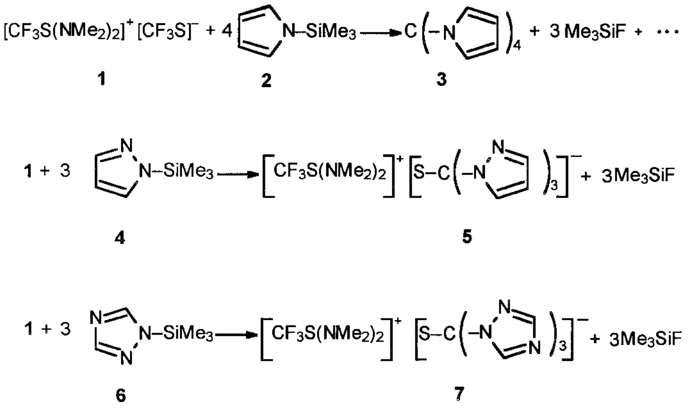
Tris(azolyl)methylthiolates: Another New Scorpionate Class?

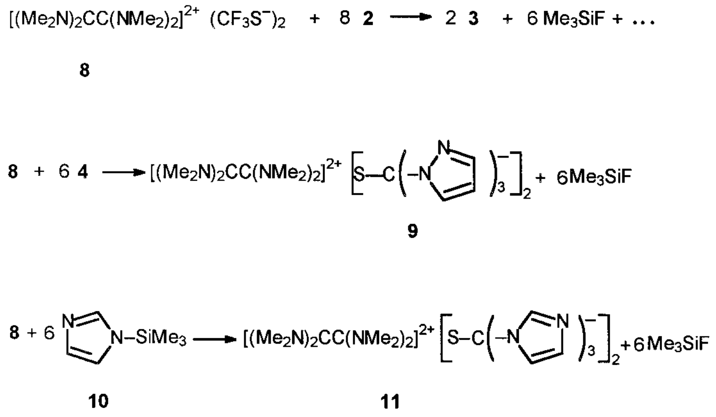
Marco Müller, Enno Lork, and Rüdiger Mews*

The trimethylsilyldifluorosilicate ion $[Me_3SiF_2]^-$ (usually used as its sulfonium salt $A^+[Me_3SiF_2]^-$ ($A^+ = [(Me_2N)_3S]^+$ (TAS),[1] $[(Me_2N)_2SCF_3]^+$ (CF$_3$BAS),[2] $[(Me_2N)_3SO]^+$ (TAOS)[3])) behaves like a "naked" fluoride due to its very weak, long[4] and thus, extremely reactive Si–F bond.[5] It is particularly well suited to the nucleophilic cleavage of Si–element bonds.[6] The considerable lengthening of the C–F bond in the anions $[OCF_3]^-$ (139 pm)[7] and, less markedly, $[SCF_3]^-$ (134–135 pm),[8] (compared to C–F bond lengths in covalent or cationic CF_3S derivatives (130–131 pm)) leads one to expect a significant activation of these bonds. Whereas $[OCF_3]^-$ only acts as a fluoride source,[9] it is known that $[SCF_3]^-$ reacts as a nucleophile to give trifluoromethylthioethers in high yield.[8, 10, 11] In reactions of $[CF_3S(NMe_2)_2]^+[SCF_3]^-$ (**1**)[12] with the silylated azoles **2**, **4**, and **6**, we have been able to show that in $[SCF_3]^-$ ions the C–F bond is so highly activated that it reacts even at temperatures below 0 °C (Scheme 1).



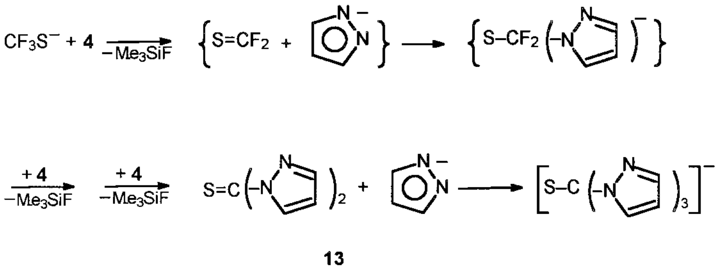
Scheme 1.

Here, a surprising reaction path is observed: the anion acts as a nucleophile and is itself the target of nucleophilic attack. Tetrapyrrolemethane (**3**) is isolated from trimethylsilylpyrrole, whereas with trimethylsilylpyrazole (**4**) and 1,2,4-trimethylsilyltriazole (**6**) the reaction stops at the tris(azolyl)methylthiolates **5** and **7**, respectively.

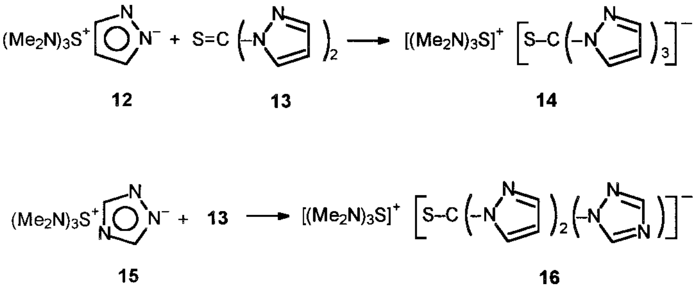


Scheme 2.

As expected, these reactions are virtually independent of the counterion. The very stable salt **8**, which was recently reported by Kolomeitsev et al.,[8] undergoes analogous reactions at slightly higher temperatures (Scheme 2). A proposal for the reaction path of the formation of the tris(azolyl)methylthiolates is given in Scheme 3. The last step of this reaction scheme is the addition of the pyrazole anion to the bis(pyrazolyl)thioketone **13**. This step was confirmed by the direct reaction of **13**[13] with **12**[14] and **15**[14], respectively. The corresponding products **14** and **16** are formed quantitatively at room temperature in CH_3CN as solvent (Scheme 4).



Scheme 3.



Scheme 4.

Kläui and co-workers recently reported the synthesis of $[(pyr)_3CSO_3]^-$ (pyr = pyrazolyl)[15] which is closely related to our tris(azolyl)methylthiolates. This tris(pyrazolyl)methanesulfonate which was synthesized from lithium tris(pyrazolyl)methane and $SO_3 \cdot NMe_3$ is a water-soluble, hydrolysis-stable analogue of the tris(pyrazolyl)borates,[16] which could play a very important role as a novel scorpionate[17] ligand in coordination chemistry. These investigations have also shown that the starting material $Li[C(pyr)_3]$ can be used as a versatile reagent for the synthesis of further tris(pyrazolyl)methane derivatives.[15] It is not known whether the thiolates we have described can be synthesized by the reaction of the salt with sulfur.

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[*] Prof. Dr. R. Mews, Dipl.-Chem. M. Müller, Dr. E. Lork
Institut für Anorganische und Physikalische Chemie
Universität Bremen
Postfach 330440, 28334 Bremen (Germany)
Fax: (+49) 421-218-4267
E-mail: mews@chemie.uni-bremen.de

The tris(azolyl)methylthiolates **5**, **7**, **9**, **11**, and **16**, as well as tetra(pyrrolyl)methane (**3**) were unambiguously characterized by X-ray structure analyses. As an example the structure of the tris(pyrazolyl) salt **5** is shown in Figure 1. Selected bond lengths and angles of the anions are compared with those of the $Tl^+[(pyr)_3CSO_3]^-$ (**A**)[16] in Table 1. Whereas the central SCN_3 framework of the tris(azolyl)thiolates is virtually independent of the particular azolyl group, we observe a considerable difference between the $[(pyr)_3CS]^-$ and the $[(pyr)_3CSO_3]^-$ ions. In particular, the C–S distance in the methanesulfonate **A** is 10 pm longer than in the thiolate anions. Coulombic repulsion between the strongly positive S^{VI} center and the, likewise, positively polarized central carbon lead to the bond lengthening, the somewhat increased coulombic attraction leads to a shortening of the C–N bonds. The higher electron density in the C–S bond of the thiolates leads to an opening of the S-C-N angle and a compression of the N-C-N angle.

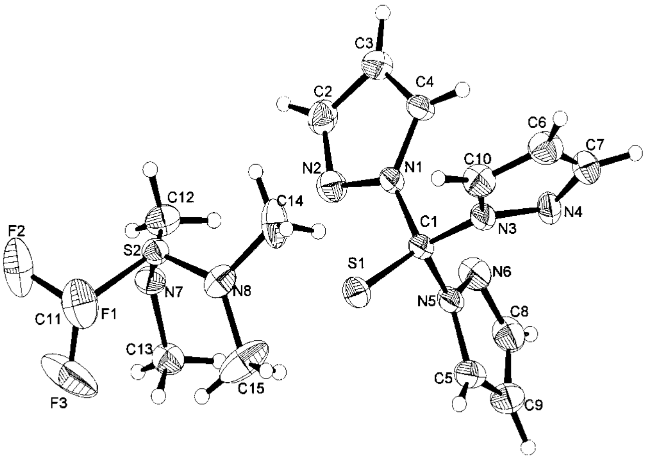
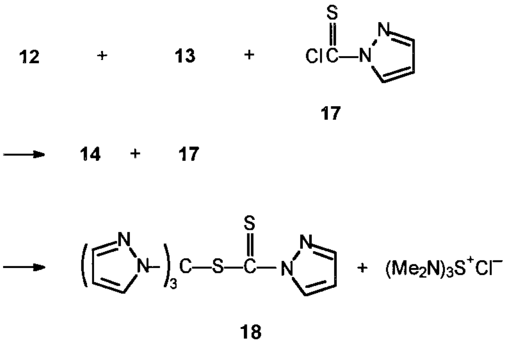


Figure 1. Structure of the salt **5** with average bond lengths [pm] and selected bond and torsion angles [°]. Anion: C1-S 178.8, C1-N1 147.6, N1-N2 135.5, N2-C2 132.6, C2-C3 139.7, C3-C4 136.6, C4-N1 135.4; N1-C1-N3 105.8(2), N3-C1-N5 107.1(2), N5-C1-N1 107.0(2), S1-C1-N1 113.1(2), S1-C1-N3 110.9(2), S1-C1-N5 112.6(5); S1-C1-N1-N2 −54.9(3), S1-C1-N3-N4 153.9(2), S1-C1-N5-N6 152.1(2); cation: C-F 131.2, S-N 160.6, C-S 185.4, C-N 147.2; N7-S2-N8 119.96(13), N8-S2-C11 100.79(14), N7-S2-C11 99.00(13); sum of the angles at N7 353.8, at N8 355.7°.

Table 1. Comparison of selected average bond lengths and angles of **A**, **5**, **9**, **7**, and **11**.

	A	5	9	7	11
S–C [pm]	189.1	178.8	177.8	176.9	177.4
C–N [pm]	145.2	147.6	148.3	148.2	148.1
N–N [pm]	137.3	135.5	135.7	–	–
N-C-S [°]	109.7	112.2	111.8	112.6	112.7
N-C-N [pm]	109.2	106.6	107.0	106.3	106.0

We expect interesting coordination chemistry for the tris(azolyl)methylthiolates and investigations are underway. This class of compounds is not only important for coordination chemistry, but also as a nucleophile in organic chemistry as shown, for example, by the reaction of $[(Me_2N)_3S]^+[pyr]^-$ (**12**) with a mixture of ClC(S)(pyr) (**17**) and bis(pyrazolyl)-thioketone **13** (Scheme 5). We isolated a mixture of $(pyr)_3CSC(S)(pyr)$ (**18**) and $[(Me_2N)_3S]^+Cl^-$. The formation of **18** can be formally explained by a nucleophilic attack by **14** on ClC(S)(pyr).



Scheme 5.

Experimental Section

General procedure: In a N_2 dry-box the salt **1** or **8** (0.75–1 mmol), respectively, was placed into one side of a two-armed lambda-shaped glass vessel fitted with a Teflon valve. A small excess of the trimethylsilylazole was placed, by a syringe, into the second arm under dry N_2. CH_3CN (10 mL) was condensed at −196 °C by using a vacuum line onto the salt **1** or **8**. At −40 °C the silylazoles were slowly poured onto the salt solutions. Whereas **1** already reacted readily at −10 °C, the reaction with **8** finished after 30 min at room temperature. The formation of tetrapyrrolemethane (**3**) from **8** and **2** required more than 24 h. In the case of the reactions of **8** the silylazoles could also be added directly to the salt solutions at room temperature. Me_3SiF, formed as by-product, was removed in vacuum, the reaction solution was layered with diethyl ether (30 mL) at −40 °C and the reaction vessel kept still in a cryostat bath at this temperature for one week. Most of the unreacted starting materials and decomposition products were removed by decantation of the liquid from the crystals. After condensing off the solvent the crystals were washed with diethyl ether and the volatiles removed under vacuum.

The tris(azolyl)methanethiolate salts were isolated in yields of 80–90%. The salts decomposed in moist air.

3: Yield 90%; m.p. 130 °C, ^1H NMR (CD_3CN, 20 °C): $\delta = 6.6$ ($^4J(AA') = 1.0$, $^3J(AB) = 3.2$, $^4J(AB') = 1.5$ Hz, 2H), 6.3 ($^3J(BB') = 2.0$ Hz, 2H).

5: Yield 92%; m.p. 119 °C, ^1H NMR (CD_3CN, 20 °C): $\delta = 3.2$ (q, $^5J(H,F) = 0.8$ Hz), 6.1 (dd, $^3J(H,H) = 2.5$, 1.6 Hz), 7.3 (dd, $^3J(H,H) = 1.6$, $^4J(H,H) = 0.9$ Hz), 8.1 (dd, $^3J(H,H) = 2.5$, $^4J(H,H) = 0.9$ Hz); ^{19}F NMR (CD_3CN, 20 °C): $\delta = -58.3$ (tridecet, $^5J(F,H) = 0.8$ Hz).

7: Yield 92%; m.p. 120 °C, ^1H NMR (CD_3CN, 20 °C): $\delta = 3.2$ (q, $^5J(H,F) = 0.8$ Hz), 7.8 (d, $^4J(H,H) = 0.7$ Hz), 8.9 (d, $^4J(H,H) = 0.7$ Hz); ^{19}F NMR (CD_3CN, 20 °C) $\delta = -58.3$ (tridecet, $^5J(F,H) = 0.8$ Hz).

9: Yield 87%; m.p. 116 °C, ^1H NMR (CD_3CN, 20 °C): $\delta = 3.0$ (s), 3.3 (s), 6.1 (dd, $^3J(H,H) = 2.5$, 1.6 Hz), 7.3 (dd, $^3J(H,H) = 1.6$, $^4J(H,H) = 0.8$ Hz), 8.0 (dd, $^3J(H,H) = 2.5$, $^4J(H.H) = 0.8$ Hz).

11: Yield 83%; m.p. 114 °C, ^1H NMR (CD_3CN, 20 °C): $\delta = 3.0$ (s), 3.3 (s), 7.1 (dd, $^3J(H,H) = 1.8$, $^4J(H,H) = 0.9$ Hz), 7.6 (dd, $^3J(H,H) = 1.8$, 1.4 Hz), 8.1 (dd, $^3J(H,H) = 1.4$, $^4J(H,H) = 0.9$ Hz).

X-ray structure analysis: Crystals were grown by slow diffusion of diethyl ether into CH_3CN solutions of the compounds at −40 °C. Crystals suitable for X-ray structure analysis were fixed to a glass fiber by Kel-F oil and measured on a Siemens P4 four-circle diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation at −100 °C.

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[17] X-ray structure analysis of **5** ($C_{15}H_{21}F_3N_8S_2$), $M_r = 434.52$; crystal size $0.5 \times 0.4 \times 0.3$ mm^3; orthorhombic, space group $P2_12_12_1$, $a = 821.70(10)$, $b = 1534.2(6)$, $c = 1574.4(2)$ pm, $V = 1.9848(9)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.454$ Mg m^{-3}, $\mu = 0.315$ mm^{-1}. Of the 5023 measured reflections ($\omega/2\theta$ scan, $2.59 < \theta < 27.51°$), 3990 independent reflections remained after averaging ($R_{int} = 0.0207$). The structure was solved by direct methods. The refinement converged at $wR_2 = 0.1013$ (refined against F^2) for all 3990 reflections and 260 variables ($R1 = 0.0396$ for 3532 reflections with $I > 2\sigma(I)$). The refinement of the absolute structure parameters gave a final value of $-0.05(8)$. The difference Fourier synthesis indicated no residual electron density beyond $+549$ and -287 e nm^{-3}. Calculations were carried out using the SHELXL-97 program package[18] and the drawings with the program DIAMOND.[19, 20]

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[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149963 (**9**), CCDC-149964 (**11**), CCDC-149965 (**7**), CCDC-149966 (**5**), and CCDC-149967 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).