Different fluoride anion sources and (trifluoromethyl)trimethylsilane: molecular structure of tris(dimethylamino)sulfonium bis(trifluoromethyl)trimethylsiliconate, the first isolated pentacoordinate silicon species with five Si–C bonds

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(Trifluoromethyl)trimethylsilane, CF_3SiMe_3 reacts with $[(Me_2N)_3S]^+[Me_3SiF_2]^-$, Q^+F^- and $Q^+[HF_2]^-$ ($Q^+ = Me_4N^+$, $[(Me_2N)_3C]^+$, $[(Me_2N)_4P]^+$) at -70 to $50\ °C$ to afford the first hypervalent silicon species, $[(CF_3)_2SiMe_3]^-$ with five Si–C bonds (stable in monoglyme up to $-10\ °C$) as the main reactive species whose molecular structure was determined by X-ray crystallography.

One of the most useful reagents for anionic trifluoromethylation of different organic and organometallic electrophiles is (trifluoromethyl)trimethylsilane.[1,2] The instability of the corresponding lithium and magnesium counterparts (CF_3Li and CF_3MgX decompose even at $-100\ °C$) and the reduced nucleophilicity of trifluoromethyl derivatives of zinc, cadmium and copper makes CF_3SiMe_3 indispensable in many cases.[3,4] For the generation of 'CF_3^-' in the presence of a catalytic[4] or stoichiometric[5] quantity of fluoride anion an intermediary hypervalent silicon species has not so far been found.[4,6a] This led to the conclusion[4] that the highly basic nature of the 'CF_3^-' anion together with the high propensity to eliminate α-fluoride renders the pentavalent CF_3 intermediate elusive. Investigation of the Me_3SiCF_3–$Me_4N^+F^-$ system in CD_3CN revealed Me_3SiF and CF_3D as the only reaction products.[4] Furthermore, if Me_3SiCF_3–$Me_4N^+F^-$ is reacted in MeCN the anion $[Me_3Si(CH_2CN)(F)]^-$ was found, but no CF_3 containing hypervalent silicon derivative was found.[6b] It is noteworthy that the generation, structures and spectral properties and reactivities of fluorosiliconates $[R_nSiF_{5-n}]^-$ and $[R_nSiF_{6-n}]^{2-}$ ($n = 1-3$) have been extensively studied.[7] Despite the fact that fluorine directly bonded to hypervalent silicon has a stabilizing effect, no reports have appeared, to the best of our knowledge, describing their isolation and reliable characterization of $[(CF_3)_2SiF_3]^-$ and $[CF_3SiF_4]^-$ in the solid state.[8a] Lithium pentaphenylsiliconate was observed in solution at $-80\ °C$.[8b] Investigation of species formed in the course of Me_3SiCF_3

interaction with fluoride ions is very important for designing selective high-yield trifluoromethylation procedures of synthetical and possible practical use.

Studying the Lewis acidic properties of $P(CF_3)_3$ we observed that a $1:2:1$ mixture of $[(Me_2N)_3S]^+[Me_3SiF_2]^-$–$CF_3SiMe_3$–$P(CF_3)_3$ in THF yielded the stable acyclic phosphoranide, $[P(CF_3)_4]^-$ at $-55\ °C$ together with $5-10\%$ $[P(CF_3)_3F]^-$ impurity.[9] However, if Me_4NF–$CF_3SiMe_3(1:2-2.5)$, forming a clear solution at $-60\ °C$ in glyme was used and $P(CF_3)_3$ was added at $-60\ °C$, analytically pure $[P(CF_3)_4]^-$ was obtained.[10] A trifluoromethylating species has been pre-generated, which we tried to elucidate by reacting CF_3SiMe_3 with a range of fluoride ion sources.

Here we report results obtained for CF_3SiMe_3 **1** reactions with $Q^+[Me_3SiF_2]^-$ **2a**,[11,12] Q^+F^-, **3b–d** and $Q^+HF_2^-$, **4b–d** [**a**: $Q^+ = (Me_2N)_3S^+$, **b**: $Q^+ = Me_4N^+$,[13] **c**: $Q^+ = [(Me_2N)_3C]^+$,[14] **d**: $Q^+ = [(Me_2N)_4P]^+$[15]].† When **1** was added to a suspension of **2a** or **3b–d** ($2:1$ ratio) in monoglyme at $-50\ °C$ or in THF at $-78\ °C$, the solids were immediately dissolved to form a stable colourless solution of the siliconates, $Q^+[(CF_3)_2SiMe_3]^-$, **6a–d** in 95% yield (Scheme 1) with δ_F in the range -63.6 to -63.8, approximately $3.2-3.6$ ppm downfield of the CF_3SiMe_3 resonance.‡§ After recrystallization of **6a** monitored by ^{19}F NMR spectroscopy only *one* species with δ_F -63.7 was present, namely $(Me_2N)_3S^+$ $[(CF_3)_2SiMe_3]^-$ **6a** the first isolated pentacoordinate silicon species having five Si–C binds, proven by single-crystal X-ray structural determination (Fig. 1).¶ The new compound is stable in the solid state upto $0\ °C$ but decomposes exothermally at $0-5\ °C$ with the formation of **2a**. The same reaction has been observed in monoglyme solution of **6b** at $-30\ °C$ with the quantitative formation of $Me_4N^+[F_2SiMe_3]^-$ **2b** proven by ^{19}F NMR and single-crystal X-ray diffraction.‖ The corresponding **6d** decomposes at $-10-0\ °C$ to give **2d**. Obviously, the size of the counter ion plays an important role in the thermal stability of $[(CF_3)_2SiMe_3]^-$.[8b] Expected reaction
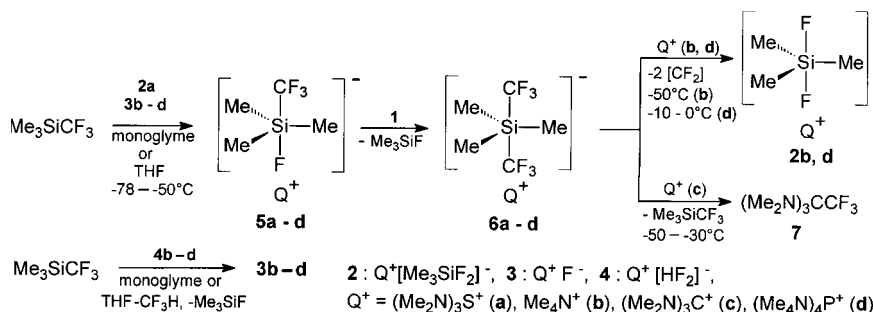
Scheme 1
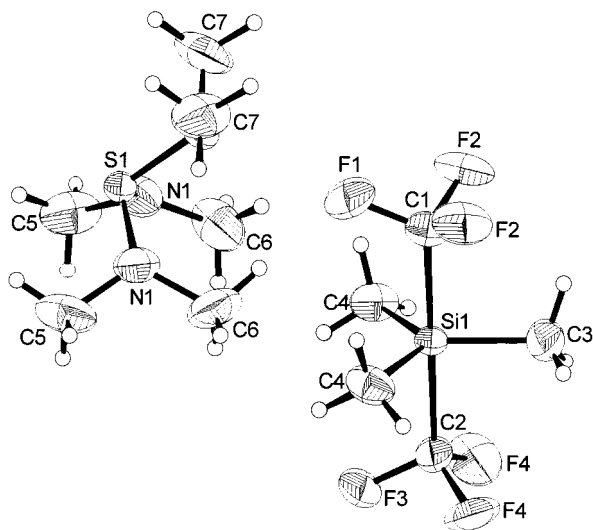
Fig. 1 Crystal structure of **6a** with thermal ellipsoids. Selected bond lengths (pm) and angles (°): Si(1)–C(1) 205.6(4), Si(1)–C(2) 206.2(4), Si(1)–C(3) 188.2(5), Si(1)–C(4) 188.6(3); C(3)–Si(1)–C(4) 120.85(12), C(3)–Si(1)–C(1) 91.0(2), C(3)–Si(1)–C(2) 89.6(2), C(1)–Si(1)–C(2) 179.40(19).

products[16] of difluorocarbene with monoglyme or THF were not detected. Addition of **1** to **3c** in THF at −80 °C afforded **6c** (δ_F −63.7) as the sole product, which upon warming to −50 °C gave slowly $(Me_2N)_3CCF_3$ **7** and **1** (Scheme 1), at −30 °C the formation of **7** proceeds much faster and was complete in 1 h along with gaseous Me_3SiF and CF_3H impurity.†† In the case of hydrogen difluorides and compound **1**, a 1 : 3 ratio has to be applied to convert **4b–d** at −80 °C into the fluorides **3b–d** under formation of CF_3H and Me_3SiF (Scheme 1) and subsequently **6b–d** are formed.

Probably the siliconates **5a–d** containing the $[(CF_3)Si(F)Me_3]^-$ anion were produced initially as intermediates releasing $[CF_3]^-$ to attack CF_3SiMe_3 yielding $[(CF_3)_2SiMe_3]^-$. So far, there is no direct spectroscopical observation of $[(CF_3)Si(F)Me_3]^-$, whereas the isoelectronic phosphorane, $(CF_3)P(F)Me_3$ could be isolated and fully characterized.[17]

The single crystal X-ray structure determination of **6a** showed almost ideal trigonal-bipyramidal geometry at silicon [C(1)–Si(1)–C(2) 179.40(19), C(3)–Si–C(1) 91.0(2) and C(3)–Si–C(4) 120.85(12)°] with a rather long[4] apical Si–C(1)F$_3$ bond [205.6(4)] and a considerably shorter equatorial Si–C(1)H$_3$ bond [188.2(5) pm] (cf. 187.4 pm in **2a**[12]). For the isoelectronic $(CF_3)_2PMe_3$ the same structure was found with shorter P–C distances[18] [P–CF$_3$ 197.4(4) and P–CH$_3$ 181.3(2) pm]. The geometry parameters of the cation $(Me_2N)_3S^+$ are similar to those investigated earlier.[12]

The use of the hypervalent trifluoromethylating silicon compounds for new carbon–carbon bond forming reactions and synthesis of trifluoromethylated phosphorus(v) derivatives is underway in our laboratories. The results of the study for CF_3SiF_3 and CF_3SiPh_3 interaction with the different fluoride anion sources including $(Et_2N)_3PF_2$ and Ph_3CF and reactions of $(Me_2N)_3CCF_3$ will be published in due course.

Notes and references

† All reactions were performed under nitrogen in carefully dried solvents. Compound **7** gave satisfactory elemental analysis. NMR spectra at 200.13 (^{1}H, TMS), 188.31 (^{19}F, CClF$_3$), 50.32 MHz (^{13}C, TMS) were recorded.

‡ General procedure for **6b–d**: to a solution of the corresponding fluoride **2a–d** (0.2 mmol) in monoglyme or THF (5 ml) has added 0.06 g (0.42 mmol) of **1**. The use of corresponding bifluorides gave the same products but the molar ratio of bifluoride to silane was 1 : 3 in this case. Selected data for **6b–d**: δ_F −63.67 (**6b**), −63.94 (**6c**), −63.82 (**6d**), −64.83 (**2b**), −64.75 (**2d**).

§ Synthesis of **6a**: to a solution of 0.41 g (1.49 mmol) **2a** in 5 ml monoglyme was condensed 0.45 g (3.13 mmol) **1** and the mixture stirred for 3 h at −55 °C, δ_F −64.04. Yield: 95%.

¶ Crystal data for **6a**: $C_{11}H_{27}F_6N_3SSi$, $M = 375.51$, monoclinic, space group $P2_1/m$, $a = 769.8(2)$, $b = 1132.1(2)$, $c = 1135.6(2)$ Å, β 105.26(1)°, $V = 0.9548(3)$ nm^3, $Z = 2$, $D_c = 1.306$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å. Siemens P4 m/v diffractometer, θ-2θ-scan type, 2.59 ⩽ θ ⩽ 24.99°, 173 K; 6512 reflections collected, 1775 independent reflections ($R_{int} = 0.0672$), full-matrix least-squares on F^2, goodness-of-fit (F^2) = 1.064, final R values [$I > 2\sigma(I)$]: $R1 = 0.0476$, $wR2 = 0.1002$, R values (all data): $R1 = 0.0774$, $wR2 = 0.1157$, extinction coefficient 0.0103(18), difference electron density: 0.264 and −0.244 e Å^3. CCDC 182/1232. See http://www.rsc.org/suppdata/cc/1999/1017/ for crystallographic files in .cif format.

‖ Selected data for **2b**: δ_F(CD$_3$CN, −30 °C) −60.10; δ_H(CD$_3$CN, −30 °C) −0.18 (s, Me$_3$Si), 3.10 (s, Me$_4$N$^+$). The geometry parameters, bond lengths and angles for the anion $[Me_3SiF_2]^-$ in **2b** are almost identical with those for **2a**[12] within the standard deviation.

†† Selected data for **7**: bp 166–170 °C (decomp.). δ_H 2.33 ($^5J_{FH}$ 1.23 Hz); δ_F −62.48; δ_C 127.35 (CF$_3$, $^1J_{CF}$ 305.6 Hz), 94.24 [C(NMe$_2$)$_3$], $^2J_{CF}$ 23.7 Hz), 39.36 (CH$_3$, $^4J_{CF}$ 2.3 Hz).

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Communication 9/01953G