

Pseudo Halide Chemistry in Ionic Liquids with Decomposable Anions

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Abstract. Several pseudohalide containing ionic liquids with quarternary ammonium counter cations of the general formula $[R_3MeN]X$ [R = ethyl (**1X**), n -butyl (**2X**) with $X^- = CN^-$, N_3^- , OCN^- , and SCN^-] were synthesized by decomposition of the corresponding trialkylammonium methylcarbonate in the reaction with Me_3Si-X . We also treated **2CN** with $OP(OMe)_3$, yielding $[nBu_3MeN][O_2P(OMe)_2]$

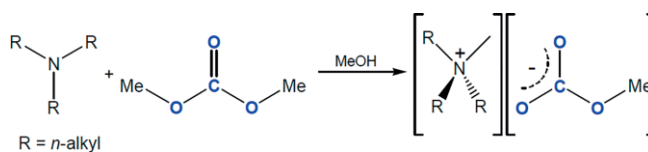
and acetonitrile (Me-CN). The double salt $[nBu_3MeN]_2\{[B(OMe)_3(CN)](CN)\}$ was obtained from the reaction of **2CN** with $B(OMe)_3$, featuring the formation of the monocyanotrimethoxyborate anion, $[B(OMe)_3(CN)]^-$, co-crystallized with $[nBu_3MeN]CN$. $[nBu_3MeN]_2\{[B(OMe)_3(CN)](CN)\}$ was fully characterized including structure elucidation.

Introduction

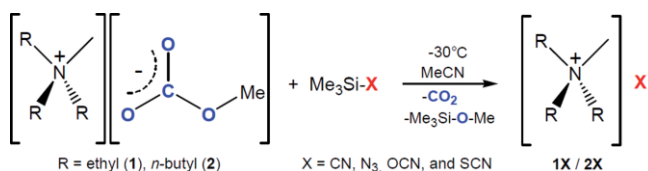
The pseudohalogen concept was first mentioned by *Birkenbach* and *Kellermann* in 1925, followed by further modifications and developments in subsequent years.^[1–5] Molecular entities X can be regarded as classical pseudohalogen when showing halogen-like chemical behavior, e.g. they can form a (i) univalent radical, (ii) singly charged anion, (iii) neutral dimer, which disproportionates and reacts with multiple bonds, (iv) interpseudoalogen compound, (v) hydrogen pseudohalogen acid, (vi) highly insoluble salt with Ag^I , Pb^{II} , and Hg^I cations, and (vii) complex compound such as $[E(X)_m]^{n-}$.^[6]

Syntheses of pseudohalide-containing ionic liquids (IL)^[7] are usually carried out in biphasic systems, in which different solubilities of salts are utilized, or via salt metathesis reactions, in which a highly insoluble salt (often a silver halide) precipitates.^[8–13] Incomplete cation exchange and dissolved traces of metal halides^[14] in the ionic liquid are known problems for this synthetic route. In addition, long drying times at elevated temperatures are necessary to remove residual water or solvents, often resulting in darkening of the ionic liquid caused by traces of decomposition products. To avoid these problems, ionic liquids containing a methylcarbonate anion^[15–20] have proven to be promising starting materials (Scheme 1). These ionic liquids are accessible by methylation of e.g. tertiary amines with organic carbonate esters (Scheme 1), first men-

tioned in a patent by *Wertz*^[21] and further discussed and examined in a series of publications.^[22,23] For the introduction of anionic species, carbonate esters can be decomposed in an additional step with Brønsted acids,^[22,24] silylated pseudohalides, or (per)silylated compounds^[25,26] bearing elements of group 15, 16, or 17 (Scheme 2 for halides). This use of decomposable cations or anions provides easy access to pure ionic liquids and low melting salts that are free of traces of metal halides and water in good, near quantitative yields.



Scheme 1. Synthesis of tetraalkylammonium methylcarbonates in methanol with dimethyl carbonate and an alkylated tertiary amine.



Scheme 2. Formation of tetraalkylammonium pseudohalides via nucleophilic desilylation of trimethylsilyl pseudohalogenes by methylcarbonate-containing ILs.

Here we report on the synthesis of ionic liquids and low temperature melting salts, which contain pseudohalide anions such as $[R_3MeN]X$ (R = ethyl (**1X**), n -butyl (**2X**) with $X^- = CN^-$, N_3^- , OCN^- , and SCN^-). Moreover, we examined the reaction of such ILs with $B(OMe)_3$ and $OP(OMe)_3$.

Results and Discussion

Synthesis of $[R_3MeN]X$ [R = ethyl (**1**), n -butyl (**2**); $X^- = CN^-$, N_3^- , OCN^- , SCN^-]

For synthesizing a set of different trialkylmethylammonium pseudohalides (**1X** and **2X**, Scheme 2) we first prepared trialk-

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201900055> or from the author.

ylmethylammonium methylcarbonates $[\text{Et}_3\text{MeN}][\text{CO}_3\text{Me}]$ (**1**) and $[\text{nBu}_3\text{MeN}][\text{CO}_3\text{Me}]$ (**2**) by a slightly changed literature protocol as illustrated in Scheme 1.^[15–20] Subsequently, the syntheses of quaternary ammonium pseudohalides was achieved in the reaction of $[\text{Et}_3\text{MeN}][\text{CO}_3\text{Me}]$ (**1**) and $[\text{nBu}_3\text{MeN}][\text{CO}_3\text{Me}]$ (**2**) with the corresponding trimethylsilyl pseudohalogen compound (Scheme 2), a synthetic approach previously reported by *Sundermeyer* and co-workers^[25] (see Supporting Information for further details). By this method, all pseudohalides **1X** and **2X** ($X = \text{CN}^-$, N_3^- , OCN^- , and SCN^-) could be obtained in nearly quantitative yields (90–99%) as colorless solids.

Thermal Properties: Melting and Decomposition Points

Melting and decomposition temperatures of all salts **1X** and **2X** are listed in Table 1. While both starting materials (**1** and **2**) are ILs, only all **2X** have melting points below 101 °C and hence can be regarded as ILs.^[27,28] Except from **1SCN**, all other **1X** salts do not show a melting point since decomposition starts prior to melting leading always to a brownish/black residue. Interestingly, substitution of ethyl by butyl leads to much lower melting points ($\Delta T_{\text{mp.}} > 100$ °C) and decomposition points ($\Delta T_{\text{dec.}} = 55$ °C CN^- , 64 °C N_3^- , 32 °C OCN^- , and 14 °C SCN^-).

Table 1. Melting and decomposition points /°C of tetraalkylammonium methylcarbonates and pseudohalides (heating rate 5 K·min⁻¹).

Compound	M.p.	Dec.	Compound	M.p.	Dec.
1	60	170	2	45	190
1CN	– a)	234	2CN	100	179
1N₃	– a)	254	2N₃	57	190
1OCN	– a)	240	2OCN	56	208
1SCN	213	221	2SCN	100	207

a) Decomposition below melting.

Our decomposition and melting points of **1CN** and **2CN**, respectively, are significantly higher than known values reported by *Simchen* et al. (215–220 °C vs. 234 °C and 78–81 °C vs. 100 °C, Table 1).^[29] This is believed to be the result of remaining traces of inorganic salts resulting from salt metathesis reactions. Such impurities can be avoided when the methylcarbonate anion is decomposed with trimethylsilyl pseudohalogen to form the desired pseudohalide salt (Scheme 2). The determined melting point for **2SCN** (100 °C) agrees well with the published value of *Strong* and *Kraus* (101 °C).^[30]

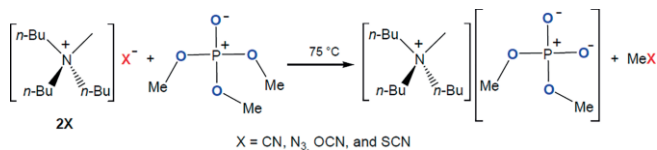
By means of ESI-TOF measurements, it was possible to observe ion pairs for all **1X** and **2X** salts in both the positive and

negative mode as shown in Table 2. This indicates that salts such as **1X** and **2X** can be transferred into the gas phase without decomposing. The main series of peaks correspond to singly charged salt cluster ions of the form $[\text{Cat}_2(\text{X})]^+$ and $[\text{Cat}(\text{X})_2]^-$.^[31] Only for **1CN** we were able to observe a cluster cation of the type $\{[\text{Et}_3\text{MeN}]_5(\text{CN})_4\}^+$ that belongs to the series $[\text{Cat}_n(\text{X})_{n-1}]^+$ with $n = 5$.^[32]

Reaction of $[\text{nBu}_3\text{MeN}]\text{X}$ with $\text{OP}(\text{OMe})_3$ and $\text{B}(\text{OMe})_3$.

To study the Lewis acidity of $\text{OP}(\text{OMe})_3$ and $\text{B}(\text{OMe})_3$ we treated both species with pure $[\text{nBu}_3\text{MeN}]\text{X}$ (**2X**) with the aim to generate ions of the type $[\text{OP}(\text{OMe})_3\text{X}]^-$ and $[\text{B}(\text{OMe})_3\text{X}]^-$, respectively.

Since methylation is preferred over cyanide complexation, treatment of $\text{OP}(\text{OMe})_3$ resulted in quantitative methylation of the cyanide ion, yielding acetonitrile and $[\text{nBu}_3\text{MeN}][\text{O}_2\text{P}(\text{OMe})_2]$ (Scheme 3). After removing all volatiles in vacuo, a light yellow solid was obtained in almost 90% yield. The light yellow solid melts at 66 °C and decomposes above 185 °C (heating rate 5 K·min⁻¹). An alternative strategy to synthesize $[\text{nBu}_3\text{MeN}][\text{O}_2\text{P}(\text{OMe})_2]$ is the methylation of the amine nBu_3N with trimethyl phosphate, reported by *Buchanan* et al.^[33]



Scheme 3. Reaction of pure **2X** with pure $\text{OP}(\text{OMe})_3$ yielding the dimethylphosphate salt and a methylated pseudohalide MeX ($X =$ pseudohalogen).

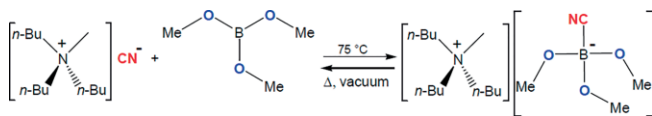
NMR spectroscopic studies of the reaction of $\text{OP}(\text{OMe})_3$ with $[\text{nBu}_3\text{MeN}]\text{X}$ ($X = \text{N}_3$, OCN , SCN), also revealed the formation of the $[\text{O}_2\text{P}(\text{OMe})_2]^-$ anion (in addition to Me-X). The $[\text{O}_2\text{P}(\text{OMe})_2]^-$ ion was always detected as a singlet resonance at 1.3 ppm in the $^3\text{P}\{^1\text{H}\}$ NMR spectra. In ESI-TOF studies the $\{[\text{nBu}_3\text{NMe}]_2[\text{O}_2\text{P}(\text{OMe})_2]\}^+$ ($m/z = 525$) as well as $\{[\text{nBu}_3\text{NMe}][\text{O}_2\text{P}(\text{OMe})_2]_2\}^-$ ($m/z = 450$) were detected. All methylated pseudohalides were characterized by NMR studies, for example, methyl azide was detected by means of $^{14}\text{N}\{^1\text{H}\}$ NMR showing three distinct singlets ($N_\alpha = -173$ ppm, $N_\beta = -130$ ppm, $N_\gamma = -321$ ppm).^[34–39] In the reaction with **2OCN**, methyl isocyanate was formed that trimerized to trimethylcyanuric acid, which was proven by two singlets at $\delta = 29$ ppm and 150 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR

Table 2. Ion pair formation, visible in the analyses of (ESI-TOF)-MS. Values for ion pairs in m/z .

Compound	Positive scan	Negative scan
1CN	$\{[\text{Et}_3\text{MeN}]_5(\text{CN})_4\}^+$	$\{[\text{Et}_3\text{MeN}](\text{CN})_2\}^-$
1N₃	$\{[\text{Et}_3\text{MeN}]_2(\text{N}_3)\}^+$	$\{[\text{Et}_3\text{MeN}](\text{N}_3)_2\}^-$
1OCN	$\{[\text{Et}_3\text{MeN}]_2(\text{OCN})\}^+$	$\{[\text{Et}_3\text{MeN}](\text{OCN})_2\}^-$
1SCN	$\{[\text{Et}_3\text{MeN}]_2(\text{SCN})\}^+$	$\{[\text{Et}_3\text{MeN}](\text{SCN})_2\}^-$
2CN	$\{[\text{nBu}_3\text{MeN}]_2(\text{CN})\}^+$	$\{[\text{nBu}_3\text{MeN}](\text{CN})_2\}^-$
2N₃	$\{[\text{nBu}_3\text{MeN}]_2(\text{N}_3)\}^+$	$\{[\text{nBu}_3\text{MeN}](\text{N}_3)_2\}^-$
2OCN	$\{[\text{nBu}_3\text{MeN}]_2(\text{OCN})\}^+$	$\{[\text{nBu}_3\text{MeN}](\text{OCN})_2\}^-$
2SCN	$\{[\text{nBu}_3\text{MeN}]_2(\text{SCN})\}^+$	$\{[\text{nBu}_3\text{MeN}](\text{SCN})_2\}^-$

spectra.^[40–42] The formation of methyl thiocyanate was detected by the appearance of two singlets in the $^{13}\text{C}\{^1\text{H}\}$ NMR at 16 and 114 ppm.^[40,41,43] In all three cases, no product isolation was performed. It should be noted that the usual way to synthesize Me-X ($X = \text{CN}, \text{N}_3, \text{OCN}, \text{SCN}$) is to methylate the pseudohalides with dimethylsulfate.^[43] In addition, $\text{OP}(\text{Ph})_3$ was used instead of $\text{OP}(\text{OMe})_3$, but in this case no formation of $[\text{O}_2\text{P}(\text{OPh})_2]^-$ or $[\text{O}_2\text{P}(\text{OPh})_3\text{X}]^-$ could be observed. Even upon activation with ultrasonic irradiation at 80°C for 3 h did not lead to any reaction.

No reaction was observed when $\text{B}(\text{OMe})_3$ was treated with $[\text{nBu}_3\text{MeN}]\text{X}$ ($X = \text{N}_3, \text{OCN}, \text{SCN}$) or $[\text{Et}_3\text{MeN}]\text{CN}$, not even at elevated temperatures of 100°C . However, when $\text{B}(\text{OMe})_3$ was added to $[\text{nBu}_3\text{MeN}]\text{CN}$, a slow reaction was detected. At the beginning of the reaction, a suspension was observed which liquefied with time. This reaction mixture was slowly heated to 75°C for one hour while the mixture was sonicated. After cooling the liquid to ambient temperature, a few crystals of $[\text{nBu}_3\text{MeN}]_2\{[\text{B}(\text{OMe})_3(\text{CN})](\text{CN})\}$ could be obtained and separated from the yellow-colored and viscous (room temperature) ionic liquid by manual crystal picking. The ionic liquid with the $[\text{B}(\text{OMe})_3(\text{CN})]^-$ anion appears to be very unstable, since heating this compound in vacuo to 70°C leads to decomposition, whereby the starting materials $[\text{nBu}_3\text{MeN}]\text{CN}$ and $\text{B}(\text{OMe})_3$ form again (Scheme 4).



Scheme 4. The synthesis of tri-*n*-butylmethylammonium trimethoxy-cyanido-borate.

Since we realized that depending on the stoichiometry $\text{B}(\text{OMe})_3 : [\text{nBu}_3\text{MeN}]\text{CN}$ either a mono-phasic or a biphasic system is formed, we used NMR techniques to examine these mixtures. A highly viscous oil is received when using an equimolar stoichiometry, leading to a broadening of the cyanide signal in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which is high-field shifted (singlet for the $\delta(\text{CN}^-) = \text{CN}$ at 136 vs. 167 ppm for $[\text{nBu}_3\text{MeN}]\text{CN}$ in CD_3CN) that gives a hint for the formation of a covalently bound cyanide species (Figure 1) [cf. $[\text{B}(\text{OMe})_2(\text{CN})_2]^-$ 132, $[\text{B}(\text{OMe})(\text{CN})_3]^-$ 129, or $[\text{B}(\text{CN})_4]^-$ 123, $[\text{BF}(\text{CN})_3]^-$ 127, $[\text{BF}_2(\text{CN})_2]^-$ 130, $[\text{BF}_3(\text{CN})]^-$ 132 ppm,

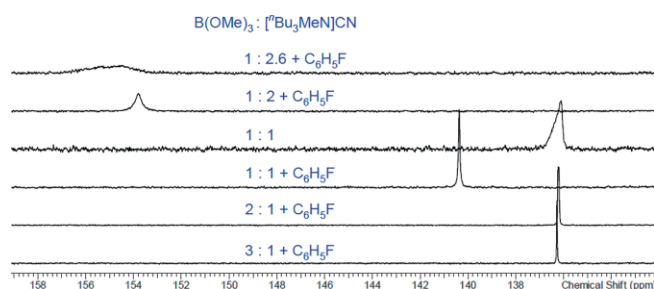


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR experiments of the reaction of $\text{B}(\text{OMe})_3$ and $[\text{nBu}_3\text{MeN}]\text{CN}$ utilizing different stoichiometries. Only cyanide signals are shown for clarity.

Table 3).^[81] A molar ratio of 3:1 and 2:1 results in a biphasic system even at elevated temperatures (75°C). A suspension is formed when adding more equivalents of ammonium cyanide, so fluorobenzene was added for homogenization. The solvent causes a downfield shift of the cyanide signal to 140 ppm in the 1:1 molar ratio. At higher cyanide concentrations (1:2 and 1:2.6) the mixture becomes more viscous and the ^{13}C signal broadens and shifts from 154 to 156 ppm, respectively. The broadening could also arise due to an equilibrium between free and covalently bound cyanide in $[\text{B}(\text{OMe})_3(\text{CN})]^-$.

Table 3. $^1\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts for different mixtures of $\text{B}(\text{OMe})_3$ and $[\text{nBu}_3\text{MeN}]\text{CN}$ (chemical shift δ in ppm).

Ratio: $\text{B}(\text{OMe})_3:\text{CN}^-$	$^1\text{B}\{^1\text{H}\}$	$^{13}\text{C}\{^1\text{H}\}$
Pure $\text{B}(\text{OMe})_3$ ^{a)}	18.5 (s)	–
3 : 1 + $\text{C}_6\text{H}_5\text{F}$ ^{b)}	12.5 (br)	136.3 (s)
2 : 1 + $\text{C}_6\text{H}_5\text{F}$ ^{b)}	9.7 (br)	136.2 (s)
1 : 1 ^{b)}	1.5 (br)	136.2 (br)
1 : 1 + $\text{C}_6\text{H}_5\text{F}$ ^{b)}	1.5 (br)	140.4 (s)
1 : 2 + $\text{C}_6\text{H}_5\text{F}$ ^{b)}	0.9 (br)	153.8 (br)
1 : 2.6 + $\text{C}_6\text{H}_5\text{F}$ ^{b)}	0.9 (br)	156.2 (br)
Pure $[\text{nBu}_3\text{MeN}]\text{CN}$ ^{a)}	–	167 (s)
$[\text{B}(\text{OMe})_3(\text{CN})]^-$ ^{a)}	5.9 (br)	150.3 (s)
$[\text{B}(\text{OMe})_2(\text{CN})_2]^-$ ^{c)}	–5.4 (q)	131.9 (s)
$[\text{B}(\text{OMe})(\text{CN})_3]^-$ ^{c)}	–18.4 (q)	128.5 (s)

a) This work, in $[\text{D}_3]$ acetonitrile. b) This work, no deuterated solvent. c) In $[\text{D}_6]$ acetone from literature.^[44]

$^1\text{B}\{^1\text{H}\}$ NMR studies show an up-field shift, compared to the trimethyl borate signal at $\delta = 19$ ppm, of the boron species at higher cyanide concentrations, starting from 13 (for 3:1) to 10 (for 2:1) to 2 ppm (for 1:1). The largest high-field chemical shift at 1 ppm was observed for a 1:2.6 ratio. A side product, presumably the $[\text{B}(\text{OMe})_2(\text{CN})_2]^-$ at -5.8 ppm in $^1\text{B}\{^1\text{H}\}$ NMR spectrum, could be detected. In summary, NMR studies (see Figure 1 and Figure 2) display that a highly dynamic system is observed, especially at high concentrations of $[\text{nBu}_3\text{MeN}]\text{CN}$, which is reflected by a large line width. An excess of $\text{B}(\text{OMe})_3$ results in an up-field shift of the $[\text{B}(\text{OMe})_3(\text{CN})]^-$ signal and the line width decreases. The polarity of the solvent has also a strong influence on the chemical shift, leading to a downfield shift of the $[\text{B}(\text{OMe})_3(\text{CN})]^-$ signal from 136 (neat without solvent) over 140 in fluorobenzene to 150 ppm in acetonitrile.

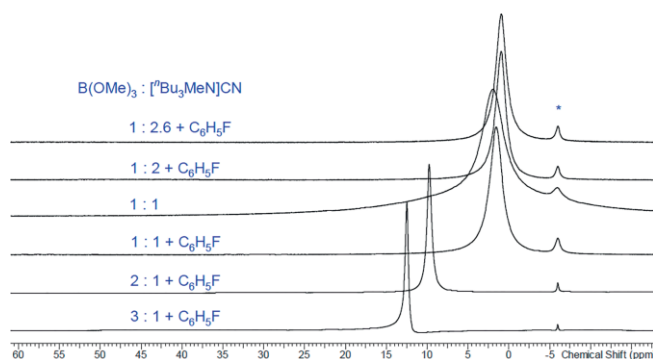


Figure 2. $^1\text{B}\{^1\text{H}\}$ NMR experiments of the reaction of $\text{B}(\text{OMe})_3$ and $[\text{nBu}_3\text{MeN}]\text{CN}$ utilizing different stoichiometries. The asterisk marks the assumed $[\text{B}(\text{OMe})_2(\text{CN})_2]^-$ anion.

The highly viscous, champagne-colored room temperature ionic liquid $[n\text{Bu}_3\text{MeN}][\text{B}(\text{OMe})_3(\text{CN})]$ can be obtained with a yield of > 99%. m.p. $-51\text{ }^\circ\text{C}$). From this IL it was possible to isolate a few crystals of the double salt $[n\text{Bu}_3\text{MeN}]_2\{[\text{B}(\text{OMe})_3(\text{CN})](\text{CN})\}$ after three days that crystallized in the orthorhombic space group *Aba2* with three independent $[n\text{Bu}_3\text{MeN}]_2\{[\text{B}(\text{OMe})_3(\text{CN})](\text{CN})\}$ moieties in the asymmetric unit. Only one independent ion pair of the double salt $[n\text{Bu}_3\text{MeN}]_2\{[\text{B}(\text{OMe})_3(\text{CN})](\text{CN})\}$ is shown in Figure 3. There are no significant interionic interactions as there are no close interionic distances. The shortest inter-anionic $[\text{B}(\text{OMe})_3(\text{CN})]^- \cdots \text{CN}^-$ distance is 5.9 \AA . The $[\text{B}(\text{OMe})_3(\text{CN})]^-$ ion adopts a slightly distorted tetrahedral arrangement (all angles around the boron atoms are between $107\text{--}111^\circ$) with almost local C_3 symmetry $[(\text{B}1\text{--C}1\text{--N}1) = 177.7(4)^\circ]$. Both the B–C [$1.700(5)\text{ \AA}$] and B–O distances (av. 1.442 \AA) are in the typical range of single bonds, although the more polar B–O bonds are significantly shorter than the B–C bond. The CN bond length of the free cyanide is slightly shorter than the CN ligand distance [cf. $1.096(5)$ vs. $1.149(5)\text{ \AA}$].

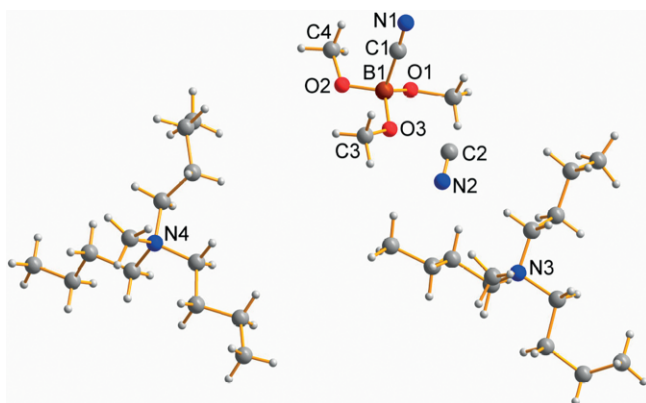


Figure 3. Ball-and-stick representation of the molecular structure of one independent ion pair of $[n\text{Bu}_3\text{MeN}]_2\{[\text{B}(\text{OMe})_3(\text{CN})](\text{CN})\}$ in the crystal. Selected bond lengths / \AA and angles $^\circ$: B1–C1 $1.700(5)$, B1–O1 $1.446(5)$, B1–O2 $1.442(5)$, B1–O3 $1.438(5)$, C1–N1 $1.149(5)$, N2–C2 $1.096(5)$; B1–C1–N1 $177.7(4)$, O1–B1–C1 $108.4(3)$, O2–B1–C1 $107.3(3)$, O3–B1–C1 $109.2(3)$, O1–B1–O2 $111.0(3)$, O1–B1–O3 $110.4(3)$, O2–B1–O3 $110.5(3)$.

Conclusions

Pseudohalide (X) containing ionic liquids such as $[\text{R}_3\text{MeN}]\text{X}$ can be synthesized easily by decomposition of the corresponding trialkylammonium methylcarbonates in the reaction with $\text{Me}_3\text{Si–X}$. Ammonium pseudohalides of the type $[n\text{Bu}_3\text{MeN}]\text{CN}$ were treated with OPOMe_3 affording $[n\text{Bu}_3\text{NMe}][\text{O}_2\text{P}(\text{OMe})_2]$ and the methylated pseudohalide, while a double salt $[n\text{Bu}_3\text{NMe}]_2\{[\text{B}(\text{OMe})(\text{CN})](\text{CN})\}$ was obtained from the reaction of $[n\text{Bu}_3\text{MeN}]\text{CN}$ with $\text{B}(\text{OMe})_3$.

Experimental Section

Caution! HCN / cyanides are highly toxic! Appropriate safety precautions (HCN detector, gas mask, low temperatures) should be taken.

Experimental and computational details including all spectra and ORTEP representations of all experimentally studied species are given in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Supporting information includes experimental details and all spectra (NMR, IR, Raman).

Acknowledgements

The authors thank Deutsche Forschungsgemeinschaft (DFG SCHU 1170/9–2), especially the priority program SPP 1708 for financial support (*Philip Stoer*).

Keywords: Pseudohalide; Borates; Ionic liquids; Structure; Synthesis

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Received: March 12, 2019

Published Online: ■

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