Pseudohalogen Chemistry in Ionic Liquids with Non-innocent Cations and Anions

Sören Arlt,[a] Kevin Bläsing,[a] Jörg Harloff,[a] Karoline Charlotte Laatz,[a] Dirk Michalik,[a] Simon Nier,[c] Axel Schulz,[a, b] Philip Stoer,[a] Alrik Stoffers,[a] and Alexander Villinger[a]
Within the second funding period of the SPP 1708 “Material Synthesis near Room Temperature”, which started in 2017, we were able to synthesize novel anionic species utilizing ionic liquids (ILs) both, as reaction media and reactant. ILs, bearing the decomposable and non-innocent methyl carbonate anion [CO₂Me]⁻, served as starting material and enabled facile access to pseudohalide salts by reaction with Me₂Si–X (X = CN, N₃, OCN, SCN). Starting with the synthesized Room temperature ionic liquid (RT-IL) [nBu₄MeN][B(OMe)₃(CN)], we were able to crystallize the double salt [nBu₄MeN][B(OMe)₃(CN)]·CN. Furthermore, we studied the reaction of [WCC][SCN] and [WCC][CN]. In addition, the highly labile anionic HCN solvates were obtained from [PPN][X] (PPN = μ-nitridos(triphénylphosphorium), X = N₃, OCN, SCN and OCP) and HCN. Crystals of [PPN][X(HCN)]₂ (X = N₃, OCN) and [PPN][SCN(HCN)]₂ were obtained when the crystallization was carried out at low temperatures. Interestingly, reaction of [PPN][OCP] with HCN was noticed, which led to the formation of [PP(HCN)]⁻, crystallizing as HCN disolvate [PPN][P(CN·HCN)₃]. Furthermore, we were able to isolate the novel cyanido(halido) silicate dianions of the type [SiCl₆₃]⁻ and [Si(CN)₆]²⁻ and the hexa-substituted [Si(CN)₆]³⁻ by temperature controlled halide/cyanide exchange reactions. By facile neutralization reactions with the non-innocent cation of [Me₃SnSb(Se)]⁺ with MOH (M = Li, K), Li₃[Si(CN)₆]·2H₂O and K₅[Si(CN)₆] were obtained, which form three dimensional coordination polymers. From salt metathesis processes of Li₃[Si(CN)₆] with different imidazolium bromides, we were able to isolate new imidazolium salts and the ionic liquid [BMIm][Si(CN)₆]. When reacting [Mes(nBuIm)][Si(CN)₆] with an excess of the strong Lewis acid B(C₆F₅)₃, the voluminous adduct anion [Si(CN·B(C₆F₅)₃)]⁻ was obtained.

1. Introduction

With this Minireview, we would like to summarize our results obtained during the 2nd period of the SPP 1708 “Material Synthesis near Room Temperature”. SPP 1708 was mainly set up to identify and demonstrate the advantages (but also the disadvantages) of ILs when used as reaction media for synthesis in contrast to common inorganic and organic solvents. In synthesis, ILs can play an active role as template, e.g. for the precipitation of nanoparticles,[11–14] or it is more or less inert providing a highly polar reaction media composed of ions.[15] Even after six years of SPP 1708, utilization of ILs as reaction media for the synthesis of inorganic compounds is still a fairly new area steadily growing and with the focus on metal/metal-oxide/metal nitride (nano)particles of different types,[16–18] semiconductors,[19] and inorganic solids (e.g. zeolites).[20–23] Besides application in classic solid state chemistry, ILs can be used as reaction media to prepare (oligomeric) metal complexes, metal organic frameworks, coordination polymers[24–28] or cluster compounds incorporating main group elements.[29–31] Within SPP 1708, the synthesis of intermetallic cluster and nanoparticles,[32–34] the controlled synthesis of polyanions and cations,[35–37] solvent-free chalcogenidometal-containing materials,[38–40] and nanocrystalline materials,[41–43] as well as the low-temperature synthesis of thermoelectric materials were investigated. Moreover, theoretical[44–46] and solubility[47–49] aspects during the synthesis process were studied. Among the publications with respect to main group molecule chemistry, some highlights are the isolation and characterization of [P₆S₆H₄]⁻ by Ruck et al.[50] and the cluster anions of the type [M₅Sn₅Se₅]⁻ (M = Mn, Zn, Cd) by Dehnen et al.[51] and the isolation of elusive hydrogen bonded poly(hydrogen halide) halogenates [XYH⁺]⁻ (X = Br, I, ClO₄⁻; Y = Cl, Br, CN) by Hasenstab-Riedel and coworkers.[52]

Following our interests in pseudohalide chemistry, we focused on the synthesis of small molecules with the primary goal to make very simple isolable compounds. During the first funding period we were able to synthesize and characterize salts bearing new heteroleptic cyanido(fluorido)phosphate anions of the general formula [PF₆–n(CN)₄+n]⁻ (n = 1 – 4),[53–58] as well as the homoleptic tetracyanidoborate anion [BC(CN)₄]⁻.[59] By very mild Lewis-acid catalyzed synthesis protocols, when starting from ILs. We succeeded in the synthesis and structural characterization of molecular pinctogen triyanides E(CN)₃ (E = Sb, Bi), which were stabilized in the IL [BMIm][OTf] (BMIm = 1-nButyl-3-methylimidazolium, [OTf] = F₃CSO₂O⁻), thus preventing these species from oligomerization.[60] Utilizing ILs, we were able to synthesize salts with homoleptic [E(CN)₅]²⁻ anions (E = Sb, Bi), but never formed any higher substituted species like [Bi(CN)₆]³⁻ or [Li₃[Si(CN)₆]·2H₂O and K₅[Si(CN)₆] were obtained, which form three dimensional coordination polymers. From salt metathesis processes of Li₃[Si(CN)₆] with different imidazolium bromides, we were able to isolate new imidazolium salts and the ionic liquid [BMIm][Si(CN)₆]. When reacting [Mes(nBuIm)][Si(CN)₆] with an excess of the strong Lewis acid B(C₆F₅)₃, the voluminous adduct anion [Si(CN·B(C₆F₅)₃)]⁻ was obtained.

[1] Dr. S. Arlt, Dr. K. Bläsing, Dr. J. Harloff, K. C. Laatz, Dr. D. Michalk, Prof. A. Schulz, P. Stoer, Dr. A. Stoffers, Dr. A. Villinger Anorganische Chemie, Institut für Chemie, Universität Rostock A.-Einstein-Str. 3a 18059 Rostock (Germany) E-mail: axel.schulz@uni-rostock.de [2] Prof. A. Schulz Materialdesign, Leibniz-Institut für Katalyse an der Universität Rostock A.-Einstein-Str. 29a 18059 Rostock (Germany) [3] S. Nier Anorganische Chemie, Institut für Chemie, Philipps-Universität Marburg Hans-Meerwein-Straße 4 35032 Marburg (Germany) E-mail: simon.nier@chemie.uni-marburg.de © 2020 The Authors. Published by Wiley-VCH GmbH
2. Synthesis of Pure Pseudohalide Containing ILs from ILs with Decomposable Anions \(^{123-125}\)

We started this project with the synthesis of various trialkylmethylammonium- \((R,M_nE_n): R = E, nPr, nBu\) \(^{123,124}\) and methyltriphenylphosphonium methylcarboxates \(^{125}\). They were formed in autoclave reactions at autogenous pressure (Scheme 1), due to a modified reaction, which was first described by Wernitz \(^{126}\) and taken up again in later years by various working groups. \(^{127-129}\)

In a subsequent reaction we synthesized the pseudohalides of the type \([R,M_nE_n]X: X = CN, N_2, OCN, SCN\) \(^{122}\) by nucleophilic desilylation of trimethylpseudoalosilanes \(Me_3Si-X\) with the reactive and non-innocent \([CO_2Me]^+\) anion (Scheme 2), a reaction developed by Sundermeyer et al. \(^{129}\) Besides the pseudohalide salt, \(Me_3Si-Ome\) and \(CO_2\) were formed, whereby the latter can be removed from the reaction solution, which shifted the reaction equilibrium in favor of the products. The formation of the stable \(Si-O\) bond \((444 \text{kJ/mol})\) is also a driving force of this reaction. These synthesized ILs (and salts with a low-temperature melting point), containing methyl carbones and pseudohalides, provided the basis for the majority of all planned reactions, which are described in the following sections.

In addition to the synthesis of the pseudohalide salts, we aimed to isolate possible intermediates such as \([CO_2X]^−\) \((X = \text{pseudohalogen})\), which are presumably formed during the decomposition reaction (Scheme 2). The fluoro- and cyanofor-mates \([COF]^−\) \(^{130}\) or \([CO_2CN]^-\) \(^{132}\) are already literature known.

\[ R + Me_3SiOme + Me_3SiX = RMe_3SiOme + Me_3SiX \]

\(T = 120 \degree C\)

MwOH

Scheme 1. Synthesis of methylcarboxates with trialkylmethylammonium \((E = N, R = E, nPr, nBu)\) or methyltriphenylphosphonium \((E = P, R = Ph)\) counter ions in methanol with dimethyl carbonate and a tertiary alkylated amine or triphenylphosphine, respectively.

\[ RMe_3SiOme + CO_2 = RMe_3Si-OMe + CO_2 \]

Scheme 3. Temperature dependant equilibrium of cyanoformate and the starting materials \([Et_3MeN]CN\) and \(CO_2\) at a \(CO_2\) pressure of 3 bar.

\[ \frac{n/4 P_4 + 2 MCN}{solvent} \rightarrow \frac{M[P(CN)_{n-1}] + MP_{n-1}}{} \]

\[ 4 P_4 + 2 MCN \rightarrow M[P(CN)_5] + MP_{15} \]

Scheme 4. Synthesis of dicyanophosphides and polyphosphonides by nucleophilic degradation of white phosphorus with cyanides \((M = [18]crown-6-Na/K, [Et_3N], [nBuN], [PPN])\).\(^{114}\)

3. Reactions of Pseudohalides Containing ILs with \(P_4\) and \(P_4S_{10}\) \(^{113}\)

As Schmidt et al. could show, white phosphorus is degraded by cyanide salts to dicyanophosphide and different polyphosphonides in solution (Scheme 4).\(^{113}\)

We wondered whether new phosphorus pseudohalide compounds could be synthesized, using the pure ILs without further solvents.\(^{113}\) To prevent the white phosphorus from sublimating, a mixture of \(P_4\) and the ILs \([nBuMeN]X:\((X = CN, N_2)\) was filled into an ampoule. This was sealed and then heated to 65°C \((X = N_2)\) and 105°C \((X = CN)\), respectively, causing the solids to liquify. When heating the mixture for 24 h, a shiny violet-black solid was formed in both reaction vessels and a red \((X = N_2)\) or colorless \((X = CN)\) liquid was formed as well. Subsequently, the reaction products were extracted with which the latter was synthesized as the \([Ph,P]^−\) salt by exposure of \(CO_2\) to a concentrated solution of \([Ph,P]^−\) in acetonitrile.

First, we tried to isolate pseudohalofomrate anions from concentrated and cooled reaction solutions of \([R,M_nE_n][CO_2Me]\) and \(Me_3Si-X\) in acetonitrile.\(^{133}\) But even at \(-40\degree C\) the release of gaseous \(CO_2\) was observed and no new signals for any \([CO_2X]^-\) species could be observed by means of \(^{13}C(\text{H})\) NMR spectroscopy. Subsequently, a solvent free process was used, from which the \([CO_2CN]^-\) anion was synthesized with \([Et_3MeN]^−\) as counter cation, when heating pure \([Et_3MeN]CN\) to 150°C in a \(CO_2\) atmosphere at a pressure of 3 bar. Initially, the salt remained solid at high temperature but then liquefied when it was cooled down to room temperature. Raman spectroscopy revealed that at room temperature the RT-IL \([Et_3MeN][CO_2CN]\) with \(ν_{CO_2}=2196\text{ cm}^{-1}\) is present, while at elevated temperature \((100\degree C)\) the \(C=O\) bond cleavage (activation barrier \(≈ 40 \text{kJ/mol}\)) and formation of the starting materials \([Et_3MeN]CN\) with \(ν_{CN}=2049\text{ cm}^{-1}\) and \(CO_2\) is observed (Scheme 3). In a closed system this process is reversible, whereby \([Et_3MeN][CO_2CN]\) is formed again upon cooling. However, when the system is opened, \(CO_2\) is irreversibly released and \([Et_3MeN]CN\) is formed.

Nevertheless, a reaction of other ammonium pseudohalides of the type \([nBuMeN]X\) \((X = N_2, OCN, SCN)\) with \(CO_2\) could not be observed under similar reaction conditions.
acetonitrile and benzene, leaving an insoluble black solid. By means of $^1$H and $^{13}$C($^1$H) NMR spectroscopic analysis of the liquid phase, the decomposition of the cation to $n$Bu$_2$N could be determined in both reactions. The reaction of $P_4$ with cyanide also resulted in the formation of traces of $[P(CN)]_4^-$ as was observed by Schmidtpeter et al.$^{[134]}$ The solid residues could not be examined further by Raman spectroscopy due to fluorescence, but elemental analyses of the substances indicated a high phosphorus content of the compound with 61% for $X=Na$ and 33.7% for $X=CN$. The formation of further unknown pseudohalide phosphorus compounds could not be observed by means of $^{31}$P NMR spectroscopy. Due to the instability of the cation, no further experiments with $[n$Bu$_3$MeN] X ($X=OCN$ and SCN) were performed.

Likewise, the aim was to investigate whether the pseudohalide salts undergo reaction with phosphorus pentasulfide, hopefully leading to the formation of new compounds via a solvent-free synthesis process. Roessky et al. already observed the formation of $[[NCPS]_2]^-$, $[[N_3]_2PS]_2^-$ and $[[NPS]_2S]_2^-$ or $[[SCN]_2PS]_2^-$, which were isolated as $[n$Pr$_2$N] salts by reaction of $MX$ (M = Na or K; $X=CN$, $N_3$ or SCN) with $P_4S_{10}$ in acetonitrile.$^{[134]}$ We heated a mixture of two equivalents of $[n$Bu$_3$MeN]CN with one equivalent of $P_4S_{10}$ at 105°C for 24 h, thus resulting in liquefaction of both reactants and formation of a homogeneous phase. In solvents such as Et$_2$O, benzene, thf or n-hexane, no formed products could be extracted, whereas in acetonitrile the complete residue was dissolved. From the complex reaction mixture, only two formed products could be assigned by $^{31}$P NMR and (ESI-TOF)-MS. One was the adamantane-like $[P_3S_2N]^-\text{anion}^{[135,136]} (\delta [^{31}P]=67$ and 33 ppm; m/z = 426) and the second was the $[[SCN]_2PS]_2^-\text{anion}^{[134]} (\delta [^{31}P]=53$ ppm, m/z = 211), which are already known from literature and are shown in Scheme 5. Interestingly, Roessky et al. prepared the $[P_3S_2N]$ anion by the reaction of $[N_3]_2PS_2^-$ with $P_4S_{10}$, while the $[[SCN]_2PS]_2^-$ was formed from $P_4S_{10}$ and KSCN.

As the products could neither be extracted from the mixture nor crystallized in different mixtures of solvents, e.g. acetonitrile/benzene or acetonitrile/diethyl ether, no further investigations with other ILs $[n$Bu$_3$MeN]X ($X=OCN$, SCN) were carried out.

### 4. Reactions of Pseudohalides containing ILs with Acids of Pseudohalides (HA)$^{[125,137,138]}$

When attempting the synthesis of $[PPN(SCN)]$ from $[PPN][Cl]$ and KSCN in H$_2$O, we surprisingly obtained crystals of $[PPN][H(NCS)]$. A direct method for the synthesis of this compound was achieved when $[PPN][SCN]$ was treated with $\textit{in situ}$ formed HNCS, generated from MeOH and Me$_3$Si–NCS (Scheme 6).

According to X-ray analysis, a slightly bent anion is formed, with one N–H–N hydrogen bridge (Figure 1, contacts a and b). Dove and Nuzzo et al. already observed the formation of molecular [H(NCS)$_2$]$^-$ ion when a solution of WCC(SCN) ([WCC] = [Ph$_4$As], [Ph$_3$P]) was treated with the acid HNCS.$^{[139,140]}$

Already in 1978, Salthouse and Waddington observed that, when HCN was added to $[n$Pr$_2$N]CN, the solution became increasingly viscous due to polymerization of the HCN and also noticed that the color of the solution quickly intensified. Crystals, which formed in the black oil, were examined by IR spectroscopy. A single band for $\nu_{CN}=2060$ cm$^{-1}$ indicated the formation of hydrogen dicyanide (HCN)$_2^-$, but a solid state structure was not determined.$^{[141]}$ Thus motivated, we tried to synthesize salts containing the [CN(HCN)$_n$]$^-$ ($n=1, 2, 3 \ldots$) ions by reaction of pure HCN with [WCC]CN ([WCC] = [Et$_3$MeN], [n$Pr$_2$N$]N,$[n$Bu$_3$MeN], [Ph$_3$P]).$^{[125]}$ In an initial study the salts were suspended in Me$_3$Si–CN and then MeOH was added to generate HCN in situ, but no crystallization could be achieved when cooling the solutions. Therefore, the [WCC]CN were dissolved directly in an excess of 15 equivalents of HCN, which was cooled to 0°C. The concentrated, highly ionic solution with the characteristics of an IL turned from yellow to brown within an hour and became increasingly viscous, which can be explained by the formation of polymeric HCN species.$^{[142]}$ Since in all cases no crystallization of a product could be achieved, different salts of the type [WCC]CN ([WCC] = [PPN], [Ph$_3$P]) were used, which contain symmetrical cations and thus crystallize faster (Scheme 7).

Colorless crystals of [Ph$_3$P]CN(HCN)$_3$ could be obtained from a solution of [Ph$_3$P]CN in pure liquid HCN, when the mixture was slowly cooled to $-20^\circ$C. The compound is sensitive

![Figure 1. Ball-and-stick representation of the [H(NCS)$_2$]$^-$ ion in the crystal of [PPN][H(NCS)$_2$]. Dashed red lines (a and b) represent hydrogen bridges.](image-url)

![Scheme 6. Synthesis of hydrogen dithiocyanate from the reaction of [PPN]SCN with [H(NCS)$_2$].](image-url)

![Scheme 7. Synthesis of dihydrogen tricyanide and trihydrogen tetracyanide containing salts by reaction of [Ph$_3$P]CN or [PPN]CN with liquid HCN.](image-url)
to temperature as well as moisture and decompose over time, observed by Raman spectroscopy. X-ray structure analysis proved the formation of molecular dihydrogen tricyanide anions \([\text{CN(HCN)}]^-\) (Figure 2). The anions form distorted chains which are formed by hydrogen bonds (Figure 2, contacts a and b). The chains are connected to each other by weak Van der Waals interaction (Figure 2, contact c) by a head-to-tail arrangement and thus form chains along the α-axis in the crystal.

Due to disorder, three other isomers can be considered besides the isomer \([\text{NC–H–CN–H–CN}^-]\) (P = 73%, major), which show the formation of hydrogen isocyanide \([\text{CN–H–CN–H–CN}^-]\), \([\text{NC–H–CN–H–NC}^-]\), \([\text{CN–H–CN–H–NC}^-]\). DFT calculations (pbe0/aug-cc-pVTZ) support this finding, since the thermodynamically preferred isomer also has the lowest energy of all four calculated linear anions. Furthermore, the energies for a rotation of the central cyanide ion in a flexible \([\text{CN(HCN)}]^-\) system were calculated. An activation energy of 7.0 kcal/mol is low enough to allow the central anion to rotate freely in solution at room temperature, thus explaining a disorder.

When [PPN]CN was used instead of \([\text{Ph}_3\text{P}]\text{CN}\), crystals with the trihydrogen tetracyanide ion \([\text{PPN}[\text{CN(HCN)}]]^-\) are formed. Intra-ionic hydrogen bonds (Figure 3, contacts a–f) and inter-ionic Van der Waals interactions (Figure 2, contacts g–j) also lead to chains along the b-axis in the crystal. Y-shaped molecular anions are built, due to the larger cavities formed by the bulky [PPN] cation, which allows the aggregation of a further HCN molecule. This Y-shaped isomer, which contains only hydrogen cyanide molecules, also represents the energetically preferred structure of all calculated isomers of the trisolvates.

In addition, we were curious, whether it is possible to stabilize and isolate HCN aggregates with other pseudohalides, such as azide, cyanate, thiocyanate and the phosphaethynolate anion in form of their [PPN]⁺ salts. Again, the pseudohalides were dissolved in cooled HCN, but unfortunately no crystals could be obtained from the concentrated and cooled phase. Hence, a rather unusual crystallization method was used. Fomblin YR-1800 perfluropolyether was placed in a low-temperature stage for crystal picking, which was cooled to −60 °C. The HCN salt mixtures were cooled until the liquid layer of the IL-like mixture slowly solidified and subsequently, small portions of the solid were transferred into the ether. Even at −60 °C, the release of gaseous HCN could be observed which resulted in formation of X-ray suitable crystals. The azide and cyanate salts crystallized as trisolvates [PPN][X(HCN)] (X = N₃, OCN) (Figure 4 and Figure 5). Both molecular anions exhibit a distorted Y-shaped geometry. Head-to-tail contacts of adjacent anions can be observed but with quite long interionic distances. Hence, the formation of anionic strands, which are located in the cavities formed by the bulky [PPN]⁺ ions, are better explained by packing effects in the crystal. Due to disorder of the central cyanate anion in [OCN(HCN)]⁺, two different isomers have to be considered. On the one hand, an isomer (52(1)%) in which two C–H–O and one C–H–N H-bridges are observed (Figure 5, left), and on the other hand an isomer (48(1)%) in which two C–H–N and one C–H–O H-bridges are found (Figure 5, right). The thiocyanate salt crystallized as HCN...
disolvate [PPN][SCN(HCN)]\textsubscript{2} forming a L-shaped molecular anion with one C–H–N and one C–H–S hydrogen bridge (Figure 6, left). Computations suggest that the energetically favored isomers exhibit a Y-shaped structure with two C–H–N H-bridges. However, the observed L-shaped geometry was found to be only 0.58 kcal/mol higher in energy. Interestingly, if the isomers exhibit a Y-shaped structure with two C–H–N H-bridges. However, the observed L-shaped geometry was found to be only 0.58 kcal/mol higher in energy. Interestingly, if the

5. Synthesis of Pseudohalogen Borate and Phosphate Species in Pseudohalide Containing \( \text{ILs}^{[123]} \)

The Lewis acidities of trimethyl phosphate OP(OMe)\textsubscript{3} and trimethyl borate B(OMe)\textsubscript{3} were investigated towards the pure

\( \text{ILs} \) [nBu\textsubscript{3}MeN]X (X = CN, N\textsubscript{3}, OCN, SCN), hopefully leading to new pseudohalide phosphates or borates. However, a reaction of [nBu\textsubscript{3}MeN]X with OP(OMe)\textsubscript{3} did not lead to the formation of new pseudohalide phosphates as hoped (Scheme 8, route A), but in all cases to methylation of the pseudohalide and to formation of [nBu\textsubscript{3}MeN][O\textsubscript{2}P(OMe)\textsubscript{3}], which could be shown clearly by means of NMR spectroscopy (Scheme 8, route B).\textsuperscript{[123]}

When heating [nBu\textsubscript{3}MeN]X and B(OMe)\textsubscript{3} in a flask, a reaction was observed exclusively with X = CN. When heating an equimolar mixture slowly to 75 °C, the RT-IL [nBu\textsubscript{3}MeN][B \textsubscript{3}O\textsubscript{2}E\textsubscript{3}] with a melting point of –51 °C, was formed. The cyanidotrimethoxyborate anion is thermally unstable and can be transferred to the starting materials in vacuum, which is accelerated when raising the temperature (Scheme 9). After cooling the RT-IL to room temperature, the formation of crystals could be observed. X-ray elucidation of the single crystals revealed the formation of the double salt [nBu\textsubscript{3}MeN][B \textsubscript{3}O\textsubscript{2}E\textsubscript{3}(CN)]\textsubscript{2}, with the novel [B(OMe)\textsubscript{3}CN]\textsuperscript{2} ion. According to a patent by Finze et al., the formation of [B(OMe)\textsubscript{3}CN]\textsuperscript{2} has only been observed as intermediate by means of NMR and MS analysis, when synthesizing [B(OMe)\textsubscript{3}],[E(CN)\textsubscript{3}](n = 2, 3), starting from [B(OMe)\textsubscript{3}]+ and cyanotrimethylsilane.)\textsuperscript{[144]}

6. Reaction of Pseudohalogen Borate ILs with Persilylated Compounds of Group 15\textsuperscript{[133]}

Since it is already known that [B(OMe)\textsubscript{3}]\textsuperscript{2} undergoes reaction with cyanotrimethylsilane to form [B(OMe)\textsubscript{3}],[E(CN)\textsubscript{3}](n = 2, 3) under elimination of MeSi–OMe, the reactivity of the synthesized [B(OMe)\textsubscript{3}],[E(CN)\textsubscript{3}] anion towards tris(trimethylsilyl)phosphane and tris(trimethylsilylamine) was investigated.\textsuperscript{[133]} The aim was to synthesize new cyanide-containing compounds by the same silyl ether elimination reaction under formation of a boron-element bond (Scheme 10).

An equimolar mixture of [nBu\textsubscript{3}MeN][B(OMe)\textsubscript{3}(CN)] and E \textsubscript{3}(SiMe\textsubscript{3})(E = N, P) was placed in a flask. In both cases, a two-phase system was formed in which the starting materials remained unchanged at room temperature, showing no reaction. When heating the mixtures to 55 °C, no reaction with N \textsubscript{3}(SiMe\textsubscript{3})\textsubscript{3} was observed according NMR analysis. However, with P

Figure 6. Left: Ball-and-stick representation of the molecular L-shaped [SCN(HCN)]\textsubscript{2} ion in the crystal of [PPN][SCN(HCN)]\textsubscript{2}. Right: Ball-and-stick representation of the molecular [PCN(HCN)]\textsubscript{2} ion in the crystal of [PPN][PCN(HCN)]\textsubscript{2}. Red dashed lines (a and b) show hydrogen bonding whereas the grey dashed lines (c and d) show head-to-tail contacts.

Scheme 8. Route A: Assumed nucleophilic addition of ammonium pseudohalides (R = nBu, X = CN, N\textsubscript{3}, OCN, SCN) to trimethoxy phosphate. Route B: Observed reaction of the ammonium pseudohalides with OP(OMe)\textsubscript{3}, and formation of ammonium dimethylphosphates via methylation of the pseudohalides.

Scheme 9. Synthesis of the RT-IL [nBu\textsubscript{3}MeN][B(OMe)\textsubscript{3}(CN)] and decomposition of the anion into its starting materials at elevated temperature in vacuum.

Scheme 10. Assumed reaction of [nBu\textsubscript{3}MeN][B(OMe)\textsubscript{3}(CN)] with E(SiMe\textsubscript{3})\textsubscript{3} (E = N, P) via Me\textsubscript{3}Si–OMe elimination reactions.
accompanied with the formation of [B(OMe)3]−.

The synthesis of hexacyanidosilicate dianions [Si(CN)6]2− was motivated by the fact that this anion, besides the already synthesized pseudohalide analogues [SiX6]2− (X = N Cs, 146,147 OCN, 148,149 SCN, 150,151 SeCN, 152 NCCICs, 153), was not yet known. The first attempt to synthesize hexacyanido silicates was performed via Cl/CN substitution reactions. 145 Heating a mixture of SiCl4, AgCN and [WCC]CN (WCC) = [nPr2MeN] or [Ph3P] in acetonitrile, led to incomplete chloro/cyanide exchange. We were able to isolate [Ph(R)]2[SiCl6-x(CN)x] as well as [nPr2MeN][Ag(CN)Cl] from the corresponding mixtures (Scheme 11, Figure 3). Portius et al. faced the same problem when synthesizing hexacyanodisilicates as they could show in their publication, which appeared at the same time as ours. 154 Hence, we thought, that utilization of IL-like reaction mixtures could help to solve this problem.

Therefore, we changed the synthesis strategy. We started with the synthesis of [RjHN]2[SiF6] (R = Et, nPr), by protonation of tertiary amines with H2SiF6 (Scheme 12, route A), and [R3MeN]2[SiF6], which were formed by decomposition reactions of H3SiF6 with the previously synthesized ILs, the ammonium methylcarbonates (Scheme 12, route B). Subsequently, the fluoro silicates were suspended in 20 equivalents of Me6Si−CN and selectively converted to [SiF(CN)6]2− and [Si(CN)6]2− by temperature-controlled F/CN substitution reactions (Scheme 12, Figure 7), which could be isolated on a preparative scale. Catalytic amounts of GaCl3 as Lewis acid shortened the reaction time when synthesizing the hexacyanodisilicate dianions.

When using decomposable cations such as [Et4HN]+, we were able to synthesize Mj[Si(CN)6] (M = Li, K) by facile neutralization reactions of [Et4HN][Si(CN)6] with LiOH or KOH (Scheme 13, top). X-ray analysis of Li3[Si(CN)6]·2·H2O and K3[Si(CN)6] revealed the formation of coordination polymers, forming a 3D network in both cases. Subsequently, the metal salts were transferred by metathesis reactions with [BMIIm][Br] (1-Butyl-3-methylimidazolium) or TAAlLi 155-157 (Tunable Aryl Alkyl Ionic Liquids) such as [R(nBu)Im]Br (R = 2-MePh, 4-MePh, 2,4,6-Me3Ph = Mes, 2-MeOPh, 2,4-FPh, 4-BrPh) 145 to novel imidazolium hexacyanodisilicates (Scheme 13, middle). But only the combination with [BMIIm]− led to formation of a new IL, [BMIIm][Si(CN)6] with Tm,p = 72 °C, which contains a double negatively charged anion.

In addition, the reaction of the hexacyanodisilicate dianion towards the Lewis acid tris(pentafluoroethyl)borane B(CF3)3, was investigated. 146 But since all synthesized ammonium and alkali metal salts were only soluble in Lewis basic solvents such as MeCN, MeOH or H2O, which react themselves with the borane, a cation was needed, which allowed the salt to dissolve in non-Lewis basic solvents such as CH2Cl2. [Mes(nBu)Im][Si(CN)6] now enabled the reaction with B(CF3)3. Initially, we aimed to abstract one cyanide moiety affording in formation of [Si(CN)6]2− and [B(CF3)3][Si(CN)6]− when one equivalent of the borane

Scheme 11. Reaction of [WCC]CN and AgCN with SiCl4 ([WCC] = [nPr2MeN], [Ph3P]).

Scheme 12. Synthesis of [RjHN]2[SiF6] and [R3MeN]2[SiF6] as well as their conversion into [RjHN][SiF(CN)], [RjHN][Si(CN)3], and [R3MeN][SiF(CN)], [R3MeN][Si(CN)3] (R = Et, nPr and nBu). For reasons of clarity, the [SiF6]2− impurities in the starting material were omitted.

Figure 7. ORTEP representation of the molecular anion structure in the crystal of [Ph3P][SiCl6-x(CN)x]-4·MeCN (left), [nPr2MeN][SiCN6] (middle) and [nPr2MeN][Si(CN)6] (right). Cations and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at 50% level of probability.

Scheme 13. Top: Synthesis of Mj[Si(CN)6] (M = Li, K) via neutralization reactions. Middle: Synthesis of imidazolium hexacyanodisilicates via salt metathesis reactions (R = 2-MePh, 4-MePh, 2,4,6-Me3Ph = Mes, 2-MeOPh, 2,4-FPh, 4-BrPh). Bottom: Synthesis of the fully functionalized Lewis acid-base adduct anion [Si(CN)6B(CF3)3]− with [Cat] = [Mes(nBu)Im] as counter ion.
is used. Unfortunately, only different hexacyanidosilicate-borane substitution patterns could be observed by means of $^{11}$B($^{1}$H) NMR spectroscopy, but no compound could be isolated from the reaction mixture. But when the borane is used in excess ($n > 6$), a complete functionalization of all cyanide ligands with the borane was found and the voluminous [Si(CN)B(C$_3$F$_5$)$_3$]$_2$ adduct anion ($V_{\text{mole}} \approx 2.77$ nm$^3$) is formed (Scheme 13, bottom; Figure 8).

8. Conclusions

In conclusion, we have shown that salts containing the methyl carbonate anion like [R$_3$MeE][CO$_2$Me] (E = N, R = Et, nPr or nBu; E = P, R = Ph) are suitable starting materials for the quantitative synthesis of the corresponding ammonium and phosphonium pseudohalides [R$_3$MeE]X (X \text{= CN, N$_2$, OCN, SCN}) as well as for hexafluorosilicate salts such as [R$_3$MeN]$_2$[SiF$_6$] (R = nPr, nBu). Reactions of pseudohalides with Lewis-acidic OP(OMe)$_3$ and B(OMe)$_3$ were investigated, resulting in formation of the [O,P(OMe)$_3$]$_2$ anion under methylation of the pseudohalide or the synthesis of the RT-IL [nBu$_3$MeN][B(OMe)$_3$(CN)], respectively. Reaction of the ILs [nBu$_3$MeN]X (X \text{= CN, N$_2$}) with white phosphorus led to decomposition of the cation, yielding a free amine and polymeric phosphorus species. No novel anionic species could be extracted from the reaction of P$_3$S$_10$ with [nBu$_3$MeN]CN. When [WCC]CN ([WCC] = unsymmetrical) is dissolved in a slight excess of HCN, forming an IL, only fast polymerization of HCN was observed and no crystalline material could be obtained. With symmetrical cations, e.g. [PPN$_3$] and [PPN], it was possible to isolate the elusive [CN(HCN)$_4$]$_2^-$ and [CN(HCN)$_3$]$_2^-$ anions from the IL-like mixtures. We were able to isolate molecular [H(NCS)$_3$]$_2^-$, when treating [PPN]SCN with in situ generated HNCS. From an unusual crystallization medium (IL-mixture + perfluoropolyether), we were able to generate and isolate [PPN][N$_2$(HCN)$_3$], [PPN][OCN(HCN)$_3$], [PPN][SCN(HCN)$_3$] as well as [PPN][P(CN(HCN)$_3$)], when treating [PPN][X (X = N$_2$, OCN, SCN, OCP)] with liquid HCN after adding perfluoropolyether. These are the first examples of solvate anions of the type [X(HY)$_n$]$_2^-$, which contain two different pseudohalides. We also managed to synthesize novel (cyanido)halidosilicates of the type [SiCl$_2$(CN)$_6$]$_2^-$, [SiF(CN)$_6$]$_2^-$ and [Si(CN)$_3$]$_2^-$ from temperature controlled halide/cyanide exchange reactions. Utilizing neutralization and salt metathesis reactions, we were able to obtain metal salts, such as Li$_3$[Si(CN)$_3$]$_2$·2H$_2$O or K$_3$[Si(CN)$_3$] and novel imidazolium salts, respectively. Further, derivatization of the hexacyanidosilicate dianion with the Lewis acid B(C$_3$F$_5$)$_3$ led to formation of the bulky adduct anion [Si(CN-B(C$_3$F$_5$)$_3$)$_3$]$_2^-$, which can be regarded as a very bulky WCA (weakly coordinating anion).

**Experimental Section**

Caution! HCN and Me$_3$Si-CN are highly toxic! Appropriate safety precautions (HCN detector, gas mask, low temperature) should be taken. All experimental data can be found in the original papers.

**Acknowledgements**

The authors thank the Deutsche Forschungsgemeinschaft (DFG SCHU 1170/9-2), especially to the priority program SPP 1708, for financial support. We would like to thank all collaborators, especially Prof. Dr. Thomas Strassner and Dr. Swantje Lerch, for the nice cooperation regarding to the chemistry of the TAAILs, and the University of Rostock for access to the cluster computer. Open access funding enabled and organized by Projekt DEAL.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** pseudohalides · hydrogen bonding · ionic liquids · silicates · borates

---

[1] J. Dupont, J. D. Scholten, Chem. Soc. Rev. 2010, 39, 1780–1804.
[2] D. Marquardt, C. Janiak, Nachr. Chem. 2013, 61, 754–757.
[3] L. Schmölke, S. Lerch, M. Bülow, M. Schön, A. Schmitz, J. Thomas, G. Dehm, C. Held, T. Strassner, C. Janiak, Nanoscale 2019, 11, 4073–4082.
[4] S. Wegner, C. Janiak, Top. Curr. Chem. 2017, 375, 65.
[5] P. Kuhn, M. Antonietti, A. Thomas, Angew. Chem. Int. Ed. 2008, 47, 3450–3453; Angew. Chem. 2008, 120, 3499–3502.
[6] Y. Gao, A. Voigt, M. Zhou, K. Sundmacher, Eur. J. Inorg. Chem. 2008, 3769–3775.
[7] H. Kaper, M. G. Willinger, I. Djerdj, S. Gross, M. Antonietti, B. M. Smarsly, J. Mater. Chem. 2008, 18, 5761–5769.
[8] L. Le Li, W. M. Zhang, Q. Yuan, Z. X. Li, C. J. Fang, L. D. Sun, L. J. Wan, C. H. Yan, Crystal Growth and Design 2008, 8, 4165–4172.
W. S. Dong, C. L. Liu, L. Liu, F. Q. Lin, J. Cryst. Growth 2008, 310, 4626–4634.

Z. X. Li, L. Li, L. Q. Yuan, W. Feng, J. Xu, L. D. Sun, W. G. Song, C. H. Yan, J. Phys. Chem. C 2008, 112, 18405–18411.

A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Batiechina, Y. Grin, Nature 2006, 443, 320–323.

H. S. Park, Y. C. Lee, B. G. Choi, W. H. Hong, J. W. Yang, ChemSusChem 2008, 1, 356–362.

Y. H. Liu, C. W. Lin, M. C. Chang, H. Shao, A. C. M. Yang, J. Mater. Sci. 2008, 43, 5005–5013.

E. R. Parnham, A. M. Z. Slawin, R. E. Morris, J. Solid State Chem. 2007, 180, 49–53.

E. R. Parnham, R. E. Morris, Acc. Chem. Res. 2007, 40, 1005–1013.

A. Thirumurugan, C. N. R. Rao, Crystal Growth and Design 2008, 8, 1640–1644.

L. Wang, Y. Xu, Y. Wei, J. Duan, A. Chen, B. Wang, H. Ma, Z. Tian, L. Lin, J. Am. Chem. Soc. 2006, 128, 7432–7433.

E. R. Parnham, P. S. Wheatley, R. E. Morris, Chem. Commun. 2006, 380–382.

E. R. Parnham, R. E. Morris, J. Mater. Chem. 2006, 16, 3682–3684.

E. R. Parnham, R. E. Morris, J. Am. Chem. Soc. 2006, 128, 2204–2205.

Z. Qiao, Z. Wang, C. Zhang, S. Yuan, Y. Zhu, J. Wang, Angew. Chem. Int. Ed. 2012, 51, 215–228.

L. Liu, Y. Kong, H. Xu, J. P. Li, J. X. Dong, Z. Lin, Microporous Mesoporous Mater. 2011, 115, 624–628.

E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Z. Slawin, J. E. Warren, R. E. Morris, Angew. Chem. Int. Ed. 2011, 50, 17965–17968.

L. Wang, Y. P. Xu, B. C. Wang, S. J. Wang, J. Y. Yu, Z. L. Tian, W. L. Lin, Chem. Eur. J. 2008, 14, 10551–10555.

Z. Lin, Y. Li, A. M. Z. Slawin, R. E. Morris, Dalton Trans. 2008, 2, 3989–3994.

F. N. Shi, T. Trindade, J. Rocha, F. A. Almeida Paz, Crystal Growth and Design 2008, 8, 3917–3920.

J. H. Liao, W. C. Huang, Inorg. Chem. Commun. 2006, 9, 1227–1231.

L. Xu, Y. E. Choi, Y. U. Kwon, Inorg. Chem. 2007, 46, 10670–10680.

W. J. Ji, Q. G. Zhai, M. C. Hu, S. N. Li, Y. C. Jiang, Y. Wang, Inorg. Chem. Commun. 2008, 11, 1455–1458.

S. Chen, J. Zhang, X. Bu, Inorg. Chem. 2008, 47, 5567–5569.

J. Zhang, S. Chen, X. Bu, Angew. Chem. Int. Ed. 2008, 120, 5514–5517.

T. Hogben, R. E. Douthwaite, L. J. Gillie, A. C. Whitwood, CrystEngComm 2006, 8, 866–868.

S. H. Zottnick, W. G. Daul, C. Kerpen, M. Finze, K. Müller-Buschbaum, Chem. Eur. J. 2018, 24, 15287–15294.

J. J. Xiang, W. C. Huang, Inorg. Chem. Commun. 2006, 9, 1227–1231.

K. G. Köpcke, P. W. Roesky, C. Feldmann, Z. Anorg. Allg. Chem. 2004, 664, 1445–1450.

A. Eich, R. Köpcke, P. W. Roesky, C. Feldmann, Z. Anorg. Allg. Chem. 2004, 664, 275–279.

Y. Lin, W. Massa, S. Dehnen, Chem. Eur. J. 2012, 18, 13427–13434.

Y. Lin, D. H. Mayrhofer, S. Lippert, B. Ewers, A. Chernikov, M. Koch, S. Dehnen, Chem. Eur. J. 2013, 19, 8806–8813.

E. Ahmed, J. Breitneritz, M. F. Groh, M. Ruck, CrystEngComm 2012, 14, 4874–4885.

M. F. Groh, A. Isea, M. Rucka, Chem. Eur. J. 2012, 18, 10886–10891.

M. Ruck, Z. Anorg. Allg. Chem. 2012, 638, 1555–1555.

E. Ahmed, M. Rud, Coord. Chem. Rev. 2011, 255, 2892–2903.

S. Essig, S. Behrens, Chemie-Ingenieur-Technik 2015, 87, 1741–1747.

M. Knies, M. Kaiser, M. Lé Alh, A. Efimova, T. Doert, M. Ruck, Inorganics 2019, 7, 45.

S. Hess, K. Reiter, F. Weigand, W. Klopfer, C. Feldmann, Inorg. Chem. 2015, 54, 3899–3904.

A. Schmitz, K. Schütte, V. Ilievski, J. Barthel, L. Burk, R. Mullhäuser, J. Yue, B. Smarsly, C. Janiak, Beilstein J. Nanotechnol. 2017, 8, 2474–2483.

M. Siebel, S. Mai, L. Schmolke, K. Schütte, J. Barthel, J. Yue, J. Thomas, B. Smarsly, A. Devi, R. A. Fischer, C. Janiak, Beilstein J. Nanotechnol. 2018, 9, 1881–1894.

G. Thiele, P. Bron, S. Lippert, F. Nietzsche, O. Oeckler, M. Koch, B. Roling, S. Dehnen, Inorg. Chem. 2019, 58, 4052–4054.

M. Loor, S. Sallourn, P. Kavuloch, S. Izadi, G. Bendl, J. Guschlbauer, J. Sundermeier, N. Perez, K. Nielssen, G. Schiening, S. Schulz, Inorg. Chem. 2020, 59, 3428–3436.

K. Klauke, I. Gruber, T. O. Kneidel, L. Schmolke, J. Barthel, H. Breitzke, G. Bunkwoski, C. Janiak, Organometallics 2018, 37, 298–308.

S. Wolf, W. Klopfer, C. Feldmann, Chem. Commun. 2018, 54, 1217–1220.
