Communications

Halonium Ions

Bissilylated Halonium Ions: [Me$_3$Si$-$X$-$SiMe$_3$][B(C$_6$F$_5$)$_4$] (X = F, Cl, Br, I)**
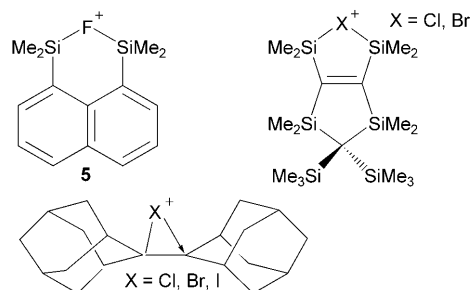
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Ions of the type [R$-$X$-$R]$^+$, where X is any halogen, are referred to as halonium ions. They may be open-chain or cyclic and are an important class of onium ions.[1,2] They play a major role in preparative chemistry as reaction intermediates, for example in Friedel–Crafts alkylation or Lewis acid catalyzed halogenation reactions.[3] Dialkyl chloro-, bromo-, and iodonium ions can be prepared as stable, long-lived ions and even isolated as stable salts by treating an excess of haloalkane with strong Lewis acids in low-nucleophilicity solvents, mostly superacidic media (Scheme 1 A).[3] However,

A) $\quad$ 2 R**X** + LA $\xrightarrow{\text{LNS}}$ $\left[\text{R}-\overset{+}{\textbf{X}}-\text{R}\right]\left[\textbf{X}-\text{LA}\right]^-$

B) Me$_3$Si**X** + [Me$_3$Si][Y] $\xrightarrow[\text{Me}_3\text{SiX}]{\text{LNS} =}$ $\left[\text{Me}_3\text{Si}-\overset{+}{\textbf{X}}-\text{SiMe}_3\right][\text{Y}]^-$
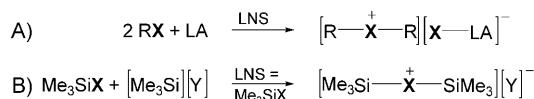
Scheme 1. A) Synthesis of halonium salts (X = Cl, Br, I; LA = Lewis acid, LNS = low-nucleophilicity solvent); B) Synthesis of bis(trimethylsilyl)halonium salts (X = F, Cl, Br, I; Y$^-$ = [B(C$_6$F$_5$)$_4$]$^-$).

no stable dialkylfluoronium ion has been obtained in the condensed phase, which has been attributed to the high electronegativity of fluorine leading to a C$-$H (or C$-$C) bond alkylation. Surprisingly, no structural data of dialkyl halonium ions are available. Only a few aryl-substituted chloronium and bromonium ions have been studied by means of X-ray analysis (Scheme 2), along with quite a large number of fully characterized salts containing iodonium ions.

As early as 1988 the [H$-$F$-$H]$^+$ ion was observed in [H$-$F$-$H][Sb$_2$F$_{11}$] (= 2HF·SbF$_5$), which was isolated from the superacidic medium HF/SbF$_5$.[4] The bulky trimethylsilicenium ion [Me$_3$Si]$^+$ may be regarded as a sterically demanding "big proton". Hence, similar to a proton which is always associated in the condensed state (e.g. in anhydrous HF$_{(l)}$ it forms [H$-$F$-$H]$^+$ or it protonates HSO$_3$F$_{(l)}$ to [H$_2$SO$_3$F]$^+$), it can be assumed that [Me$_3$Si]$^+$ is also always solvated and adds to the solvent to form the corresponding analogous cations.[5,6] Thus, the idea was to react [Me$_3$Si]$^+$ salts with trimethylha-

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Scheme 2. Structurally characterized fluoronium, chloronium, and bromonium salts with the halogen attached either to a C or a Si atom.[10–12]

logenosilanes Me$_3$Si$-$X (X = F, Cl, Br, and I) to give bis(trimethylsilyl)halonium cations [Me$_3$Si$-$X$-$SiMe$_3$]$^+$, where Me$_3$Si$-$X is both solvent and reactant (Scheme 1 B). [Me$_3$Si]$^+$ salts are only stable in the presence of chemically robust, weakly coordinating anions[7] such as carborate ions (e.g. [HCB$_{11}$F$_{11}$]$^-$)[6,8] or tetrakis(pentafluorophenyl)borate, [B(C$_6$F$_5$)$_4$]$^-$.[5] Hence, the system Me$_3$Si$-$X/[Me$_3$Si][Y] ([Y]$^-$ = weakly coordinating anion) can be considered as a super Lewis acidic silylating medium.[8,9] Herein, we report on the synthesis and full characterization of the first acyclic fluoronium cation [Me$_3$Si$-$F$-$SiMe$_3$]$^+$ (**1**) as well as on the hitherto unknown analogous chloronium (**2**), bromonium (**3**), and iodonium (**4**) cations, providing a complete set of the same type of halonium ions, which have been fully characterized as their tetrakis(pentafluorophenyl)borate salts.

With respect to the solvent, two strategies could be followed to prepare halonium salts of the type [Me$_3$Si$-$X$-$SiMe$_3$]$^+$. Me$_3$Si$-$X could be directly silylated by a [Me$_3$Si]$^+$ salt either in a [Me$_3$Si]$^+$-salt-stable solvent such as toluene[5] or in an excess of liquid Me$_3$Si$-$X. Liquid Me$_3$Si$-$X (b.p. for X = F: 19, Cl: 57, Br: 79, and I: 107 °C) was chosen as solvent because of its low basicity, relatively high dielectric constant, and ease of drying and removal, and because it can act as both starting material and solvent (Scheme 1 B).

[Me$_3$Si][B(C$_6$F$_5$)$_4$] undergoes immediate reaction with Me$_3$Si$-$X to yield clear colorless solutions of the [Me$_3$Si$-$X$-$SiMe$_3$]$^+$ salts dissolved in the excess of Me$_3$Si$-$X (1 mmol of [Me$_3$Si][B(C$_6$F$_5$)$_4$] in a 30- to 50-fold molar excess of Me$_3$Si$-$X). Removal of the solvent yields in all cases colorless, thermally stable crystals of [Me$_3$Si$-$X$-$SiMe$_3$][B(C$_6$F$_5$)$_4$] (**1**[B(C$_6$F$_5$)$_4$]–**4**[B(C$_6$F$_5$)$_4$]; yield > 91 %). All salts are extremely air- and moisture-sensitive but are stable under argon atmosphere over a long period as solids and in Me$_3$Si$-$X solutions.

Salts of **1**–**4** are easily prepared in bulk and are stable indefinitely when stored in a sealed tube in the dark and kept at ambient temperatures. They are thermally stable to above 115 °C (F: 150; Cl: 116, Br: 123, and I: 120 °C), which is quite surprising. In contrast to **1**[B(C_6F_5)$_4$], the heavier halonium salts **2**[B(C_6F_5)$_4$]–**4**[B(C_6F_5)$_4$] crystallize as solvates of the corresponding halogenosilane Me_3Si-X, which can easily be removed at elevated temperatures in vacuo. Decomposition starts upon melting. **Caution**: Salts of **1**–**4** decompose vigorously, and appropriate safety precautions should be taken when dealing with large quantities at temperatures above 100 °C.

In the case of **1**, the shift at $\delta[^{19}F] = -131.6$ ppm in the ^{19}F NMR spectrum (in neat Me_3Si-F, $\delta = -132.0$ ppm in C_6D_6) is characteristic for bissilylated fluoronium ions (cf. **5**: $\delta[^{19}F] = -144$ ppm), revealing a strongly shielded fluorine atom. However, owing to a rapid exchange process,[13] which has already been described for [R_3Si][B(C_6F_5)$_4$] in various solvents,[5] no specific ^{1}H, ^{13}C, and ^{29}Si resonances could be detected for **1**–**4**. This dynamic exchange is also indicated by a considerable signal broadening ($t_{1/2} \approx 420$ Hz) of the ^{19}F resonance in the NMR spectrum of Me_3Si-F in the Me_3Si-F/[$Me_3Si-F-SiMe_3$]$^+$ reaction mixture. Furthermore, in the ^{1}H, ^{13}C, and ^{29}Si spectra, the doublet splitting arising from ^{19}F coupling in Me_3Si-F disappears. In addition, when C_6D_6 was used as solvent, NMR resonances (^{1}H, ^{13}C, and ^{29}Si) of neither the halonium ions nor Me_3Si-X were observed. Moreover, the salts of [$Me_3Si-X-SiMe_3$]$^+$ start to decompose within hours in C_6D_6 but are stable in Me_3Si-X.[14]

To obtain single crystals suitable for X-ray diffraction experiments, saturated solutions of [$Me_3Si-X-SiMe_3$][B-(C_6F_5)$_4$] were stored at −25 °C for one hour, resulting in the deposition of colorless crystals of [$Me_3Si-X-SiMe_3$][B-(C_6F_5)$_4$]. Figure 1 contains the structures of the cations; selected structural data can be found in Table 1. Salt **1**[B-(C_6F_5)$_4$] crystallizes in the monoclinic space group *C*2/*c* with four formula units per cell. Several relatively close contacts between anion and cation can be detected. However, all contacts are beyond the sum of the van der Waals radii, thus indicating the absence of strong interactions between the cation and the anion (d_{vdW}: F···F 2.8, H···F 2.4 Å). As depicted in Figure 1, the cation adopts a staggered C_2-symmetric conformation with a large Si-F-Si angle of 163.0(3)°, in accord with DFT computations (see below). Formally, this cation can also be regarded as the isoelectronic analogue of hexamethyldisiloxane, $Me_3Si-O-SiMe_3$, which adopts a distorted C_s-symmetric arrangement with a Si-O-Si angle of 148.6(1)°.[15] In cation **5** (Scheme 2), prepared by Müller and co-workers, a Si-F-Si angle of 129.9° was found.[10] These experimental data indicate the ease with which the Si-X-Si angle can be deformed and explain the fairly large deviation of the theoretically obtained data (Table 2, see below). The coordination geometry around both Si atoms in **1** is strongly distorted tetrahedral (sum of angles: **1**: 348.0° (Table 1); **5**: 345.9/347.7°,[10] Me_3Si-F: 334.5°,[16] [Me_3Si]$^+$ as [$HCB_{11}F_{11}$] salt: 354.4°[8]). The deviation from planarity[17] of the Si atom amounts to 0.369 Å (cf. Me_3Si-F: 0.551, [Me_3Si]$^+$: 0.250 Å[8]).

The Si−F bonds, the most prominent structural feature, of 1.753(9) Å are substantially longer than the sum of the
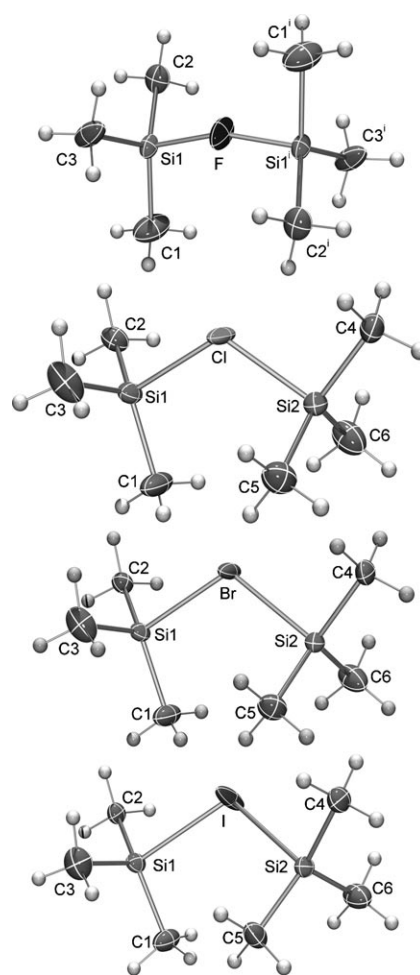

Figure 1. ORTEP drawing of the molecular structure of **1**–**4** in crystals of **1**[B(C_6F_5)$_4$]–**4**[B(C_6F_5)$_4$]. Thermal ellipsoids with 50% probability at 173 K.

Table 1: Selected structural data from single crystal X-ray analyses (Figure 1). Distances in Å, angles in °.[a]

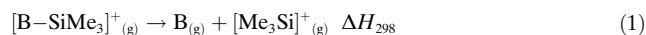|	F	Cl	Br	I
Si1−X	1.753(9)	2.238(5)	2.385(3)	2.584(5)
Si2−X	1.753(9)	2.215(5)	2.380(3)	2.551(4)
Si1−C$_{average}$	1.818(2)	1.818(3)	1.825(3)	1.829(6)
Si2−C$_{average}$	1.818(2)	1.819(3)	1.830(3)	1.832(6)
Si-X-Si	163.0(3)	119.0(2)	114.2(1)	111.8(1)
$\Sigma\angle$ C-Si1-C	348.0(1)	346.2(2)	345.9(2)	345.5(3)
$\Sigma\angle$ C-Si2-C	348.0(1)	345.1(2)	345.3(2)	345.2(3)
dfp-Si[17]	0.369(1)	0.395(2)	0.402(2)	0.408(4)
	0.369(1)	0.412(2)	0.411(2)	0.413 (4)

[a] Owing to a positional disorder two positions for X are observed. The given value corresponds to the position with the largest occupation.

covalent radii (d_{cov}(Si−F) = 1.7; cf. d(Si−F) in **5**: 1.755/1.763 Å[10]), which indicates a Si−F bond order smaller than one (Table 1). For comparison, the Si−F distance in Me_3Si-F of 1.600(1) Å represents a typical Si−F single bond.[16] In pentacoordinate fluorido-bridged anionic bis(siliconates), Tamao et al. always found a short (1.700–1.898 Å) and a long Si−F separation (2.090–2.369 Å).[18] Another example

with an asymmetric fluorine bridge is the product of the reaction of 1,8-bis(diphenylmethylium)naphthalenediyl dication with fluoride, as shown by Gabaï and co-workers. In this case, the fluorine atom is connected through a typical C–F bond of 1.424(2) Å and forms a long interaction of 2.444(2) Å with the other methylium center.[13]

The heavier $[Me_3Si–X–SiMe_3][B(C_6F_5)_4]$ salts (X = Cl, Br, and I) crystallize isotypically in the orthorhombic space group *Pbca* with eight formula units per cell. In contrast to the fluoronium salt, one molecule of the solvent ($Me_3Si–X$) is found along with a slightly distorted C_2-symmetric cation and the $[B(C_6F_5)_4]^-$ ion in the asymmetric unit (Figure 1). Comparing the structural data with respect to the Si-X-Si angles and the deviation from planarity, the following trends can be established (Table 1): The Si-X-Si angles decrease along the series F, Cl, Br, I, while the distance between the Si atom and the plane defined by the three methyl C atoms in the Me_3Si fragment increases. Since all three $[Me_3Si–X–SiMe_3][B(C_6F_5)_4]$ salts (X = Cl, Br, and I) crystallize as solvate with one molecule $Me_3Si–X$, the bridging Si-X distance (Cl: 2.238(5), Br: 2.385(3), I: 2.584(5) Å) can easily be compared to the Si–X distance in $Me_3Si–X$ (Cl: 2.055(2), Br: 2.242(2), I: 2.479(2) Å). As expected, the bridging Si–X distance is always larger, but interestingly the difference $\Delta(d_{Si-XSi} - d_{Si-X})$ significantly decreases along Cl, Br, I (Cl: 0.183, Br: 0.143, I: 0.105 Å).

$[Me_3Si–X–SiMe_3]^+$ ions can be considered as solvent complexes between $Me_3Si–X$ and $[Me_3Si]^+$. In these complexes the Me_3Si fragment has almost completely lost its silicenium character (strong deviation from planarity, Table 1), as a stable covalently bonded tetracoordinated Si center is formed. In this context, and in analogy to the proton affinity, a trimethylsilicenium affinity (TMSA) can be defined as the enthalpy change associated with the dissociation of the conjugated acid [Eq. (1), B = base].[1,2,19]

$$[B–SiMe_3]^+_{(g)} \rightarrow B_{(g)} + [Me_3Si]^+_{(g)} \quad \Delta H_{298} \qquad (1)$$

Using the pbe1pbe and MP2 levels of theory and an aug-cc-pwCVDZ basis set,[20] we have computed the TMSA and Gibbs free energies of all considered species at 298 K (B = $Me_3Si–X$; X = F, Cl, Br, and I). Along the series of $Me_3Si–X$ bases, the largest TMSA value was found for $Me_3Si–F$ (pbe1pbe: 34.8 kcal mol^{-1}), which decreased to 31.1 kcal mol^{-1} for $Me_3Si–Cl$. Interestingly, from Cl to I the TMSA slightly increases (Br: 31.8, I: 33.1 kcal mol^{-1}; for MP2 and ΔG_{298} values see Table S3 in the Supporting Information).[20]

In agreement with computational results for dimethyl halonium ions[21,22] at different DFT levels and the experimental data (see above), all C_2-symmetric structures are bent, with the Si-X-Si angles decreasing in the series F, Cl, Br, I (Table 1 and Table 2); however, there are fairly large deviations between theory and experiment, especially for the fluoronium ion. The reason is that the energy potentials for the variation of the Si-X-Si angle are very flat. For example, in the case of the fluoronium ion the difference between the linear C_{3h} (eclipsed) and bent C_2 (staggered) species amounts only to 0.5 kcal mol^{-1} (ΔE_0) at the pbe1pbe level of theory, while ΔH_{298} favors the linear species by 1.4 kcal mol^{-1}.[23]

Table 2: Partial charges (q) and charge transfer (Q_{CT}) in e, selected NBO data, TMSA values (kcal mol^{-1}), and selected calculated structural data (distances in Å, angles in °) of $[Me_3Si–X–SiMe_3]^+$ ions at the pbe1pbe/aug-cc-pwCVDZ level of theory.[20]

	F	Cl	Br	I
q[a]	−0.64	−0.30	−0.17	+0.01
	(−0.67)	(−0.43)	(−0.36)	(−0.26)
Q_{CT}[b]	0.18	0.35	0.42	0.51
c_{Si}/c_X[c]	0.28/0.96	0.40/0.92	0.43/0.90	0.48/0.88
$h_X = sp^\lambda$[c]	1.29	2.88	4.16	5.34
sp^λ LP[d]	6.78	1.05	0.63	0.43
TMSA	34.8	31.1	31.8	33.1
Si–X	1.830	2.276	2.422	2.630
X-Si-X	148.4	117.3	112.3	106.8

[a] Values in parenthesis are the partial charges in $Me_3Si–X$. [b] Charge transfer from $Me_3Si–X$ to $[Me_3Si]^+$. [c] Natural bond orbital: $\phi_{NBO}(Si–X) = c_{Si}h_{Si} + c_Xh_X$ with the hybrid orbital $h = sp^\lambda$. [d] Hybridization of the sp^λ-type lone pair; the second lone pair is composed of a pure p atomic orbital.

Thus, small interactions of the cation with the environment in the crystal can have a large influence on the Si-X-Si angle. The Si-X-Si angles reflect the steric repulsion of the Me_3Si groups and suggest that in $[Me_3Si–I–SiMe_3]^+$ the steric repulsion is less pronounced, and the angle approaches the structures of a p orbital bonding, in accord with the NBO data (see below and Table 2) and with computed results of the series of $[Me–X–Me]^+$ ions, where this effect is even more pronounced (Cl: 105°, Br: 101.1°, I: 97.8°).[22] As expected, all Si–X bonds are highly polarized, but this polarization decreases considerably for the heavier halogens (q in Table 2), in accord with the computed partial charges. In contrast to the negatively charged F, Cl, and Br atoms in $[Me_3Si–X–SiMe_3]^+$ ions, for iodine a small positive net charge is found. Upon silylation, the fluorine partial charge does not change significantly ($\Delta q_X = q_X(Me_3Si–X–SiMe_3]^+) - q_X(Me_3Si–X)$; $\Delta q_F = 0.03$ e) but increase along Cl (0.13 e), Br (0.19 e), and I (0.25 e). Compared to the overall charge transfer Q_{CT} (see Table 2), the contribution of the F atom is negligible, and thus Q_{CT} stems mainly from the other Me_3Si group, while in the heavier analogue $[Me_3Si–I–SiMe_3]^+$, the I atom contributes almost half to the overall charge transfer (Table 2).

The NBO Lewis picture[20] shows two equivalent Si–X σ bonds and two lone pairs (LPs) localized at the halogen atom (a pure p-type LP and a sp^λ-hybridized LP). A detailed study of the NBO data reveals that the heavier the halogen is, the larger is the p contribution in the hybrid orbitals of the halogen forming the Si–X σ bond. In contrast, the s character of the sp^λ-hybridized LP significantly increases along F < Cl < Br < I (Table 2).

In conclusion, we present herein a straightforward, facile synthetic procedure to form bissilylated halonium salts. By means of this approach it was possible to prepare in high yields the first example of an acyclic bissilylated fluoronium cation with a slightly bent Si-F-Si unit, which can be regarded as the silyl analogue of the well-known $[H–F–H]^+$ ion. The fact that $Me_3Si–F$ acts as both solvent and reactant combined with the easy handling of $Me_3Si–F$ (b.p. 19 °C, moisture- and

oxygen-stable) makes the reaction mixture $Me_3Si-F/[Me_3Si-F-SiMe_3]^+$ salt an interesting reaction medium for several applications, such as C—F bond activation[24] or $[Me_3Si]^+$ transfer reactions. This unusual reaction medium may also serve as a true alternative to anhydrous HF/SbF_5 mixtures. Moreover, we have shown that this synthetic approach can be extended to all other halogens, leading to analogous $Me_3Si-X/[Me_3Si-X-SiMe_3]^+$ media stable at room temperature. It can be assumed that this method is also applicable to pseudohalide systems, which are currently under investigation.

Experimental Section

Synthesis of the salts of **1–4**: A minimum of the corresponding Me_3Si-X (30- to 50-fold molar excess) was added dropwise (or condensed in vacuo at 0°C in the case of Me_3Si-F) to neat $[Me_3Si][B(C_6F_5)_4]$ (0.752 g, 1.0 mmol) at ambient temperatures with stirring and gentle heating to 60°C, resulting in a clear, colorless solution. Cooling to −25°C for a period of one hour results in the deposition of colorless crystals. Removal of excess trimethylhalogenosilane by decantation and drying in vacuo gives the corresponding $[Me_3Si-X-SiMe_3]$ $[B(C_6F_5)_4]$ (X = F, Cl, Br, I) as a colorless solid in almost quantitative yield (91–98%).[25]

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[25] Synthesis and characterization of all starting materials including X-ray data of $[Ph_3C][B(C_6F_5)_4]$ and detailed analytical data of all products are given in the Supporting Information.