoborate-ILs interesting compounds for potential applications in materials sciences. Furthermore, the Li salt of the $[CH_3OB(CN)_3]^-$ ions was prepared and found to provide a significantly higher solubility in propylene carbonate compared to lithium tetracyanoborate. Alkali metal salts Li[CH₃OB(CN)₃]·H₂O, Na[CH₃OB(CN)₃]·H₂O, K[CH₃OB(CN)₃], Na[C₂H₅OB(CN)₃], and Na[CF₃CH₂OB(CN)₃]·0.5H₂O have been characterized by single-crystal X-ray diffraction.

stimulated the search for alternative anions in particular by modification of the parent tetrafluoroborate $[BF_4]^-$ anion.

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The formal replacement of all four fluorine against cyano groups in $[BF_4]^-$ leads to the tetracyanoborate anion $[B(CN)_4]^-$ (**TCB**, Fig. 1) that was reported independently by Willner *et al.*⁶ and Kouvetakis *et al.*⁷ in 2000. The **TCB** anion is hydrolytically stable^{6,8} and in 2003 first **TCB**-ILs have been reported.^{5,9,10} **TCB**-ILs have superior properties such as low viscosity and high specific conductivity in conjunction with high electrochemical and thermal stability compared to tetrafluoroborate-ILs.^{5,9,10} Therefore, they have been tested in many different applications, in particular in electrochemical and optoelectronic devices,^{3,10} *e.g.* electrical storage devices, *i.e.* batteries,¹¹ supercapacitors^{12,13} and dye-sensitized solar cells (DSSCs).^{13,14}

Later, it was found that ionic liquids based on mixed-substituted cyanoborate anions often exhibit properties that are even superior



Fig. 1 Tricyanoborate anions $[RB(CN)_3]^-$ (R = CN,^{5,9} H,¹⁵ F,⁵ Cl,¹⁸ perfluoroalkyl^{19,20})¹⁰ that have been used for the design of very low-viscosity room temperature ionic liquids (RTILs) and the ions $[B(CN)_4]^-$ (**TCB**) and $[BF(CN)_3]^-$ (**MFB**) in the crystals of their $[CH_3NH_3]^+$ salts.¹⁷

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compared to those of the respective TCB-ILs.^{5,10} In particular, mixed-substituted dicyano- and tricyanoborate anions are of interest (Fig. 1), since these anions retain the hydrolytical and chemical stability of the parent TCB anion, in general. Examples are the cyanohydridoborate anions $[BH(CN)_3]^-$ (MHB) and $[BH_2(CN)_2]^-$ (DHB)¹⁵ and the cyanofluoroborate anions $[BF(CN)_3]^-$ (MFB, Fig. 1) and $[BF_2(CN)_2]^-$ (DFB).^{16,17} Most likely, the reduced symmetry of such mixed-substituted borate anions is the reason for the improved properties of ILs based on them, such as lower viscosity and higher conductivity.

Perfluoroalkyl(fluoro)cyanoborate anions $[R^FBF_n(CN)_{3-n}]^ (R^F = perfluoroalkyl, <math>n = 0-2$) are a further class of mixed-substituted cyanoborate anions that provide access to low-viscosity RTILs with high thermal, chemical, and electrochemical stabilities.¹⁹⁻²¹ Salts of the anions $[R^FBF_n(CN)_{3-n}]^ (R^F = perfluoroalkyl, <math>n = 0-2$) are conveniently accessible from the corresponding perfluoroalkyltrifluoroborates²² using trimethylsilylcyanide as the cyanide source.^{17,19,20,23}

In addition to their use as components of ionic liquids, cyanoborate anions are applied as counterions for metal ions^{24–26} and reactive nonmetal cations, *e.g.* the trityl ion, Ph_3C^{+27} and the oxonium ion, $H_3O^{+.10,26,28}$ Furthermore, cyanoborate anions serve as versatile starting compounds for unprecedented and valuable borate anions and boranes, *e.g.* the very weakly coordinating anion $[B(CF_3)_4]^{-,29}$ the carboxylatoborate anion $[B\{C(O)OH\}_4]^{-,30}$ the anions $[(CF_3)_3BCPnic]^-$ (*Pnic* = N, P, As),³¹ the boron-centered nucleophile $B(CN)_3^{2^-,32}$ and the borane carbonyl $(CF_3)_3BCO.^{33}$

All cyanoborate-ILs mentioned above show exceptional properties making them interesting materials for diverse applications. However, there is still demand for cyanoborate anions having similar advantageous, tunable properties that are very easily accessible. In particular, for industrial applications, the aspect of availability is of outmost importance.

Here we report on a set of alkoxycyanoborate anions, which have in part been previously mentioned in patent applications by Lonza AG (Basel, Switzerland)³⁴ and Merck KGaA (Darmstadt, Germany).³⁵ Structures of alkali metal salts of the anions $[ROB(CN)_3]^-$ ($R = CH_3$, C_2H_5 , CH_2CF_3) are discussed. Furthermore, the syntheses and physicochemical properties of the respective EMIm-ILs are described.

2. Results and discussion

Synthesis of alkoxycyanoborates $Kt[(RO)_xB(CN)_{4-x}]$ (x = 1, 2, *Kt* = cation)

The different syntheses developed by us providing highly convenient access to dialkoxydicyanoborates and alkoxytricyanoborates are summarized in Scheme 1. Methoxy, ethoxy, and 1,1,1trifluoroethoxy groups have been selected as substituents since we are particularly interested in low-viscosity and highly conducting RTILs for which ions with a low molecular weight are beneficial.³⁶

Tetrafluoroborates, tetraalkoxyborates, and tetrahydridoborates have been successfully employed as starting compounds. Despite these easy-to-handle salts, trimethoxyborane (trimethyl borate) was used as a starting material, as well. These compounds





are all cost-effective and readily available boron-containing commodities. In all cases trimethylsilylcyanide (TMSCN) served as a cyanide source that was prepared also *in situ* from trimethylsilylchloride and potassium or sodium cyanide.

Yields of up to 99% have been achieved, *e.g.* starting from Li[BF₄], TMSCN, and (CH₃)₃SiOCH₃, surprisingly, even at room temperature (Scheme 1). This latter reaction is noteworthy since the well-known tricyanofluoroborate anion ([BF(CN)₃]⁻, **MFB**) is not formed under these reaction conditions (Scheme 1). Similarly, Na[BF₄] was converted into [ROB(CN)₃]⁻ (R = CH₃, C₂H₅) in yields of 74–76% (Scheme 1). The slightly higher yield starting from Li[BF₄] instead of Na[BF₄] may be attributed to the higher fluoride ion affinity of the Li⁺ cation, which results in a more efficient replacement of fluorine against cyano and alkoxy groups at boron. Furthermore, the higher solubility of Li[BF₄] compared to Na[BF₄] might have a beneficial influence on the conversion, as well. A similar beneficial effect of Li⁺ was reported by us earlier for the conversion of tetrafluoroborates into tricyanofluoroborates.¹⁶

Tetrahydridoborates were converted into tetraalkoxyborates in a first step, followed by the reaction with TMSCN to give alkoxytricvanoborates (Scheme 1). Again, high vields have been achieved (up to 91%). The application of trimethoxyborane as the starting compound was demonstrated by its conversion into alkoxytricyanoborates in a one pot reaction with sodium methoxide and TMSCN (Scheme 1). A related synthesis for K[CH₃OB(CN)₃] starting from trimethoxyborane was described in a patent application filed by Lonza AG (Basel, Switzerland), earlier.34 However, KCN and TMSCN in conjunction with trimethoxyborane were used in the aforementioned patent and not NaOCH3 and TMSCN as described herein.

Dialkoxydicyanoborates $Na[(RO)_2B(CN)_2]$ (R = CH₃, CF₃CH₂) were selectively obtained via careful tuning of the reaction conditions. The formation of Na[(CH₃O)₂B(CN)₂] was achieved by using two equivalents of TMSCN. The stronger electronwithdrawing and slightly more sterically demanding 1,1,1trifluoroethoxy group results in a slower replacement against a cyano group. Thus, the preparation of $Na[(CF_3CH_2O)_2B(CN)_2]$ was accomplished by simply lowering the reaction temperature to room temperature compared to the synthesis of Na[CF₃CH₂OB(CN)₃] that was performed at 80 °C (Scheme 1).

Alkoxytricyanoborates are stable in aqueous solution and tolerate dilute basic and acidic conditions, as well. In contrast, dialkoxydicyanoborates decompose in air.

The protocols presented in Scheme 1 offer cost-efficient entries to alkoxytricyanoborates $M[ROB(CN)_3]$ (M = Na, K) using cheap and commercially available chemicals. Hence, these borates are interesting reagents for further derivatizations, for instance for the conversion into tetracyanoborates (Scheme 2).³⁷

Furthermore, these borates are valuable starting materials for metatheses. In Scheme 3 the preparation of various organic salts including EMIm- and BMPL-ILs with alkoxytricyanoborate anions is presented. Both EMIm- and BMPL-ILs are hydrophobic and thus separate from aqueous solution during metathesis. The synthesis of Li[CH₃OB(CN)₃] starting from Na[CH₃OB(CN)₃] exemplifies the preparation of metal alkoxytricyanoborates via metathesis.

Spectroscopic characterization

The cyanoborates have been characterized by multinuclear NMR and vibrational spectroscopy. In Fig. 2 the ¹H and ¹³C

	– (CH ₃) ₃ SiOCH ₃ (CH ₃) ₃ SiCN (CH ₃) ₃ SiCI (cat)					
K[CH ₃ OB(CN) ₃] + (CH ₃) ₃ SiCN	250 °C, 11 h autoclave	not isolated				
	[EMIm] H ₂ O	CI ➤ [EMIm][B(CN) ₄] (31%)				
Scheme 2 Conversion of K[CH ₃ O	B(CN) ₃] into K[B(CN) ₄]. ³⁷				

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[(C₂H₅)₄N][CH₃OB(CN)₃]↓

(84%)

[ROB(CN)3]⁻ + NaCl

[CH₃OB(CN)₃]⁻ + NaCl

CH₂Cl₂

(70-91%)

H₂O

H₂C

CH₂Cl₂

C₄H₀

(83%)

Li[CH₃OB(CN)₃] + NaCl↓

(99%)



NMR spectra of the EMIm-ILs are depicted. The ¹H NMR signals of the methoxy group in [CH₃OB(CN)₃]⁻ and of the CH₂ units in $[C_2H_5OB(CN)_3]^-$ and $[CF_3CH_2OB(CN)_3]^-$ show ³J coupling to ¹¹B as evident from the splitting of the signals into quartets of lines with equal intensities. In cases of $[C_2H_5OB(CN)_3]^-$ and $[CF_3CH_2OB(CN)_3]^-$, additional couplings to the CH₃ and CF₃ units are observed, respectively. Similarly, the ¹³C NMR spectra provide clear evidence for the presence of the respective cyanoborate anions, e.g. by the signals of the cyano groups that show the splitting into quartets of equal intensities due to the ¹J coupling to ¹¹B and, in addition, the ¹⁰B satellites that are septets of equal intensities (Fig. 2).

 H_2O , CH_2CI_2

The IR and Raman spectra of selected trimethoxyborates are depicted in Fig. 3. In all Raman spectra, the strongest signal at approximately 2206–2249 cm^{-1} refers to the CN stretching mode. In contrast, in the IR spectrum the corresponding bands are very weak and often their intensity is below the detection limit. The IR spectra of Li[CH₃OB(CN)₃]·H₂O and Li[CH₃OB(CN)₃] provide clear evidence for the effective removal of water upon drying since the bands typical for water are fully absent in the spectrum of Li[CH₃OB(CN)₃].

In Table 1 the band positions of the CN stretching modes of selected alkali metal alkoxytricyanoborates and related cyanoborates and their EMIm-ILs are listed. A comparison of $\nu \sim$ (CN) of the EMIM-ILs nicely demonstrates the decreasing electron density at boron in the order $[ROB(CN)_3]^-$ (R = CH₃, C_2H_5 < $[CF_3CH_2OB(CN)_3]^-$ < $[CF_3B(CN)_3]^- \approx [B(CN)_4]^-$, which is in line to the calculated band positions at the



Fig. 2 Sections of the ¹H, ¹H(¹⁹F), and ¹H(¹¹B) NMR spectra of the OCH_x units (x = 2 or 3; top) and ¹³C(¹H) NMR spectra of EMIm-alkoxytricyanoborates in (CD₃)₂CO.



B3LYP/6-311++G(d,p) level of theory (Table 1). The decrease in electron density is attributed to the electronic properties of the substituent bonded to the $B(CN)_3$ unit, *e.g.* alkoxy groups are more electron rich than perfluoroalkyl or cyano groups. This difference in electron density relates to the coordinative properties of the cyanoborate anions, thus, alkoxytricyanoborates are expected

to be better donors or ligands in coordination chemistry than perfluoroalkyltricyanoborates or the parent **TCB** ion, in general. However, the difference should be rather small.

The wavenumber of ν (CN) for the methoxytricyanoborates decreases in the order Li⁺ > Na⁺ > K⁺ > [EMIm]⁺. So, a weaker interaction of the cation with the cyanoborate anion results in a lower wavenumber, which is a typical feature for cyanoboron compounds as exemplified by a comparison to the literature known **TCB** salts^{6,8,15} listed in Table 1.

Structural characterization

Crystals of three alkali metal salts of the methoxytricyanoborate anions were characterized by single-crystal X-ray diffraction (Fig. 4 and Table 2). Li[CH₃OB(CN)₃] and Na[CH₃OB(CN)₃] crystallize with one water molecule per formula unit in the monoclinic space group Cc with Z = 4 and in the triclinic space group $P\overline{1}$ with Z = 2, respectively. In contrast, the potassium salt K[CH₃OB(CN)₃] crystallizes as anhydrous compounds in the monoclinic space group C2/c with Z = 8. The lithium cation in Li[CH₃OB(CN)₃]·H₂O is coordinated by three N atoms and the O atom of the water molecule resulting in a distorted tetrahedral arrangement. The sodium cation in Na[CH₃OB(CN)₃]·H₂O has a distorted octahedral coordination sphere composed of four N atoms and two O atoms. The O atoms belong to water molecules that are μ_2 -coordinated to two Na atoms. Thus, the O atom of the $[CH_3OB(CN)_3]^-$ anion is not coordinated to the metal ion in $M[CH_3OB(CN)_3] \cdot H_2O$ (M = Li, Na). The aqua ligands in both salts are involved in O···H-O hydrogen bonds with the cyanoborate anions as depicted in Fig. 4.

In K[CH₃OB(CN)₃] two crystallographically independent potassium atoms are present that are located on special positions (Fig. 4). One K atom has a distorted octahedral environment with six N atoms in the coordination sphere. The second K atom has the coordination number 8 and a strongly distorted square antiprismatic geometry. The K atom is connected to six N atoms, as well, and in addition to two O atoms. So, in contrast to the lithium and sodium salt, the O atom of the methoxytricyanoborate anion is involved in the coordination to potassium.

Na[C₂H₅OB(CN)₃] and Na[CF₃CH₂OB(CN)₃]·0.5H₂O crystallize in the triclinic space group $P\overline{1}$ (Z = 2) and in the monoclinic space group C2/c (Z = 8), respectively. The coordination sphere of the Na atom in Na[C₂H₅OB(CN)₃] is a distorted trigonal bipyramid with four N atoms and one O atom. So, one of the cyano groups bridges two Na atoms. In contrast, the sodium atom in the structure of the partially fluorinated cyanoborate anion has a distorted octahedral coordination sphere. Four N atoms, a single F atom of the CF₃ group, and the O atom of the H₂O solvate molecule are coordinated to sodium. One of the N atoms and the O atom of water are coordinated to two Na atoms.

The bond parameters of the alkoxytricyanoborate anions are listed in Table 2. The experimental and calculated bond lengths and angles are very close. Furthermore, the bond parameters of the three closely related anions are very similar. Thus, most of the differences of the experimental values are not significant $(>3\sigma)$. The calculated bond parameters of the non-fluorinated

 Table 1
 Experimental (Raman) and calculated CN stretching band positions of alkoxytricyanoborates and selected related cyanoborates

Anion	Li^+	Na^+	\mathbf{K}^{+}	$[\mathbf{EMIm}]^+$	Calcd ^a
$[CH_3OB(CN)_3]^-$ $[C_2H_5OB(CN)_3]^-$ $[CF_3CH_2OB(CN)_3]^-$ $[CF_3B(CN)_3]^-$ $[B(CN)_4]^-$	2249 n.d. ^b n.d. n.d. 2263 ⁸	2224 2240/2228/2220 2236 n.d. 2252 ⁸	$2221 \\ n.d. \\ n.d. \\ 2237/2231^{20} \\ 2233^{6}$	2206220722112223c 20222315	229922992305231420231515

^{<i>a</i>} B3LYP/6-311++G(d,p), mean value where applicable. ^{<i>b</i>} n.d. = not determined. ^{<i>c</i>} II



 Table 2
 Selected experimental and calculated^a bond lengths [Å] and angles [°] of alkoxytricyanoborate anions^b

Anion	Cation	<i>d</i> (B–C)	<i>d</i> (B–O)	$d(C \equiv N)$	<i>d</i> (O–C)	<i>d</i> (C–C)	≾ (С-В-С)	≾ (С-В-О)	≰(B-C≡N)	д (В−О−С)
[CH ₃ OB(CN) ₃] ⁻	Li ⁺ Na ⁺ K ⁺ B3LVP	1.613(2) 1.6140(15) 1.6197(19) 1.6167	1.449(2) 1.4249(12) 1.4277(16) 1.4504	$1.146(2) \\ 1.1355(15) \\ 1.1430(18) \\ 1.1570$	1.441(2) 1.4129(13) 1.4276(16) 1.4080		107.66(12) 107.38(8) 107.48(10) 108.11	111.21(13) 111.49(8) 111.39(10) 110.81	$177.02(17) \\ 178.84(11) \\ 177.70(13) \\ 178.20$	115.55(12) 117.78(8) 116.80(10) 117.82
$[C_2H_5OB(CN)_3]^-$	Na ⁺ B3LYP	1.619(2) 1.6166	1.4314(14) 1.4511	1.1370 1.146(2) 1.1570	1.4030 1.435(2) 1.4117	1.5054(16) 1.5226	106.59(10) 108.09	110.81 112.23(9) 110.83	178.20 178.59(12) 178.29	117.82 115.95(9) 118.32
$[CF_3CH_2OB(CN)_3]^-$	Na ⁺ B3LYP	1.6143(17) 1.6104	1.4509(15) 1.4642	1.1447(15) 1.1565	1.4149(13) 1.3904	1.4973(18) 1.5167	108.49(9) 108.64	110.41(9) 110.29	177.40(12) 177.91	115.39(8) 117.53
^{<i>a</i>} B3LYP/6-311++G(d,p). ^{<i>b</i>} Mean value where applicable.										

anions $[ROB(CN)_3]^-$ (R = CH₃, C₂H₅) are similar, as well. In contrast, small deviations are predicted for the partially fluorinated analogue. The B–C and C \equiv N distances are shorter while the *d*(B–O) distance is longer. These differences are attributed to the less electron rich CF₃CH₂O group compared to its non-fluorinated counterparts. The shorter and thus stronger C \equiv N bonds in $[CF_3CH_2OB(CN)_3]^-$ are in agreement to the slightly higher wavenumber for ν (CN) (Table 1). The short B–C bonds in $[CF_3CH_2OB(CN)_3]^-$ compared to $[ROB(CN)_3]^-$ (R = CH₃, C₂H₅) indicate stronger B–C bonds.

Thermal properties

The thermal stability of the alkali metal salts and EMIm-ILs of selected alkoxytricyanoborates was studied by DTA and TG measurements and the results are summarized in Table 3.

In Fig. 5 the TG and DTA curves for the decomposition of $Li[CH_3OB(CN)_3]$ ·H₂O are depicted and the DSC curve is shown in Fig. S2 (ESI‡). The hydrate melts at approximately 100 °C. The melting process is followed by a loss in weight of 12.4%

and results in solid, anhydrous Li[CH₃OB(CN)₃], which is stable up to 313 °C. At this temperature decomposition of the anion starts and gas evolution takes place. The IR spectrum of the gas evolved corresponds to the spectrum of B(OCH₃)₃ with minor amounts of HCN (Fig. 5). The mass loss of 27.0% fits well to the mass loss calculated for trimethoxyborane of 23.9%. The black solid residue in the crucible is hardly soluble in water and insoluble in organic solvents. The ¹¹B NMR spectrum of the water extract shows a number of signals including a weak signal that is assigned to the [B(CN)₄]⁻ ions.

The formation of $B(OCH_3)_3$ during decomposition of $Li[CH_3OB(CN)_3]$ may be rationalized by a dismutation initiated by the Li^+ cation that attacks the borate anion. In Scheme 4 the respective first step of this dismutation that results in a dimethoxyboron species is depicted. Further methoxy transfer steps would yield the experimentally observed $B(OCH_3)_3$.

The sodium and potassium salts $M[CH_3OB(CN)_3]$ (M = Na, K) exhibit similar thermal stabilities to the corresponding lithium salt with decomposition temperatures of ~310 and 304 °C.

Salt	$T_{\rm g} \left[{}^{\circ} { m C} ight]$	$T_{\rm mp} \left[^{\circ} { m C} \right]$	$T_{\rm dec} \left[^{\circ} \mathrm{C}\right]$
$\text{Li}[CH_3OB(CN)_3] \cdot H_2O^b$ Na[CH_2OB(CN)_2] \cdot H_2O^d	n.o. ^c	$(58)^b$ 298	$313 \sim 310^e$
$K[CH_3OB(CN)_3]$ $N_2[CH_3OB(CN)_3]$	n.o.	242	304
$Na[CF_3CH_2OB(CN)_3]$ $Na[CF_3CH_2OB(CN)_3] \cdot 0.5H_2O^{f}$	n.o. n.o.	320 265	$\sim 340^{\circ}$ 337
[EMIm][CH ₃ OB(CN) ₃] [EMIm][C ₂ H ₅ OB(CN) ₃]	-93 -86	n.o. n.o.	230 243
[EMIm][CF ₃ CH ₂ OB(CN) ₃]	-85	-21	285

^{*a*} Temperatures are onset values of the DSC measurements (plots of the DSC curves are depicted in the ESI); T_{dec} = decomposition temperature; T_{mp} = melting point; T_g = glass transition temperature; T_{dec} and T_{mp} were confirmed visually. ^{*b*} Li[CH₃OB(CN)₃]·H₂O melts at 58 °C and loses water at 95 °C to give solid Li[CH₃OB(CN)₃] that decomposes at 313 °C (Fig. S2, ESI). ^{*c*} n.o. = not observed. ^{*d*} Loss of water starts at 44 °C (Fig. S3, ESI). ^{*e*} Decomposition starts during melting. ^{*f*} Loss of water starts at 86 °C. An irreversible phase transition is observed at 170 °C (Fig. S10, ESI).



Fig. 5 DTA (blue) and TG curve (green) of Li[CH₃OB(CN)₃]·H₂O (bottom) and IR spectra of H₂O lost at 100 °C (onset) and of the volatile decomposition product $B(OCH_3)_3$ with traces of HCN (*) released at 309 °C (onset).

However, both salts $M[CH_3OB(CN)_3]$ (M = Na, K) melt before decomposition (Table 3) whereas $Li[CH_3OB(CN)_3]$ remains solid until decomposition. In all cases, $B(OCH_3)_3$ is formed as a gaseous decomposition product.

The sodium salts of $[ROB(CN)_3]^-$ (R = C₂H₅, CF₃CH₂) are slightly more stable than Na[CH₃OB(CN)₃] (Table 3). According to the TG measurements and the respective IR spectra of the



B(OCH₃)₃↑ + decomposition products

Scheme 4 First step proposed for the dismutation of $Li[CH_3OB(CN)_3]$.

volatile decomposition products, all three sodium salts decompose under loss of the respective borane $B(OR)_3$ (R = CH₃, C₂H₅, CF₃CH₂).

The three EMIm-ILs [EMIm][ROB(CN)₃] (R = CH₃, C₂H₅, CF₃CH₂) are thermally very robust with decomposition temperatures well above 200 °C (Table 3). The stability increases in the order [EMIm][CH₃OB(CN)₃] (230 °C) < [EMIm][C₂H₅OB(CN)₃] (243 °C) < [EMIm][CF₃CH₂OB(CN)₃] (285 °C).

The EMIm-ILs decompose under release of the respective trialkoxyborane as the main gaseous product, which is rationalized by dismutation reactions similar to the one depicted for Li[CH₃OB(CN)₃] in Scheme 4. HCN was identified in the IR spectra as a minor component. The significantly higher thermal stability of [EMIm][CF₃CH₂OB(CN)₃] is attributed to the stronger electron withdrawing effect of the partially fluorinated alkoxy group at boron that results in stronger bonds of boron to its substituents, which is in line with the shorter and thus stronger B-C bonds in the partially fluorinated anion (Table 2). The electron density at oxygen in $[CF_3CH_2OB(CN)_3]^-$ is lower compared to its non-fluorinated counterparts $[ROB(CN)_3]^-$ (R = CH_3 , C_2H_5). Both, the stronger bonds of boron to its substituents and the comparably low electron density at oxygen are expected to result in an increase of the energy of the transition state of dismutation reactions such as the one presented in Scheme 4. The glass transition temperatures of the three EMIm-ILs are in the range of -85 to -93 °C. Cold crystallization and melting were observed for [EMIm][CF₃CH₂OB(CN)₃] at -42 and -20 °C, only. The DSC traces of the non-fluorinated ILs [EMIm][CH₃OB(CN)₃] and [EMIm][C₂H₅OB(CN)₃] do not show any crystallization.

Physicochemical properties of EMIm-ILs

Electrochemical properties. The three neat ionic liquids $[EMIm][ROB(CN)_3]$ (R = CH₃, C₂H₅, and CF₃CH₂) were studied by cyclic voltammetry using a glassy carbon (GC) working electrode (Fig. 6). All three RTILs are electrochemically surprisingly stable with electrochemical windows of up to 4.4 V, which are similar to related EMIm-cyanoborate-ILs, for example [EMIm]TCB ($\Delta E = 4.4$ V,¹⁵ Table 4). The oxidation of the different anions occurs at 1.8–2.0 V and reduction of the $[EMIm]^+$ cations at -2.4 V. Both electrochemical reductions and oxidations proceed irreversibly.

Density and viscosity. The dynamic viscosity (η) and density (ρ) of [EMIm][*R*OB(CN)₃] ($R = CH_3$, C₂H₅, and CF₃CH₂) was determined using a rolling ball viscometer (Table 4). The density



Fig. 6 Cyclic voltammograms of neat [EMIm][$ROB(CN)_3$] ($R = CH_3$, C_2H_5 , and CF_3CH_2) measured at 20 °C with a scan rate of 50 mV s⁻¹ using a glassy carbon working electrode.

of $[EMIm][CH_3OB(CN)_3]$ and $[EMIm][C_2H_5OB(CN)_3]$ is almost identical and similar to the one of [EMIm]TCB.¹⁵ As expected from the data of our study on perfluoroalkyl(cyano)fluoroborate-ILs,²⁰ the introduction of fluorine into the alkyl chain of the borate anion results in a significant increase in density of $[EMIm][CF_3CH_2OB(CN)_3]$ (Table 4).

Surprisingly, $[EMIm][CH_3OB(CN)_3]$ reveals a lower dynamic viscosity than the well-established $[EMIm]TCB^{15}$ (Table 4). An increasing alkyl chain length of the alkoxy group results in an increase in dynamic viscosity, which is in accordance with the trend of higher viscosities of perfluoroalkylcyanoborates with longer perfluoroalkyl chains.²⁰ The dynamic viscosity of $[EMIm][CF_3-CH_2OB(CN)_3]$ is slightly lower compared to $[EMIm][C_2H_5OB(CN)_3]$. In spite of the increase of the anion mass, the electron withdrawing effect of the trifluoromethyl group in CF_3CH_2O results in weaker cation–anion interactions and thus leads to a lower viscosity. The dynamic viscosity of all four ILs including $[EMIm]TCB^{15}$ decreases with the increasing temperature as depicted in Fig. 7.

Specific conductivity and diffusivity. [EMIm][CH₃OB(CN)₃] has the highest specific conductivity σ (10.1 mS cm⁻¹ at 20 °C) of the three alkoxytricyanoborate-ILs studied (Fig. 7 and Table 4). The specific conductivity of [EMIm][C₂H₅OB(CN)₃] and [EMIm][CF₃CH₂OB(CN)₃] is very close as can be expected on the basis of the similar dynamic viscosities. Although [EMIm][CH₃OB(CN)₃] reveals a slightly lower viscosity than [EMIm]TCB,¹⁵ the tetracyanoborate-IL possesses a slightly higher



Fig. 7 Temperature dependence of the dynamic viscosities (top) and conductivities (bottom) of EMIm-ILs of $[ROB(CN)_3]^-$ ($R = CH_3$, C_2H_5 , and CF_3CH_2) and $[B(CN)_4]^-$.

specific conductivity of 12.1 mS cm⁻¹. This observation may be rationalized by a stronger ion pairing or ion interaction in [EMIm][CH₃OB(CN)₃] compared to [EMIm]**TCB** as evident from the ionicity,³⁸ which is defined as the ratio of the molar conductivity based on impedance measurements Λ_{imp} and the molar conductivity derived from NMR diffusion coefficients Λ_{NMR} (Fig. 8). Most likely, the methoxy group in [CH₃OB(CN)₃]⁻ results in stronger cation–anion interactions in [EMIm][CH₃OB(CN)₃] compared to [EMIm][B(CN)₄], *e.g. via* hydrogen bonding between the [EMIm]⁺ cation and the [CH₃OB(CN)₃]⁻ ion. The ionicity further decreases in the order [EMIm][C₂H₅OB(CN)₃] > [EMIm][CF₃CH₂OB(CN)₃]. This behaviour may reflect an increase in ion pairing. So, the CF₃ unit in [CF₃CH₂OB(CN)₃]⁻ may be involved in additional, weak hydrogen bonding to the [EMIm]⁺ ions.

Table 4 Selected physical	l and ele	ctroche	pchemical properties ^a of [EMIm][ROB(CN) ₃] (R = CH ₃ , C ₂ H ₅ , and CF ₃ CH ₂) and [EMIm][B(CN) ₄] ([EMIm] TCB) at 20 °C										
Salt	η [mPa s]	ρ [g cm ⁻	c ⁻³] [mol L ⁻	D^+ $[10^{-11}]$	$m^2 s^{-1}$] $[10^{-11} m^2 s^{-1}]$	σ [mS cm ⁻	$\Lambda_{\rm NMR}$ [cm ² S mol ⁻¹]	$\Lambda_{ m imp}$ $[m cm^2 S$ $^{-1}] m mol^{-1}]$	Ι	Е _с [V]	E_{a} [V]	ΔE [V]	$n_{ m D}^{20}$
[EMIm][CH ₃ OB(CN) ₃]	18.8	1.04	4.48	7.2	5.5	10.1	4.84	2.25	0.46	-2.4	1.9	4.3	1.450
[EMIm][C ₂ H ₅ OB(CN) ₃]	25.2	1.03	4.19	5.8	3.9	5.6	3.71	1.34	0.36	-2.4	1.8	4.2	1.450
[EMIm][CF ₃ CH ₂ OB(CN) ₃]	24.4	1.18	3.93	6.9	5.0	5.5	4.55	1.40	0.31	-2.4	2.0	4.4	1.422
[EMIm][B(CN) ₄] ¹⁵	22.6	1.04	4.60	6.3	5.4	12.1	4.47	2.64	0.59	-2.4	2.0	4.4	1.450

^{*a*} Dynamic viscosity η ; density ρ ; concentration *c*; diffusion coefficients of cations (D^+) and anions (D^-) ; specific conductivity σ measured *via* impedance spectroscopy; molar conductivities calcd by $\Lambda_{\text{NMR}} = (D^+ + D^-)N_{\text{A}}e^2k^{-1}T^{-1}$ and $\Lambda_{\text{imp}} = \sigma M \rho^{-1}$; ionicity $I = \Lambda_{\text{ump}}\Lambda_{\text{NMR}}^{-1}$; cathodic and anodic limits E_c and E_a ; electrochemical window $\Delta E = E_a - E_c$.



Fig. 8 Ionicity of EMIm-ILs of $[ROB(CN)_3]^-$ ($R = CH_3$, C_2H_5 , and CF_3CH_2) and $[B(CN)_4]^-$.

The molar conductivities $\Lambda_{\rm imp}$ and $\Lambda_{\rm NMR}$ were determined at 20, 40, and 60 °C (Table S3 and Fig. S1 in the ESI‡) and both $\Lambda_{\rm imp}$ and $\Lambda_{\rm NMR}$ increase with the increasing temperature. Within the temperature range studied, $\Lambda_{\rm NMR}$ reveals a stronger increase with the increasing temperature than $\Lambda_{\rm imp}$ and, thus, the ionicity slightly decreases with the increasing temperature (Fig. 8).

Refractive indices. The refractive indices (n_D^{20}) of the [EMIm]-ILs depend on the number of fluorine atoms (Table 4). So, the



Fig. 9 Cyclic voltammogram (20 °C; scan rate: 50 mV s⁻¹, glassy carbon working electrode, top) and temperature dependence of the conductivity (bottom) of a saturated solution of Li[CH₃OB(CN)₃] in propylene carbonate (0.50 mol L⁻¹).

 $[\rm EMIm]^+$ salts of the non-fluorinated ions $[\rm CH_3OB(CN)_3]^-$ and $[\rm C_2H_5OB(CN)_3]^-$ exhibit the same refractive index as $[\rm EMIm]\rm TCB,^5$ whereas the value found for $[\rm EMIm]\rm [CF_3CH_2OB(CN)_3]$ is lower, which is typical for fluorine-containing ILs. 5

Electrochemical properties of Li[CH₃OB(CN)₃]

The lithium salt Li[CH₃OB(CN)₃] is either accessible *via* direct cyanation of Li[B(OCH₃)₄] or Li[BF₄] (Scheme 1) or by salt metathesis from Na[CH₃OB(CN)₃] (Scheme 3). The solubility of Li[CH₃OB(CN)₃] in propylene carbonate (PC) at room temperature is 0.50 mol L⁻¹, which is much higher than the solubility of Li**TCB** of 0.10 mol L⁻¹. The solution of Li[CH₃OB(CN)₃] in PC possesses a large electrochemical window of *ca.* 5 V (Fig. 9).

The specific conductivity of this solution is 1.86 mS cm^{-1} at 20 °C and it increases with the increasing temperature and reaches 4.67 mS cm⁻¹ at 80 °C (Fig. 9).

3. Conclusions

Alkali metal salts of alkoxytricyanoborate ions and dialkoxydicyanoborate ions have become accessible using different commercially available boron-based starting materials. In particular, alkoxytricyanoborates exhibit high stabilities, which make them interesting building blocks for material applications. Room temperature ionic liquids with [EMIm]⁺ ions have been synthesized via metathesis. These ILs possess low melting and low viscous properties and they exhibit high specific conductivities as well as high thermal, chemical, and electrochemical stabilities. Thus, ILs based on these anions fulfill key requirements for potential applications in electrochemical devices. In addition, Li[CH₃OB(CN)₃] was prepared. This Li salt provides a 5-times higher solubility in propylene carbonate than LiTCB and it provides a decent conductivity. The high yield and easily scalable syntheses of alkoxytricyanoborates combined with the interesting properties of their salts make them promising alternatives to tetracyanoborates.

4. 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 (Rettberg, Göttingen) under argon using Schlenk-line techniques. High pressure reactions (>5 bar) were conducted in a Carl Roth autoclave model I (working volume = 100 mL and inner volume = 135 mL). ¹H, ¹¹B, ¹³C, and ¹⁹F NMR spectra were recorded at 25 °C in (CD₃)₂CO or CD₃CN on a Bruker Avance 500 NMR spectrometer. The NMR signals were referenced against TMS (¹H, ¹³C), BF₃·OEt₂ in CDCl₃ with Ξ (¹¹B) = 32.083974 MHz, and CFCl₃ with Ξ (¹⁹F) = 94.094011 MHz as external standard.³⁹ ¹H and ¹³C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively (δ (¹H): (CD₃)(CD₂H)CO 2.05 ppm, CD₂HCN 1.94 ppm; δ (¹³C): (CD₃)₂CO 206.26 and 29.84 ppm, CD₃CN 118.26 and 1.32 ppm).⁴⁰ IR spectra were recorded at room temperature 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 room temperature with a MultiRAM FT-Raman spectrometer using the 1064 nm excitation line of an Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of $3500-100 \text{ cm}^{-1}$. (–)-ESI mass spectra were recorded on a Thermo Scientific Extractive Plus mass spectrometer equipped with an Orbitrap mass analyser. Elemental analysis (C, H, N) was performed with an Elementar Varion Micro Cube instrument. Thermal analyses were performed with a DSC 204 F1 Phoenix (Netzsch) in the temperature range of -150 to 500 °C with a heating rate of 10 K min⁻¹ and DTA measurements were performed with a STA 449 F3 Perseus (Netzsch), connected to an Alpha FTIR spectrometer (Bruker) for the analysis of the gaseous decomposition products, in the temperature range of 30 to 500 °C with a heating rate of 10 K min⁻¹. The water content of the ILs was determined by Karl-Fischer titration with a Metrohm 831 KF Coulometer. The water content of the ILs was < 50 ppm. Viscosities and densities were measured with a rolling-ball viscometer Lovis 2000 ME combined with a DMA 4100 M density meter (Anton Paar) at different angles and temperatures.

Chemicals

Sodium and potassium tetraalkoxyborates were synthesized similar to a literature procedure for Na[B(OCH₃)₄]⁴¹ from Na[BH₄] or K[BH₄] and the corresponding alcohol (MeOH, EtOH, trifluoroethanol).⁴² Li[B(OCH₃)₄] was prepared from LiOCH₃ and B(OCH₃)₃ in methanol.⁴³ Li**TCB** was synthesized similar to a literature procedure.²⁵

Caution. Alkali metal cyanides and trimethylsilyl cyanides are highly toxic. Peroxides are potentially hazardous. Thus, the decomposition of peroxides during the work-up procedures had to be secured with Quantofix Peroxide 100 test sticks (Machery-Nagel).

Lithium methoxytricyanoborate, Li[CH₃OB(CN)₃]. Method A

A solution of Li[BF₄] (15.0 g, 160.0 mmol) in acetonitrile (40 mL) was mixed with trimethylsilyl cyanide (TMSCN, 75.0 mL, 597.6 mmol). Gas evolution (trimethylsilyl fluoride, TMSF) was observed. After the gas evolution had ceased, trimethylmetoxysilane (TMSOCH₃, 25.0 mL, 182.1 mmol) was added. The reaction mixture was stirred for 2 days at 40 °C. All volatiles were removed under vacuum. The residue was dissolved in acetone (25 mL). Slow addition of CHCl₃ (150 mL) resulted in Li[CH₃OB(CN)₃] as a precipitate, which was isolated by filtration and dried under vacuum. Yield: 20.2 g (159.3 mmol, 99%). ¹H NMR ((CD₃)₂CO): δ : 3.20 (q, ³*J*(¹¹B,¹H) = 4.1 Hz, 3H). ¹³C NMR ((CD₃)₂CO): δ : 128.56 (q, ¹*J*(¹³C, ¹¹B) = 70.3 Hz, 3C, CN), 53.05 (qq, ¹*J*(¹³C, ¹H) = 140.0 Hz, ²*J*(¹³C, ¹¹B) < 1 Hz, 1C, OCH₃). ¹¹B NMR ((CD₃)₂CO): δ : -18.42 (q, ³*J*(¹¹B,¹H) = 3.7 Hz, 1B). Raman (cm⁻¹): 2247, 2239 (ν (CN)).

Elemental analysis was performed on a material derived from crystals of $Li[CH_3OB(CN)_3] \cdot H_2O$ that have been briefly dried. Drying resulted in loss of part of the solvate molecules and in salt of the approximate composition $Li[CH_3OB(CN)_3] \cdot$ 0.75H₂O. Anal. calculated for C₄H_{4.5}BLiN₃O_{1.75}: C, 34.23%; H, 3.23%; N, 29.94%. Found: C, 34.72%; H, 3.09%; N, 31.25%.

Method B

Li[BF₄] (15.0 g, 160.0 mmol) was dissolved in a mixture of TMSCN (120.0 mL, 956.2 mmol) and TMSOCH₃ (150 mL, 1092.3 mmol). The reaction mixture was stirred at room temperature for 2 days. The resulting suspension was filtered, and the colorless solid was washed with CH_2Cl_2 (20 mL) and dissolved in acetone (50 mL). CH_2Cl_2 (350 mL) was slowly added to give Li[$CH_3OB(CN)_3$] as a precipitate that was filtered off and dried under vacuum. Yield: 20.1 g (158.5 mmol, 99%).

Method C

 $Na[CH_3OB(CN)_3]$ (1.0 g, 7.0 mmol) was added to a solution of LiCl (296 mg, 7.0 mmol) in acetone (150 mL) under vigorous stirring. The precipitate (NaCl) was filtered off. The volume of the filtrate was reduced to approximately 5 mL with a rotary evaporator. Chloroform (100 mL) was added to give Li[CH_3OB(CN)_3] as a precipitate that was filtered off and dried under vacuum. Yield: 874 mg (6.9 mmol, 99%).

Sodium methoxytricyanoborate, Na[CH₃OB(CN)₃]. Method A

Na[B(OCH₃)₄] (3.0 g, 19.0 mmol) was mixed with TMSCN (100.0 mL, 796.8 mmol). The reaction mixture was stirred for 2 days at 60 °C. The excess of TMSCN and the byproduct TMSOMe was distilled off. The residue was dissolved in an aqueous solution of H2O2 (30% w/w, 20 mL), mixed with Na₂CO₃ (ca. 1 g) and stirred for 4 h. Subsequently, the mixture was treated with Na₂S₂O₅. The solution was extracted with THF (3 \times 20 mL). The combined THF phases were dried with Na_2CO_3 (ca. 10 g), filtered and the solvent was evaporated under vacuum. The residue was dissolved in acetone (5 mL). The addition of CH2Cl2 (100 mL) yielded colorless Na[CH₃OB(CN)₃] as a precipitate. The solid was filtered off and dried under vacuum. Yield: 2.5 g (17.5 mmol, 92%). ¹H NMR $((CD_3)_2CO): \delta: 3.21 (q, {}^{3}J({}^{11}B, {}^{1}H) = 3.8 Hz, OCH_3, 3H). {}^{13}C NMR$ $((CD_3)_2CO): \delta: 128.50 \text{ (q, } {}^1J({}^{13}C, {}^{11}B) = 70.2 \text{ Hz, CN, 3C}), 52.97 \text{ (qq, })$ ${}^{1}f({}^{13}C, {}^{1}H) = 139.6 \text{ Hz}, {}^{2}f({}^{13}C, {}^{11}B) \approx 1 \text{ Hz}, 1C, \text{ OCH}_{3}$. ${}^{11}B \text{ NMR}$ $((CD_3)_2CO): \delta: -18.42 (q, {}^{3}J({}^{11}B, {}^{1}H) = 3.8 Hz, 1B). (-)-ESI$ MS calculated for (C₄H₃BN₃O)⁻: 120.0 (100%), 119.0 (25%), 121.0 (6%). Found: 120.4 (100%), 119.4 (22%), 121.4 (5%). Raman (cm⁻¹): 2231, 2224, 2217 (ν (CN)).

A sample of $Na[CH_3OB(CN)_3]$ was crystallized from wet acetone to give $Na[B(CN)_3OCH_3]$ ·H₂O. Anal. calculated for C₄H₅BN₃NaO₂: C, 29.86%; H, 3.13%; N, 26.12%. Found: C, 29.94%; H, 2.79%; N, 26.22%.

Method B

Na[BH₄] (10.0 g, 264.3 mmol) was slowly added to methanol (600 mL). After the exothermic reaction had stopped, the solution was evaporated using a rotary evaporator and the solid residue was dried under vacuum. The solid was dissolved in TMSCN (250 mL, 1992.0 mmol) and the reaction mixture was stirred for 5 days at 60 °C. Subsequently, all volatiles were distilled off. The residue was treated with H_2O_2 (30% w/w, 25 mL) and mixed with Na₂CO₃ in portions (*ca.* 2 g). Na₂S₂O₅

was added to destroy the excess peroxide. The crude product was extracted from the aqueous phase with THF (5×100 mL). The combined THF phases were dried with Na₂CO₃, filtered and the solvent was removed under vacuum. The beige solid residue was washed with CH₂Cl₂ (3×50 mL) to result in a colourless solid that was dried under vacuum. Yield: 34.3 g (240.0 mmol, 91%).

Method C

NaOCH₃ (1.0 g, 18.5 mmol) was suspended in acetonitrile (5 mL). B(OCH₃)₃ (1.9 g, 2.1 mL, 18.3 mmol) and TMSCN (9.0 mL, 71.7 mmol) were added. The reaction mixture was stirred for 4 days at 50 °C. Subsequently, all volatiles were removed under vacuum. The residue was treated with H₂O₂ (30% w/w, 10 mL) and mixed with Na₂CO₃ in portions (*ca.* 0.5 g). Excess H₂O₂ was destroyed with the addition of Na₂S₂O₅. The crude product was extracted from the aqueous phase with THF (3×50 mL). The combined THF phases were dried with Na₂CO₃, filtered and evaporated under vacuum to dryness. The beige solid was washed with CH₂Cl₂ (50 mL) on a glass frit (D4) and dried under vacuum. Yield: 1.8 g (12.6 mmol, 69%).

Method D

Na[BF₄] (25.0 g, 227.6 mmol) was suspended in a mixture of TMSCN (100 mL, 796.8 mmol) and TMSOCH₃ (100 mL, 728.4 mmol). The mixture was heated to reflux for 2 d. All volatiles were removed in a vacuum and the residue was washed with CH₂Cl₂ (70 mL). The solid was dissolved in acetonitrile (100 mL) and, after stirring for 5 min, insoluble Na[BF₄] was filtered off. The filtrate was evaporated to dryness using a rotary evaporator, the residue was rinsed onto a glass frit (D4) using dichloromethane (*ca.* 150 mL), and the solid was subsequently dried under vacuum. Yield: 24.1 g (168.6 mmol, 74%). The crude material contained Na[BF₄] (4%) and Na[BF₂(CN)₂] (9%) as identified by ¹¹B NMR spectroscopy.

Potassium methoxytricyanoborate, K[CH₃OB(CN)₃]

K[BH₄] (10.0 g, 185.4 mmol) was slowly added to methanol (500 mL). After the exothermic reaction had ceased, the reaction mixture was refluxed for further 2 h. The resulting solution was evaporated using a rotary evaporator and the colorless $K[B(OCH_3)_4]$ (¹¹B NMR spectroscopy) was dried overnight under vacuum. In a parallel reaction, NaCN (60.0 g, 1.22 mol) and [EMIm]Cl (10 g, 68.2 mmol) were dissolved in acetonitrile (20 mL) and TMSCl (140.0 mL, 1.103 mol) was added. The suspension was stirred for 2 d at room temperature and the formation of TMSCN was periodically checked by ¹³C NMR spectroscopy. The freshly prepared TMSCN that still contained some TMSCl was distilled at 150 °C to the colorless $K[B(OCH_3)_4]$. The resulting suspension was stirred at room temperature for 2 d. All volatiles were removed under vacuum and the colorless residue was rinsed onto a glass frit (D4) with CH₂Cl₂ (ca. 200 mL). Yield: 17.2 g (108.2 mmol, 58%). Anal. calculated for C₄H₃BKN₃O: C, 30.22%; H, 1.90%; N, 26.43%. Found: C, 30.10%; H, 1.96%; N, 27.36%. ¹H NMR ((CD₃)₂CO): δ : 3.19 (q, ³*J*(¹¹B, ¹H) = 3.8 Hz, 3H). ¹³C NMR ((CD₃)₂CO): δ : 128.50 (q, ¹*J*(¹³C, ¹¹B) = 70.2 Hz, 3C, CN),

Tetraethylammonium methoxytricyanoborate, $[(C_2H_5)_4N][CH_3OB(CN)_3]$

An aqueous solution of tetraethylammonium hydroxide (35% w/w, 20.2 g, 48.0 mmol) was added to Na[CH₃OB(CN)₃] (6.8 g, 47.6 mmol) dissolved in distilled water (5 mL) under vigorous stirring. CH₂Cl₂ (50 mL) was added to the emulsion and the organic phase was separated. The CH₂Cl₂ phase was subsequently washed with distilled water (3 × 5 mL), dried with MgSO₄, filtered, and evaporated using a rotary evaporator. The residue was dried under fine vacuum at 60 °C. Yield: 10.0 g (40.0 mmol, 84%). ¹H{¹¹B} NMR ((CD₃)₂CO): δ : 3.44 (q, 8H, CH₂), 3.20 (s, 3H, OCH₃), 1.38 (tt, ³*J*(¹H, ¹H) = 7.3 Hz, 12H, CH₃). ¹³C{¹H} NMR ((CD₃)₂CO): δ : 128.74 (q, ¹*J*(¹³C, ¹¹B) = 70.1 Hz, 3C, CN), 54.93 (q, ²*J*(¹³C, ¹¹B) ≈ 1 Hz, 1C, OCH₃), 53.02 (s, 4, CH₂), 7.66 (s, 4C, CH₃). ¹¹B{¹H} NMR ((CD₃)₂CO): δ : -18.44 (s, 1B). Raman (cm⁻¹): 2204, 2214 (ν (CN)).

Tetrabutylammonium methoxytricyanoborate, [(C₄H₉)₄N][CH₃OB(CN)₃]. Method A

A solution of Na[CH₃OB(CN)₃] (5.2 g, 36.4 mmol) in bidistilled water (10 mL) was mixed with an aqueous solution of [Bu₄N]OH (40% w/w, 1.5 mol L⁻¹, 25.0 mL, 38.3 mmol). CH₂Cl₂ (50 mL) was added to the emulsion and stirred for 10 min. The CH₂Cl₂ phase was separated, washed with bidistilled water $(3 \times 5 \text{ mL})$, dried with MgSO₄, and filtered. The solution was evaporated using a rotary evaporator and the highly viscous liquid was dried under vacuum. Yield: 11.6 g (32.0 mmol, 88%). Anal. calculated for C₂₀H₃₉BN₄O: C, 66.29%; H, 10.85%; N, 15.46%. Found: C, 66.11%; H, 9.74%; N, 15.44%. ¹H{¹¹B} NMR ((CD₃)₂CO): δ: 3.39 (m, 8H, CH₂), 3.21 (s, 3H, OCH₃), 1.80 (m, 8H, CH₂), 1.44 (m, 8H, CH₂), 0.98 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4, 12H, CH_{3}$). ${}^{13}C{}^{1}H$ NMR ((CD₃)₂CO): δ : 128.84 (q, ¹f(¹³C, ¹¹B) = 70.1 Hz, 3C, CN), 59.48 $(t, {}^{1}f({}^{15}N, {}^{13}C) = 2.9 \text{ Hz}, 4C, \text{ NCH}_{2}), 53.04 (q, {}^{2}f({}^{13}C, {}^{11}B) \approx 1 \text{ Hz}, 1C,$ OCH₃), 24.47 (s, 4C, CH₂), 20.42 (t, 4C, CH₂), 13.88 (s, 4C, CH₃). ¹¹B{¹H} NMR ((CD₃)₂CO): δ : -18.44 (s, 1B). Raman (cm⁻¹): 2202, 2212 (v(CN)).

Method B

Na[B(OCH₃)₄] (300 mg, 1.90 mmol) was suspended in $(CH_3)_3SiCN$ (50.0 mL, 398.4 mmol). The reaction mixture was stirred at 60 °C for 2 d. All volatiles were removed under reduced pressure and the residue was dissolved in aqueous H_2O_2 (15% w/w, 20 mL). K₂CO₃ was added to this solution, and the mixture was stirred at 50 °C for 1 h. Tetrabutylammonium bromide (806 mg, 2.50 mmol) was added and the resulting emulsion was extracted with CH_2Cl_2 (3 × 5 mL). The dichloromethane phase was separated, washed with distilled water (3 × 2 mL), dried with MgSO₄, and evaporated to dryness under vacuum to result in a highly viscous liquid. Yield: 600 mg (1.66 mmol, 87%).

1-Ethyl-3-methylimidazolium methoxytricyanoborate, [EMIm][CH₃OB(CN)₃]. Method A

Na[CH₃OB(CN)₃] (8.0 g, 56.0 mmol) and [EMIm]Cl (8.2 g, 55.9 mmol) were dissolved in bidistilled water (10 mL) and stirred vigorously for 15 min. CH2Cl2 (50 mL) was added and the emulsion was stirred for another 15 min. The CH₂Cl₂ phase was separated, washed with bidistilled water (3 \times 2 mL), dried with MgSO₄, and filtered. The solution was evaporated under vacuum and the ionic liquid was dried under fine vacuum. Yield: 9.1 g (39.4 mmol, 70%). Anal. calculated for C₁₀H₁₄BN₅O: C, 51.98%; H, 6.11%; N, 30.31%. Found: C, 51.35%; H, 6.35%; N, 30.76%. ¹H₁¹¹B} NMR ((CD₃)₂CO): δ : 8.95 (s, 1H, CH), 7.72 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 1.8$ Hz, 1H, CH), 7.65 $(t, {}^{3}J({}^{1}H, {}^{1}H) = 1.7 \text{ Hz}, 1H, CH), 4.38 (q, {}^{3}J({}^{1}H, {}^{1}H) = 7.3 \text{ Hz}, 2H, CH_{2}),$ 4.04 (s, 3H, CH₃), 3.19 (s, 3H, OCH₃), 1.57 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.3$, 3H, CH₃). ${}^{13}C{}^{1}H$ NMR ((CD₃)₂CO): δ : 136.91 (s, 1C, CH), 128.60 $(q, {}^{1}J({}^{13}C, {}^{11}B) = 70.0 \text{ Hz}, 3C, CN), 124.69 (s, CH, 1C), 123.02$ (s, 1C, CH), 52.98 (q, ${}^{2}J({}^{13}C,{}^{11}B) \approx 1$ Hz, 1C, OCH₃), 45.70 (s, 1C, CH₂), 36.61 (s, 1C, CH₃), 15.49 (s, 1C, CH₃). ${}^{11}B_1^{(1)}H_1^{(1)}$ NMR $((CD_3)_2CO)$: δ : -18.48 (s, 1B). Raman (cm⁻¹): 2205, 2214 (ν (CN)).

Method B

Solutions of Li[CH₃OB(CN)₃] (2.25 g, 17.7 mmol) in bidistilled water (10 mL) and [EMIm]Cl (2.80 g, 19.1 mmol) in bidistilled water (10 mL) were combined and vigorously stirred for 15 min. CH₂Cl₂ (100 mL) was added and the resulting emulsion was stirred for 15 min. The CH₂Cl₂ phase was separated, washed with bidistilled water (3×5 mL), dried with MgSO₄, and filtered. The solution was evaporated under vacuum and the ionic liquid was dried under a fine vacuum. Yield: 3.45 g (14.9 mmol, 84%).

N-butyl-*N*-methylpyrrolidinium methoxytricyanoborate, [BMPL][CH₃OB(CN)₃]

Na[CH₃OB(CN)₃] (6.0 g, 42.0 mmol) and [BMPL]Cl (7.5 g, 42.2 mmol) were dissolved in bidistilled water (10 mL) and stirred for 10 min. The resulting emulsion was extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic phases were washed with bidistilled water (3 \times 5 mL), dried with MgSO₄, filtered, and evaporated using a rotary evaporator. The ionic liquid was dried under a fine vacuum at 60 °C. Yield: 9.1 g (34.7 mmol, 83%). Anal. calculated for C₁₃H₂₃BN₄O: C, 59.56%; H, 8.84%; N, 21.37%. Found: C, 59.60%; H, 9.65%; N, 21.47%. ¹H{¹¹B} NMR ((CD₃)₂CO): δ : 3.68 (m, 4H, CH₂), 3.49 (m, 2H, CH₂), 3.22 (s, 3H, CH₃), 3.20 (s, OCH₃, 3H), 2.31 (m, 4H, CH₂), 1.89 (m, 2H, CH₂), 1.43 (m, 2H, CH₂), 0.98 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4$ Hz, 3H, CH₃). ¹³C{¹H} NMR ((CD₃)₂CO): δ : 128.71 (q, ¹J(¹³C, ¹¹B) = 70.1 Hz, 3C, CN), 65.20 (s, 2C, CH₂), 65.00 (s, 1C, CH₂), 53.04 (q, ${}^{2}J({}^{13}C, {}^{11}B) = 0.8$ Hz, 1C, OCH₃), 48.98 (s, 1C, CH₃), 26.17 (s, 1C, CH₂), 22.23 (s, 2C, CH₂), 20.30 (s, 1C, CH₂), 13.64 (s, 1C, CH₃). ¹¹B{¹H} NMR ((CD₃)₂CO): δ : -18.44 (s, 1B). Raman (cm⁻¹): 2204, 2214 (v(CN)).

Sodium ethoxytricyanoborate, Na[C2H5OB(CN)3]. Method A

 $Na[B(OC_2H_5)_4]$ (2.0 g, 9.3 mmol) was suspended in TMSCN (20.0 mL, 159.4 mmol) and stirred for 2 d at 60 °C. The excess TMSCN and the byproduct trimethylethoxysilane were distilled

off. The slimy residue was dissolved in an aqueous solution of H₂O₂ (30% w/w, 15 mL) and treated with Na₂CO₃ (ca. 0.5 g). The excess peroxide was destroyed with the addition of Na₂S₂O₅. The reaction mixture was extracted with THF (4 \times 50 mL) and the combined THF phases were dried with Na₂CO₃, filtered, and evaporated using a rotary evaporator. The residue was dissolved in acetone and the product was precipitated by the addition of a 1:1 mixture of CH₂Cl₂/CHCl₃. Na[C₂H₅OB(CN)₃] was filtered off and dried under fine vacuum. Yield: 0.8 g (5.1 mmol, 55%). Anal. calculated for C5H5BN3NaO: C, 38.27%; H, 3.21%; N, 26.78%. Found: C, 38.10%; H, 3.20%; N, 27.33%. ¹H NMR ((CD₃)₂CO): δ : 3.42 (qq, ³J(¹H, ¹H) = 7.0 Hz, ${}^{3}J({}^{11}B,{}^{1}H) = 1.7 \text{ Hz}, 2H, \text{ OCH}_{2}), 1.09 (t, {}^{3}J({}^{1}H,{}^{1}H) = 7.0 \text{ Hz}, 3H,$ CH₃). ${}^{13}C{}^{1}H$ NMR ((CD₃)₂CO): δ : 128.82 (q, ${}^{1}J{}^{13}C{}^{11}B$) = 69.9 Hz, 3C, CN), 61.12 (s, 1C, OCH₂), 17.57 (q, ${}^{3}J({}^{13}C, {}^{11}B) = 3.2$ Hz, 1C, CH₃). ¹¹B NMR ((CD₃)₂CO): δ : -18.99 (t, ³J(¹¹B, ¹H) = 1.7 Hz, 1B). (-)-ESI MS calculated for (C₅H₅BN₃O)⁻: 134.1 (100%), 133.1 (24%). Found: 134.1 (100%), 133.3 (29%). Raman (cm⁻¹): 2238, 2227, 2219 (v(CN)).

Method B

Na[BH₄] (10.0 g, 264.3 mmol) was added to ethanol (600 mL) and the reaction mixture was refluxed for 12 h. Excess ethanol was removed using a rotary evaporator at 70 °C to give $Na[B(OC_2H_5)_4]$. In a parallel reaction, NaCN(80.0 g, 1632.3 mmol)and TMSCl (200.0 mL, 1.576 mol) were reacted for 2 d in acetonitrile (25 mL) in the presence of NaI (10.0 g, 66.7 mmol) to give a suspension containing TMSCN. The Na $[B(OC_2H_5)_4]$ was added to this suspension. The reaction mixture was stirred for 6 d at 25 °C. All volatiles were removed under vacuum to give a dark brown residue that was dissolved in H₂O₂ (30% w/w, 200 mL). Na₂CO₃ (ca. 5g) was added in portions and the reaction mixture was stirred for 1 d at room temperature. The excess peroxide was destroyed by the addition of Na₂S₂O₅. The aqueous phase was extracted with THF (5 \times 100 mL). The yellow THF solution was dried with Na2CO3, filtered, and evaporated under vacuum until dryness. The residue was dissolved in acetone at 60 °C and the product was precipitated by the addition of CH_2Cl_2 (300 mL). The yellowish solid was filtered off and dried under fine vacuum. Yield: 37.3 g (237.7 mmol, 90%).

Method C

NaCN (3.0 g, 61.2 mmol) was suspended in a mixture of acetonitrile (10 mL), (CH₃)₃SiCl (7.0 mL, 55.2 mmol), C₂H₅OH (0.72 mL, 12.3 mmol), and a few drops of triethylamine. Na[BF₄] (0.78 g, 7.1 mmol) was subsequently added to this mixture, and the reaction mixture was stirred at room temperature for 2 d. The suspension was rendered alkaline with aqueous NaOH and was evaporated to dryness. The residue was extracted with THF (5×5 mL), dried with MgSO₄ and filtered. The THF phase was evaporated to a residual volume of about 5 mL, and colorless Na[C₂H₅OB(CN)₃] was precipitated by the addition of CH₂Cl₂ (25 mL). The product was filtered off and dried under fine vacuum. Yield: 0.85 g (5.4 mmol, 76%).

Tetrabutylammonium ethoxytricyanoborate, $[(C_2H_5)_4N][C_2H_5OB(CN)_3]$

Na[C₂H₅OB(CN)₃] (5.0 g, 31.9 mmol) was dissolved in bidistilled water (15 mL) and mixed with an aqueous solution of $[nBu_4]$ N]OH (40% w/w, 1.5 mol L⁻¹, 22.0 mL, 33.7 mmol). The solution was extracted with CH_2Cl_2 (5 × 50 mL). The combined CH_2Cl_2 phases were washed with bidistilled water (3 \times 5 mL), dried with MgSO₄, and filtered. The solution was evaporated under reduced pressure and the residue was dried under vacuum. Yield: 10.9 g (29.0 mmol, 91%). Anal. calculated for C21H25BN4O: C, 67.01%; H, 10.98%; N, 14.89%. Found: C, 66.63%; H, 12.34%; N, 13.78%. ${}^{1}H{}^{11}B$ NMR ((CD₃)₂CO): δ : 3.42 (q, ${}^{3}J({}^{1}H, {}^{1}H) = 7.0$ Hz, 2H, OCH₂), 3.39 (m, 8H, CH₂), 1.82 (m, 8H, CH₂), 1.44 (m, 8H, CH₂), 1.13 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.0$ Hz, 3H, CH₃), 0.99 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4$ Hz, 12H, CH₃). ${}^{13}C\{{}^{1}H\}$ NMR $((CD_3)_2CO): \delta: 129.01 \text{ (q, } {}^1J({}^{13}C, {}^{11}B) = 69.8 \text{ Hz, } 3C, \text{ CN}), 61.17$ (s, 1C, OCH₂), 59.48 (t, ${}^{1}J({}^{15}N, {}^{13}C) = 2.9$ Hz, 4C, NCH₂), 24.47 $(s, 4C, CH_2), 20.39 (t, 4C, CH_2), 17.78 (q, {}^{3}J({}^{13}C, {}^{11}B) = 3.2 Hz, 1C,$ CH₃), 13.86 (s, 4C, CH₃). ¹¹B{¹H} NMR ((CD₃)₂CO): δ : -18.96 (s, 1B).

1-Ethyl-3-methylimidazolium ethoxytricyanoborate, [EMIm][C₂H₅OB(CN)₃]

Na[C₂H₅OB(CN)₃] (3.77 g, 24.0 mmol) was dissolved in bidistilled water (15 mL) and mixed with a solution of [EMIm]Cl (3.69 g, 25.2 mmol) in bidistilled water (20 mL) under vigorous stirring. CH₂Cl₂ (100 mL) was added and the resulting emulsion was agitated for 15 min. The CH2Cl2 phase was separated, washed with bidistilled water (3 \times 10 mL), dried with MgSO₄, and filtered. The solution was evaporated under reduced pressure and the ionic liquid was dried under fine vacuum. Yield: 5.32 g (21.7 mmol, 90%). Anal. calculated for C₁₁H₁₆BN₅O: C, 53.91%; H, 6.58%; N, 28.57%. Found: C, 53.45%; H, 6.87%; N, 27.81%. ¹H{¹¹B} NMR ((CD₃)₂CO): δ : 8.97 (s, 1H, CH), 7.73 (t, ³J(¹H, ¹H) = 1.8 Hz, 1H, CH), 7.66 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 1.7$ Hz, 1H, CH), 4.38 $(q, {}^{3}J({}^{1}H, {}^{1}H) = 7.3 Hz, 2H, CH_{2}), 4.05 (s, 3H, CH_{3}), 3.43$ $(q, {}^{3}J({}^{1}H, {}^{1}H) = 7.0 \text{ Hz}, 2H, \text{ OCH}_{2}), 1.57 (t, {}^{3}J({}^{1}H, {}^{1}H) = 7.3 \text{ Hz},$ 3H, CH₃), 1.10 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.0$ Hz, 3H, CH₃). ${}^{13}C{}^{1}H$ NMR ((CD₃)₂CO): δ : 137.00 (s, CH, 1C), 129.01 (q, ${}^{1}J({}^{13}C, {}^{11}B) = 69.8$ Hz, 3C, CN), 124.76 (s, CH, 1C), 123.09 (s, CH, 1C), 61.17 (s, 1C, OCH₂), 45.75 (s, CH₂, 1C), 36.66 (s, 1C, CH₃), 17.73 (q, ${}^{3}J({}^{13}C, {}^{11}B) = 3.2$ Hz, 1C, CH₃), 15.42 (s, 1C, CH₃). ¹¹B{¹H} NMR ((CD₃)₂CO): δ : -19.03 (s, 1B). Raman (cm⁻¹): 2204, 2216 (ν (CN)).

Sodium trifluoroethoxytricyanoborate, Na $[CF_3CH_2OB(CN)_3]$. Method A

Na[B(OCH₂CF₃)₄] (1.0 g, 2.33 mmol) was stirred in TMSCN (15.0 mL, 119.5 mmol) for 2 d at 80 °C. All volatiles were removed under reduced pressure and the black residue was dissolved in an aqueous solution of H₂O₂ (30% w/w, 20 mL). The solution was treated with Na₂CO₃ (*ca.* 0.5 g) in portions. The excess peroxide was destroyed by the addition of Na₂S₂O₅. The solution was extracted with THF (3 × 20 mL). The combined THF phases were dried with Na₂CO₃, filtered, the solvent was removed under reduced pressure, and the solid was dried under fine vacuum. Yield: 443 mg (2.10 mmol, 90%).

¹H NMR ((CD₃)₂CO): δ : 3.80 (qq, ³*J*(¹⁹F, ¹H) = 9.1 Hz, ³*J*(¹¹B, ¹H) = 2.0 Hz, 2H, OCH₂). ¹³C{¹H} NMR ((CD₃)₂CO): δ : 127.47 (q, ¹*J*(¹³C, ¹¹B) = 71.7 Hz, 3C, CN), 125.82 (qq, ¹*J*(¹⁹F, ¹³C) = 277.2 Hz, ³*J*(¹³C, ¹¹B) = 5.0 Hz, 1C, CF₃), 64.21 (q, ²*J*(¹⁹F, ¹³C) = 34.5 Hz, 1C, OCH₂). ¹⁹F NMR ((CD₃)₂CO): δ : -76.08 (t, ³*J*(¹⁹F, ¹H) = 8.8 Hz, 1H). ¹¹B NMR ((CD₃)₂CO): δ : -19.03 (t, ³*J*(¹⁹F, ¹H) = 2.0 Hz, 1B). (-)-ESI MS calculated for (C₅H₂BF₃N₃O)⁻: 188.0 (100%), 187.0 (24%), 189.0 (7%). Found: 187.7 (100%), 186.7 (29%), 188.7 (10%). Raman (cm⁻¹): 2236, 2228 (ν (CN)).

Elemental analysis was performed on crystals of $Na[CF_3CH_2OB(CN)_3]$ ·0.5H₂O. Anal. calculated for $C_5H_3BF_3N_3NaO_{1.5}$: C, 27.31%; H, 1.38%; N, 19.11%. Found: C, 27.09%; H, 1.29%; N, 18.77%.

Method B

Na[B(OCH₂CF₃)₄] (5.0 g, 11.63 mmol) was stirred in TMSCN (20.0 mL, 159.4 mmol) for 17 h at 80 °C. The formation of a colorless precipitate was observed. Subsequently, all volatiles were removed under vacuum. The residue was dissolved in THF (5 mL). The addition of CH₂Cl₂ resulted in the precipitation of a colorless solid. Yield: 1.96 g (9.29 mmol, 80%).

Sodium bis(methoxy)dicyanoborate, Na[(CH₃O)₂B(CN)₂]

TMSCN (1.0 mL, 7.97 mmol) was added to a suspension of Na[B(OCH₃)₄] (592 mg, 3.75 mmol) in dry acetonitrile (30 mL) and stirred for 12 h at room temperature. The stirring was stopped, and the precipitant could settle. The clear liquid phase was transferred into a second flask, all volatiles were removed under reduced pressure, and the product was dried under a fine vacuum. Yield: 440 mg (2.97 mmol, 79%). ¹H NMR (CD₃CN): δ : 3.21 (q, ³J_{B-H} = 3.3 Hz, 6H) ppm. ¹H{¹¹B} NMR (CD₃CN): δ : 3.21 (s, 6H). ¹³C NMR (CD₃CN): δ : 131.85 (q, ¹J(¹³C, ¹¹B) = 68.4 Hz, 2C, CN), 50.91 (q, ³J(¹³C, ¹H) = 139.5 Hz, 2C, CH₃). ¹¹B NMR (CD₃CN): δ : -5.40 (q, ³J(¹¹B, ¹H) = 3.2 Hz, 1B).

Sodium bis(1,1,1-trifluoroethoxy)dicyanoborate, Na[(CF₃CH₂O)₂B(CN)₂]. Method A

Na[B(OCH₂CF₃)₄] (2.0 g, 4.7 mmol) was stirred in TMSCN (20.0 mL, 159.4 mmol) for 2 d at room temperature. All volatiles were distilled off and the colorless residue was dried under vacuum. The crude product was dissolved in acetone (*ca.* 5 mL) and precipitated by the addition of CHCl₃ (50 mL). The solid was filtered off and dried under fine vacuum. Yield: 1.2 g (4.2 mmol, 89%). ¹H NMR ((CD₃)₂CO): δ : 3.78 (qq, ³*f*(¹⁹F,¹H) = 9.4 Hz, ³*f*(¹¹B,¹H) = 1.6 Hz, 4H, OCH₂).¹³C{¹H} NMR ((CD₃)₂CO): δ : 130.23 (q, ¹*f*(¹³C,¹¹B) = 73.8 Hz, 2C, CN), 126.40 (qq, ¹*f*(¹⁹F,¹³C) = 280.9 Hz, ²*f*(¹³C,¹¹B) = 4.4 Hz, 2C, CF₃), 62.15 (q, ²*f*(¹⁹F,¹³C) = 34.1 Hz, 2C, OCH₂). ¹¹B NMR ((CD₃)₂CO): δ : -76.11 (t, ³*f*(¹⁹F,¹H) = 9.3 Hz, 6F, CF₃). (-)-ESI MS calculated for (C₅H₂BF₃N₃O)⁻: 261.0 (100%), 260.0 (24%), 262.0 (7%). Found: 261.3 (100%), 260.3 (25%), 262.3 (1%). Raman (cm⁻¹): 2229, 2222, 2215 (ν(CN)).

Method B

 $Na[B(OCH_2CF_3)_4]$ (15.0 g, 34.9 mmol) was stirred in TMSCN (45.0 mL, 358.6 mmol) for 2 d at room temperature. All volatiles

were distilled off and the colorless residue was dried under vacuum. The solid was redissolved in THF (10 mL) and precipitated by the addition of CH_2Cl_2 (200 mL). The product was isolated by filtration and dried under fine vacuum. Yield: 8.0 g (28.2 mmol, 81%).

1-Ethyl-3-methylimidazolium trifluoroethoxytricyanoborate, [EMIm][CF₃CH₂OB(CN)₃]

Na[CF₃CH₂OB(CN)₃] (1.50 g, 7.11 mmol) was dissolved in bidistilled water (10 mL) and mixed with a solution of [EMIm]Cl (1.16 g, 7.91 mmol) in bidistilled water (10 mL). Dichloromethane (50 mL) was added to the reaction mixture and the emulsion was stirred for 15 min. The CH₂Cl₂ phase was separated, washed with bidistilled water (3 \times 5 mL), dried with MgSO₄, and filtered. The solution was evaporated under reduced pressure and the ionic liquid was dried under fine vacuum. Yield: 1.93 g (6.45 mmol, 91%). Anal. calculated for C11H13BF3N5O: C, 44.18%; H, 4.38%; N, 23.42%. Found: C, 44.01%; H, 4.67%; N, 24.72%. ¹H NMR ((CD₃)₂CO): δ: 8.99 (s, 1H, CH), 7.73 (t, ${}^{3}f({}^{1}H,{}^{1}H) = 1.8$ Hz, 1H, CH), 7.66 (t, ${}^{3}f({}^{1}H,{}^{1}H) = 1.7$ Hz, 1H, CH), 4.39 (q, ${}^{3}/({}^{1}H, {}^{1}H) = 7.3$ Hz, 2H, CH₂), 4.05 (s, 3H, CH₃), 3.79 $(qq, {}^{3}f({}^{19}F, {}^{1}H) = 9.1 \text{ Hz}, {}^{3}f({}^{11}B, {}^{1}H) = 2.0 \text{ Hz}, \text{ OCH}_{2}, 2H), 1.57$ $(t, {}^{3}J({}^{1}H, {}^{1}H) = 7.3, 3H, CH_{3})$. ${}^{13}C{1H} NMR ((CD_{3})_{2}CO): \delta: 136.70 (s, 136.70)$ CH, 1C), 127.11 (q, ¹/₁(¹³C, ¹¹B) = 71.7 Hz, 3C, CN), 124.45 (s, CH, 1C), 123.52 (qq, ${}^{1}J({}^{19}F, {}^{13}C) = 277.2$ Hz, ${}^{3}J({}^{13}C, {}^{11}B) = 5.0$ Hz, 1C, CF₃), 122.78 (s, CH, 1C), 64.21 (q, ${}^{2}J({}^{19}F, {}^{13}C) = 34.5$ Hz, 1C, OCH₂), 45.45 (s, CH₂, 1C), 36.32 (s, 1C, CH₃), 15.24 (s, 1C, CH₃). ¹⁹F NMR ((CD₃)₂CO): δ : -75.96 (t, ${}^{3}_{I}$ (${}^{19}F$, ${}^{1}H$) = 9.09 Hz, 1H). ${}^{11}B$ NMR ((CD₃)₂CO): δ : -19.07 $(t, {}^{3}J({}^{11}B, {}^{1}H) = 2.0 \text{ Hz}, 1B)$. Raman (cm^{-1}) : 2211 $(\nu(CN))$.

1-Ethyl-3-methylimidazolium tetracyanoborate, [EMIm][B(CN)₄]

K[CH₃OB(CN)₃] (2.5 g, 15.72 mmol) was placed into an autoclave and TMSCN (90.0 mL, 674.91 mmol) and TMSCl (10.0 mL, 79.16 mmol) were added. The reaction mixture was heated for 11 h to 250 °C while stirring. The maximum pressure was 70 bar. After cooling to room temperature all volatiles were removed under reduced pressure. The residue was dissolved in water (50 mL). The suspension was treated with an aqueous solution of H₂O₂ (30% w/w, 100 mL) and the pH was adjusted to about 3 by the addition of aqueous HCl (37% w/w). The mixture was stirred overnight. All volatiles were removed using a rotary evaporator (50 °C) and the residue was extracted with acetone (30 mL). Acetone was removed using the rotary evaporator and the residue was dissolved in water (10 mL) and treated with [EMIm]CI (2.5 g, 11.17 mmol). The aqueous solution was extracted with dichloromethane (20 mL) and the organic phase was washed with bidistilled water (3 \times 1 mL). Subsequently, dichloromethane was removed using the rotary evaporator and the ionic liquid was dried under fine vacuum. Yield: 1.1 g (4.87 mmol, 31%). The analytical data are consistent with those reported earlier.15

Electrochemical measurements

All electrochemical studies were performed on the neat ILs under an argon atmosphere with a Metrohm PGSTAT30 potentiostat and a Microcell HC set-up with a Eurotherm temperature controller (rhd instruments). A 0.1 mL Pt-cell TSC-70 closed (rhd instruments) served as a counter electrode and was equipped with a glassy carbon working electrode (surface area: 3.14×10^{-2} cm²). Specific conductivities (σ) were determined at different temperatures (20, 40, 60, 70, and 80 °C) by impedance spectroscopy from 500×10^3 to 800 Hz. The cell constant was determined on a 1413 µS cm⁻¹ conductivity solution HI 70031 (HANNA instruments). Cyclic voltammetry was conducted at 20 °C with a scan rate of 50 mV s⁻¹ using the same set-up and an additional Ag/Ag⁺ micro reference electrode (acetonitrile, rhd instruments).

Single-crystal X-ray diffraction

Single-crystals of Li[CH₃OB(CN)₃]·H₂O, K[CH₃OB(CN)₃], Na[C₂H₅OB(CN)₃], and Na[CF₃CH₂OB(CN)₃]·0.5H₂O were studied with a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped using Cu-K_α radiation (micro-focus sealed X-ray tube, $\lambda = 1.54184$ Å) and single-crystal of Na[CH₃OB(CN)₃]·H₂O was investigated using an Oxford Xcalibur equipped with an EOS detector using Mo-K_α radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods,^{44,45} and refinements are based on full-matrix least-squares calculations on $F^{2,44,46}$ All nonhydrogen atoms were refined anisotropically. The positions of all H atoms were located from electron density difference maps. In the final steps of the refinements, idealized bond lengths and angles were introduced for most of the H atoms.

All calculations were performed with the ShelXle graphical interface.⁴⁷ Molecular structure diagrams were drawn with the program Diamond 4.6.3.⁴⁸ Experimental details, crystal data, and the CCDC numbers are collected in Tables S4–S6 in the ESI. \ddagger

DFT calculations

Density functional calculations $(DFT)^{49}$ using the hybrid functional B3LYP⁵⁰ and Pople-type basis sets 6-311++G(d,p) were performed with the Gaussian16 program suite.⁵¹ All structures represent true minima with no imaginary frequency on the respective hypersurface.

Conflicts of interest

There are no conflicts to declare.

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