Syntheses, X-ray Crystal Structure Analyses, and Solid-State NMR Studies of Some Zwitterionic Organofluorosilicates

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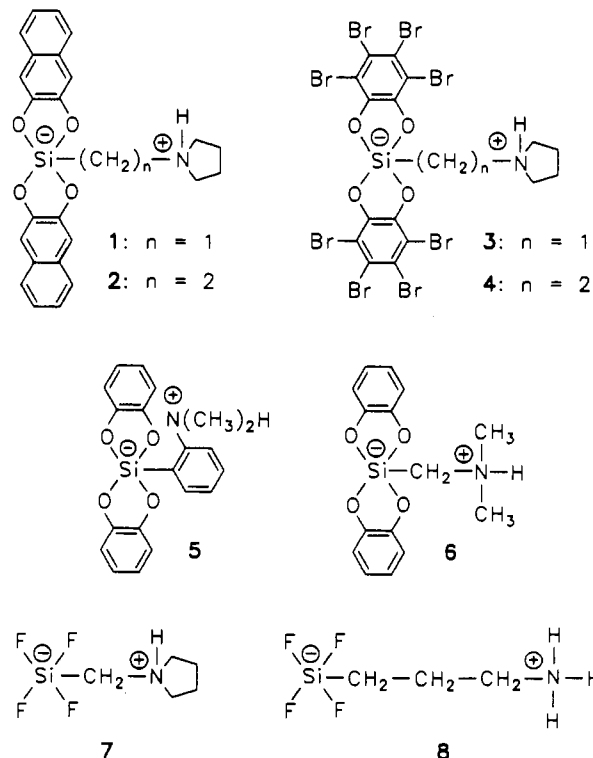Postfach 101251, D-8580 Bayreuth, Germany

Reaction of dimethoxy(methyl)(pyrrolidinomethyl)silane [Me(MeO)$_2$SiCH$_2$NC$_4$H$_8$, NC$_4$H$_8$ = pyrrolidino] and methoxy(methyl)phenyl(pyrrolidinomethyl)silane [MePh(MeO)SiCH$_2$NC$_4$H$_8$] with hydrogen fluoride at 0 °C in ethanol/hydrofluoric acid yielded trifluoro(methyl)(pyrrolidiniomethyl)silicate [F$_3$Si(Me)CH$_2$N(H)C$_4$H$_8$ (**9**), N(H)-C$_4$H$_8$ = pyrrolidinio] (yield 90% and 89%, respectively). The related trifluoro(phenyl)(pyrrolidiniomethyl)silicate [F$_3$Si(Ph)CH$_2$N(H)C$_4$H$_8$ (**10**)] was obtained by reaction of dimethoxy(phenyl)(pyrrolidinomethyl)silane [Ph-(MeO)$_2$SiCH$_2$NC$_4$H$_8$] with HF (yield 81%). **9** and **10** are the first zwitterionic (ammonioalkyl)organotrifluorosilicates. Crystal data for these two compounds are as follows. **9**: space group $P2_1/n$, a = 8.359(3) Å, b = 11.388(4) Å, c = 9.076(2) Å, β = 93.40(3)°, V = 862.4(5) Å^3, T = –100 °C, Z = 4, R = 0.037, R_w = 0.037. **10**: space group $P2_1/n$, a = 9.542(4) Å, b = 12.536(4) Å, c = 10.996(3) Å, β = 114.13(3)°, V = 1200.4(7) Å^3, T = –100 °C, Z = 4, R = 0.043, R_w = 0.043. The zwitterionic organofluorosilicates **9** and **10** contain a pentacoordinate silicon atom (formally negatively charged) and a tetracoordinate nitrogen atom (formally positively charged). In the crystal, the coordination polyhedrons around the silicon atoms can be described as distorted trigonal bipyramids: two of the fluorine atoms occupy the axial sites, whereas the third fluorine atom and the two carbon atoms are found in the equatorial positions. The zwitterionic species also exist in solution (**9**, CD$_3$CN, CDCl$_3$; **10**, CD$_3$CN; ^{1}H, ^{13}C, and ^{19}F NMR), displaying a rapid ligand exchange at room temperature (one ^{19}F resonance). Solid-state NMR studies (^{15}N, ^{29}Si) on authentic tetrafluoro(pyrrolidiniomethyl)silicate [F$_4$SiCH$_2$N(H)C$_4$H$_8$ (**7**)] and on (3-ammoniopropyl)tetrafluorosilicate [F$_4$Si(CH$_2$)$_3$NH$_3$ (**8**)] revealed evidence that **8** is indeed the earlier postulated product formed in the reaction of (3-aminopropyl)triethoxysilane [(EtO)$_3$Si(CH$_2$)$_3$NH$_2$] with HF in ethanol/hydrofluoric acid (**7**, δ(^{15}N) = –318.5 ppm, δ(^{29}Si) = –121.1 ppm; **8**, δ(^{15}N) = –345.3 ppm, δ(^{29}Si) = –112.4 ppm).

Introduction

During the last few years, numerous papers on the synthesis and structure of *ionic* organosilicates have been published.[1,2] In contrast, only a small number of *zwitterionic* organosilicates have been described[3–10] (for a recent review, see ref 11). Most of these zwitterions belong to the class of spirocyclic silicates (examples: **1**·1/4CH$_3$CN,[5,8] **2**·CH$_3$CN,[4,8] **3**·CH$_3$CN,[6,8] **4**,[8] **4**·H$_2$O,[8] **5**,[7,8] and **6**[8]), whereas compound **7**[10] represents the only authentic zwitterionic organofluorosilicate that has been characterized by X-ray diffraction and NMR-spectroscopic studies (Scheme I). In this context it should be mentioned that the existence of the structurally related zwitterionic (ammonioalkyl)tetrafluorosilicate **8** (Scheme I) was already postulated nearly two decades previously.[12] As its identity was based only on an elemental analysis, the authenticity of this compound, however, has remained uncertain. We now wish to report the syntheses and crystal structures of the

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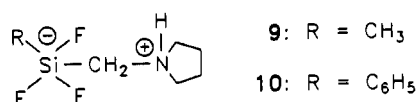† Universität Karlsruhe.
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§ Universität Bayreuth.
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Scheme I

first zwitterionic (ammonioalkyl)organotrifluorosilicates **9** and **10** (Scheme II). In addition, the results of solid-state NMR studies on **7**, **9**, and **10** are described. In order to establish its

Scheme II

$$9: \quad R = CH_3$$
$$10: \quad R = C_6H_5$$

identity unequivocally, compound **8** was resynthesized and included in these investigations.

Experimental Section

(a) Syntheses. Except for the reactions with hydrofluoric acid, all syntheses were carried out under dry nitrogen. The solvents used were dried according to standard procedures and stored under nitrogen. The reactions with hydrofluoric acid were carried out in polypropylene or Nalgene beakers under normal atmospheric conditions; for filtrations polypropylene suction flasks, polypropylene Büchner funnels, and normal commercial filter paper were used. Melting points were determined with a Leitz Laborlux S microscope, equipped with a heater (Leitz, Model M 310). The ^{1}H, ^{13}C and ^{19}F solution-state NMR spectra were recorded on a Bruker AC-250 spectrometer (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz; ^{19}F, 235.4 MHz). The ^{29}Si NMR spectra were recorded with a Bruker WP-300 (59.6 MHz) spectrometer. Except for some low-temperature studies with **9**, all solution-state NMR experiments were carried out at room temperature; CD$_3$CN, CDCl$_3$ and CD$_3$OD were used as solvents. Chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H, δ 7.25), CDCl$_3$ (^{13}C, δ 77.05), CD$_3$OH (^{1}H, δ 4.85), CD$_3$OD (^{13}C, δ 49.0), CD$_2$HCN (^{1}H, δ 1.93), CD$_3$CN (^{13}C, δ 1.3), and relative to internal TMS (^{29}Si, δ 0) and CFCl$_3$ (^{19}F, δ 0). Assignment of the ^{13}C NMR data was supported by DEPT experiments. Mass spectra were obtained with a Varian MAT-711 and a Finnigan MAT-8430 mass spectrometer (EI MS, 70eV; FAB MS, 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source). The selected m/z values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{19}F, and ^{28}Si.

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Tetrafluoro(pyrrolidiniomethyl)silicate (7). Synthesis as described in ref 10.

(3-Ammoniopropyl)tetrafluorosilicate (8). A solution of **11** (11.1 g, 50.1 mmol) in ethanol (30 mL) was added dropwise at 0 °C during 5 min to a stirred solution of 40% hydrofluoric acid (14.0 g, 280 mmol of HF) in ethanol (20 mL). After 2 h stirring at 0 °C, the precipitate was filtered off and recrystallized from water to give 6.53 g (yield 80%) of tabular, colorless crystals; sublimation at 190 °C. ^{1}H NMR (CD$_3$OD): δ 0.70–0.76 (m, 2 H, SiCH$_2$C), 1.70–1.82 (m, 2 H, CCH$_2$C), 2.85–2.91 (m, 2 H, NCH$_2$C). ^{13}C NMR (CD$_3$OD): δ 13.2 (SiCH$_2$C), 24.3 (CCH$_2$C), 43.3 (NCH$_2$C). EI MS: m/z 143 (15%, [M – HF]$^+$), 30 (100%, CH$_2$=NH$_2$$^+$). Anal. Calcd for C$_3H_9F_4$NSi: C, 22.08; H, 5.56; F, 46.57; N, 8.58. Found: C, 22.2; H, 5.6; F, 46.3; N, 8.6.

Trifluoro(methyl)(pyrrolidiniomethyl)silicate (9). Method A. A solution of **12** (2.84 g, 15.0 mmol) in ethanol (10 mL) was added dropwise at 0 °C during 10 min to a stirred solution of 40% hydrofluoric acid (3.75 g, 75.0 mmol of HF) in ethanol (10 mL). After 2 h stirring at 0 °C, the precipitate was filtered off and recrystallized from ethanol to give 2.50 g (yield 90%) of prismatic, colorless crystals; sublimating at 115 °C, dec 170 °C. Recrystallization from methanol, acetonitrile and water gave the same results. For analytical data, see below.

Method B. A solution of **15** (1.00 g, 4.25 mmol) in ethanol (5 mL) was added dropwise at 0 °C during 5 min to a stirred solution of 40% hydrofluoric acid (0.64 g, 12.8 mmol of HF) in ethanol (10 mL). After 2 h stirring at 0 °C, the precipitate was filtered off and recrystallized from ethanol to give 0.70 g (yield 89%) of prismatic, colorless crystals; sublimating at 115 °C, dec 170 °C. ^{1}H NMR (CD$_3$CN): δ –0.01 (s, 3 H, SiCH$_3$), 1.9–2.1 (m, 4 H, CCH$_2$C), 2.51 (s, 2 H, SiCH$_2$N), 2.8–3.0 and 3.5–3.7 (m, 4 H, NCH$_2$C), 6.8–7.6 (broad s, 1 H, NH). ^{13}C NMR (CD$_3$CN): δ 23.7 (CCH$_2$C), 50.5 (SiCH$_2$N), 58.0 (NCH$_2$C), SiCH$_3$ resonance not detectable (overlapping with the reference signal). ^{19}F NMR (CD$_3$CN): δ –102.2 (broad s). ^{1}H NMR (CDCl$_3$): δ 0.13 (s, 3 H, SiCH$_3$), 1.95–2.15 (m, 4 H, CCH$_2$C), 2.60 (d, 2 H, SiCH$_2$N), 2.7–2.9 and 3.7–3.8 (m, 4 H, NCH$_2$C), 8.0 (broad s, 1 H, NH). ^{13}C NMR (CDCl$_3$): δ 2.1 (SiCH$_3$), 23.9 (CCH$_2$C), 50.5 (SiCH$_2$N), 58.0 (NCH$_2$C). ^{19}F NMR (CDCl$_3$, 20 °C): δ –106.0 (broad s; $\nu_{1/2} \approx$ 1995 Hz). ^{19}F NMR (CDCl$_3$, –70 °C): δ –91.5 (s, 2 F$_{ax}$; $J_{SiF(ax)}$ = 242.9 Hz), –138.6 (s, 1 F$_{eq}$; $J_{SiF(eq)}$ = 212.5 Hz). ^{29}Si NMR (CD$_3$CN and CDCl$_3$): Experiments failed (under the same conditions as used successfully for 7[10]). EI MS: m/z 165 (10%, [M – HF]$^+$), 84 (100%, CH$_2$=NC$_4$H$_8$$^+$). FAB MS (negative ions): m/z 184 (54%, M – H$^+$), 153 (100%, matrix). FAB MS (positive ions): m/z 166 (100%, M – F$^-$). Anal. Calcd for C$_6$H$_{14}$F$_3$NSi: C, 38.90; H, 7.62; F, 30.76; N, 7.56. Found: C, 39.1; H, 7.6; F, 30.8; N, 7.6.

Trifluoro(phenyl)(pyrrolidiniomethyl)silicate (10). A solution of **13** (2.51 g, 9.98 mmol) in ethanol (10 mL) was added dropwise at 0 °C during 5 min to a stirred solution of 40% hydrofluoric acid (2.8 g, 56 mmol of HF) in ethanol (10 mL). After stirring for 2 h at 0 °C, the precipitate was filtered off and recrystallized from methanol [cooling of a saturated (20 °C) solution to –30 °C] to give 2.01 g (yield 81%) of prismatic, colorless crystals; mp 125 °C. ^{1}H NMR (CD$_3$CN): δ 1.85–2.05 (m, 4 H, CCH$_2$C), 2.56 (s, 2 H, SiCH$_2$N), 2.85–3.0 and 3.5–3.7 (m, 4 H, NCH$_2$C), 6.9–7.9 (m, 5 H, SiC$_6$H$_5$), NH resonance not resolved. ^{13}C NMR (CD$_3$CN): δ 23.8 (CCH$_2$C), 48.4 (SiCH$_2$N), 58.1 (NCH$_2$C), 127.9 (C-3/C-5, SiC$_6$H$_5$), 129.2 (C-2/C-6, SiC$_6$H$_5$), 129.6 (C-4, SiC$_6$H$_5$), 137.9 (C-1, SiC$_6$H$_5$). ^{19}F NMR (CD$_3$CN): δ –118.8 (broad s). ^{29}Si NMR (CD$_3$CN): Experiments failed (under the same conditions as used successfully for 7[10]). EI MS: m/z 227 (26%, [M – HF]$^+$), 84 (100%, CH$_2$=NC$_4$H$_8$$^+$). Anal. Calcd for C$_{11}H_{16}F_3$NSi: C, 53.42; H, 6.52; F, 23.04; N, 5.66. Found: C, 53.4; H, 6.6; F, 23.1; N, 5.7.

(3-Aminopropyl)triethoxysilane (11) was obtained from Wacker-Chemie GmbH, Burghausen, Germany.

Dimethoxy(methyl)(pyrrolidinomethyl)silane (12). Synthesis as described in ref 5.

Dimethoxy(phenyl)(pyrrolidinomethyl)silane (13). A Grignard reagent was prepared from chlorobenzene (13.5 g, 120 mmol) and magnesium turnings (2.92 g, 120 mmol) in tetrahydrofuran (100 mL) and was then added dropwise at 0 °C during 1 h to a stirred solution of **14** (24.0 g, 117 mmol) in diethyl ether (250 mL). The mixture was stirred for 16 h at room temperature and then heated under reflux for 8 h. The precipitate was filtered off and washed with *n*-pentane (3 × 50 mL), the filtrate was combined with the washings, and the solvent was removed by distillation at normal pressure. The residue was distilled *in vacuo* (Vigreux column) to give 15.9 g (yield 54%) of a colorless liquid; bp 89 °C (0.02 Torr). ^{1}H NMR (CDCl$_3$): δ 1.68–1.71 (m, 4 H, CCH$_2$C), 2.29 (s, 2 H, SiCH$_2$N), 2.43–2.47 (m, 4 H, NCH$_2$C), 3.60 (s, 6 H, SiOCH$_3$), 7.34–7.41 and 7.65–7.68 (m, 5 H, SiC$_6$H$_5$). ^{13}C NMR

Table I. Crystallographic Data for **9** and **10**

	9	10
chem formula	$C_6H_{14}F_3NSi$	$C_{11}H_{16}F_3NSi$
fw	185.3	247.3
space group	$P2_1/n$	$P2_1/n$
T, °C	–100	–100
a, Å	8.359(3)	9.542(4)
b, Å	11.388(4)	12.536(4)
c, Å	9.076(2)	10.996(3)
β, deg	93.40(3)	114.13(3)
V, Å^3	862.4(5)	1200.4(7)
Z	4	4
ρ_{calcd}, g·cm^{-3}	1.427	1.369
μ(Mo Kα), cm^{-1}	2.53	2.00
no of unique reflns	1521	2118
no of reflns, used for refinement	1182	1448
R^a	0.037	0.043
$R_w{}^b$	0.037	0.043
S, goodness of fit	1.72	1.36

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

(CDCl$_3$): δ 23.9 (CCH$_2$C), 42.6 (SiCH$_2$N), 50.8 (SiOCH$_3$), 58.0 (NCH$_2$C), 127.9 (C-3/C-5, SiC$_6$H$_5$), 130.2 (C-4, SiC$_6$H$_5$), 132.8 (C-1, SiC$_6$H$_5$), 134.4 (C-2/C-6, SiC$_6$H$_5$). ^{29}Si NMR (CDCl$_3$): δ –20.6. EI MS: m/z 251 (12%, M$^+$), 84 (100%, CH$_2$=NC$_4$H$_8$$^+$). Anal. Calcd for C$_{13}H_{21}NO_2$Si: C, 62.11; H, 8.42; N, 5.57. Found C, 62.3; H, 8.4; N, 5.5.

Trimethoxy(pyrrolidinomethyl)silane (14). Synthesis as described in ref 5.

Methoxy(methyl)phenyl(pyrrolidinomethyl)silane (15). A Grignard reagent was prepared from bromobenzene (1.57 g, 10.0 mmol) and magnesium turnings (243 mg, 10.0 mmol) in diethyl ether (10 mL) and was then added dropwise at 0 °C during 20 min to a stirred solution of **12** (1.89 g, 9.98 mmol) in diethyl ether (50 mL). The mixture was stirred for 20 h at room temperature and then heated under reflux for 2 h. The precipitate was filtered off and washed with n-pentane (50 mL), the filtrate was combined with the washings, and the solvent was removed by distillation at normal pressure. The residue was distilled *in vacuo* (micro-Vigreux column) to give 1.19 g (yield 51%) of a colorless liquid; bp 88 °C (0.05 Torr). ^{1}H NMR (CDCl$_3$): δ 0.05 (s, 3 H, SiCH$_3$), 1.73–1.78 (m, 4 H, CCH$_2$C), 2.34 (s, 2 H, SiCH$_2$N), 2.48–2.54 (m, 4 H, NCH$_2$C), 3.51 (s, 3 H, SiOCH$_3$), 7.36–7.42 and 7.62–7.66 (m, 5 H, SiC$_6$H$_5$). ^{13}C NMR (CDCl$_3$): δ –3.5 (SiCH$_3$), 24.5 (CCH$_2$C), 45.9 (SiCH$_2$N), 51.4 (SiOCH$_3$), 58.6 (NCH$_2$C), 128.6 (C-3/C-5, SiC$_6$H$_5$), 130.2 (C-4, SiC$_6$H$_5$), 134.2 (C-2/C-6, SiC$_6$H$_5$), 137.0 (C-1, SiC$_6$H$_5$). ^{29}Si NMR (CDCl$_3$): δ 4.1. EI MS: m/z 235 (19%, M$^+$), 84 (100%, CH$_2$=NC$_4$H$_8$$^+$). Anal. Calcd for C$_{13}H_{21}$NOSi: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.4; H, 8.9; N, 6.0.

(b) X-ray Diffraction Studies. Cell parameters were obtained from least-squares fits to the settings of 25 reflections in the range 15° ≤ Θ ≤ 20° centered on a Siemens P4 diffractometer by using Mo Kα radiation. Intensities were collected for colorless, prismatic crystals of **9** and **10** at –100 °C for 2Θ ≤ 50°. No significant deviations in intensity were registered for three monitor reflections recorded at regular intervals. Crystallographic parameters and additional details of the data collection and refinement are given in Table I. A total of 1521 (R_{int} = 0.015) and 2118 (R_{int} = 0.029) independent reflections were measured for **9** and **10**, respectively. On the basis of the rejection criterion $F_o{}^2 \leq 2\sigma(F_o{}^2)$ 1182 and 1448 reflections were used for subsequent refinements. The structures were solved by direct methods and refined by full-matrix least-squares[13] with anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 14. Corrections for absorption were applied after isotropic least-squares refinement for the non-hydrogen atoms by use of the program DIFABS.[15] All the hydrogen atoms were located in difference Fourier syntheses and their positions included in the least-squares refinement together with isotropic temperature factors. The function minimized during the refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + pF_o{}^2]^{-1}$, p = 0.0001 for **9** and 0.0003 for **10**. Atom coordinates

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for **9**

atom	x	y	z	U(eq)^a
Si	2003(1)	143(1)	2924(1)	23(1)
F(1)	91(2)	472(1)	3460(1)	26(1)
F(2)	3872(2)	–294(1)	2571(2)	37(1)
F(3)	1435(2)	–1226(1)	2898(2)	40(1)
C(1)	1709(4)	1031(3)	1217(3)	34(1)
C(2)	2914(3)	774(2)	4720(3)	26(1)
C(3)	2616(4)	1706(3)	7204(3)	31(1)
C(4)	1837(4)	2833(3)	7648(3)	34(1)
C(5)	1688(4)	3511(3)	6219(3)	39(1)
C(6)	1246(4)	2603(2)	5058(3)	35(1)
N	1846(2)	1440(2)	5692(2)	21(1)

^{a} The equivalent isotropic temperature factor U(eq) is defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for **10**

atom	x	y	z	U(eq)^a
Si	630(1)	3295(1)	4221(1)	34(1)
F(1)	500(2)	4645(1)	3944(1)	33(1)
F(2)	672(2)	1991(1)	4593(2)	61(1)
F(3)	–1225(2)	3298(1)	3780(2)	47(1)
C(1)	1303(3)	3051(2)	2869(3)	37(1)
C(2)	1888(4)	3515(3)	6052(3)	39(1)
C(3)	3337(4)	4794(3)	7943(3)	46(1)
C(4)	4764(5)	5432(3)	8224(4)	58(2)
C(5)	4852(4)	5626(3)	6909(3)	56(2)
C(6)	3891(4)	4764(3)	6001(3)	48(2)
C(12)	2250(4)	2191(3)	2902(4)	56(2)
C(13)	2727(5)	2004(4)	1879(6)	76(2)
C(14)	2241(5)	2665(5)	795(5)	81(2)
C(15)	1293(5)	3507(4)	716(4)	72(2)
C(16)	844(4)	3697(3)	1742(3)	50(1)
N	2631(3)	4577(2)	6455(2)	32(1)

^{a} The equivalent isotropic temperature factor U(eq) is defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

Table IV. Selected Bond Distances (Å) and Angles (deg) for **9** and **10**

	9	10
Si–F(1)	1.738(2)	1.715(2)
Si–F(2)	1.689(2)	1.681(2)
Si–F(3)	1.630(2)	1.633(2)
Si–C(1)	1.854(3)	1.870(4)
Si–C(2)	1.899(3)	1.896(3)
C(2)–N	1.498(3)	1.487(4)
C(3)–N	1.512(3)	1.518(4)
C(6)–N	1.513(3)	1.498(5)
C(3)–C(4)	1.504(4)	1.498(6)
C(4)–C(5)	1.509(4)	1.503(6)
C(5)–C(6)	1.500(4)	1.502(5)
F(1)–Si–F(2)	173.1(1)	174.5(1)
F(1)–Si–F(3)	86.5(1)	87.4(1)
F(1)–Si–C(1)	92.2(1)	92.5(1)
F(1)–Si–C(2)	90.4(1)	90.8(1)
F(2)–Si–F(3)	89.3(1)	89.4(1)
F(2)–Si–C(1)	94.6(1)	93.0(1)
F(2)–Si–C(2)	86.9(1)	86.7(1)
F(3)–Si–C(1)	119.1(1)	116.5(1)
F(3)–Si–C(2)	118.4(1)	117.0(2)
C(1)–Si–C(2)	122.5(1)	126.4(2)
Si–C(2)–N	118.3(2)	117.7(2)

are listed in Tables II and III, selected bond lengths and angles in Table IV. The atomic numbering schemes are given in Figures 1 and 2.

(c) Solid-State NMR Studies. High-resolution solid-state ^{15}N and ^{29}Si NMR spectra of **7** and **8** have been obtained on a Bruker MSL-300 NMR spectrometer operating at 30.4 (^{15}N) and 59.6 (^{29}Si) MHz, respectively. Chemical shifts are given with respect to external TMS (0 ppm, ^{29}Si) and solid NH$_4$NO$_3$ (NO$_3^-$ resonance, 0 ppm, ^{15}N). The Hartmann–Hahn matching condition for ^{1}H → ^{15}N experiments was set on slow-spinning solid NH$_4$NO$_3$, using a 5-μs ^{1}H 90° pulse. The experimental parameters for the ^{1}H → ^{15}N CP MAS spectra of **7** and

(13) Sheldrick, G. M. SHELX-76. University of Cambridge, Cambridge, England, 1976. SHELXTL PLUS. Siemens Analytical X-Ray Instruments Inc., 1990.

(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–149.

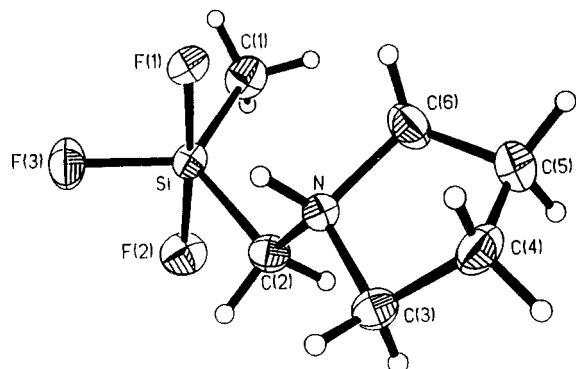(15) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

Figure 1. Molecular structure of **9** (ORTEP plot) in the crystal, showing the atomic numbering scheme. The thermal ellipsoids are drawn at a 50% probability level.
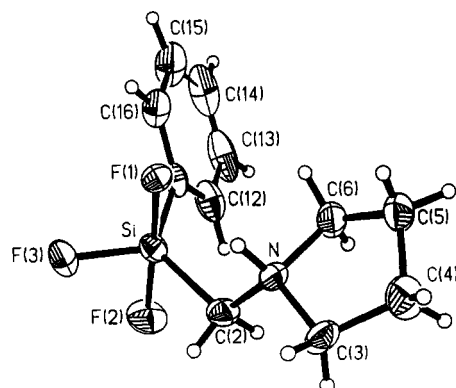

Figure 2. Molecular structure of **10** (ORTEP plot) in the crystal, showing the atomic numbering scheme. The thermal ellipsoids are drawn at a 50% probability level.
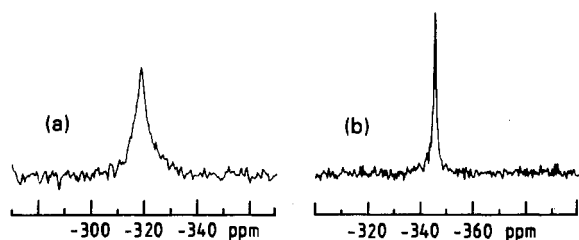

Figure 3. ^{1}H → ^{15}N CP MAS spectra of (a) **7** and (b) **8**. Key: (a) spinning rate = 2.9 kHz, contact time = 8 ms, recycle delay time = 20 s, 3188 transients, no exponential line broadening, $\delta(^{15}$N$) = -318.5$ ppm, $\nu_{1/2} = 140$ Hz; (b) spinning rate = 3.0 kHz, contact time = 5 ms, recycle delay time = 8 s, 922 transients, no exponential line broadening, $\delta(^{15}$N$) = -345.3$ ppm, $\nu_{1/2} = 35$ Hz.

8 are given in the respective figure caption (Figure 3). The procedure for setting the Hartmann–Hahn matching condition for ^{19}F → ^{29}Si CP MAS experiments (using a 5-μs ^{19}F 90° pulse) on topaz, [Al$_2$(F,OH)$_2$-(SiO$_4$)] (with >95% fluorine content), as well as the necessary spectrometer hardware modifications, has been described elsewhere.[16] Again, experimental parameters of the ^{19}F → ^{29}Si CP MAS and of the single-pulse ^{29}Si MAS spectra with high-power ^{19}F-decoupling are given in the respective figure caption (Figure 4). ^{1}H → ^{29}Si CP MAS experiments were set up using Q$_8$M$_8$ and a 5-μs ^{1}H 90° pulse.

Results and Discussion

(a) Syntheses. Tetrafluoro(pyrrolidiniomethyl)silicate[10] (**7**) was synthesized as described in the literature. (3-Ammonio-propyl)tetrafluorosilicate (**8**) was prepared analogously by reaction of commercially available (3-aminopropyl)triethoxysilane (**11**) with an excess of hydrogen fluoride in ethanol/hydrofluoric acid at 0 °C, following the strategy outlined in ref 12, but using a modified procedure (Scheme III). **8** was isolated with 80%
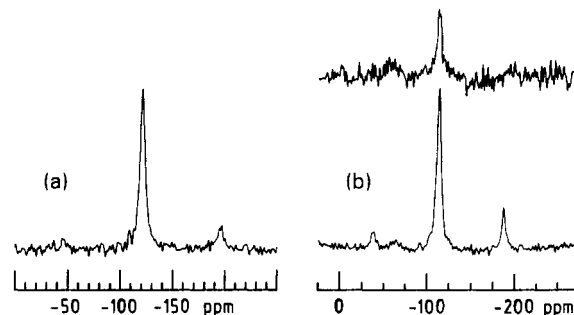
(16) Sebald, A.; Merwin, L. H.; Schaller, T.; Knöller, W. *J. Magn. Reson.* **1992**, *96*, 159–164.

Figure 4. ^{29}Si MAS spectrum of (a) **7** as well as ^{29}Si MAS and ^{19}F → ^{29}Si CP MAS spectra of (b) **8**. Key: (a) ^{19}F high-power decoupled ^{29}Si MAS spectrum of **7**, spinning rate = 4.5 kHz, 30° ^{29}Si pulse, recycle delay time = 30 s, 2271 transients, exponential line broadening of 25 Hz, $\delta(^{29}$Si$) = -121.1$ ppm, $\nu_{1/2} = 350$ Hz; (b) ^{19}F → ^{29}Si CP MAS spectrum of **8** (top), with spinning rate = 4.5 kHz, contact time = 10 ms, recycle delay time = 15 s, 1167 transients, exponential line broadening of 25 Hz, and ^{19}F high-power decoupled ^{29}Si MAS spectrum of **8** (bottom) with spinning rate = 4.5 kHz, 30° ^{29}Si pulse, recycle delay time = 30 s, 2165 transients, exponential line broadening of 25 Hz, $\delta(^{29}$Si$) = -112.4$ ppm, $\nu_{1/2} = 300$ Hz.
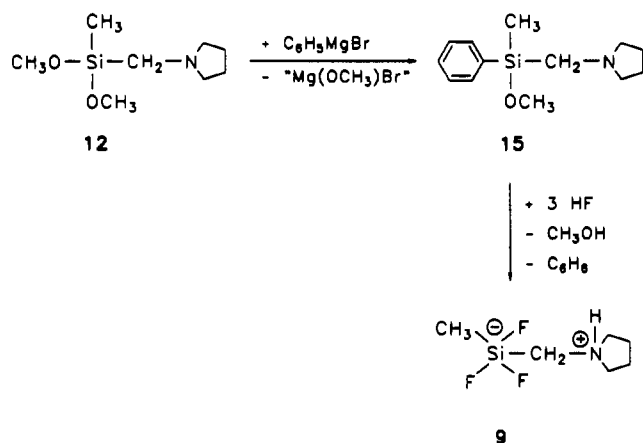
Scheme III

Scheme IV

	R
9,12	CH$_3$
10,13	C$_6$H$_5$
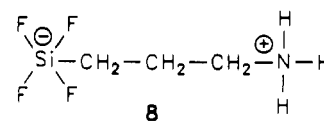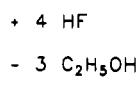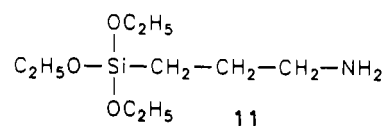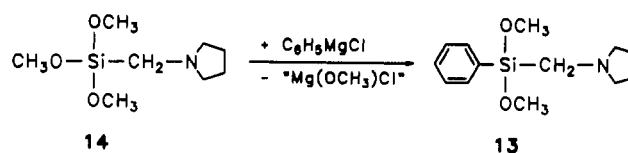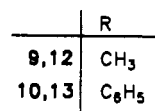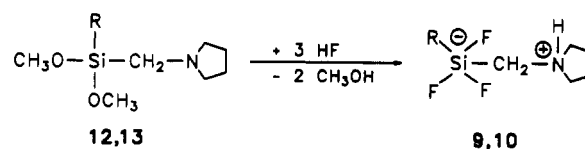
yield (lit.[12a] 50%) as a colorless crystalline solid. Similarly, trifluoro(methyl)(pyrrolidiniomethyl)silicate (**9**) and trifluoro-(phenyl)(pyrrolidiniomethyl)silicate (**10**) were synthesized by reaction of dimethoxy(methyl)(pyrrolidinomethyl)silane (**12**) and dimethoxy(phenyl)(pyrrolidinomethyl)silane (**13**), respectively, with an excess of hydrogen fluoride in ethanol/hydrofluoric acid at 0 °C (Scheme IV). The new zwitterionic organofluorosilicates were isolated with 90% (**9**) and 81% (**10**) yield as colorless crystalline solids. **9** and **10** are the first representatives of the hitherto unknown class of zwitterionic (ammonioalkyl)organo-trifluorosilicates.

Scheme V

CH₃O—Si(CH₃)(OCH₃)—CH₂—N(pyrrolidine) + C₆H₅MgBr / − "Mg(OCH₃)Br" → C₆H₅—Si(CH₃)(OCH₃)—CH₂—N(pyrrolidine)

12 → **15**

+ 3 HF / − CH₃OH / − C₆H₆

→ **9** (CH₃)(F)(F)(F)Si—CH₂—N⁺H(pyrrolidine) zwitterion

Alternatively, **9** was obtained by reaction of methoxy(methyl)-phenyl(pyrrolidinomethyl)silane (**15**) with an excess of hydrogen fluoride in ethanol/hydrofluoric acid at 0 °C (yield 89%; Scheme V). In addition to the Si–O bond cleavage (generation of methanol), the formation of **9** from **15** involves a chemoselective Si–C bond cleavage (generation of benzene). No indications were found for the formation of methane (Si–CH₃ cleavage) or 1-methylpyrrolidine (Si–CH₂NC₄H₈ cleavage). In this context it should be mentioned that the zwitterionic organofluorosilicate **10** was found to decompose almost completely *via* a Si–C₆H₅ cleavage (formation of benzene) upon heating in CDCl₃ at 50 °C for 5 hours (¹H and ¹³C NMR).

The starting materials used for the synthesis of the zwitterionic silicates **9** and **10** were prepared according to the literature (**12**,[5] **14**[5]) or were synthesized for the first time (**13**, Scheme IV; **15**, Scheme V). Details of the preparation and characterization of the new silanes **13** and **15** are given in the Experimental Section.

The identity of **8** was proven by elemental analyses (C, H, F, N), by mass-spectrometric investigations (EI MS), and by solution and solid-state NMR studies (solution in CD₃OD, ¹H and ¹³C NMR; solid state, ¹⁵N and ²⁹Si NMR). These investigations (see the Experimental Section and Solid-State NMR Data) unequivocally establish the zwitterionic structure of **8** as was postulated in ref 12.

The identity of **9** and **10** was established by elemental analyses (C, H, F, N), mass-spectrometric investigations (**9**, EI MS, FAB MS; **10**, EI MS) and solution-state NMR studies (see Experimental Section). In addition, the crystal structures of **9** and **10** were established by X-ray diffraction (see Crystal Structures).

The zwitterionic nature of **9** and **10** is reflected by their low solubility in organic solvents. For solutions of **9** (CD₃CN, CDCl₃) and **10** (CD₃CN) similar ¹H and ¹³C NMR spectra for the respective pyrrolidiniomethyl groups were obtained (see Experimental Section). The chemical shifts for the NCH₂C protons of the pyrrolidinio moiety (multiplets at 2.8–3.0 and 3.5–3.8 ppm) are typical of methylene groups bound to an ammonium-type nitrogen. This interpretation is supported by the ¹H NMR spectrum of **9** in CDCl₃, showing a resonance signal at δ = 8.0, which is typical of an NH function of an ammonium group. In contrast to the related zwitterionic organofluorosilicate **7** [δ-(²⁹Si) = −120.8; solution in CD₃CN],[10] all attempts to detect a ²⁹Si resonance at room temperature for solutions of **9** (CD₃CN, CDCl₃) and **10** (CD₃CN) failed.[17] Thus, pentacoordination of the silicon atoms in solution could not be established directly. However, as the ¹H and ¹³C NMR data for the pyrrolidiniomethyl group of **9** and **10** are very similar to those observed for **7** (whose pentacoordination was proved directly), it is concluded that the

zwitterions **9** and **10** also exist in solution. This assumption is strongly supported by low-temperature solution-state ¹⁹F NMR studies of **9** in CDCl₃. At 20 °C a single broad ¹⁹F-resonance signal, centered at −106.0 ppm ($\nu_{1/2} \approx 1995$ Hz), was observed, indicating a rapid exchange of the four fluorine atoms. On cooling, however, this ligand exchange becomes significantly slower, and at −70 °C two sharp ¹⁹F-resonance signals at δ = −91.5 (relative intensity = 2; $J_{SiF(ax)}$ = 242.9 Hz) and δ = −138.6 (relative intensity = 1; $J_{SiF(eq)}$ = 212.5 Hz) as well as ¹⁹F/²⁹Si spin-spin coupling were observed. These data are consistent with a trigonal-bipyramidal geometry of **9** in solution, with two fluorine atoms in the axial sites and one fluorine atom in an equatorial position. This is in accordance with the geometries observed for **9** and **10** in the crystal.

(b) Crystal Structures. The molecular structures of the zwitterionic fluorosilicates **9** and **10** in the crystal are depicted in Figures 1 and 2. The fluorine atoms F(1) and F(2) occupy the axial sites in a distorted trigonal bipyramid (TBP), F(3) and the carbon atoms C(1) and C(2) the equatorial positions. As may be gathered from Table IV, both molecules display similar deviations from an idealized TBP. The observed distortions are not in accordance with angular movements on the Berry pseudorotation pathway toward a square-pyramidal geometry.

The equatorial bond angles in **9** reflect the greater steric requirements of the bulkier pyrrolidiniomethyl and methyl group in comparison to the fluorine atom F(3). As a consequence, the C(1)–Si–C(2) angle is 122.5(1)° accompanied by a concomitant narrowing of the F(3)–Si–C(1) and F(3)–Si–C(2) angles to 119.1-(1) and 118.4(1)°, respectively. Increased steric demands of the phenyl group leads to more pronounced deviations from the idealized equatorial angles in **10**. The C(1)–Si–C(2) angle displays a value of 126.4(2)°; the F(3)–Si–C(1) and F(3)–Si–C(2) angles are 116.5(1) and 117.0(2)°. The axial bond angles F(1)–Si–F(2) also deviate from the idealized value of 180° [173.1-(1) and 174.5(1)°, respectively]. The deformation parameter Δ,[2j] defined as the sum of the axial and equatorial bond angle displacements from the ideal values of 180 and 120°, is 9.4 and 11.9° in **9** and **10**, respectively [angles used for these calculations: F(1)–Si–F(2), C(1)–Si–C(2)]. Similar values have been reported for ionic diorganotrifluorosilicates, for instance 8.7, 11.4, and 12.4° in the anions Ph₂SiF₃⁻,[2f,2j] Mes₂SiF₃⁻,[2o] and *t*-BuPhSiF₃⁻,[2n] respectively. The deviations of the F_{ax}–Si–F_{eq} and F_{ax}–Si–C_{eq} angles from the ideal value of 90° are clearly a result of the steric requirements of the bulky equatorial groups. Whereas both the F(1)–Si–C(1) and F(2)–Si–C(1) angles in **9** and **10** are significantly wider than 90° [range 92.2(1)–94.6-(1)°], the former axial fluorine atom is displaced toward F(3), with the latter displaced toward C(2).

Inspection of Figures 1 and 2 indicates that the pyrrolidinio-methyl groups in **9** and **10** both adopt conformations, which lead to short intramolecular F(1)···N contacts. The torsion angles F(1)–Si–C(2)–N in **9** and **10** are −10.0(2) and −17.4(3)°, respectively, the F(1)···N distances 2.67 and 2.68 Å. However, the intramolecular (N)H···F(1) distances of 2.25 and 2.19 Å are not indicative of a significant degree of hydrogen bonding; **9** and **10** display Si–C(2)–N–H torsion angles of 51 and 48°, respectively. Relatively weak intermolecular N–H···F(1) hydrogen bonds [F(1)···N distance 2.85 Å] lead to the formation of centrosymmetric dimers in the case of **9**. The intermolecular (N)H···F(1) distance is 1.96 Å; the N–H···F(1) angle is 152°. For **10** intermolecular N···F(1) and N···F(3) distances of 3.00 and 2.95 Å accompanied by (N)H···F(1) and (N)H···F(3) distances of 2.26 and 2.14 Å are observed for analogous molecule pairs related by a crystallographic center of symmetry. Both pyrrolidinio ring systems display an envelope conformation with C(4) displaced by 0.59 Å from the plane of the remaining atoms in **9**. In contrast, the atoms C(3), C(4), C(5), and N are effectively coplanar in **10**, with C(6) displaced by 0.50 Å from this plane.

---

(17) The failure to observe ²⁹Si resonances at room temperature for solutions of **9** and **10** may have to be attributed to motional processes involving the SiF₃ moiety as has also been discussed for related ionic compounds (see for example refs 1c,e,f and 2i,m,n,t).

The equatorial Si-F(3) bond lengths of 1.630(2) and 1.633(2) Å in the zwitterions 9 and 10 are similar to those observed for ionic diorganotrifluorosilicates.[2n,2s] The axial Si-F(1) bond is significantly longer than the opposite Si-F(2) bond in both 9 (difference 0.049 Å) and 10 (difference 0.034 Å). A similar phenomenon has been reported for ionic diorganotrifluorosilicates with 18-crown-6 potassium as the cation.[2n,2s] In each case the axial fluorine atom of the longer Si-F_{ax} bond participates in the coordination sphere of the potassium cation and the relevant F_{ax}-Si-F_{eq} angle is markedly smaller than 90°, as is observed in 9 and 10. Different axial Si-F bond distances were also found for the zwitterionic organotetrafluorosilicate 7 (differences 0.045 and 0.049 Å, respectively),[10] which may be explained by dipolar F···N interactions. The lengthening of the Si-F(1) with respect to the Si-F(2) distances in the zwitterionic silicates 9 and 10 may also be a result of dipolar F(1)···N interactions displayed by the former axial fluorine atom. In the case of 9, intermolecular N-H···F hydrogen bonds may also play a role.

A dihedral angle of 57.8° is observed in 10 between the plane of the phenyl ring and the equatorial plane of the TBP. The corresponding dihedral angle in [N(n-Bu)$_4$][PhMeSiF$_3$] is 78.2°.[2j]

(c) Solid-State NMR Data. The zwitterionic organofluorosilicates 7-10 were studied by solid-state NMR spectroscopy (7, 8, ^{15}N; 7-10, ^{29}Si). ^{15}N CP MAS and ^{29}Si MAS and CP MAS spectra of 7 and 8 are shown in Figures 3 and 4.

The ^{15}N chemical shifts for 7 (-318.5 ppm) and 8 (-345.3 ppm) clearly characterize these ^{15}N resonances as due to ammonium-type nitrogen.[18] The larger line width of the ^{15}N resonance of 7 ($\nu_{1/2}$ = 140 Hz) as compared to 8 ($\nu_{1/2}$ = 35 Hz) may have to be attributed to some residual ^{19}F-^{15}N dipolar interactions in 7; the average ^{19}F···^{15}N distances in 7 should be shorter than those in 8. An alternative explanation can be found on the basis of the X-ray crystallographic data for 7.[10] First, there are two crystallographically independent molecules per asymmetric unit, information which is apparently not resolved in the ^{1}H → ^{15}N CP MAS spectrum of 7 (neither are the two expected ^{29}Si resonances resolved in the ^{29}Si MAS spectrum of 7, see Figure 4). Thus, the presence of two unresolved ^{15}N resonances may account for some increase in the observed line width. Second and more important, some dynamic disorder phenomena (along with a phase transition occurring near -10 °C) has been claimed for 7 on the basis of variable-temperature X-ray diffraction studies.[10] This latter crystallographic finding is in fact corroborated by the occurrence of a broadened ^{15}N resonance. Another NMR-spectroscopic result further confirms this interpretation: while there is no problem to obtain a ^{29}Si single-pulse MAS spectrum of 7 (under ^{19}F high-power decoupling conditions, see Figure 4), all our attempts to obtain a ^{19}F → ^{29}Si CP MAS spectrum of 7 failed. A wide range of ^{19}F → ^{29}Si cross polarization contact times (ranging from 1 to 25 ms) have been used unsuccessfully. Taking the spin dynamics of the CP MAS experiment into account, motional processes, like the mentioned dynamic disorder phenomena for 7 or intramolecular exchange processes involving the SiF$_4$ moiety, can partially (or fully) average the respective dipolar interactions, thus rendering the cross polarization process fairly (or totally) inefficient. Under such circumstances also MAS rates of only a few kilohertz may interfer with the CP process, leading to well-known modulations in the CP matching curves[19] and to the potential complete failure of CP MAS methods for such cases. Further low-temperature CP MAS studies should enable us to prove this interpretation for compounds 7 and 8.

Along with the ^{29}Si MAS spectrum of 7, Figure 4 also depicts the ^{29}Si MAS and ^{19}F → ^{29}Si CP MAS spectra of 8. The ^{29}Si

resonances of both 7 and 8 show similar half-height line widths under ^{19}F high-power decoupling (7: 350 Hz; 8: 300 Hz). As mentioned before, the two ^{29}Si resonances for 7 which one would expect on the basis of the single-crystal X-ray diffraction studies[10] are not resolved. Line widths of the order of 300 Hz certainly have to be considered substantial for ^{29}Si MAS or CP MAS spectra of crystalline silicates. In the case of compounds 7 and 8 it may only seem too tempting to ascribe this broadening entirely to some residual ^{1}H-^{29}Si dipolar interactions.[20] However, also for 8 the cross polarization efficiency for the ^{19}F → ^{29}Si CP MAS experiment is fairly poor as may be seen in Figure 4. In the absence of motion ^{19}F → ^{29}Si cross polarization has been shown to be a highly efficient process[16,21] so that it seems reasonable to postulate a certain degree of SiF$_4$ nonrigidity also for compound 8. Another indication for the presence of such SiF$_4$ nonrigidity in solid 7 and 8 can be obtained from the respective ^{1}H → ^{29}Si CP MAS spectra. 7 yields a ^{1}H → ^{29}Si CP MAS resonance ($\nu_{1/2}$ = 350 Hz, excellent CP efficiency with CP contact times of approximately 5 ms) which displays no fine structure due to the interplay of scalar and dipolar ^{19}F/^{29}Si interactions. We may thus speculate that motional processes in solid 7 at room temperature should be restricted to the SiF$_4$ moiety, leaving the ^{1}H-^{29}Si interactions rather undisturbed. In fact, exchange processes similar to those shown for related ionic compounds in solution (see for example refs 1c,e,f and 2i,m,n,t), would be fully in agreement with our various CP MAS findings.

Finally, it should be mentioned that the isotropic ^{29}Si chemical shifts of 7 (-121.1 ppm; in CD$_3$CN -122.9 ppm[10]) and 8 (-112.4 ppm) are in good agreement with the existence of pentacoordinate silicon in these zwitterions.

For compounds 9 and 10 we can only report a complete failure to obtain either ^{29}Si MAS spectra with ^{19}F high-power decoupling or ^{19}F → ^{29}Si CP MAS spectra. Using similar experimental parameters as for 7 and 8 to record the ^{29}Si (^{19}F decoupled) MAS spectra (i.e. spinning rates of 4-5 kHz, ^{29}Si pulse widths of 30°, and recycle delays of 30-60 s) yielded no detectable ^{29}Si resonances for 9 and 10. Various ^{19}F → ^{29}Si CP MAS experiments on 9 and 10 were equally unsuccessful. We have no reason to believe that the ^{29}Si longitudinal relaxation times T_1 for 9 and 10 could be much longer than for 7 and 8. Therefore, similarly conservative pulse conditions (i.e. small ^{29}Si flip angles and rather long relaxation delays) as used successfully for 7 and 8 should yield reasonable ^{29}Si MAS spectra for 9 and 10. We have to come to the conclusion that for both 9 and 10 the ^{29}Si resonances (even under ^{19}F high-power decoupling conditions) at room temperature are broadened beyond detection. Again, this could be a combined effect of substantial residual ^{1}H-^{29}Si dipolar interactions (more for 9 and 10 than for 7 and 8) and/or motional processes which would have to be in the coalescence regime near room temperature in order to broaden the ^{29}Si resonances of 9 and 10 to such an extent.

(18) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, London, 1987.
(19) (a) Mehring, M. *Principles of High Resolution NMR in Solids*; Springer-Verlag: Berlin, 1983. (b) Wind, R. A.; Dec, S. F.; Lock, H.; Maciel, G. E. *J. Magn. Reson.* **1988**, *79*, 136-139.
(20) No ^{1}H high-power decoupling in addition to the ^{19}F high-power decoupling could be used as this would require a triply-tuned probe circuit: our probe is only doubly-tuned and matched for ^{19}F/X-nucleus frequencies. Accordingly, ^{1}H → ^{29}Si CP MAS experiments had to be carried out in the absence of ^{19}F high-power decoupling.
(21) Schaller, T.; Dingwell, D. B.; Keppler, H.; Knöller, W.; Merwin, L. H.; Sebald, A. *Geochim. Cosmochim. Acta* **1992**, *56*, 701-707.