

Preparation and characterization of $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$

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Received 18th February 2010, Accepted 26th March 2010

First published as an Advance Article on the web 14th April 2010

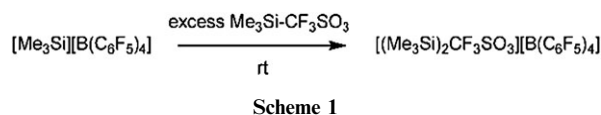
DOI: 10.1039/c0cc00013b

Using tetrakis(pentafluorophenyl)borate, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, as weakly coordinating counterion, the bis(trimethylsilyl)trifluoromethylsulfonium cation, $[\text{CF}_3\text{SO}_3(\text{Me}_3\text{Si})_2]^+$, is readily isolated for X-ray, NMR and IR structural characterization.

Recently it was shown by Kornath *et al.*¹ that sulfurtrioxide reacts with the superacidic solutions^{2–5} XF/SbF_5 ($\text{X} = \text{H}, \text{D}$) to form the corresponding salts $[\text{X}_2\text{SO}_3\text{F}]^+ [\text{SbF}_6]^-$, which are the protonated forms of fluorosulfonic acid. On the Hammett^{2,3,6} acidity scale fluorosulfonic acid reaches an H^0 value of -15.1 , which is in the region of a superacid. By definition, acids with a lower H^0 value than that of sulfuric acid ($H^0 = -12.1$) are superacids. Trifluoromethanesulfonic acid, $\text{CF}_3\text{SO}_3\text{H}$, represents a similarly strong superacid with an H^0 value of -14.1 .⁷ The silylated species trifluoromethylsulfonato trimethylsilane (also known as trimethylsilyl trifluoromethanesulfonate), $\text{CF}_3\text{SO}_3\text{SiMe}_3$, is frequently used as Me_3Si^+ transfer reagent.

The bulky trimethylsilicenium ion $[\text{Me}_3\text{Si}]^+$ may be regarded as a sterically demanding big proton.⁸ Thus, the reaction mixture $\text{Me}_3\text{Si}-\text{Y}/[\text{Me}_3\text{Si}][\text{wca}]$ (wca = weakly coordinating anion⁹ such as $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and Y = weakly basic moiety such as a halogen) can be considered as super Lewis acid silylating medium.^{8,10,11} By applying this approach the full series of salts containing the bisilylated halonium cations $[\text{Me}_3\text{Si}-\text{Y}-\text{SiMe}_3]^+$ ($\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) have been generated and isolated in the super Lewis acid silylating medium $\text{Me}_3\text{Si}-\text{Y}$ (as solvent) and $[\text{Me}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ as silylating reagent.⁸

Beside carborane anions the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion is amongst the least coordinating,⁹ least basic and most chemically inert anions presently known. Even the least coordinating anions presently known form four-coordinate species of the type $\text{R}_3\text{Si}-\text{wca}$,¹² which, although mostly ion-like, nevertheless retain some degree of covalence. Weakly basic solvents such as $\text{Me}_3\text{Si}-\text{Y}$ (Y = halogen),⁸ acetonitrile¹³ or toluene^{12,14} have been shown to displace the wca 's, forming isolable salts of the type $[\text{R}_3\text{Si}-\text{solvent}]^+ [\text{wca}]^-$ with a four-coordinate silicon species. In the present communication, we show that a solvent as weakly coordinating as trifluoromethylsulfonato trimethylsilane, $\text{CF}_3\text{SO}_3\text{SiMe}_3$, also forms a stable adduct-cation with the Me_3Si^+ ion analogous to its lighter congener FSO_3H .



The salt, $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**1**) was prepared in a good yield (83%) in a one step synthesis according to Scheme 1.

$[\text{Me}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ undergoes immediate reaction with one equivalent of $\text{Me}_3\text{Si}-\text{X}$ yielding a clear colorless solution of **1** dissolved in the excess of $\text{CF}_3\text{SO}_3\text{SiMe}_3$ (1 mmol of $[\text{Me}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ in a 10 to 20 fold molar excess of $\text{CF}_3\text{SO}_3\text{SiMe}_3$ when gently heated to 60 °C). The resulting clear colourless solution is concentrated to incipient crystallisation.† Storage at 5 °C for ten hours results in the deposition of colourless crystals. Removal of the supernatant by decantation, washing with 2 mL of neat trimethylsilyl-trifluoromethylsulfonate and drying *in vacuo* yields **1** as colourless crystals. $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) is extremely air and moisture sensitive but stable under argon atmosphere over a long period as solid and in $\text{CF}_3\text{SO}_3\text{SiMe}_3$ solutions. Compound **1** is easily prepared in bulk and is thermally stable up to 127 °C. Decomposition starts at these temperatures upon melting.

$[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ crystallizes in the triclinic space group $P\bar{1}$ with two units per cell. The molecular structure is shown in Fig. 1, confirming an essentially C_s symmetrical cation that is well separated from the borate anion. The C_s symmetric SO_3 core is structurally characterized by two longer S–O bonds ($d(\text{S}-\text{O}1) = 1.477(1)$ and $d(\text{S}-\text{O}2) = 1.477(1)$ Å) and one considerably shorter S–O bond ($d(\text{S}-\text{O}3) = 1.411(1)$; cf. $[\text{H}_2\text{SO}_3\text{F}]^+$: $d_{\text{long}}(\text{S}-\text{O}) = 1.475(3)/1.485(3)$ Å and $d_{\text{short}}(\text{S}-\text{O}) = 1.395(3)$ Å),¹ which indicates double bond character for all S–O bonds (cf. $\Sigma r_{\text{cov}}(\text{S}-\text{O}) = 1.7$, $\Sigma r_{\text{cov}}(\text{S}=\text{O}) = 1.50$).¹⁵ It should be mentioned that polar covalent bonds tend to be shorter than would be expected on the basis of the sum of covalent radii, and it can be assumed that the bonding along the S–O–Si fragment is highly polar (see below).¹⁵ Hence, S=O double bond character can be questioned.¹⁶ As expected the S–O bond lengths increase upon silylation. The Si–O bond lengths ($d(\text{Si}1-\text{O}1) = 1.813(2)$, $d(\text{Si}2-\text{O}2) = 1.824(1)$ Å) are significantly elongated compared to those found in $\text{Me}_3\text{Si}-\text{O}-\text{SiMe}_3$ (1.626(2) Å).¹⁷

The coordination geometry around both Si atoms in **1** is strongly distorted tetrahedral as displayed by $\sum \angle \text{C}-\text{Si}-\text{C} = 347.4^\circ$ (cf. $\text{Me}_3\text{Si}-\text{O}-\text{SiMe}_3$: 330.4° ,¹⁷ $\text{Me}_3\text{Si}-\text{F}$: 334.5° ,¹⁸ $\text{Me}_3\text{Si}-\text{F}-\text{SiMe}_3$: 348.0° ,⁸ $[\text{Me}_3\text{Si}]^+$: 354.4° as $[\text{HCB}_{11}\text{F}_{11}]\text{-salt}$).¹⁹ The Si–O–S angles with $132.16(7)^\circ$ and $135.01(8)^\circ$, respectively, are widened due to steric strain. The coordination geometry around the sulfur is also distorted tetrahedral since the steric demand of the short S=O double bond requires

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† Electronic supplementary information (ESI) available: Experimental and computational details. CCDC 766935. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc00013b

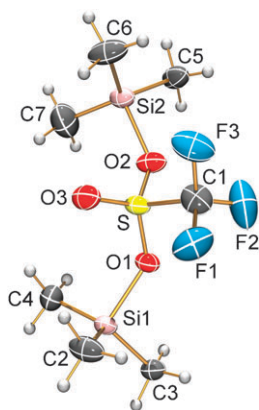


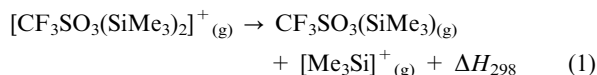
Fig. 1 ORTEP drawing of the cation of **1** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths (Å) and angles (°): S–O3 1.411(1), S–O1 1.477(1), S–O2 1.477(1), S–C1 1.830(2), Si1–O1 1.813(2), Si2–O2 1.824(1); O1–Si1–C3 99.67(6), O1–Si1–C4 102.33(7), O1–Si1–C2 104.08(7), C3–Si1–C4 115.91(9), C3–Si1–C2 115.65(9), C4–Si1–C2 115.8(1), S–O1–Si1 132.16(7), S–O2–Si2 135.01(8), O3–S–O1 116.77(8), O3–S–O2 116.76(8), O1–S–O2 106.64(8).

more space as depicted by the two significantly enlarged O–S–O angles (O3–S–O1 116.77(8), O3–S–O2 116.76(8) vs. O1–S–O2 106.64(8)°).

Besides the C–Si–C angles, the ^{29}Si NMR chemical shift can also be used as a measure for the silicenium ion character. The ^{29}Si NMR chemical shift of $\delta(^{29}\text{Si}) = 75.4$ (d_6 -benzene), which is detected for the cation, $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+$, indicates considerable charge accumulation at the silicon atoms. This chemical shift is characteristic for bisilylated cations, and similar values are reported for e.g. $[\text{Pr}_3\text{Si}(\text{SO}_2)][\text{CHB}_{11}\text{H}_5\text{Br}_6]$ with 85 or 77.2 for a disilylfluoronium ion with a naphthyl backbone.^{12,20}

According to NBO²¹ analysis both Si–O bonds are highly polarized in $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+$ and in agreement with the computed partial charges ($q(\text{Si}) = +1.998e$, $q(\text{O}) = -0.983e$). The silylation is associated with an overall charge transfer $Q_{\text{CT}} = 0.238e$ corresponding to a Me_3Si -group charge of 0.762e.

The cation $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+$ can be regarded as solvent complexes between $\text{CF}_3\text{SO}_3(\text{SiMe}_3)$ and $[\text{Me}_3\text{Si}]^+$. Analogous to the proton affinity, the trimethylsilicenium affinity (TMSA) is defined as the enthalpy change associated with the dissociation of the conjugated Lewis acid as illustrated in eqn (1).^{8,22}



Utilizing the pbe1pbe DFT level of theory and an aug-cc-pwVDZ basis set,²⁰ we have computed the TMSA of $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+_{(\text{g})}$ and $[\text{FSO}_3(\text{SiMe}_3)_2]^+_{(\text{g})}$ at 298 K. As for the protonated species, for which similar proton affinities are observed, similar TMSA were computed for both silylated species which amount to 41.3 and 44.3 kcal mol^{−1}. These TMSA are considerably larger than those calculated for the halonium ions of the type $[\text{Me}_3\text{Si}-\text{X}-\text{SiMe}_3]^+$ (X = F, Cl, Br, I), which lie between 31.1 (X = Cl) and 34.8 (X = F) kcal mol^{−1}.

The reactivity of $[\text{CF}_3\text{SO}_3(\text{SiMe}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**1**) as silylating agent has been shown in the reaction of **1** with

excess of diethyl ether, which yields in a straightforward reaction $[\text{Et}_2\text{OSiMe}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**2**) in almost quantitative yield. Compound **2** was fully characterized (see ESI†). The structure was already reported by Driess *et al.*²³

In conclusion, we have shown that bisilyl(trifluoromethyl)sulfonic acid **1** is easily prepared in very good yields analogous to the protonated acid and can be utilized as “soft” silylating agent. In addition the better solubility of **1** in organic solvents compared to pure Me_3Si^+ -salts might be useful in Me_3Si^+ transfer reactions.

Notes and references

† To neat trimethylsilicenium tetrakis(pentafluorophenyl)borate $[\text{Me}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.752 g, 1.0 mmol), a minimum of trifluoromethyl sulfonyl trimethylsilane (10 to 20 fold molar excess) was added dropwise at ambient temperatures with stirring, followed by gently heating to 60 °C. The resulting clear colourless solution is concentrated to incipient crystallisation. Storage at 5 °C for ten hours results in the deposition of colourless crystals. Removal of the supernatant by decantation, washing with 2 mL of neat (trimethylsilyl)trifluoromethyl sulfonate and drying *in vacuo* yields 0.811 g (0.832 mmol, 83%) bis(trimethylsilyl)trifluoro-methylsulfonium tetrakis pentafluorophenylborate $[(\text{Me}_3\text{Si})_2\text{CF}_3\text{SO}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) as colourless crystals. Mp 127 °C (dec.). Anal. Calc. % (found): C 38.21 (40.71); H 1.86 (1.80); ^1H NMR (25 °C, C_6D_6 , 250.13 MHz): $\delta = -0.06$ (s, 18H, $[(\text{CH}_3)_3\text{Si}]_2\text{CF}_3\text{SO}_3^+$). ^{11}B NMR (25 °C, C_6D_6 , 96.3 MHz): $\delta = -15.9$. $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, C_6D_6 , 75.5 MHz): $\delta = -0.92$ (s, $[(\text{CH}_3)_3\text{Si}]_2\text{CF}_3\text{SO}_3^+$), 117.7 (q, $[(\text{CH}_3)_3\text{Si}]_2\text{CF}_3\text{SO}_3^+$), $^1J(^{13}\text{C}-^{19}\text{F}) = 321$ Hz), 125 (br, *ipso*-C), 136.9 (dm, *m*-CF, $^1J(^{13}\text{C}-^{19}\text{F}) = 246$ Hz), 138.8 (dm, *p*-CF, $^1J(^{13}\text{C}-^{19}\text{F}) = 246$ Hz), 149.0 (dm, *o*-CF, $^1J(^{13}\text{C}-^{19}\text{F}) = 242$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (25 °C, C_6D_6 , 282.4 MHz): $\delta = -167.1$ (m, 8F, *m*-CF), -163.2 (m, 4F, *p*-CF), -132.1 (m, 8F, *o*-CF), -74.1 (s, 3F, $[(\text{CH}_3)_3\text{Si}]_2\text{CF}_3\text{SO}_3^+$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (25 °C, C_6D_6 , 59.6 MHz): $\delta = 75.4$ (s, $[(\text{CH}_3)_3\text{Si}]_2\text{CF}_3\text{SO}_3^+$). X-Ray crystal data for **1** (CCDC 766935): $\text{C}_{31}\text{H}_{18}\text{BF}_{23}\text{O}_3\text{Si}_2$, $M = 974.50$, triclinic, $P\bar{1}$; $a = 10.319(6)$, $b = 13.300(7)$, $c = 15.086(9)$ Å, $\alpha = 68.29(1)$, $\beta = 82.48(1)$, $\gamma = 76.86(2)^\circ$. $V = 1871(2)$ Å³, $Z = 2$, $\rho = 1.730$, $\mu = 0.300$ mm^{−1}, $T = 173(2)$ K, measured reflections 38916, independent reflections 10715, $R_{\text{int}} = 0.0259$, $R_1 = 0.0360$, $wR_2 = 0.1035$, GooF = 1.053.

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