

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

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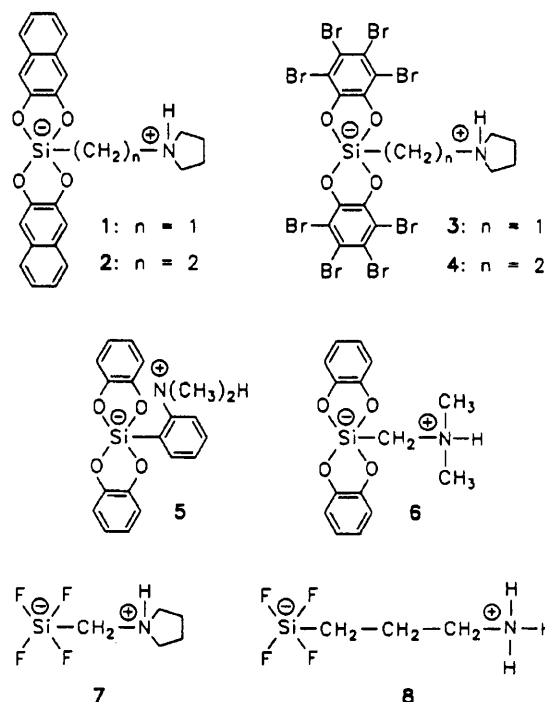
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Reaction of dimethoxy(methyl)(pyrrolidinomethyl)silane [Me(MeO)₂SiCH₂NC₄H₈, NC₄H₈ = pyrrolidino] and methoxy(methyl)phenyl(pyrrolidinomethyl)silane [MePh(MeO)SiCH₂NC₄H₈] with hydrogen fluoride at 0 °C in ethanol/hydrofluoric acid yielded trifluoro(methyl)(pyrrolidinomethyl)silicate [F₃Si(Me)CH₂N(H)C₄H₈ (9), N(H)-C₄H₈ = pyrrolidino] (yield 90% and 89%, respectively). The related trifluoro(phenyl)(pyrrolidinomethyl)silicate [F₃Si(Ph)CH₂N(H)C₄H₈ (10)] was obtained by reaction of dimethoxy(phenyl)(pyrrolidinomethyl)silane [Ph(MeO)₂SiCH₂NC₄H₈] 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 P2₁/n, a = 8.359(3) Å, b = 11.388(4) Å, c = 9.076(2) Å, β = 93.40(3)°, V = 862.4(5) Å³, T = -100 °C, Z = 4, R = 0.037, R_w = 0.037. 10: space group P2₁/n, a = 9.542(4) Å, b = 12.536(4) Å, c = 10.996(3) Å, β = 114.13(3)°, V = 1200.4(7) Å³, 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, CD₃CN, CDCl₃; 10, CD₃CN; ¹H, ¹³C, and ¹⁹F NMR), displaying a rapid ligand exchange at room temperature (one ¹⁹F resonance). Solid-state NMR studies (¹⁵N, ²⁹Si) on authentic tetrafluoro(pyrrolidinomethyl)silicate [F₄SiCH₂N(H)C₄H₈ (7)] and on (3-ammoniopropyl)tetrafluorosilicate [F₄Si(CH₂)₃NH₃ (8)] revealed evidence that 8 is indeed the earlier postulated product formed in the reaction of (3-aminopropyl)triethoxysilane [(EtO)₃Si(CH₂)₃NH₂] with HF in ethanol/hydrofluoric acid (7, δ(¹⁵N) = -318.5 ppm, δ(²⁹Si) = -121.1 ppm; 8, δ(¹⁵N) = -345.3 ppm, δ(²⁹Si) = -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 described³⁻¹⁰ (for a recent review, see ref 11). Most of these zwitterions belong to the class of spirocyclic silicates (examples: 1-1/4CH₃CN,^{3,8} 2-CH₃CN,^{4,8} 3-CH₃CN,^{6,8} 4-H₂O,⁸ 5,^{7,8} and 6⁸), whereas compound 7¹⁰ 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

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

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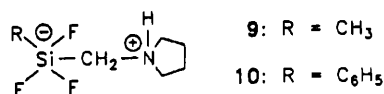
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Scheme II



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 ¹H, ¹³C and ¹⁹F solution-state NMR spectra were recorded on a Bruker AC-250 spectrometer (¹H, 250.1 MHz; ¹³C, 62.9 MHz; ¹⁹F, 235.4 MHz). The ²⁹Si 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; CD₃CN, CDCl₃ and CD₃OD were used as solvents. Chemical shifts (ppm) were determined relative to internal CHCl₃ (¹H, δ 7.25), CDCl₃ (¹³C, δ 77.05), CD₃OH (¹H, δ 4.85), CD₃OD (¹³C, δ 49.0), CD₃HCN (¹H, δ 1.93), CD₃CN (¹³C, δ 1.3), and relative to internal TMS (²⁹Si, δ 0) and CFC₃ (¹⁹F, δ 0). Assignment of the ¹³C 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 ¹H, ¹²C, ¹⁴N, ¹⁶O, ¹⁹F, and ²⁹Si.

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

(3-Ammionopropyl)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. ¹H NMR (CD₃OD): δ 0.70–0.76 (m, 2 H, SiCH₂C), 1.70–1.82 (m, 2 H, CCH₂C), 2.85–2.91 (m, 2 H, NCH₂C). ¹³C NMR (CD₃OD): δ 13.2 (SiCH₂C), 24.3 (CCH₂C), 43.3 (NCH₂C). EI MS: *m/z* 143 (15%, [M – HF]⁺), 30 (100%, CH₂=NH₂⁺). Anal. Calcd for C₃H₉F₄NSi: 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)pyrroldinylsilicate (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. ¹H NMR (CD₃CN): δ –0.01 (s, 3 H, SiCH₃), 1.9–2.1 (m, 4 H, CCH₂C), 2.51 (s, 2 H, SiCH₂N), 2.8–3.0 and 3.5–3.7 (m, 4 H, NCH₂C), 6.8–7.6 (broad s, 1 H, NH). ¹³C NMR (CD₃CN): δ 23.7 (CCH₂C), 50.5 (SiCH₂N), 58.0 (NCH₂C), SiCH₃ resonance not detectable (overlapping with the reference signal). ¹⁹F NMR (CDCl₃): δ –102.2 (broad s). ¹H NMR (CDCl₃): δ 0.13 (s, 3 H, SiCH₃), 1.95–2.15 (m, 4 H, CCH₂C), 2.60 (d, 2 H, SiCH₂N), 2.7–2.9 and 3.7–3.8 (m, 4 H, NCH₂C), 8.0 (broad s, 1 H, NH). ¹³C NMR (CDCl₃): δ 2.1 (SiCH₃), 23.9 (CCH₂C), 50.5 (SiCH₂N), 58.0 (NCH₂C). ¹⁹F NMR (CDCl₃, 20 °C): δ –106.0 (broad s; *ν*_{1/2} ≈ 1995 Hz). ¹⁹F NMR (CDCl₃, –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). ²⁹Si NMR (CD₃CN and CDCl₃): Experiments failed (under the same conditions as used successfully for **7**¹⁰). EI MS: *m/z* 165 (10%, [M – HF]⁺), 84 (100%, CH₂=NC₄H₈⁺). 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 C₆H₁₄F₃NSi: 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)pyrroldinylsilicate (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. ¹H NMR (CD₃CN): δ 1.85–2.05 (m, 4 H, CCH₂C), 2.56 (s, 2 H, SiCH₂N), 2.85–3.0 and 3.5–3.7 (m, 4 H, NCH₂C), 6.9–7.9 (m, 5 H, SiC₆H₅), NH resonance not resolved. ¹³C NMR (CD₃CN): δ 23.8 (CCH₂C), 48.4 (SiCH₂N), 58.1 (NCH₂C), 127.9 (C-3/C-5, SiC₆H₅), 129.2 (C-2/C-6, SiC₆H₅), 129.6 (C-4, SiC₆H₅), 137.9 (C-1, SiC₆H₅). ¹⁹F NMR (CD₃CN): δ –118.8 (broad s). ²⁹Si NMR (CD₃CN): Experiments failed (under the same conditions as used successfully for **7**¹⁰). EI MS: *m/z* 227 (26%, [M – HF]⁺), 84 (100%, CH₂=NC₄H₈⁺). Anal. Calcd for C₁₁H₁₆F₃NSi: 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-Aminoopropyl)triethoxysilane (11) was obtained from Wacker-Chemie GmbH, Burghausen, Germany.

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

Dimethoxy(phenyl)pyrroldinylsilane (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). ¹H NMR (CDCl₃): δ 1.68–1.71 (m, 4 H, CCH₂C), 2.29 (s, 2 H, SiCH₂N), 2.43–2.47 (m, 4 H, NCH₂C), 3.60 (s, 6 H, SiOCH₃), 7.34–7.41 and 7.65–7.68 (m, 5 H, SiC₆H₅). ¹³C NMR

Table I. Crystallographic Data for 9 and 10

	9	10
chem formula	C ₈ H ₁₄ F ₃ NSi	C ₁₁ H ₁₆ F ₃ NSi
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 _{calc} , 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

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

(CDCl₃): δ 23.9 (CCH₂C), 42.6 (SiCH₂N), 50.8 (SiOCH₃), 58.0 (NCH₂C), 127.9 (C-3/C-5, SiC₆H₅), 130.2 (C-4, SiC₆H₅), 132.8 (C-1, SiC₆H₅), 134.4 (C-2/C-6, SiC₆H₅). ²⁹Si NMR (CDCl₃): δ -20.6. EI MS: m/z 251 (12%, M⁺), 84 (100%, CH₂=NC₄H₉⁺). Anal. Calcd for C₁₃H₂₁NO₂Si: 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). ¹H NMR (CDCl₃): δ 0.05 (s, 3 H, SiCH₃), 1.73–1.78 (m, 4 H, CCH₂C), 2.34 (s, 2 H, SiCH₂N), 2.48–2.54 (m, 4 H, NCH₂C), 3.51 (s, 3 H, SiOCH₃), 7.36–7.42 and 7.62–7.66 (m, 5 H, SiC₆H₅). ¹³C NMR (CDCl₃): δ -3.5 (SiCH₃), 24.5 (CCH₂C), 45.9 (SiCH₂N), 51.4 (SiOCH₃), 58.6 (NCH₂C), 128.6 (C-3/C-5, SiC₆H₅), 130.2 (C-4, SiC₆H₅), 134.2 (C-2/C-6, SiC₆H₅), 137.0 (C-1, SiC₆H₅). ²⁹Si NMR (CDCl₃): δ 4.1. EI MS: m/z 235 (19%, M⁺), 84 (100%, CH₂=NC₄H₉⁺). Anal. Calcd for C₁₃H₂₁NOSi: 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_o² ≤ 2σ(F_o²) 1182 and 1448 reflections were used for subsequent refinements. The structures were solved by direct methods and refined by full-matrix least-squares¹³ 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 Σw(|F_o| - |F_c|)² with w = [σ²(F_o) + pF_o²]⁻¹, p = 0.0001 for 9 and 0.0003 for 10. Atom coordinates

Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) 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 (×10⁴) and Temperature Factors (Å² × 10³) 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 ¹⁵N and ²⁹Si NMR spectra of 7 and 8 have been obtained on a Bruker MSL-300 NMR spectrometer operating at 30.4 (¹⁵N) and 59.6 (²⁹Si) MHz, respectively. Chemical shifts are given with respect to external TMS (0 ppm, ²⁹Si) and solid NH₄NO₃ (NO₃⁻ resonance, 0 ppm, ¹⁵N). The Hartmann-Hahn matching condition for ¹H → ¹⁵N experiments was set on slow-spinning solid NH₄NO₃, using a 5-μs ¹H 90° pulse. The experimental parameters for the ¹H → ¹⁵N CP MAS spectra of 7 and

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

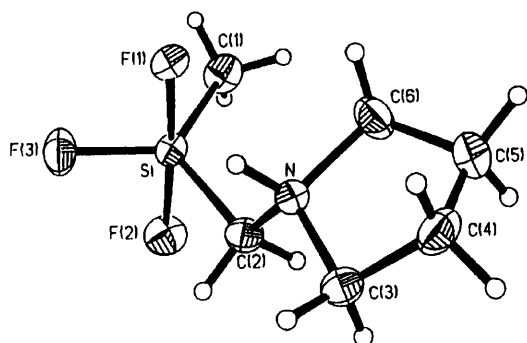


Figure 1. Molecular structure of **9** (ORTEP plot) in the crystal, showing the atomic numbering scheme. The thermal ellipsoids are drawn at a 50% probability level.

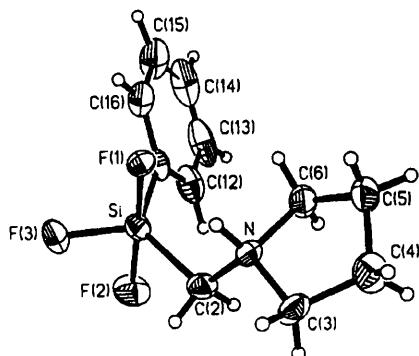


Figure 2. Molecular structure of **10** (ORTEP plot) in the crystal, showing the atomic numbering scheme. The thermal ellipsoids are drawn at a 50% probability level.

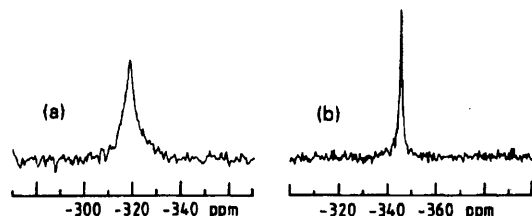


Figure 3. $^1\text{H} \rightarrow ^{15}\text{N}$ CP MAS spectra of (a) **7** and (b) **8**. Key: (a) spinning rate = 2.9 kHz, contact time = 8 ms, recycle delay time = 20 s, 3188 transients, no exponential line broadening, $\delta(^{15}\text{N}) = -318.5$ ppm, $\nu_{1/2} = 140$ Hz; (b) spinning rate = 3.0 kHz, contact time = 5 ms, recycle delay time = 8 s, 922 transients, no exponential line broadening, $\delta(^{15}\text{N}) = -345.3$ 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 $^{19}\text{F} \rightarrow ^{29}\text{Si}$ CP MAS experiments (using a $5\text{-}\mu\text{s}$ ^{19}F 90° pulse) on topaz, $[\text{Al}_2(\text{F},\text{OH})_2(\text{SiO}_4)]$ (with >95% fluorine content), as well as the necessary spectrometer hardware modifications, has been described elsewhere.¹⁶ Again, experimental parameters of the $^{19}\text{F} \rightarrow ^{29}\text{Si}$ 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). $^1\text{H} \rightarrow ^{29}\text{Si}$ CP MAS experiments were set up using Q_6M_8 and a $5\text{-}\mu\text{s}$ ^1H 90° pulse.

Results and Discussion

(a) **Syntheses.** Tetrafluoro(pyrrolidinomethyl)silicate¹⁰ (**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%

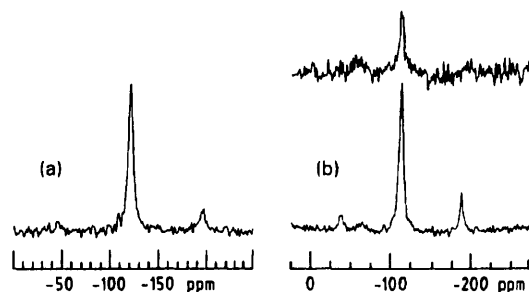
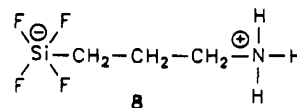
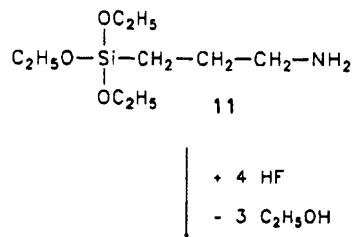
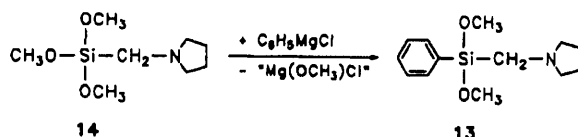
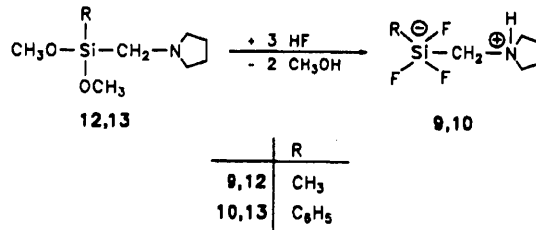


Figure 4. ^{29}Si MAS spectrum of (a) **7** as well as ^{29}Si MAS and $^{19}\text{F} \rightarrow ^{29}\text{Si}$ CP MAS spectra of (b) **8**. Key: (a) ^{19}F high-power decoupled ^{29}Si MAS spectrum of **7**, spinning rate = 4.5 kHz, 30° ^{29}Si pulse, recycle delay time = 30 s, 2271 transients, exponential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

Scheme III



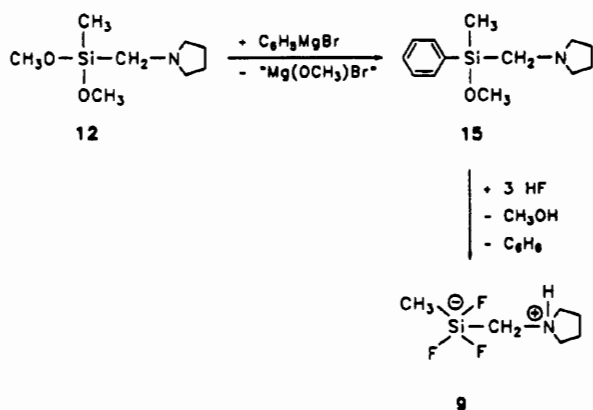
Scheme IV



yield (lit.^{12a} 50%) as a colorless crystalline solid. Similarly, trifluoro(methyl)(pyrrolidinomethyl)silicate (**9**) and trifluoro(phenyl)(pyrrolidinomethyl)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.

(16) Sebald, A.; Merwin, L. H.; Schaller, T.; Knöller, W. *J. Magn. Reson.* 1992, 96, 159–164.

Scheme V



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**) 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 pyrrolidinomethyl groups were obtained (see Experimental Section). The chemical shifts for the NCH₂C protons of the pyrrolidino 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 pyrrolidinomethyl 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 (ν_{1/2} ≈ 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 pyrrolidinomethyl 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 Δ₂²¹ 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 pyrrolidinomethyl 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 pyrrolidino 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.^{2a,2b} 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.^{2a,2b} 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 \cdots 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) \cdots N interactions displayed by the former axial fluorine atom. In the case of **9**, intermolecular N-H \cdots 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][PhMeSiF₃] is 78.2°.^{2j}

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

The ¹⁵N chemical shifts for **7** (-318.5 ppm) and **8** (-345.3 ppm) clearly characterize these ¹⁵N resonances as due to ammonium-type nitrogen.¹⁸ The larger line width of the ¹⁵N 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 ¹⁹F-¹⁵N dipolar interactions in **7**; the average ¹⁹F \cdots ¹⁵N 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 ¹H \rightarrow ¹⁵N CP MAS spectrum of **7** (neither are the two expected ²⁹Si resonances resolved in the ²⁹Si MAS spectrum of **7**, see Figure 4). Thus, the presence of two unresolved ¹⁵N 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 ¹⁵N resonance. Another NMR-spectroscopic result further confirms this interpretation: while there is no problem to obtain a ²⁹Si single-pulse MAS spectrum of **7** (under ¹⁹F high-power decoupling conditions, see Figure 4), all our attempts to obtain a ¹⁹F \rightarrow ²⁹Si CP MAS spectrum of **7** failed. A wide range of ¹⁹F \rightarrow ²⁹Si 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 SiF₄ 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 interfere with the CP process, leading to well-known modulations in the CP matching curves¹⁹ 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 ²⁹Si MAS spectrum of **7**, Figure 4 also depicts the ²⁹Si MAS and ¹⁹F \rightarrow ²⁹Si CP MAS spectra of **8**. The ²⁹Si

resonances of both **7** and **8** show similar half-height line widths under ¹⁹F high-power decoupling (**7**: 350 Hz; **8**: 300 Hz). As mentioned before, the two ²⁹Si resonances for **7** which one would expect on the basis of the single-crystal X-ray diffraction studies¹⁰ are not resolved. Line widths of the order of 300 Hz certainly have to be considered substantial for ²⁹Si 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 ¹H-²⁹Si dipolar interactions.²⁰ However, also for **8** the cross polarization efficiency for the ¹⁹F \rightarrow ²⁹Si CP MAS experiment is fairly poor as may be seen in Figure 4. In the absence of motion ¹⁹F \rightarrow ²⁹Si cross polarization has been shown to be a highly efficient process^{16,21} so that it seems reasonable to postulate a certain degree of SiF₄ nonrigidity also for compound **8**. Another indication for the presence of such SiF₄ nonrigidity in solid **7** and **8** can be obtained from the respective ¹H \rightarrow ²⁹Si CP MAS spectra. **7** yields a ¹H \rightarrow ²⁹Si 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 ¹⁹F/²⁹Si interactions. We may thus speculate that motional processes in solid **7** at room temperature should be restricted to the SiF₄ moiety, leaving the ¹H-²⁹Si 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 ²⁹Si chemical shifts of **7** (-121.1 ppm; in CD₃CN -122.9 ppm¹⁰) 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 ²⁹Si MAS spectra with ¹⁹F high-power decoupling or ¹⁹F \rightarrow ²⁹Si CP MAS spectra. Using similar experimental parameters as for **7** and **8** to record the ²⁹Si (¹⁹F decoupled) MAS spectra (i.e. spinning rates of 4-5 kHz, ²⁹Si pulse widths of 30°, and recycle delays of 30-60 s) yielded no detectable ²⁹Si resonances for **9** and **10**. Various ¹⁹F \rightarrow ²⁹Si CP MAS experiments on **9** and **10** were equally unsuccessful. We have no reason to believe that the ²⁹Si 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 ²⁹Si flip angles and rather long relaxation delays) as used successfully for **7** and **8** should yield reasonable ²⁹Si MAS spectra for **9** and **10**. We have to come to the conclusion that for both **9** and **10** the ²⁹Si resonances (even under ¹⁹F high-power decoupling conditions) at room temperature are broadened beyond detection. Again, this could be a combined effect of substantial residual ¹H-²⁹Si 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 ²⁹Si resonances of **9** and **10** to such an extent.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, Wacker-Chemie GmbH (Burghausen, Germany) and Bayer AG (Leverkusen and Wuppertal-Elberfeld, Germany) is gratefully acknowledged.

Supplementary Material Available: For **9** and **10**, respectively, anisotropic thermal parameters (Tables S1 and S4), hydrogen atom parameters (Tables S2 and S5), and additional bond angles and distances (Tables S3 and S6) (6 pages). Ordering information is given on any current masthead page.

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(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 ¹H high-power decoupling in addition to the ¹⁹F high-power decoupling could be used as this would require a triply-tuned probe circuit: our probe is only doubly-tuned and matched for ¹⁹F/*X*-nucleus frequencies. Accordingly, ¹H \rightarrow ²⁹Si CP MAS experiments had to be carried out in the absence of ¹⁹F high-power decoupling.

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