CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000289

Pseudohalonium Ions: $[Me_3Si–X–SiMe_3]^+$ (X = CN, OCN, SCN, and NNN)

Axel Schulz*[a, b] and Alexander Villinger*[a]

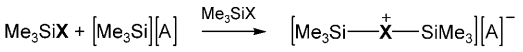
Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday

Abstract: By utilizing reaction mixtures, such as $Me_3Si–X/[Me_3Si–X–SiMe_3]^+$ (X = CN, OCN, SCN, and NNN), it was possible to prepare the first examples of bissilylated pseudohalonium cations in high yields. The structure and bonding of a whole series of salts containing pseudohalonium cations is discussed on the basis of experimentally observed (X-ray diffraction, Raman, and IR spectroscopy, and mass spectrometry) and theoretically obtained data. Salts containing pseudohalonium cations are only stable in the presence of weakly coordinating anions, such as the well-known tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$.

Keywords: azides · main group chemistry · pseudohalonium ions · weakly coordinating anions · X-ray diffraction

Introduction

Similar to a proton, the bulky trimethylsilicenium ion $[Me_3Si]^+$ (“big proton”)[1] is also always solvated and silylates the solvent forming the corresponding cation.[2,3,4] The full series of salts that contain bissilylated halonium cations $[Me_3Si–X–SiMe_3]^+$ (X = F, Cl, Br, and I) has been generated and fully characterized in the super Lewis acidic silylating medium $Me_3Si–X$ by using the $[Me_3Si]^+$ salt as the silylating reagent in the presence of the chemically robust, weakly coordinating, anion[5] tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$(Scheme 1).[1,2] Here, $Me_3Si–X$ is both solvent and reactant. Thus it was of great interest to see if, by means of this synthetic approach, it was also possible to prepare salts incorporating the bissilylated pseudohalonium cation (X = CN, OCN, SCN, and NNN), and to prove and extend the pseudohalogen concept. To the best of our knowledge, salts incorporating silylated pseudohalonium cations have not been reported yet.



$$Me_3SiX + [Me_3Si][A] \xrightarrow{Me_3SiX} [Me_3Si–\overset{+}{X}–SiMe_3][A]^-$$

Scheme 1. Synthesis of halonium (X = F, Cl, Br, and I) and pseudohalonium salts (X = CN (**1**), OCN (**2**), SCN (**3**), and NNN (**4**); $[A]^- = [B(C_6F_5)_4]^-$).

The pseudohalogen concept was introduced by Birckenbach and Kellermann in 1925 and further developed and justified in a series of publications in the following years.[6] Anions such as CN^-, CNO^-, NNN^-, OCN^-, and SCN^- can be regarded as classical linear pseudohalides, as these species fulfill the following criteria with respect to halogen-like chemical behavior:[7,8] A pseudohalogen (X) forms i) a strongly bound univalent radical ($X^•$), ii) a singly charged anion (X^-), iii) a pseudohalogen hydrogen acid of the type HX, iv) salts of the type $M(X)_n$ with silver, lead, and mercuric salts of low solubility, v) a neutral dipseudohalogen compound (X–X), which disproportionates in water and can be added to double bonds, and vi) interpseudohalogen species (X–Y).[8,9] In this study, we want to show that this concept can be extended by the criterion that a pseudohalogen should also form a pseudohalonium ion, for example, of the type $[Me_3Si–X–SiMe_3]^+$. Here we report the first examples of the synthesis and full characterization of salts that incorporate the homoleptic, bissilylated pseudohalonium ions $[Me_3Si–CN–SiMe_3]^+$ (**1**), $[Me_3Si–OCN–SiMe_3]^+$ (**2**), $[Me_3Si–SCN–SiMe_3]^+$ (**3**), and the intriguing $[(Me_3Si)_2NNN]^+$ (**4**) (Scheme 1). The trialkylsilylation of a weak base is known (solvents, arenes, weakly coordinating anions, silanes, etc.)[2,3,10] and hence we assumed that the lone pairs on both ends or on one end of an ambidentate pseudohalogen anion can be silylated. Notably, despite the lack of two sets of lone

---

[a] Prof. Dr. A. Schulz, Dr. A. Villinger
Institut für Chemie
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)

[b] Prof. Dr. A. Schulz
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-4986382
E-mail: axel.schulz@uni-rostock.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000289.

pairs, hydride-bridged bissilyl cations of the type $[R_3Si–H–SiR_3]^+$, in which the bonding is best described by a two-electron three-center bond in contrast to the four-electron three-center bond found in the analogous halonium ions, have been reported by the groups of Sekiguchi, Müller, and Reed.[10,11]

Results and Discussion

According to Scheme 1, pseudohalonium ions **1**–**4** are easily obtained when $Me_3Si–X$ (X = CN, OCN, SCN, and NNN (for **1**–**4**, respectively); 30 to 50 fold molar excess) is added dropwise to neat $[Me_3Si][B(C_6F_5)_4]$ (0.752 g, 1.0 mmol) at ambient temperatures with stirring, which results in a clear colorless solution (b.p. $Me_3Si–CN$ 114 °C; $Me_3Si–NNN$ 95 °C; $Me_3Si–NCO$ 90 °C; $Me_3Si–NCS$ 143 °C; $Me_3Si–NCSe$ 75 °C (175 mm/Hg)). Cooling to −25 °C over a period of one hour, results in the deposition of colorless crystals. Removal of excess trimethylpseudohalogenosilane by decantation and drying in vacuo gives the corresponding $[Me_3Si–X–SiMe_3][B(C_6F_5)_4]$ salt (X = CN, OCN, SCN, and NNN), as a colorless solid in almost quantitative yield (90–95 %). It should be noted that the synthesis of $[Me_3Si–NCSe–SiMe_3][B(C_6F_5)_4]$ was also attempted, but only decomposition products were observed on silylation even at very low temperatures.

All salts are extremely air and moisture sensitive, but stable under an argon atmosphere over a long period, as solids and in $Me_3Si–X$ solutions. Salts of **1**–**4** are easily prepared in bulk and are stable if stored in a sealed tube and kept at ambient temperatures. They are even thermally stable up to 120–190 °C (CN 188 °C; NNN 183 °C; OCN 164 °C; SCN 128 °C). Although **4**$[B(C_6F_5)_4]$ is a covalently bound azide, it is neither heat nor shock sensitive. Decomposition starts above 183 °C, which is quite astonishing.

Caution: Salts of **1**–**4** decompose vigorously and appropriate safety precautions should be taken when dealing with large quantities at temperatures above 100 °C.

The IR and Raman data of all considered pseudohalonium salts show sharp bands in the expected region $\tilde{\nu} = 2000–2350\ cm^{-1}$, which can be assigned to the stretching frequencies ν_{CN} (**1**–**3**) and $\nu_{as,NNN}$ (**4**), respectively. As previously shown for neutral R–CN adducts, the coordination of $B(C_6F_5)_3$ to a NC–R species causes a significant band shift to higher wavenumbers,[12] which is also observed upon silylation for **1**–**4** ($\Delta\nu_{IR}$ **1**: 57, **2**: 82, **3**: 136, **4**: 53 cm^{-1}). Hence, both IR and Raman spectroscopy ($\Delta\nu_{Raman}$ **1**: 56, **2**: 77, **3**: 120, **4**: 52 cm^{-1})[13,14] are particularly well suited to distinguish between pseudohalonium ions $[Me_3Si–X–SiMe_3]^+$ and the free solvents $Me_3Si–X$, whereas NMR spectroscopy is not suited. Owing to a rapid exchange process,[15] which has already been described for $[R_3Si][B(C_6F_5)_4]$ and bissilylated halonium ions,[1] no specific ^1H, ^{13}C, and ^{29}Si resonances could be detected for the pseudohalonium ions **1**–**4**.

X-ray quality crystals were obtained from saturated solutions of **1**–**4** at −25 °C. Single-crystal X-ray studies revealed the expected $[Me_3Si–X–SiMe_3][B(C_6F_5)_4]$ salts (X = pseudohalogen) without solvent molecules in the cell.[16]

The isoelectronic analogue of bis(trimethylsilyl)acetylene, $Me_3Si–C{\equiv}C–SiMe_3$, $[Me_3Si–C{\equiv}N–SiMe_3]^+$ crystallizes as the $[B(C_6F_5)_4]^-$ salt in the monoclinic space group $P2_1/c$ with four units per cell (Table 1). As depicted in Figure 1, the cation adopts an almost staggered, C_3-symmetric conforma-

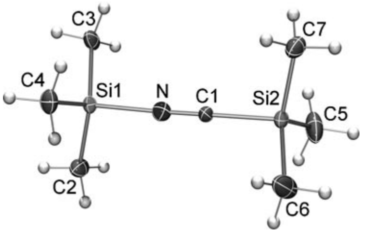


Figure 1. ORTEP drawing of the molecular structure of **1** in the crystal. Thermal ellipsoids with 50 % probability at 173 K. Selected bond lengths [Å] and angles [°]: Si2−C1 1.890(2), N−C1 1.157(2), Si1−N 1.888(2); C1-N-Si1 176.8(2), N-C1-Si2 178.5(2).

Table 1. Crystallographic details of **1**–**4**.[30]

	1	2	3	4
formula	$C_{31}H_{18}BF_{20}NSi_2$	$C_{31}H_{18}BF_{20}NOSi_2$	$C_{31}H_{18}BF_{20}NSSi_2$	$C_{30}H_{18}BF_{20}N_3Si_2$
M_w [g mol^{-1}]	851.45	867.45	883.51	867.46
color	colorless	colorless	colorless	colorless
system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2/c$	$P2_1/n$	$Pbcn$
a [Å]	8.208(4)	21.486(12)	11.195(7)	18.683(6)
b [Å]	17.811(9)	8.078(5)	18.966(13)	18.366(6)
c [Å]	24.084(13)	21.686(13)	17.077(11)	19.722(7)
β [°]	91.017(14)	112.117(13)	104.476(13)	90.00
V [Å^3]	3520(3)	3487(4)	3511(4)	6767(4)
Z	4	4	4	8
ρ_{calcd} [g cm^{-3}]	1.607	1.652	1.672	1.703
μ [mm^{-1}]	0.232	0.238	0.293	0.245
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)	173(2)
measured reflns	38 721	41 107	36 363	23 913
independent reflns	10 115	10 157	9278	8533
$I > 2\sigma(I)$	6952	7131	6925	4803
$R_{int.}$	0.0431	0.0355	0.0401	0.0482
$F(000)$	1696	1728	1760	3456
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0434	0.0422	0.0379	0.0439
wR_2 (F^2)	0.1197	0.1185	0.1069	0.0973
GoF	1.077	1.070	1.051	0.928
parameters	502	531	511	514

tion with large C-N-Si and N-C-Si angles of 176.8(3) and 178.5(2)°, in accord with DFT computations (see Table 2). The C−N bond length is 1.157(2) Å, which agrees with the C−N distance of 1.132 Å found in $[\mathrm{R{-}NC{-}Me}]^+$ (R = *N*-(2,6-dimethylphenyl)).[17] By comparison with typical Si−N bond lengths (1.70–1.76 Å),[18] the Si−N distance of 1.888(2) Å is very long, and similar to those in $[i\mathrm{Pr_3Si^+(NCCH_3)}]$ (1.82(2)[19] or $[\mathrm{Me_3Si^+(NC}t\mathrm{Bu)}]$ 1.822(5),[20] $[\mathrm{Me_3Si^+(NCCH_3)}]$ 1.845 (2) Å).[21] $[\mathrm{(Bu_2MeSi)_3Si^+(NCCH_3)}]$ has also been reported, but without structural data.[22]

Besides the observed 1,2-bissilylated CN cation, $[\mathrm{Me_3Si{-}C{\equiv}N{-}SiMe_3}]^+$, the *N,N'* ($[\mathrm{(Me_3Si)_2NC}]^+$) and, *C,C'* ($[\mathrm{(Me_3Si)_2CN}]^+$) silylated constitution isomers are also possible, but represent high-energy isomers ($\Delta E^0_{\mathrm{rel.}}$: 0 ($[\mathrm{Me_3Si{-}CN{-}SiMe_3}]^+$), 38.2 kcal mol^{-1} $[\mathrm{(Me_3Si)_2NC}]^+$), according to computations at the pbe1pbe/aug-cc-pwCVDZ level of theory.[23] The N-substituted isomer is often referred to as the "nitrilium" ion, a term that was adopted by Hantzsch in 1931 for products of the reaction of nitriles with acids.[24] Nitrilium ions are assumed to be intermediates in reactions such as Friedel–Crafts type reactions like the Gatterman and Houben–Hoesch reactions, as well as the Ritter reaction, or are used in [3+2] cycloadditions of alkyl azides with nitrilium ions to yield tetrazoles.[25,26] A series of N-substituted nitrilium salts was isolated,[27,28] and also the existence of protonated nitrilium salts of the type $[\mathrm{R{-}C{\equiv}NH}]^+$ was reported,[29] but so far structural data are only known for one arylated $[\mathrm{R{-}NC{-}Me}][\mathrm{BF_4}]$ (R = *N*-(2,6-dimethylphenyl),[17] and one silylated acetonitrile derivative $[\mathrm{R{-}NC{-}Me}][\mathrm{CB_9H_5Br_5}]$ (R = triisopropylsilyl).[19a] The proton analogue $[\mathrm{HC{\equiv}NH}]^+$ is known to be a stable ion in the gas phase[31,32,33] and of substantial interest to astrochemistry,[34,35] since it exists in interstellar molecular clouds. In the condensed phase protonation of hydrogen cyanide was achieved in strong acid systems $\mathrm{FSO_3H/SbF_5/SO_2}$ and studied by NMR spectroscopy,[36] but isolation of $[\mathrm{HC{\equiv}NH}]^+$ salts have not yet been reported and thus X-ray data are not available.

Almost nothing is known about bis-alkylated and -arylated OCN and SCN cations of the type $[\mathrm{R_2NCY}]^+$ or $[\mathrm{R{-}NCY{-}R}]^+$ (Y = O, S). The presence of $[\mathrm{R_2NCO}]^+$ in the reaction of *N,N*-dialkyl carbamide acid chloride $(\mathrm{R_2NC(Cl)O})$[37] with $\mathrm{SbCl_5}$ was assumed, but Schmidt and co-workers showed that, instead of the $[\mathrm{R_2NCO}]^+$ ion, an adduct of the type $[\mathrm{R_2NC(Cl)O{-}SbCl_5}]$ is formed.[38] In agreement with theory, for **2** and **3**, the 1,3-silylated isomer is experimentally observed (Figure 2). The, *N,N'* and the *Y,Y'* silylated species (Y = O or S) are energetically unfavored ($\Delta E^0_{\mathrm{rel}}$:O: 0 $[\mathrm{Me_3Si{-}OCN{-}SiMe_3}]^+$, 0.6 $[\mathrm{(Me_3Si)_2NCO}]^+$, 40.2 kcal mol^{-1} $[\mathrm{(Me_3Si)_2OCN}]^+$; S: 0 $[\mathrm{Me_3Si{-}SCN{-}SiMe_3}]^+$, 3.8 $[\mathrm{(Me_3Si)_2NCS}]^+$, 28.8 $[\mathrm{(Me_3Si)_2SCN}]^+$; Se: 0 $[\mathrm{Me_3Si{-}SeCN{-}SiMe_3}]^+$, 6.9 $[\mathrm{(Me_3Si)_2NCSe}]^+$, 27.4 kcal mol^{-1} $[\mathrm{(Me_3Si)_2SeCN}]^+$).[23]

$[\mathrm{Me_3Si{-}NCO{-}SiMe_3}][\mathrm{B(C_6F_5)_4}]$ and $[\mathrm{Me_3Si{-}NCS{-}SiMe_3}]$ $[\mathrm{B(C_6F_5)_4}]$ crystallize in the monoclinic space groups *P*2/*c* and, *P*2$_1$/*n*, respectively, with four units per cell (Table 1). In both ions the silyl group attached to the nitrogen atom forms an almost linear Si-N-C moiety (**2**: 173.9(8), **3**: 169.3(2)°), whereas a fairly small angle is found for the silyl group attached to the chalcogen atom (**2**: 128.2(5), **3**: 98.42(6)°), in accord with DFT computations, which indicate smaller angles for the heavier chalcogens (O: 132.1, S: 100.1, Se: 96.8°).[23] Within the slightly bent N–C–Y moieties (**2**: 176.9(5), **3**: 177.2(2); Y = O, S) two significantly different bonds are experimentally observed: i) A short C−N bond of 1.069(6) (**2**) and 1.147(2) Å (**3**), respectively, which is close to a triple bond ($\Sigma r_{\mathrm{cov}}(\mathrm{C{\equiv}N})$ = 1.15 Å), and ii) a C−O bond of 1.282(6) and C−S 1.640(2) Å, which corresponds to a typical C=Y bond (**2**: $\Sigma r_{\mathrm{cov}}(\mathrm{C{=}O})$ = 1.23, **3**: $\Sigma r_{\mathrm{cov}}(\mathrm{C{=}S})$ = 1.61 Å; Y = O, S).[39]

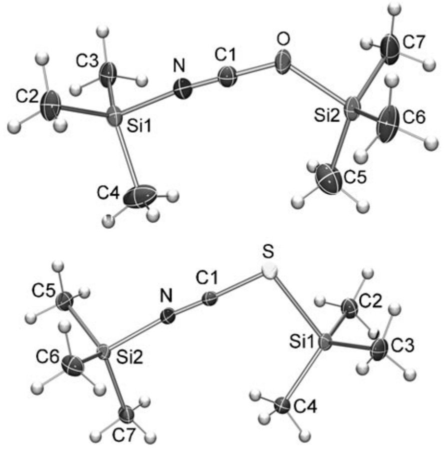


Figure 2. ORTEP drawing of the molecular structure of **2** (top) and **3** (bottom) in the crystal. Thermal ellipsoids with 50 % probability at 173 K. Selected bond lengths [Å] and angles [°] of **2**: C1−N1 1.069(6), C1−O1 1.282(6), O1−Si2 1.840(6), N1−Si1 1.775(5); N1-C1-O1 176.9(5), C1-O1-Si2 128.2(5), C1-N1-Si1 173.9(8). **3**: S−C1 1.640(2), S−Si1 2.296(2), Si2−N 1.816(2), N−C1 1.147(2); C1-S-Si1 98.42(6), C1-N-Si2 169.3(2), N-C1-S 177.2(2).

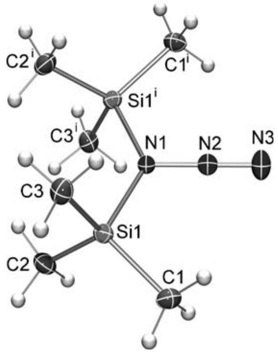


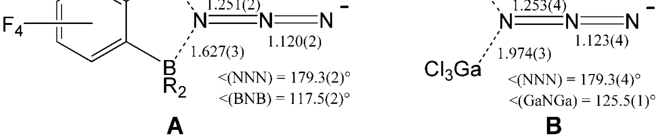
Figure 3. ORTEP drawing of the molecular structure of one independent molecule of **4** in the crystal. Thermal ellipsoids with 50 % probability at 173 K. Selected bond lengths [Å] and angles [°]: Si1−N1 1.876(1), N1−N2 1.280(3), N1−Si1^i 1.876(1), N2−N3 1.111(3); N2-N1-Si1^i 115.61(7), N2-N1-Si1 115.61(7), Si1^i-N1-Si1 128.8(1), N3-N2-N1 180.000(1). Symmetry code: i: $-x, y, -z+1/2$.

In contrast to the structures of **2** and **3**, X-ray studies of bissilylated azide cation (**4**), $[\mathrm{(Me_3Si)_2NNN}]^+$, reveal that both silyl groups are attached to one nitrogen atom (Figure 3, Table 1), in agreement with our computation. Interestingly, the difference between the 1,1- and 1,3-silylated isomer (aminodiazonium vs. iminodiazenium structure) is very small ($\Delta E^0_{\mathrm{rel}}$: 0 $[\mathrm{(Me_3Si)_2NNN}]^+$, 2.4 kcal mol^{-1} $[\mathrm{(Me_3Si)NNN(SiMe_3)}]^+$).[23] As mentioned in the introduction, the $\mathrm{Me_3Si}$ group can be considered as a "big proton", and as early as

1966 Schmidt reported the preparation of $[H_2NNN][SbCl_6]$ from the reaction of HNNN with $SbCl_5$ and HCl.[40] The aminodiazonium structure was unequivocally established by Olah and co-workers when they studied mixtures of HNNN in HF/SbF_5, HF/BF_3, and HSO_3F/SbF_5 by means of ^1H and ^{15}N NMR spectroscopy.[41] The experimentally determined structure of the $[H_2NNN]^+$ ion as a $[SbF_6]^-$ salt was first reported by Christe and co-workers in 1993.[42] Furthermore aryl- and alkyl-substituted aminodiazonium ions are discussed as intermediates in a couple of reactions, such as the Schmidt reaction.[43]

$[(Me_3Si)_2NNN][B(C_6F_5)_4]$ crystallizes in the orthorhombic space group *Pbcn* with eight units per cell (Table 1). In addition to an almost perfectly tetrahedral $[B(C_6F_5)_4]^-$ ion, the asymmetric unit contains two independent cations. There are only weak (aryl)F···H(Me_3Si) and (aryl)F···N(azide) contacts with the shortest F···H and F···N interionic contacts found at 2.560 and 2.909 Å, respectively ($\Sigma r_{vdW}(F\cdots H) = 2.7$, $\Sigma r_{vdW}(F\cdots N) = 3.1$ Å).[39] In contrast to the nonplanar $[H_2NNN]^+$ ion with a pyramidal H_2N moiety, the $[(Me_3Si)_2NNN]^+$ ion is C_{2v} symmetric and planar with both silyl groups symmetrically attached to the same nitrogen (Figure 3). Hence a linear N–N–N group is found (175.3° in $[H_2NNN]^+$) with two different N–N distances (d(N1–N2) = 1.280(3) vs. d(N2–N3) = 1.111(3) Å), in accord with the analogous bond lengths in the $[H_2NNN]^+$ ion (1.295(5) vs. 1.101(3) Å).[42] According to natural bond orbital (NBO) analysis[44] the planarity of **4** (in contrast to $[H_2NNN]^+$) may be partly attributed to hyperconjugation effects, such as the intramolecular donor–acceptor interaction between σ(Si–N1) and π*(N2–N3) bonds (14 kcal mol^{-1})[23] or between the lone pair at N1 (p-type atomic orbital) and the antibonding σ*(Si–C) bonds (1–3 kcal mol^{-1}). As expected, owing to steric repulsion the Si1^i-N1-Si1 angle with 128.8(1)° is significantly larger than the N2-N1-Si1 angle (115.61(7)°).

Related to the $[(Me_3Si)_2NNN]^+$ ion are Lewis acid (LA) adduct azide anions of the type $[LA–NNN–LA]^-$. Two examples, which contain a N,N-dicoordinated azide anion, are the borane complex **A**[45] or the $[GaCl_3–NNN–GaCl_3]^-$ ion **B**[46] (structural data are shown in Scheme 2). Lewis acids of the type ER_3 (E = Group 13 element, R = organic or inorganic group) can be considered isolobal to the Me_3Si^+ ion. Hence the structural data of **A** and **B** are very similar to those found in **4**. There are many examples of N,N-dicoordinated azide compounds in main group chemistry.[47] The latter compounds are not exactly silylated, but they are still closely related to the $[(Me_3Si)_2NNN]^+$ ion with respect to the molecular structure.



A **B**

Scheme 2. Structural data of known Lewis-acid (LA) adduct azide anions **A**[45] and **B**[46] (bond lengths in Å; R = C_6F_5).

In analogy to the bissilylated halonium ions, pseudohalonium ions of the type $[Me_3Si–X–SiMe_3]^+$ (X = pseudohalogen) can be regarded as solvent complexes between $Me_3Si–X$ and $[Me_3Si]^+$. In this context the trimethylsilicenium affinity (TMSA), which describes the enthalpy change associated with the dissociation of the conjugated acid,[1,48] has been calculated at the pbe1pbe level of theory by utilizing an aug-cc-pwCVDZ basis set.[23] The largest TMSA value was found for $[Me_3Si–CN–SiMe_3]^+$ with 54.4 (34.8 kcal mol^{-1} for X = F), decreasing along the series $[Me_3Si–NNN–SiMe_3]^+$ (44.2) > $[Me_3Si–NCSe–SiMe_3]^+$ (43.3) > $[Me_3Si–NCS–SiMe_3]^+$ (41.1) > $[Me_3Si–NCO–SiMe_3]^+$ (39.3 kcal mol^{-1}).[23]

According to NBO analysis all Si–X bonds are highly polarized, but this polarization decreases considerably if the heavier atoms S and Se are linked to the Si atom (Table 2), in accord with the computed partial charges. Interestingly, all pseudohalonium units composed of second-row elements display a similar charge transfer between 0.21–0.27 *e* (Table 2). A significantly larger charge transfer is found for X = SCN and SeCN with 0.45 and 0.51 *e*, respectively. In **1**, **2**, and **4** the pseudohalogen moiety contributes almost half to the overall charge transfer, whereas the YCN (Y = S, Se) unit dominates the charge transfer in the $[Me_3Si–YCN–SiMe_3]^+$ ions (see Table 2, Δq vs. Q_{CT}).

Table 2. Charge values and selected calculated structural data[a] of $[Me_3Si–X–SiMe_3]^+$ ions at the pbe1pbe/aug-cc-pwCVDZ level of theory.[23]

X =	CN	NNN	OCN	SCN	SeCN
q(X) [e]	−0.34 (−0.47)[b]	−0.46 (−0.59)[b]	−0.51 (−0.62)[b]	−0.28 (−0.63)[b]	−0.21 (−0.64)[b]
Δq [e] [c]	0.13	0.13	0.11	0.35	0.43
Q_{CT} [e] [d]	0.26	0.27	0.21	0.45	0.51
TMSA [kcal mol^{-1}]	54.4	44.2	39.3	41.1	43.3
YN [Å][e]	1.157	1.123 1.252	1.165	1.166	1.165
SiNZ [°][f]	180.0	115.3	176.3	176.4	177.3
SiYZ [°][g]	180.0	115.3	132.1	100.1	96.8
X [°]	–	180.0	177.8	177.3	177.3

[a] Only the lowest lying isomers are considered. [b] Values in parentheses are the partial charges of X in $Me_3Si–X$. [c] $\Delta q = q(X_{cation}) - q(X_{Me_3SiX})$. [d] Charge transfer from $Me_3Si–X$ to $[Me_3Si]^+$. [e] Y = N for NNN and C for all other. [f] Z = N for NNN, C for all other. [g] Y = O, S, Se and Z = C, for NNN Y = Z = N.

As the partial charge (q) at the pseudohalogen unit remains negative even upon bissilylation (Table 2), in accord with the analogous halonium ions $[Me_3Si–X–SiMe_3]^+$ (X = F, Cl, Br; CN, NNN, OCN, SCN and SeCN), but not $[Me_3Si–I–SiMe_3]^+$ for which $q(I) = 0.01$ e,[1] we would like to comment on the name halonium and pseudohalonium, respectively. According to IUPAC[49] onium ions are cations derived by addition of a H^+ ion to a mononuclear parent hydride of the nitrogen (H_3E, E = element of Group 15), chalcogen

(H_2E, E = element of Group 16) and halogen families (HE, E = element of Group 17) or derivatives formed by substitution of the parent ions (H_4E^+, H_3E^+, H_2E^+) by univalent groups. Hence ions of the type $[R–E–R]^+$, for which E is any halogen or pseudohalogen, are referred to as halonium ions or pseudohalonium ions, respectively, which may be open-chain or cyclic.[50,51] This naming does *not* imply that the central atom is positively charged, which may be the case for the heavier group elements, but certainly not for the electronegative elements, such as N or O, as in the ammonium (NH_4^+) or oxonium (H_3O^+) ions.

Conclusion

In conclusion, we present here a straightforward synthetic procedure to bissilylated pseudohalonium salts by utilizing the reaction mixture $Me_3Si–X/[Me_3Si–X–SiMe_3]^+$ (X = pseudohalogen)—a concept which was first applied to halogens.[1] By means of this approach it was possible to prepare the first bissilylated pseudohalonium cations in high yields, proving and extending the pseudohalogen concept.[7] Thus it can be said, that, in analogy to halogen chemistry, a pseudohalogen should form pseudohalonium ions of the type $[R–X–R]^+$ in the presence of a weakly coordinating anion.

Experimental Section

Synthesis of 1–4: To neat $[Me_3Si][B(C_6F_5)_4]$ (0.752 g, 1.0 mmol),[1,2] $Me_3Si–X$ (30 to 40 fold molar excess) was added dropwise at ambient temperatures with stirring, followed by gently heating to 60 °C. This resulted in a clear colorless solution. Cooling to −25 °C over a period of one hour resulted in the deposition of colorless crystals. In the case of **3** the solution was concentrated to promote crystallization prior to cooling. Removal of excess $Me_3Si–X$ by decantation and drying in vacuo gave the corresponding $[Me_3Si–X–SiMe_3]$ $[B(C_6F_5)_4]$ (X = CN, OCN, SCN, NNN) salt as a colorless solid in almost quantitative yield (90–95 %).[52]

Acknowledgements

We are indebted to Mathias Lehmann (University of Rostock) for the NMR study and Johannes Thomas (University of Rostock) for measuring the Raman spectra. We thank both reviewers for most valuable comments.

---

[1] M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem.* **2009**, *121*, 7580–7583; *Angew. Chem. Int. Ed.* **2009**, *48*, 7444–7447.

[2] a) J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1994**, *13*, 2430–2443; b) J. B. Lambert, S. Zhang, *J. Chem. Soc. Chem. Commun.* **1993**, 383–384.

[3] C. A. Reed, Z. Xie, R. Bau, A. Benesi, *Science* **1993**, *262*, 402–404.

[4] a) G. K. S. Prakash, S. Keyaniyan, R. Aniszfeld, L. Heiliger, G. A. Olah, R. C. Stevens, H.-K. Choi, R. Bau, *J. Am. Chem. Soc.* **1987**, *109*, 5123–5126; b) J. B. Lambert, W. J. Schulz, J. A. McConnell, W. Schilf, *J. Am. Chem. Soc.* **1988**, *110*, 2201–2210.

[5] Reviews: a) I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116–2142; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090; b) C. Reed, *Acc. Chem. Res.* **1998**, *31*, 133–139; c) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927–942, and references therein.

[6] a) L. Birckenbach, K. Kellermann, *Ber.* **1925**, *58B*, 786–794; b) L. Birckenbach, K. Kellermann, *Ber.* **1925**, *58B*, 2377–2386; c) L. Birckenbach, K. Huttner, W. Stein, *Ber.* **1929**, *62B*, 2065–2075 and L. Birckenbach, K. Huttner, W. Stein, *Ber.* **1929**, *62B*, 2261–2277; d) L. Birckenbach, M. Linhard, *Ber.* **1930**, *63B*, 2528–2544, L. Birckenbach, M. Linhard, *Ber.* **1930**, *63B*, 2544–258 and L. Birckenbach, M. Linhard, *Ber.* **1930**, *63B*, 2588.

[7] A. M. Golub, H. Köhler, *Chemie der Pseudohalogenide*, VEB Deutscher Verlag der Wissenschaften, Berlin, **1979**.

[8] H. Brand, A. Schulz, A. Villinger, *Z. Anorg. Allg. Chem.* **2007**, *633*, 22–35.

[9] Not all criteria are always met. Although many linear pseudohalogens (e.g., CN, OCN, CNO, NNN, SCN) are known, often the corresponding pseudohalide acids, dipseudohalogens, and interpseudohalogens are thermodynamically highly unstable (e.g., HNNN, OCN–NCO, NC–SCN) with respect to N_2/CO elimination or polymerization or indeed, remain unknown (e.g., N_3–N_3).

[10] a) R. Panisch, M. Bolte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676–9682; b) T. Mori, S. V. Lindeman, J. K. Kochi, *Chem. Commun.* **1998**, 927–928; c) R. S. Brown, R. W. Nagorski, A. J. Bennet, R. E. D. McClung, G. H. M. Aarts, M. Klobukowski, R. McDonald, B. D. Santarsiero, *J. Am. Chem. Soc.* **1994**, *116*, 2448–2456; d) A. Avelar, F. S. Tham, C. A. Reed, *Angew. Chem.* **2009**, *121*, 3543–3545; *Angew. Chem. Int. Ed.* **2009**, *48*, 3491–3493; e) M. Arshadi, D. Johnels, U. Edlund, C.-H. Ottosson, D. Cremer, *J. Am. Chem. Soc.* **1996**, *118*, 5120–5131; f) T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem.* **2007**, *119*, 6462–6465; *Angew. Chem. Int. Ed.* **2007**, *46*, 6346–6349; g) M. Kira, T. Hino, H. Sakurai, *J. Am. Chem. Soc.* **1992**, *114*, 6697–6700; h) H. E. Katz, *J. Am. Chem. Soc.* **1985**, *107*, 1420–1421; i) H. E. Katz, *J. Org. Chem.* **1985**, *50*, 5027–5032; j) P. D. Lickiss, P. C. Masangane, W. Sohal, G. L. Veneziani, in *Organosilicon Chemistry V* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2003**, p. 45.

[11] a) T. Müller, *Angew. Chem.* **2001**, *113*, 3123–3126; *Angew. Chem. Int. Ed.* **2001**, *40*, 3033–3036; b) T. Müller in *Organosilicon Chemistry V* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2003**, p. 34; c) A. Sekiguchi, A. Muratami, N. Fukaya, Y. Kabe, *Chem. Lett.* **2004**, *33*, 530–531; d) S. P. Hoffmann, T. Kato, F. S. Tham, C. A. Reed, *Chem. Commun.* **2006**, 767–769.

[12] H. Jacobsen, H. Berke, S. Doering, G. Kehr, G. Erker, R. Froehlich, O. Meyer, *Organometallics* **1999**, *18*, 1724–1735.

[13] Owing to the presence of two independent $[(Me_3Si)_2NNN]^+$ ions in the unit cell, the antisymmetric stretching mode is split (Raman: $\tilde{\nu}$ = 2190/2177 and IR: $\tilde{\nu}$ = 2189/2175 cm^{-1}).

[14] A. Bernsdorf, H. Brand, R. Hellmann, M. Köckerling, A. Schulz, A. Villinger, K. Voss, *J. Am. Chem. Soc.* **2009**, *131*, 8958–8970.

[15] H. Wang, C. E. Webster, L. M. Perez, M. B. Hall, F. P. Gabbaï, *J. Am. Chem. Soc.* **2004**, *126*, 8189–8196.

[16] Crystals of **1** contain one equivalent of the solvent (Me_3SiCN), which can be removed by recrystallization from benzene.

[17] A. K. Gjøystdal, C. Romming, *Acta Chem. Scandinavica* **1977**, *31b*, 56–62.

[18] W. S. Sheldrick in *The Chemistry of Organic Silicon Compounds*, (Eds.: S. Patai, Z. Rappoport), Wiley, New York, 1989, p. 227.

[19] a) Z. Xie, D. J. Liston, T. Jelínek, V. Mitro, R. Bau, C. A. Reed, *J. Chem. Soc. Chem. Commun.* **1993**, 384–386; b) S. Bahr, P. Boudjouk, *J. Am. Chem. Soc.* **1993**, *115*, 4514–4519.

[20] M. Ichinohe, H. Fukui, A. Sekiguchi, *Chem. Lett.* **2000**, *29*, 600–601.

[21] Synthesis and structural data of this compound is given in the Supporting Information (compound **5**).

[22] M. Nakamoto, T. Fukawa, A. Sekiguchi, *Chem. Lett.* **2004**, *33*, 38–39.

[23] See the Supporting Information for the computational details, E_0, H_{298} and, G_{298} values, relative energies, structural data, frequencies, and details of the NBO analysis.

[24] A. Hantzsch, *Chem. Ber.* **1931**, *64*, 667–678.

[25] E. Vilsmaier, R. Schneider, J. Schiitz, *Liebigs Ann. Chem.* **1980**, 1064–1074.
[26] H. Quast, L. Bieber, G. Meichsner, *Liebigs Ann. Chem.* **1987**, 469–475.
[27] H. Meerwein, P. Laasch, R. Mersch, J. Spille, *Chem. Ber.* **1956**, *89*, 209–224.
[28] F. Klages, W. Grill, *Liebigs Ann. Chem.* **1955**, *594*, 21–32.
[29] F. Klages, R. Ruhnau, W. Hauser, *Liebigs Ann. Chem.* **1959**, *626*, 60–70.
[30] CCDC-764307 (**1**), CCDC-764310 (**2**), CCDC-764311 (**3**), and CCDC-764309 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[31] R. S. Altman, M. W. Crofton, T. Oka, *J. Chem. Phys.* **1984**, *80*, 3911–3912.
[32] M. Kajita, K. Kawaguchi, E. Hirota, *J. Mol. Spectrosc.* **1988**, *127*, 275–276.
[33] T. Amano, K. Hashimoto, T. Hirao, *J. Mol. Struct.* **2006**, *795*, 190–193.
[34] M. Araki, H. Ozeki, S. Saito, *Astrophys. J. Lett.* **1998**, *496*, L53–L55.
[35] L. M. Ziurys, B. E. Turner, *Astrophys. J. Lett.* **1986**, *302*, L31–L36.
[36] G. A. Olah, T. E. Kiovsky, *J. Am. Chem. Soc.* **1968**, *90*, 4666–4672.
[37] F. Klages, G. Lucasczyk, *Chem. Ber.* **1963**, *96*, 2066–2069.
[38] D. Beierl, A. Schmidt, *Chem. Ber.* **1973**, *106*, 1637–1642.
[39] *Holleman Wiberg—Lehrbuch der Anorganischen Chemie*, 102. Ed.: Walter de Gruyter, Berlin, **2007**.
[40] A. Schmidt, *Chem. Ber.* **1966**, *99*, 2976–2983.
[41] A. Mertens, K. Lammertsma, M. Arvanaghi, G. A. Olah, *J. Am. Chem. Soc.* **1983**, *105*. 5657–5660.
[42] K. O. Christe, W. W. Wilson, D. A. Dixon, S. I. Khan, R. Bau, T. Metzenthin, R. Lu, *J. Am. Chem. Soc.* **1993**, *115*, 1836–1842.
[43] W. H. Pearson, R. Walavalkar, J. M. Schkeryantz, W. Fang, J. D. Blickensdorf, *J. Am. Chem. Soc.* **1993**, *115*, 10183–10194.
[44] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*; b) J. E. Carpenter, F. Weinhold, *THEOCHEM* **1988**, *169*, 41–62; c) F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum Press, **1988**, 227; d) F. Weinhold, C. Landis, *Valency and Bonding. A Natural Bond Orbital Donor–Acceptor Perspective*, Cambridge University Press, Cambridge, **2005**, and references therein.
[45] J. Chai, S. P. Lewis, S. Collins, T. J. J. Sciarone, L. D. Henderson, P. A. Chase, G. J. Irvine, W. E. Piers, M. R. J. Elsegood, W. Clegg, *Organometallics* **2007**, *26*, 5667–5679.
[46] D. Michalik, A. Schulz, A. Villinger, N. Weding, *Angew. Chem.* **2008**, *120*, 6565–6568; *Angew. Chem. Int. Ed.* **2008**, *47*, 6465–6468.
[47] For example: a) M. Veith, A. Rammo, *Z. Anorg. Allg. Chem.* **2001**, *627*, 662–668; b) T. M. Klapötke, H. Nöth, T. Schmitt, M. Warchhold, *Angew. Chem.* **2000**, *112*, 2197–2199; *Angew. Chem.* **2000**, *112*, 2197–2199; *Angew. Chem. Int. Ed.* **2000**, *39*, 2108–2109; c) R. Haiges, A. Vij, J. A. Boatz, S. Schneider, T. Schroer, M. Gerken, K. O. Christe, *Chem. Eur. J.* **2004**, *10*, 508–517.
[48] M. Swart, E. Rösler, M. Bickelhaupt, *J. Comput. Chem.* **2006**, *27*, 1486–1493.
[49] *Compendium of Chemical Terminology*, 2nd ed. (Eds.: A. D. McNaught, A. Wilkinson), Blackwell Science, New York, **1997**.
[50] G. A. Olah, *Halonium Ions*, Wiley-Interscience, New York, **1975**.
[51] A. Olah, G. K. S. Prakash, J. Sommer, *Superacids*, Wiley, New York, **1985**.
[52] Synthesis and characterization of starting materials including the X-ray data of [Me–C≡N–SiMe$_3$][B(C$_6$F$_5$)$_4$] and detailed analytical data of all products are given in the Supporting Information.

Received: February 2, 2010
Revised: March 22, 2010