2520 *Inorg. Chem.* **2001,** *40,* 2520−2527

Monocyclic Zwitterionic λ^5*Si*-Silicates with an *Si*O_2FC_2 Framework: Syntheses and Structural Characterization in the Solid State and in Solution

Reinhold Tacke,* Rüdiger Bertermann, Olaf Dannappel, Ruth E. Neugebauer,
Melanie Pülm, and Reiner Willeke

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received December 27, 2000

Treatment of the acyclic zwitterionic pentacoordinate silicate $F_3MeSiCH_2NMe_2H$ with 1 molar equiv of $Me_3SiOC_6H_4OSiMe_3$, $Me_3SiOCH_2C(O)OSiMe_3$, $Me_3SiOC(Ph){=}NOSiMe_3$, or $Me_3SiOC(O)C(O)OSiMe_3$ (solvent CH_3CN, room temperature) yielded the respective monocyclic zwitterionic pentacoordinate silicates $\mathrm{FMe(\overline{OC_6H_4O)Si}CH_2NMe_2H}$ (**11a**), $\mathrm{FMe(\overline{OCH_2C(O)O)Si}CH_2NMe_2H}$ (**12a**), $\mathrm{FMe(\overline{OC(Ph){=}NO)Si}CH_2NMe_2H}$ (**13a**), and $\mathrm{FMe(\overline{OC(O)C(O)O)Si}CH_2NMe_2H}$ (**14a**), along with 2 molar equiv of Me_3SiF. The derivatives **11b**−**14b** with a 2,2,6,6-tetramethylpiperidinio substituent instead of the dimethylammonio group were prepared analogously, starting from $F_3MeSiCH_2NR_2H$ (NR_2H = 2,2,6,6-tetramethylpiperidinio). Single-crystal X-ray diffraction studies showed that the Si-coordination polyhedra of **11a**·1.5CH_3CN, **12a**−**14a**, and **11b**−**14b** are distorted trigonal bipyramids, the axial positions being occupied by the fluorine atom and one of the two oxygen atoms (**12a**/**12b**, carboxylate oxygen atom; **13a**/**13b**, carbon-linked oxygen atom). These results are in agreement with the NMR data (^1H, ^{13}C, ^{19}F, ^{29}Si) obtained for these compounds in solution. The chiral (C_1 symmetry) zwitterions **11a**−**14a** and **11b**−**14b** exist as pairs of (*A*)- and (*C*)-enantiomers in solution. VT ^1H NMR studies with **11b**−**14b** in CH_3CN in the temperature range 25−85 °C gave no indications for an enantiomerization process [(*A*)/(*C*)-enantiomerization] at the silicon atom.

Introduction

In context with our systematic investigations on higher-coordinate silicon compounds, a series of acyclic and spirocyclic zwitterionic λ^5*Si*-silicates have been synthesized and structurally characterized over the past few years.[1] Compounds **1**,[2] **2**,[2] **3**,[3] **4**,[4] **5**,[5] **6**,[6] **7**,[7] and **8**[8] are examples of this particular type of compound (Chart 1) (for reviews dealing with pentacoordinate silicon compounds, see refs 1 and 9−18). These zwitterionic λ^5*Si*-silicates contain a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom. Their silicate moiety is built up by an *Si*F_4C (**1**), *Si*F_3C_2 (**2**), *Si*O_4C (**3**−**6**), *Si*O_5 (**7**), or *Si*O_2N_2C skeleton (**8**).

In a recent paper, the syntheses of monocyclic zwitterionic λ^5*Si*-silicates with *Si*ONF_2C and *Si*$ONFC_2$ frameworks, compounds **9** and **10**, have been reported (Chart 1).[19] We have now succeeded in preparing a series of related monocyclic λ^5*Si*-silicates with an *Si*O_2FC_2 skeleton. We report here on the syntheses of compounds **11a**/**11b**−**14a**/**14b** (Chart 2) and their structural characterization in the solid state and in solution. The studies presented here were carried out with a special emphasis on the static and dynamic stereochemistry of these pentacoordinate silicon compounds. Preliminary results of these investigations have already been reported elsewhere.[1,20]

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* To whom correspondence should be addressed. E-mail: r.tacke@mail.uni-wuerzburg.de. Phone: (+49)931-888-5250. Fax: (+49)931-888-4609.

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10.1021/ic0014484 CCC: $20.00

Chart 1

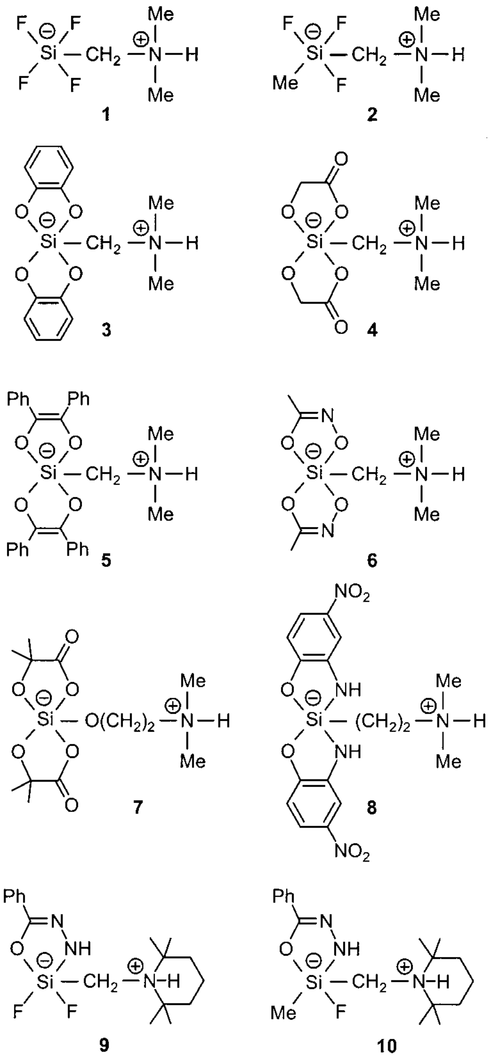
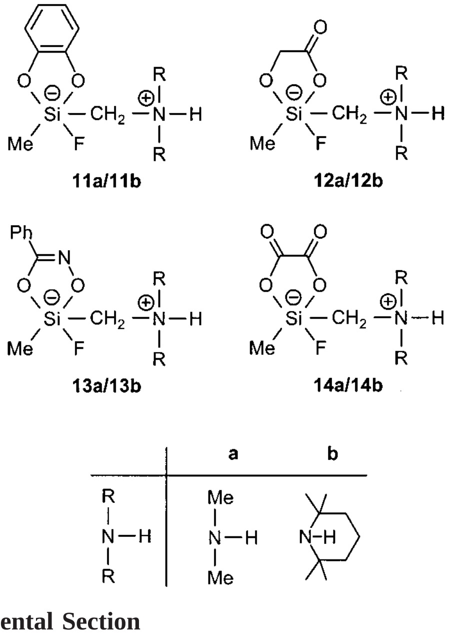


Chart 2



Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Leitz Biomed microscope equipped with a heater (Leitz, Model M 350). The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si solution NMR spectra were recorded at 22 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{19}F, 282.4 MHz; ^{29}Si, 59.6 MHz) or Bruker AMX-400 NMR spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{19}F, 376.4 MHz). $CDCl_3$ and [D$_6$]DMSO were used as solvents. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), [D$_5$]DMSO (^{1}H, δ 2.49; [D$_6$]DMSO), [D$_6$]DMSO (^{13}C, δ 39.5; [D$_6$]DMSO), external $CFCl_3$ (^{19}F, δ 0; $CDCl_3$, [D$_6$]DMSO), and external TMS (^{29}Si, δ 0; $CDCl_3$, [D$_6$]DMSO). Assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H COSY experiments, and the ^{1}H spin systems were analyzed by using the program *WIN-DAISY*.[21] Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer at 79.5 MHz with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 20−300 mg of sample [external standard, TMS (δ 0); spinning rate, 5000 Hz; contact time, 5 ms; 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s].

[(Dimethylammonio)methyl]trifluoro(methyl)silicate (2). This compound was synthesized according to ref 2.

[Benzene-1,2-diolato(2−)][(dimethylammonio)methyl]fluoro(methyl)silicate (11a). Compound **15** (800 mg, 3.14 mmol) was added to a stirred solution of **2** (500 mg, 3.14 mmol) in acetonitrile (20 mL) (formation of a precipitate ca. 5 h after combining the reactants) and the reaction mixture stirred at room temperature for 4 days. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (60 °C) to room temperature]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 706 mg (yield 98%) of a colorless solid. Mp: 159 °C. ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ 0.04 (d, $^3J_{FH}$ = 7.9 Hz, 3 H, $SiCH_3$), 2.43 (δ_A) (A part of an ABX system, B partly overlapped by internal standard, $^2J_{AB}$ = 15.9 Hz, $^3J_{AX}$ not detected, $^3J_{BX}$ = 5.0 Hz, 2 H, $F_XSiCH_AH_BN$), 2.70 (s, 6 H, NCH_3), 6.36−6.49 (m, 4 H, C_6H_4), 8.3 (br s, 1 H, N*H*). ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO): δ 4.1 (d, $^2J_{FC}$ = 38.2 Hz, $SiCH_3$), 45.4 (NCH_3), 46.3 (NCH_3), 52.4 (d, $^2J_{FC}$ = 47.7 Hz, $SiCH_2N$), 109.9 (*C*4/*C*5, C_6H_4), 116.9 (*C*3/*C*6, C_6H_4), 150.6 (d, $^3J_{FC}$ = 2.9 Hz, *C*1/*C*2, C_6H_4). ^{19}F NMR (376.4 MHz, [D$_6$]DMSO): δ −89.6 (s). ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ −74.6 (d, $^1J_{FSi}$ = 241.2 Hz). ^{29}Si VACP/MAS NMR (2913 transients): δ −66.5 (br s). Anal. Calcd for $C_{10}H_{16}FNO_2Si$: C, 52.38; H, 7.03; N, 6.11. Found: C, 52.5; H, 7.1; N, 6.0.

[Benzene-1,2-diolato(2−)]fluoro(methyl)[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (11b). Compound **15** (498 mg, 1.96 mmol) was added to a stirred solution of **19** (500 mg, 1.96 mmol) in acetonitrile (10 mL) and the reaction mixture kept undisturbed at room temperature for 2 days. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (20 °C) to −30 °C]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 472 mg (yield 74%) of colorless crystals. Mp: 159 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.24 (d, $^3J_{FH}$ = 8.5 Hz, 3 H, $SiCH_3$), 1.04 (s, 3 H, $NCCH_3$), 1.28 (s, 3 H, $NCCH_3$), 1.32 (s, 3 H, $NCCH_3$), 1.51 (s, 3 H, $NCCH_3$), 1.60−1.93 (m, 6 H, CCH_2C), 2.55 (δ_A) (A_2X system, $^3J_{AX}$ = 3.4 Hz, 2 H, $SiCH_2N$), 6.55−6.78 (m, 4 H, C_6H_4), 7.6 (br s, 1 H, N*H*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 2.3 (d, $^2J_{FC}$ = 38.5 Hz, $SiCH_3$), 15.9 ($NCCCH_2C$), 20.2 ($NCCH_3$), 20.4 ($NCCH_3$), 29.5 ($NCCH_3$), 30.5 ($NCCH_3$), 39.0 (d, $^2J_{FC}$ = 62.5 Hz, $SiCH_2N$), 39.2 ($NCCH_2C$), 63.36 ($NCCH_3$), 63.41 ($NCCH_3$), 111.4 (*C*4/*C*5, C_6H_4), 118.5 (*C*3/*C*6, C_6H_4), 149.7 (d, $^3J_{FC}$ = 2.5 Hz, *C*1/*C*2, C_6H_4). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ −95.3 (s). ^{29}Si{^{1}H} NMR ($CDCl_3$): δ −74.8 (d, $^1J_{FSi}$ = 244.4 Hz). ^{29}Si VACP/MAS NMR (2601 transients): δ −78.0 (d, $^1J_{FSi}$ = 254 Hz). Anal. Calcd for $C_{17}H_{28}FNO_2Si$: C, 62.73; H, 8.67; N, 4.30. Found: C, 62.7; H, 8.3; N, 4.5.

[(Dimethylammonio)methyl]fluoro[glycolato(2−)-*O*^{1},*O*^{2}]methylsilicate (12a). Compound **16** (705 mg, 3.20 mmol) was added to a stirred solution of **2** (505 mg, 3.17 mmol) in acetonitrile (20 mL)

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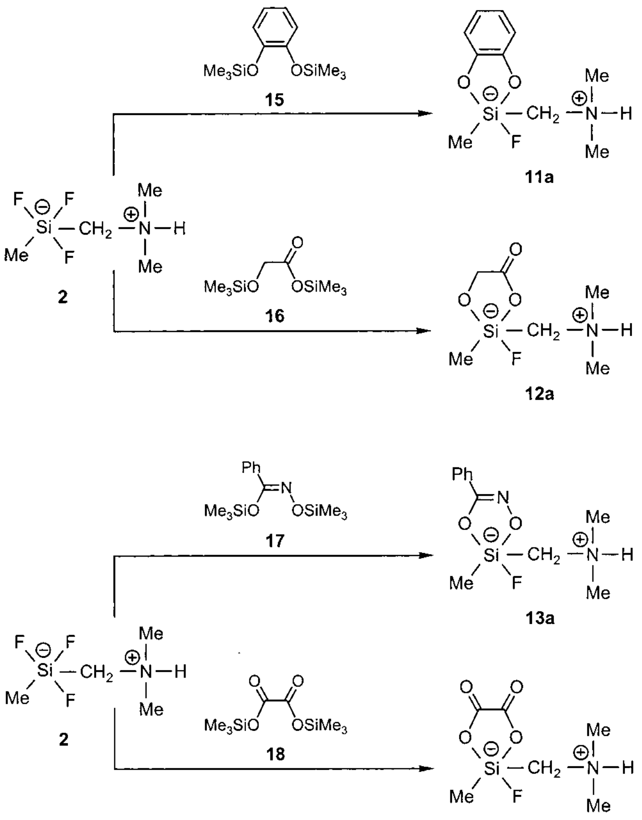
(21) Program *WIN-DAISY 4.0*, Bruker-Franzen GmbH, Bremen, Germany, 1998. Weber, U.; Germanus, A.; Thiele, H. *Fresenius J. Anal. Chem.* **1997**, *359*, 46−49.

(formation of a precipitate ca. 15 min after combining the reactants) and the reaction mixture stirred at room temperature for 24 h. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (60 °C) to room temperature]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 483 mg (yield 78%) of colorless crystals. Mp: 164 °C. ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ −0.01 (d, $^{3}J_{FH}$ = 8.0 Hz, 3 H, SiCH_3), 2.37 (δ_A) and 2.44 (δ_B) (ABX system, $^{2}J_{AB}$ = 15.7 Hz, $^{3}J_{AX}$ not detected, $^{3}J_{BX}$ = 5.5 Hz, 2 H, F$_X$SiCH_AH_BN), 2.70 (s, 6 H, NCH_3), 3.75 (s, 2 H, OCH_2C), 8.3 (br s, 1 H, NH). ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO): δ 3.5 (d, $^{2}J_{FC}$ = 36.2 Hz, SiCH$_3$), 46.0 (br s, NCH$_3$), 52.4 (d, $^{2}J_{FC}$ = 39.2 Hz, SiCH$_2$N), 62.7 (d, $^{3}J_{FC}$ = 6.0 Hz, OCH$_2$C), 175.0 (C=O). ^{19}F NMR (376.4 MHz, [D$_6$]DMSO): δ −98.5 (s). ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ −74.6 (d, $^{1}J_{FSi}$ = 248.2 Hz). ^{29}Si VACP/MAS NMR (13168 transients): δ −73.2 (d, $^{1}J_{FSi}$ = 221 Hz). Anal. Calcd for $C_6H_{14}FNO_3Si$: C, 36.91; H, 7.23; N, 7.17. Found: C, 36.9; H, 7.3; N, 7.1.

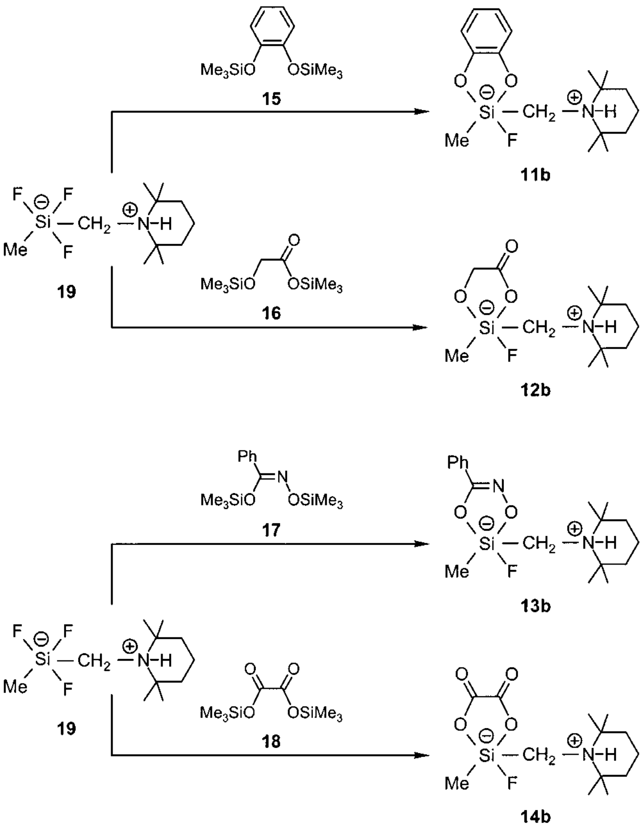
Fluoro[glycolato(2−)-*O*^{1},*O*^{2}]methyl[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (12b). Compound **16** (432 mg, 1.96 mmol) was added to a stirred solution of **19** (500 mg, 1.96 mmol) in acetonitrile (10 mL) and the reaction mixture kept undisturbed at room temperature for 2 days. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (20 °C) to −30 °C]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 401 mg (yield 70%) of colorless crystals. Mp: 176−178 °C. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 0.18 (d, $^{3}J_{FH}$ = 8.5 Hz, 3 H, SiCH_3), 1.32 (s, 6 H, NCCH_3), 1.34 (s, 3 H, NCCH_3), 1.41 (s, 3 H, NCCH_3), 1.58−1.90 (m, 6 H, CCH_2C), 2.39 (δ_A) and 2.55 (δ_B) (ABMX system, $^{2}J_{AB}$ = 17.2 Hz, $^{3}J_{AX}$ = 3.8 Hz, $^{3}J_{AM}$ < 0.8 Hz, $^{3}J_{BX}$ = 3.6 Hz, $^{3}J_{BM}$ = 1.8 Hz, 2 H, F$_X$SiCH_AH_BNH$_M$), 4.01 (δ_A) and 4.12 (δ_B) (AB system, $^{2}J_{AB}$ = 16.4 Hz, 2 H, OCH_AH_BC), 6.3 (br s, 1 H, NH). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 1.7 (d, $^{2}J_{FC}$ = 37.8 Hz, SiCH$_3$), 15.7 (NCCCH$_2$C), 20.0 (d, $^{5}J_{FC}$ = 1.5 Hz, NCCH$_3$), 20.1 (d, $^{5}J_{FC}$ = 1.5 Hz, NCCH$_3$), 30.2 (NCCH$_3$), 30.4 (d, $^{5}J_{FC}$ = 1.0 Hz, NCCH$_3$), 38.88 (NCCH$_2$C), 38.93 (NCCH$_2$C), 39.2 (d, $^{2}J_{FC}$ = 44.0 Hz, SiCH$_2$N), 63.5 (d, $^{3}J_{FC}$ = 5.8 Hz, OCH$_2$C), 64.3 (NCCH$_3$), 64.6 (NCCH$_3$), 176.6 (C=O). ^{19}F{^{1}H} NMR (282.4 MHz, CDCl$_3$): δ −103.4 (s). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −74.3 (d, $^{1}J_{FSi}$ = 244.5 Hz). ^{29}Si VACP/MAS NMR (4399 transients): δ −74.8 (d, $^{1}J_{FSi}$ = 268 Hz). Anal. Calcd for $C_{13}H_{26}FNO_3Si$: C, 53.58; H, 8.99; N, 4.81. Found: C, 53.5; H, 9.1; N, 4.9.

[Benzohydroximato(2−)][(dimethylammonio)methyl]fluoro(methyl)silicate (13a). Compound **17** (550 mg, 1.95 mmol) was added to a stirred solution of **2** (300 mg, 1.88 mmol) in acetonitrile (20 mL) (formation of a precipitate ca. 5 min after combining the reactants) and the reaction mixture stirred at room temperature for 24 h. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (60 °C) to room temperature]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 286 mg (yield 59%) of colorless crystals. Mp: 155−156 °C. ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ 0.04 (d, $^{3}J_{FH}$ = 7.6 Hz, 3 H, SiCH_3), 2.43 (δ_A) and 2.50 (δ_B) (ABX system, $^{2}J_{AB}$ = 15.5 Hz, $^{3}J_{AX}$ not detected, $^{3}J_{BX}$ = 5.3 Hz, 2 H, F$_X$SiCH_AH_BN), 2.73 (s, 6 H, NCH_3), 7.30−7.38 and 7.62−7.71 (m, 5 H, C$_6H_5$), 8.3 (br s, 1 H, NH). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]DMSO): δ 4.0 (d, $^{2}J_{FC}$ = 36.5 Hz, SiCH$_3$), 45.8 (br s, NCH$_3$), 52.3 (d, $^{2}J_{FC}$ = 44.8 Hz, SiCH$_2$N), 125.2 ($C$3/$C$5, C$_6$H$_5$), 128.0 ($C$2/$C$6, C$_6$H$_5$), 128.8 ($C$4, C$_6$H$_5$), 131.5 (d, $^{4}J_{FC}$ = 2.6 Hz, $C$1, C$_6$H$_5$), 162.3 (d, $^{3}J_{FC}$ = 1.6 Hz, C=N). ^{19}F{^{1}H} NMR (282.4 MHz, [D$_6$]DMSO): δ −94.1 (s). ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ −75.6 (d, $^{1}J_{FSi}$ = 255.4 Hz). ^{29}Si VACP/MAS NMR (796 transients): δ −73.8 (d, $^{1}J_{FSi}$ = 281 Hz). Anal. Calcd for $C_{11}H_{17}FN_2O_2Si$: C, 51.54; H, 6.68; N, 10.93. Found: C, 51.6; H, 6.7; N, 10.9.

Scheme 1



Scheme 2



[Benzohydroximato(2−)]fluoro(methyl)[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (13b). Compound **17** (1.11 g, 3.94 mmol) was added to a stirred solution of **19** (1.00 g, 3.92 mmol) in acetonitrile (10 mL) and the reaction mixture kept undisturbed at room temperature for 2 days. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (20 °C) to −30 °C]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 1.23 g (yield 89%) of colorless crystals. Mp: 165 °C. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 0.22 (d, $^{3}J_{FH}$ = 8.1 Hz, 3 H, SiCH_3), 1.20 (s, 3 H, NCCH_3), 1.29 (s, 3 H, NCCH_3), 1.33 (s, 3 H, NCCH_3), 1.51 (s, 3 H, NCCH_3), 1.58−1.90 (m,

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of **11a**·1.5CH$_3$CN, **11b**, and **12a**/**12b**

	11a·1.5CH$_3$CN	**11b**	**12a**	**12b**
empirical formula	$\mathrm{C_{10}H_{16}FNO_2Si\cdot 1.5CH_3CN}$	$\mathrm{C_{17}H_{28}FNO_2Si}$	$\mathrm{C_6H_{14}FNO_3Si}$	$\mathrm{C_{13}H_{26}FNO_3Si}$
formula mass, g mol^{-1}	290.91	325.49	195.27	291.44
collection T, K	173(2)	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$Pbca$ (61)	$P2_1/c$ (14)	$P2_1/n$ (14)
a, Å	12.693(3)	9.611(2)	9.067(2)	11.730(2)
b, Å	5.7643(12)	16.524(3)	12.873(3)	9.809(2)
c, Å	20.933(4)	22.098(4)	8.676(2)	14.010(3)
β, deg	91.05(3)	90	110.73(3)	110.05(3)
V, Å^3	1531.4(5)	3509.4(12)	947.1(3)	1514.2(5)
Z	4	8	4	4
D(calcd), g cm^{-3}	1.262	1.232	1.369	1.278
μ, mm^{-1}	0.167	0.150	0.235	0.170
F(000)	620	1408	416	632
cryst dimens, mm	0.3 × 0.3 × 0.2	0.6 × 0.6 × 0.5	0.3 × 0.3 × 0.2	0.5 × 0.4 × 0.4
2θ range, deg	6.42−52.76	4.94−49.66	4.80−56.18	5.56−52.88
index ranges	$-15 \le h \le 15$, $0 \le k \le 7$, $0 \le l \le 26$	$0 \le h \le 11$, $0 \le k \le 19$, $0 \le l \le 26$	$-12 \le h \le 11$, $-14 \le k \le 15$, $-11 \le l \le 11$	$-14 \le h \le 13$, $0 \le k \le 12$, $0 \le l \le 17$
no. of collected reflns	11524	29859	7984	15221
no. of indep reflns	3050	3021	2135	3100
R_{int}	0.0353	0.0864	0.0492	0.0557
no. of reflns used	3050	3021	2135	3100
no. of params	199	208	165	251
S^a	1.043	1.117	0.969	0.919
wt params a/b^b	0.0914/1.1043	0.0352/3.4611	0.0487/0.0000	0.0501/0.0000
R1^c [$I > 2\sigma(I)$]	0.0535	0.0578	0.0343	0.0348
wR2^d (all data)	0.1484	0.1107	0.0842	0.0835
max/min residual electron density, e Å^{-3}	+0.435/−0.444	+0.255/−0.219	+0.273/−0.288	+0.380/−0.282

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = number of reflections; p = number of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $\mathrm{R1} = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $\mathrm{wR2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

6 H, $\mathrm{CC_3}H_6\mathrm{C}$), 2.51 ($\delta_A$) and 2.54 ($\delta_B$) (ABMX system, $^2J_{AB} = 17.3$ Hz, $^3J_{AX} = 3.3$ Hz, $^3J_{AM} < 0.5$ Hz, $^3J_{BX} = 3.8$ Hz, $^3J_{BM} < 1.0$ Hz, 2 H, $\mathrm{F_XSiC}H_AH_B\mathrm{NH_M}$), 7.1 (br s, 1 H, N$H$), 7.30−7.37 and 7.80−7.87 (m, 5 H, $\mathrm{C_6H_5}$). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 2.3 (d, $^2J_{FC} = 37.4$ Hz, SiCH$_3$), 15.8 (NCCCH$_2$C), 20.1 (NCCH$_3$), 20.3 (NCCH$_3$), 29.7 (NCCH$_3$), 30.6 (NCCH$_3$), 39.0 (NCCH$_2$C), 39.2 (NCCH$_2$C), 39.2 (d, $^2J_{FC} = 58.9$ Hz, SiCH$_2$N), 63.66 (NCCH$_3$), 63.73 (NCCH$_3$), 125.5 ($C$3/$C$5, C$_6$H$_5$), 128.1 ($C$2/$C$6, C$_6$H$_5$), 129.3 ($C$4, C$_6$H$_5$), 130.5 (d, $^4J_{FC} = 1.8$ Hz, $C$1, C$_6$H$_5$), 162.0 (C=N). ^{19}F{^{1}H} NMR (282.4 MHz, CDCl$_3$): δ −95.9 (s). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −74.9 (d, $^1J_{FSi} = 254.2$ Hz). ^{29}Si VACP/MAS NMR (4096 transients): δ −74.1 (d, $^1J_{FSi} = 263$ Hz). Anal. Calcd for $\mathrm{C_{18}H_{29}FN_2O_2Si}$: C, 61.33; H, 8.29; N, 7.95. Found: C, 61.4; H, 8.3; N, 7.8.

[(Dimethylammonio)methyl]fluoro(methyl)[oxalato(2−)-*O*^{1},*O*^{2}]-silicate (14a). Compound **18** (1.62 g, 6.91 mmol) was added to a stirred solution of **2** (1.10 g, 6.91 mmol) in acetonitrile (20 mL) (formation of a precipitate ca. 20 min after combining the reactants) and the reaction mixture stirred under reflux for 8 h. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (20 °C) to −20 °C]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 6 h) to give 1.09 mg (yield 75%) of colorless crystals. Mp: 192 °C. ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ 0.18 (d, $^3J_{FH} = 7.9$ Hz, 3 H, SiCH_3), 2.62 (δ_A) and 2.70 (δ_B) (ABX system, $^2J_{AB} = 22$ Hz, $^3J_{AX} = 5.7$ Hz, $^3J_{BX} = 5.1$ Hz, 2 H, $\mathrm{F_XSiC}H_AH_B\mathrm{N}$), 2.71 (s, 3 H, NC$H_3$), 2.73 (s, 3 H, NC$H_3$), 8.5 (br s, 1 H, N$H$). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]DMSO): δ 2.7 (d, $^2J_{FC} = 34.9$ Hz, SiCH$_3$), 45.5 (d, $^4J_{FC} = 2.2$ Hz, NCH$_3$), 46.1 (NCH$_3$), 50.7 (d, $^2J_{FC} = 39.6$ Hz, SiCH$_2$N), 159.38 (C=O), 159.43 (C=O). ^{19}F{^{1}H} NMR (282.4 MHz, [D$_6$]DMSO): δ −96.6 (s). ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ −78.8 (d, $^1J_{FSi} = 263.1$ Hz). ^{29}Si VACP/MAS NMR (451 transients): δ −74.8 (d, $^1J_{FSi} = 260$ Hz). Anal. Calcd for $\mathrm{C_6H_{12}FNO_4Si}$: C, 34.44; H, 5.78; N, 6.69. Found: C, 34.7; H, 5.8; N, 6.2.

Fluoro(methyl)[oxalato(2−)-*O*^{1},*O*^{2}][(2,2,6,6-tetramethylpiperidinio)-methyl]silicate (14b). Compound **18** (459 mg, 1.96 mmol) was added to a stirred solution of **19** (500 mg, 1.96 mmol) in acetonitrile (10 mL) and the reaction mixture kept undisturbed at room temperature for 2 days. The solvent was removed in vacuo and the solid crude product recrystallized from acetonitrile [cooling of a saturated solution (20 °C) to −30 °C]. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20 °C, 4 h) to give 437 mg (yield 73%) of colorless crystals. Mp: 199 °C. ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ 0.17 (d, $^3J_{FH} = 7.9$ Hz, 3 H, SiCH_3), 1.28 (s, 6 H, NCCH_3), 1.30 (s, 3 H, NCCH_3), 1.32 (s, 3 H, NCCH_3), 1.60−2.04 (m, 6 H, CCH_2C), 2.53 (δ_A) and 2.79 (δ_B) (ABMX system, $^2J_{AB} = 17.7$ Hz, $^3J_{AX}$ or $^3J_{AM} = 5$ or 3.8 Hz, $^3J_{BX}$ not detected, $^3J_{BM} = 2.8$ Hz, 2 H, $\mathrm{F_XSiC}H_AH_B\mathrm{N}H_M$), 6.0 (br s, 1 H, N$H$). ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]DMSO): δ 2.6 (d, $^2J_{FC} = 37.0$ Hz, SiCH$_3$), 15.3 (NCCCH$_2$C), 19.3 (d, $^5J_{FC} = 1.8$ Hz, NCCH$_3$), 19.6 (d, $^5J_{FC} = 1.8$ Hz, NCCH$_3$), 28.9 (d, $^5J_{FC} = 2.5$ Hz, NCCH$_3$), 29.3 (NCCH$_3$), 36.7 (NCCH$_2$C), 37.0 (NCCH$_2$C), 37.6 (d, $^2J_{FC} = 32.7$ Hz, SiCH$_2$N), 64.8 (NCCH$_3$), 65.4 (NCCH$_3$), 159.39 (C=O), 159.42 (C=O). ^{19}F{^{1}H} NMR (282.4 MHz, [D$_6$]DMSO): δ −92.8 (s). ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ −79.2 (d, $^1J_{FSi} = 265.8$ Hz). ^{29}Si VACP/MAS NMR (40138 transients): δ −78.6 (d, $^1J_{FSi} = 278$ Hz). Anal. Calcd for $\mathrm{C_{13}H_{24}FNO_4Si}$: C, 51.12; H, 7.92; N, 4.59. Found: C, 50.3; H, 8.1; N, 4.8.

1,2-Bis(trimethylsilyloxy)benzene (15). This compound was synthesized according to ref 22.

(Trimethylsilyloxy)acetic Acid Trimethylsilyl Ester (16). This compound was synthesized according to ref 23.

***O*-(Trimethylsilyl)benzohydroximic Acid Trimethylsilyl Ester (17).** This compound was synthesized according to ref 6.

Oxalic Acid Bis(trimethylsilyl) Ester (18). This compound was synthesized according to ref 24.

Trifluoro(methyl)[(2,2,6,6-tetramethylpiperidinio)methyl]-silicate (19). This compound was synthesized according to ref 19.

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(22) Niederprüm, H.; Voss, P.; Beyl, V. *Liebigs Ann. Chem.* **1973**, 20−32.

(23) (a) Wissner, A. *Tetrahedron Lett.* **1978**, 2749−2752. (b) Wissner, A. *J. Org. Chem.* **1979**, *44*, 4617−4622.

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Table 2. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of **13a**/**13b** and **14a**/**14b**

	13a	**13b**	**14a**	**14b**
empirical formula	$C_{11}H_{17}FN_2O_2Si$	$C_{18}H_{29}FN_2O_2Si$	$C_6H_{12}FNO_4Si$	$C_{13}H_{24}FNO_4Si$
formula mass, g mol^{-1}	256.36	352.52	209.26	305.42
collection T, K	173(2)	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group (No.)	*Pbca* (61)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)
a, Å	10.967(2)	17.284(4)	8.8777(18)	11.678(2)
b, Å	10.812(7)	7.832(2)	10.859(2)	9.605(2)
c, Å	22.586(2)	14.709(3)	10.350(2)	14.286(3)
β, deg	90	109.77(3)	110.60(3)	109.91(3)
V, Å^3	2678(2)	1873.6(7)	933.9(3)	1506.7(5)
Z	8	4	4	4
D(calcd), g cm^{-3}	1.272	1.250	1.488	1.346
μ, mm^{-1}	0.180	0.147	0.252	0.179
F(000)	1088	760	440	656
cryst dimens, mm	0.6 × 0.4 × 0.4	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.4
2θ range, deg	5.18−45.74	5.00−52.24	5.64−52.74	5.54−56.08
index ranges	$-2 \le h \le 11$, $0 \le k \le 11$, $-24 \le l \le 5$	$-21 \le h \le 20$, $0 \le k \le 9$, $0 \le l \le 18$	$-11 \le h \le 9$, $0 \le k \le 13$, $0 \le l \le 12$	$-15 \le h \le 14$, $0 \le k \le 12$, $0 \le l \le 18$
no. of collected reflns	2016	20102	9980	17550
no. of indep reflns	1828	3712	1809	3590
R_{int}	0.0186	0.0823	0.0304	0.0297
no. of reflns used	1828	3712	1809	3590
no. of params	162	227	154	277
S^a	1.020	0.886	1.048	1.034
wt params a/b^b	0.0436/1.3254	0.0493/0.0000	0.0515/0.1454	0.0488/0.0816
R1^c [$I > 2\sigma(I)$]	0.0316	0.0391	0.0303	0.0284
wR2^d (all data)	0.0846	0.0936	0.0814	0.0759
extinction coefficient	0.0085(8)	0.0056(9)		
max/min residual electron density, e Å^{-3}	+0.230/−0.207	+0.289/−0.264	+0.301/−0.266	+0.286/−0.201

[a−d] See footnotes of Table 1.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **11a**·1.5CH_3CN, **11b**, and **12a**/**12b**−**14a**/**14b**

	11a·1.5CH_3CN	**11b**	**12a**	**12b**	**13a**	**13b**	**14a**	**14b**
Si−F	1.7281(13)	1.673(2)	1.7053(11)	1.6885(11)	1.6844(12)	1.6712(12)	1.6609(11)	1.6824(8)
Si−O1	1.8255(16)	1.874(2)	1.8679(13)	1.8734(13)	1.8478(14)	1.8783(14)	1.9107(13)	1.8710(9)
Si−O2	1.7062(15)	1.710(2)	1.6827(13)	1.6730(14)	1.703(2)	1.706(2)	1.7351(12)	1.7280(10)
Si−C1	1.934(2)	1.914(2)	1.904(2)	1.904(2)	1.898(2)	1.913(2)	1.9001(17)	1.8915(11)
Si−C2	1.844(2)	1.863(3)	1.864(2)	1.873(2)	1.862(2)	1.865(2)	1.857(2)	1.8611(13)
F−Si−O1	170.46(7)	170.35(8)	173.68(6)	175.81(6)	170.29(7)	170.94(7)	172.33(6)	172.62(4)
F−Si−O2	86.84(7)	88.32(7)	87.72(6)	89.60(6)	86.98(7)	88.50(7)	88.37(6)	88.35(4)
F−Si−C1	90.63(8)	88.09(8)	93.67(7)	93.77(6)	93.28(8)	88.98(7)	89.68(6)	94.52(4)
F−Si−C2	94.08(9)	96.37(12)	95.07(8)	95.10(8)	95.23(9)	95.93(8)	96.62(8)	96.75(5)
O1−Si−O2	86.57(7)	86.31(7)	87.08(6)	87.04(6)	84.98(7)	84.37(7)	84.70(6)	85.65(4)
O1−Si−C1	87.01(8)	88.65(8)	85.63(7)	85.60(7)	86.31(8)	90.21(7)	90.44(6)	84.55(5)
O1−Si−C2	95.16(9)	93.19(11)	90.77(8)	88.80(8)	93.50(9)	92.42(8)	89.68(8)	89.90(5)
O2−Si−C1	121.96(8)	126.38(9)	118.08(7)	117.98(8)	121.57(9)	122.94(8)	116.18(7)	118.15(5)
O2−Si−C2	119.18(10)	116.07(11)	122.98(8)	121.43(8)	119.95(10)	118.96(9)	119.77(8)	118.50(5)
C1−Si−C2	118.84(10)	117.49(11)	118.52(9)	119.86(10)	118.19(10)	118.00(10)	123.79(8)	122.37(6)

Crystal Structure Analyses. Suitable single crystals of **11b** and **12a/12b**−**14a/14b** were obtained by crystallization from acetonitrile (slow cooling of a boiling saturated solution to room temperature). A suitable single crystal of **11a**·1.5CH_3CN was obtained by slow cooling of a saturated solution from room temperature to −10 °C. The crystals were mounted in inert oil on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer [**11a**·1.5CH_3CN, **11b**, **12a/12b**, **13b**, **14a/14b**, Stoe IPDS diffractometer; **13a**, Enraf-Nonius CAD4 diffractometer; monochromated Mo Kα radiation (λ = 0.71073 Å)]. All structures were solved by direct methods.[25] The non-hydrogen atoms were refined anisotropically.[26] A riding model was employed in the refinement of the CH hydrogen atoms of **11a**·1.5CH_3CN, **11b**, and **13a/13b**. The CH hydrogen atoms of the other compounds and the NH hydrogen atoms of all compounds were localized in difference Fourier syntheses and refined freely. The silicon-linked methyl groups of **11a**·1.5CH_3CN and **11b** showed a rotational disorder, which was refined to an occupation of 0.5:0.5 in both cases.

VT ^{1}H NMR Studies. The experiments were carried out analogously to the standard ^{1}H NMR measurements using a Bruker DRX-300 NMR spectrometer. CD_3CN was used as solvent. The thermocouple used with the probe was calibrated for high temperatures according to ref 27 using an 80% solution of 1,2-ethanediol in [D_6]DMSO. Spectra were recorded in the range of 25−85 °C. The time required for temperature equilibration was 15 min.

Results and Discussion

Syntheses. The zwitterionic λ^5*Si*-silicates **11a**−**14a** were synthesized according to Scheme 1 by reaction of the zwitter-

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(26) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

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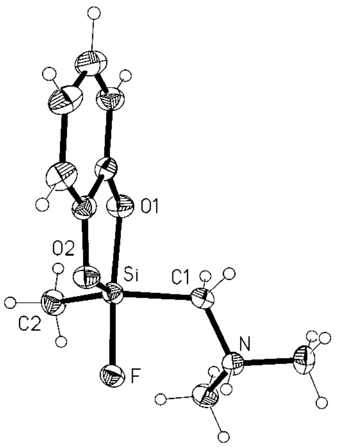

Figure 1. Molecular structure of **11a** in the crystal of **11a**·1.5CH_3CN (probability level of displacement ellipsoids 50%).

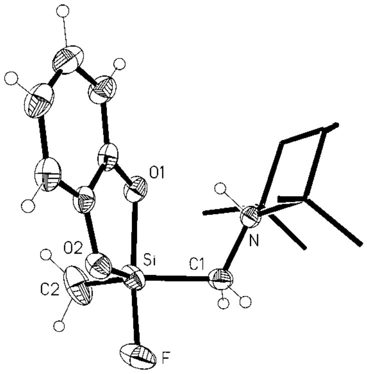

Figure 2. Molecular structure of **11b** in the crystal (probability level of displacement ellipsoids 50%; tetramethylpiperidinio moiety represented as stick model for clarity).

ionic λ^5Si-trifluorosilicate **2** with 1 molar equiv of 1,2-$Me_3SiOC_6H_4OSiMe_3$ (**15**), $Me_3SiOCH_2C(O)OSiMe_3$ (**16**), $Me_3SiOC(Ph){=}NOSiMe_3$ (**17**), or $Me_3SiOC(O)C(O)OSiMe_3$ (**18**) (→ formation of 2 molar equiv of Me_3SiF). The derivatives **11b**−**14b** were prepared analogously, starting from the zwitterionic λ^5Si-trifluorosilicate **19** (Scheme 2). All reactions were carried out in acetonitrile at room temperature, and compounds **11a**/**11b**−**14a**/**14b** were isolated, after recrystallization from acetonitrile and subsequent drying in vacuo, as colorless crystalline solids (yields: **11a**,[28] 98%; **11b**, 74%; **12a**, 78%; **12b**, 70%; **13a**, 59%; **13b**, 89%; **14a**, 75%; **14b**, 73%).

The identities of compounds **11a**/**11b**−**14a**/**14b** were established by elemental analyses (C, H, N), multinuclear solution NMR studies (^1H, ^{13}C, ^{19}F, ^{29}Si), solid-state ^{29}Si VACP/MAS experiments, and crystal structure analyses.

Crystal Structure Analyses. Compounds **11a**·1.5CH_3CN, **11b**, and **12a**/**12b**−**14a**/**14b** were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these experiments are summarized in Tables 1 and 2; selected interatomic distances and angles are listed in Table 3. The structures of the zwitterions **11a**/**11b**−**14a**/**14b** in the crystal are depicted in Figures 1−8.

The zwitterions **11a**/**11b**−**14a**/**14b** are chiral. The respective crystals are built up by pairs of (*A*)- and (*C*)-enantiomers. As

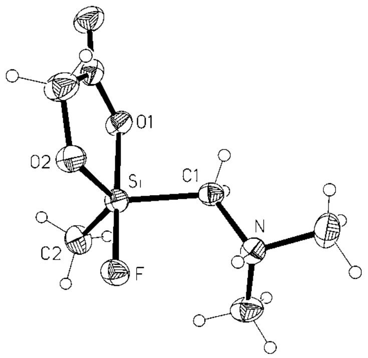

Figure 3. Molecular structure of **12a** in the crystal (probability level of displacement ellipsoids 50%).

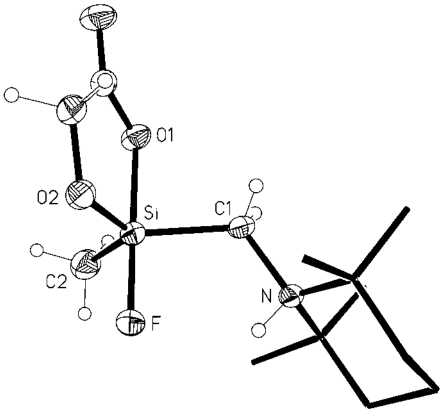

Figure 4. Molecular structure of **12b** in the crystal (probability level of displacement ellipsoids 50%; tetramethylpiperidinio moiety represented as stick model for clarity).

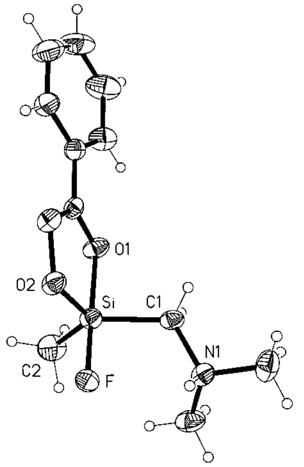

Figure 5. Molecular structure of **13a** in the crystal (probability level of displacement ellipsoids 50%).

can be seen from Figures 1−8 and Table 3, the Si-coordination polyhedra of **11a**/**11b**−**14a**/**14b** are distorted trigonal bipyramids, with the fluorine atom and one of the two oxygen atoms in the axial positions (carboxylate oxygen atom in the case of **12a**/**12b**; carbon-linked oxygen atom in the case of **13a**/**13b**). The sums of the three equatorial bond angles (O1−Si−C1, O1−Si−C2, C1−Si−C2) amount to 359−360°, indicating that the respective silicon atoms lie in the plane generated by their three equatorial ligand atoms. The axial F−Si−O1 angles are in the range 170.29(7)−175.81(6)°. The Si−F bond lengths amount to 1.6609(11)−1.7281(13) Å, and the axial Si−O1 distances are in the range 1.8255(16)−1.9107(13) Å, the shortest Si−F distance being correlated with the longest Si−O1 bond length

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(28) Compound **11a** crystallized as the acetonitrile solvate **11a**·1.5CH_3CN (see Crystal Structure Analyses); however, the solvent could be easily removed by drying in vacuo. The analytical data reported for **11a** refer to the solvent-free product.

(29) Hydrogen-bonding systems were analyzed by using the program *PLATON*: Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 1998.

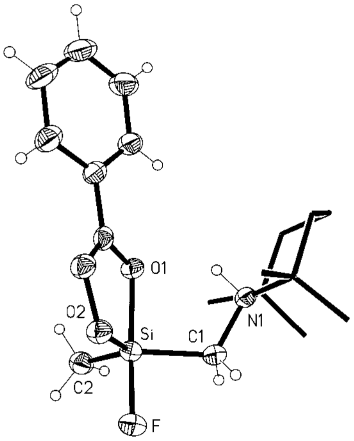

Figure 6. Molecular structure of **13b** in the crystal (probability level of displacement ellipsoids 50%; tetramethylpiperidinio moiety represented as stick model for clarity).

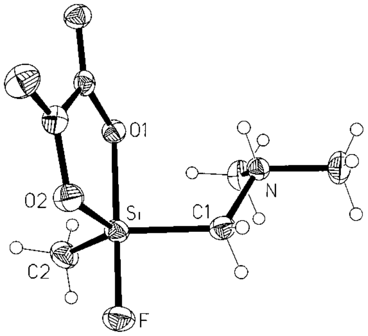

Figure 7. Molecular structure of **14a** in the crystal (probability level of displacement ellipsoids 50%).

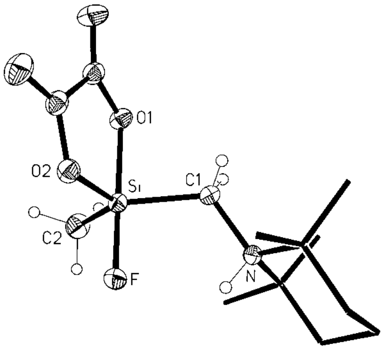

Figure 8. Molecular structure of **14b** in the crystal (probability level of displacement ellipsoids 50%; tetramethylpiperidinio moiety represented as stick model for clarity).

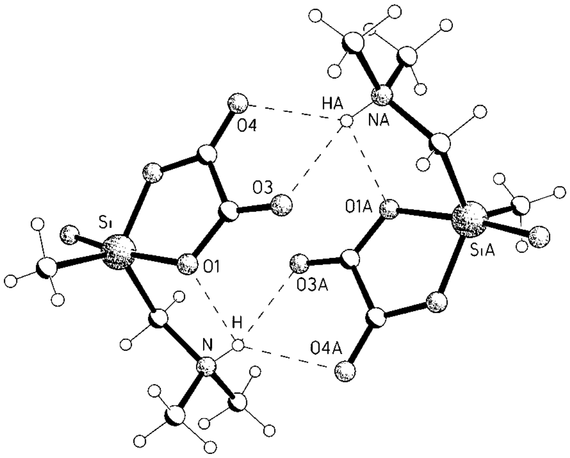

Figure 9. Hydrogen-bonding system in the crystal of **14a** leading to the formation of centrosymmetric dimers.

(compound **14a**). In all cases the axial Si−O distances [Si−O1, 1.8255(16)−1.9107(13) Å] are significantly longer than the equatorial ones [Si−O2, 1.6730(14)−1.7351(12) Å]. There is also a differentiation between the two Si−C bond lengths, the Si−C1 distances [1.8915(11)−1.934(2) Å] being significantly longer than the Si−C2 bond lengths [1.844(2)−1.873(2) Å].

As expected from the presence of the potential NH donor functions and acceptor atoms (F, N, O), hydrogen bonds were observed in all crystal structures (Table 4). The zwitterions **11a**−**14a** [molecules with a (dimethylammonio)methyl group] form trifurcate hydrogen bonds, with one intramolecular and two intermolecular interactions, leading to the formation of centrosymmetric dimers (**11a** and **12a**, N−H···F/FA/O2A; **13a**, N1−H1···F/O2A/N2A; **14a**, N−H···O1/O3A/O4A). As an example of this, the dimer of **14a** is depicted in Figure 9. For the derivatives **11b**−**14b** [molecules with a (2,2,6,6-tetramethylpiperidinio)methyl group] two totally different types of hydrogen bonds were observed, depending on the conformation of these zwitterions. Compounds **11b** and **13b** [conformations

Table 4. Hydrogen-Bonding Geometries for **11a**·1.5CH$_3$CN, **11b**, and **12a**/**12b**−**14a**/**14b** in the Crystal[a]

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
11a·1.5CH$_3$CN[b]	N−H···F (intra)	0.94(2)	2.36(2)	2.743(2)	104.2(18)
	N−H···FA (inter)	0.94(2)	2.03(3)	2.833(2)	143(2)
	N−H···O2A (inter)	0.94(2)	2.14(2)	2.896(2)	137(2)
11b	N−H···O1 (intra)	0.92(2)	1.85(2)	2.596(2)	136.9(18)
12a[c]	N−H···F (intra)	0.864(19)	2.366(16)	2.7529(18)	107.6(13)
	N−H···FA (inter)	0.864(19)	2.051(19)	2.8410(19)	151.5(17)
	N−H···O2A (inter)	0.864(19)	2.378(19)	3.057(2)	135.7(16)
12b[d]	N−H···F (intra)	0.89(2)	2.18(2)	2.8055(19)	127.6(17)
	N−H···FA (inter)	0.89(2)	2.30(2)	3.1369(19)	157.7(18)
13a[e]	N1−H1···F (intra)	0.90(2)	2.31(2)	2.723(3)	107.6(17)
	N1−H1···O2A (inter)	0.90(2)	2.39(2)	2.995(3)	125.0(18)
	N1−H1···N2A (inter)	0.90(2)	2.01(2)	2.826(3)	151(2)
13b	N1−H1···O1 (intra)	0.91(2)	1.94(2)	2.677(2)	137(2)
14a[f]	N−H···O1 (intra)	0.85(2)	2.40(2)	2.7787(19)	107.0(2)
	N−H···O3A (inter)	0.85(2)	2.17(2)	2.8500(19)	135.9(17)
	N−H···O4A (inter)	0.85(2)	2.39(2)	3.078(2)	137.5(17)
14b[g]	N−H···F (intra)	0.900(15)	2.202(15)	2.8111(12)	124.4(13)
	N−H···FA (inter)	0.900(15)	2.359(15)	3.2223(13)	160.5(13)

[a] Data calculated by using the program *PLATON*.[29] [b] F···H···FA = 83.7(9)°, F···H···O2A = 107.6(10)°, FA···H···O2A = 69.0(8)°. [c] F···H···FA = 84.4(6)°, F···H···O2A = 99.4(7)°, FA···H···O2A = 63.5(5)°. [d] F···H···FA = 74.7(7)°. [e] F···H1···O2A = 90.6(8)°, F···H1···N2A = 96.1(9)°, O2A···H1···N2A = 36.6(4)°. [f] O1···H···O3A = 84.5(7)°, O1···H···O4A = 101.1(7)°, O3A···H···O4A = 76.9(7)°. [g] F···H···FA = 75.0(5)°.

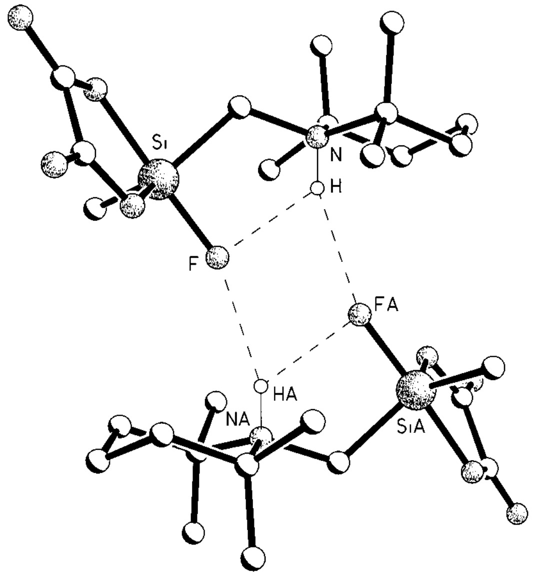

Figure 10. Hydrogen-bonding system in the crystal of **14b** leading to the formation of centrosymmetric dimers (hydrogen atoms except for the N*H* atoms are omitted for clarity).

with the oxygen atom O1 and the nitrogen atom N (N1) in *cis*-position to each other] form intramolecular N−H···O1 (N1−H1···O1) hydrogen bonds in the crystal. By contrast, compounds **12b** and **14b** (conformations with the fluorine and nitrogen atom in *cis*-position to each other) form bifurcate N−H···F/FA hydrogen bonds, with one intramolecular and one intermolecular interaction. This particular hydrogen-bonding system leads to the formation of centrosymmetric dimers in the crystal. As an example of this, the dimer of **14b** is depicted in Figure 10.

NMR Studies. The zwitterions **11a/11b−14a/14b** were studied by multinuclear NMR experiments (^{1}H, ^{13}C, ^{19}F, ^{29}Si) in solution (**11a−14a** and **14b**, [D$_6$]DMSO; **11b−13b**, CDCl$_3$). In addition, all compounds were characterized by solid-state ^{29}Si VACP/MAS NMR spectroscopy. All experiments were performed at 22 °C. In addition, compounds **11b−14b** were studied by VT NMR spectroscopy in solution (see VT ^{1}H NMR Studies).

The structures of compounds **11a/11b−14a/14b** in solution can be correlated with their crystal structures (for the NMR data, see Table 5 and the Experimental Section). The solution ^{29}Si NMR spectra of these zwitterions feature chemical shifts of $\delta(^{29}\mathrm{Si}) = -74.3$ to -79.2, with doublets due to a $^1J_{\mathrm{FSi}}$ coupling ($^1J_{\mathrm{FSi}} = 241.2-265.8$ Hz). This coupling is also present in the ^{19}F NMR spectra of **11a/11b−14a/14b** (^{29}Si satellites) (^{19}F chemical shifts for **11a/11b−14a/14b**: $\delta(^{19}\mathrm{F}) = -89.6$ to -103.4). The ^{29}Si chemical shifts of **11a/11b−14a/14b** in solution are very similar to the respective isotropic chemical shifts determined in the solid-state ^{29}Si NMR studies, indicating that the pentacoordinate silicate skeletons are also present in solution. As the ammonium protons could also be detected in the ^{1}H NMR spectra of all compounds (characteristic NH resonance signals), it is concluded that the zwitterions **11a/11b−14a/14b** exist in solution as well.

The zwitterions **11a/11b−14a/14b** are chiral (C_1 symmetry) and exist as pairs of (*A*)- and (*C*)-enantiomers in solution. These enantiomers are configurationally stable on the NMR time scale at room temperature, as is evident from the ^{1}H and ^{13}C NMR spectra. The chiral nature of the λ^5*Si*-silicate skeletons of **11a−14a** is reflected by the ABX spin systems observed for the two diastereotopic SiCH$_2$N protons in the ^{1}H NMR spectra (^{19}F as X nucleus). In addition, signal pairs for the two diastereotopic NCH$_3$ groups are resolved in the ^{13}C NMR spectra of **11a** and **14a** (one broad resonance signal each in the ^{13}C NMR spectra of **12a** and **13a**). Likewise, the chiral nature of **12b−14b** is reflected by the ABMX spin systems observed for the two diastereotopic SiCH$_2$N protons in the ^{1}H NMR spectra (N*H* as M nucleus, ^{19}F as X nucleus). By contrast, an A$_2$X spin system (^{19}F as X nucleus) was observed for the SiCH$_2$N protons of **11b** (accidentally isochronous). Besides other resolved pairs for diastereotopic groups of the 2,2,6,6-tetramethylpiperidinio substituent, signal pairs for the respective diastereotopic NC*C*H$_3$ groups are resolved in the ^{13}C NMR spectra of **11b−14b**.

Table 5. ^{29}Si and ^{19}F NMR Data for **11a/11b−14a/14b**[a]

	$\delta(^{29}\mathrm{Si})$ ($^1J_{\mathrm{FSi}}$)		$\delta(^{19}\mathrm{F})$
compd	cryst[b]	soln[c]	soln[c]
11a	−66.5[d]	−74.6 (241.2)	−89.6
11b	−78.0 (254)	−74.8 (244.4)	−95.3
12a	−73.2 (221)	−74.6 (248.2)	−98.5
12b	−74.8 (268)	−74.3 (244.5)	−103.4
13a	−73.8 (281)	−75.6 (255.4)	−94.1
13b	−74.1 (263)	−74.9 (254.2)	−95.9
14a	−74.8 (260)	−78.8 (263.1)	−95.8
14b	−78.6 (278)	−79.2 (265.8)	−92.8

[a] Spectra recorded at 22 °C, chemical shifts (δ values) in ppm, coupling constants in Hz. [b] Isotropic chemical shifts obtained by ^{29}Si VACP/MAS NMR experiments. [c] Solvents [D$_6$]DMSO (**11a−14a**, **14b**) or CDCl$_3$ (**11b−13b**). [d] Sample obtained by removal of CH$_3$CN from **11a**·1.5CH$_3$CN.

VT ^{1}H NMR Studies. To get information about the stereodynamics of the title compounds in solution, the zwitterions **11b−14b** were studied in acetonitrile in the temperature range 25−85 °C. Interestingly, enantiomerization at the silicon atom [(*A*)/(*C*)-enantiomerization], which might be observed by coalescence of the SiC*H*$_2$N AB systems in the ^{1}H NMR spectra of **11b−14b**, was not observed up to 85 °C. Furthermore, the "ammonium-nitrogen inversion" process reported for compound **10**[19] was not observed as well. This particular exchange process (which can be described as a combination of a deprotonation at the ammonium-nitrogen atom followed by nitrogen inversion and reprotonation) could not be detected up to 85 °C.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and the Bayer AG (Leverkusen and Wuppertal, Germany) and Merck KGaA (Darmstadt, Germany) for various gifts of chemicals.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **11a**·1.5CH$_3$CN, **11b**, and **12a/12b−14a/14b**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0014484