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New Zwitterionic Pentacoordinate Silicates with *Si*ONFC$_2$, *Si*ONF$_2$C, and *Si*O$_2$N$_2$C Frameworks: Synthesis, Structure, and Dynamic Stereochemistry

Daniel Kost,*,† Inna Kalikhman,*,† Sonia Krivonos,† Rüdiger Bertermann,‡
Christian Burschka,‡ Ruth E. Neugebauer,‡ Melanie Pülm,‡ Reiner Willeke,‡ and
Reinhold Tacke*,‡

Department of Chemistry, Ben Gurion University, Beer-Sheva 84105, Israel, and Institut für Anorganische Chemie, Universität Würzburg, D-97074 Würzburg, Germany

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The zwitterionic monocyclic λ^5*Si*-monofluorosilicates **3a**−**c** were synthesized by reaction of the zwitterionic λ^5*Si*-trifluorosilicates **1a**−**c** with 1 molar equiv of (*Z*)-$Me_3SiO(Ph)C{=}N{-}N(H)SiMe_3$ (**2**). The zwitterionic monocyclic λ^5*Si*-difluorosilicate **8** and the zwitterionic spirocyclic λ^5*Si*-silicate **9** (isolated as the isomer **9-I**) were prepared in an analogous manner, starting from the zwitterionic λ^5*Si*-tetrafluorosilicate **7** and using 1 (→ **8**) or 2 (→ **9**) molar equiv of **2**. Single-crystal X-ray diffraction studies showed that the *Si*-coordination polyhedra of **1a**, **3a**, **8**, **9-I**·$CHCl_3$, and **9-I**·CH_3CN are distorted trigonal bipyramids. The axial positions are occupied by two fluorine atoms (**1a**), one fluorine atom and one oxygen atom (**3a**, **8**), or two oxygen atoms (**9-I**·$CHCl_3$, **9-I**·CH_3CN). These results are in agreement with the NMR data obtained for these compounds in solution. The chiral monocyclic compounds (**3a**−**c** and **8**) undergo two distinct rate processes, inversion of absolute configuration of the chiral λ^5*Si*-silicate skeleton (enantiomerization) and a novel "ammonium-nitrogen inversion", measured by variable-temperature and selective inversion recovery NMR experiments (activation barrier for "ammonium-nitrogen inversion": **3a**−**c**, 17.0 ± 0.3 kcal mol^{-1}; **8**, 20.8 ± 0.3 kcal mol^{-1}; activation barrier for inversion of absolute configuration at the silicon atom: **3c**, 20.7 ± 0.3 kcal mol^{-1}; **8**, 11.7 ± 0.3 kcal mol^{-1}). In the spirocyclic λ^5*Si*-silicate **9-I** only one of these processes, the "ammonium-nitrogen inversion" ($\Delta G^{\ddagger} = 20.8 \pm 0.3$ kcal mol^{-1}), could be observed, while inversion of absolute configuration at the silicon atom could not be detected by NMR spectroscopy. Furthermore, no interconversion of diastereomers **9-I** $\rightleftarrows$ **9-II** was observed.

Introduction

The chemistry of complexes of pentacoordinate silicon has been studied extensively.[1−14] Among this class of compounds, a particular group of complexes has drawn our attention: pentacoordinate silicon complexes possessing a zwitterionic character, whereby the silicon atom is formally negatively charged while a neighboring ammonium group bears a positive charge.[14−41] Two main classes of zwitterionic complexes have been de-

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† Ben Gurion University.

‡ Universität Würzburg.

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scribed: spirocyclic λ^5*Si*-silicates with an *Si*O_4C framework, based on two five- or six-membered chelate rings built up by the silicon atom and diolato(2−) ligands [such as benzene-1,2-diolato(2−), *cis*-1,2-diphenylethene-1,2-diolato(2−), ethane-1,2-diolato(2−), oxalato(2−), glycolato(2−), salicylato(2−), aceto- or benzohydroximato-(2−), or similar bidentate ligands],[14−32] and acyclic λ^5*Si*-fluorosilicates with an *Si*F_nC_{5-n} ($n = 3$, 4) framework.[33−37] All these complexes have an Si−C bond connecting the silicon atom and the ammonium group through a $(CH_2)_n$ or an aromatic bridge. In addition, zwitterionic spirocyclic λ^5*Si*-silicates with an *Si*O_5,[14,28,38] *Si*O_2N_2C,[14,39] or *Si*O_2S_2C[14] skeleton and zwitterionic monocyclic λ^5*Si*-silicates with an *Si*O_2FC_2 framework[14,40,41] have been described in the literature.

Another series of neutral higher-coordinate silicon compounds with bidentate ligands, based on the hydrazonato(1−) backbone and coordinated to silicon through a nitrogen and oxygen atom, have been synthesized and described in recent years.[42−50] These ligands are attached to silicon by reaction of the respective trimethylsilyl derivatives [$Me_3SiO(R)C{=}NNMe_2$; R = alkyl, aryl] with halosilanes (formation of Me_3SiX, X = halogen), to form a variety of neutral penta- and hexacoordinate silicon complexes. Utilizing a new type of bidentate ligand, benzohydrazonato(2−) ([*O*(Ph)C=N*N*H]$^{2-}$), we have now synthesized a series of zwitterionic pentacoordinate silicates with a nitrogen-containing framework (*Si*ONFC_2, *Si*ONF_2C, *Si*O_2N_2C) and have explored their structure in the solid state and in solution, as well as their chemistry and stereodynamics.

The [*O*(Ph)C=N*N*H]$^{2-}$ ligand is isoelectronic with the benzohydroximato(2−) ligand, [*O*(Ph)C=N*O*]$^{2-}$, which has been used for the synthesis of zwitterionic λ^5*Si*-silicates with *Si*O_4C and *Si*O_2FC_2 skeletons.[14,29,32,40] Zwitterionic pentacoordinate silicon compounds with an *Si*O_2N_2C framework are already known,[14,39] whereas zwitterions with an *Si*ONF_2C or *Si*ONFC_2 skeleton have not yet been reported.

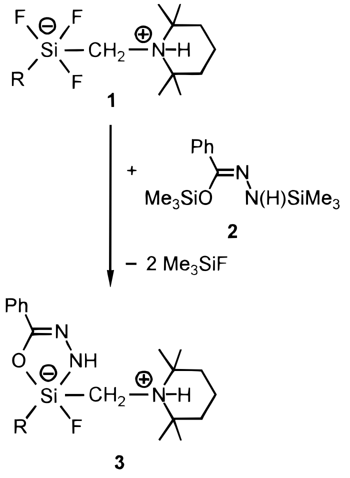
Results and Discussion

Syntheses. The zwitterionic monocyclic λ^5*Si*-silicates **3a**−**c** were obtained according to Scheme 1 by reaction of the respective zwitterionic λ^5*Si*-trifluorosilicates **1a**−**c** with 1 molar equiv of (*Z*)-$Me_3SiO(Ph)C{=}NN(H)SiMe_3$ (**2**) in CH_3CN (**3a**, **3c**) or in $CDCl_3$ (**3b**) at room temperature. Compounds **3a** and **3c** were prepared on a preparative scale (yield: **3a**, 70%; **3c**, 54%), whereas the derivative **3b** was only synthesized on an analytical scale. The precursors **1a** and **1b** were prepared in analogy with the synthesis of **1c**[36] (**4** → **6a** → **1a**, Scheme 2; **5** → **6b** → **1b**, Scheme 3) and isolated in 93% and 89% yield, respectively.

When an equimolar mixture of the zwitterionic λ^5*Si*-tetrafluorosilicate **7** and compound **2** is refluxed in $CHCl_3$ for 2 h, the NMR spectra show complete conversion to the zwitterionic monocyclic λ^5*Si*-difluorosilicate **8** (Scheme 4). This product is remarkably stable in solution as long as no excess of **2** is present. Using boiling CH_3CN as solvent, compound **8** was synthesized on a preparative scale and isolated in 58% yield as a crystalline solid.

A mixture of the zwitterionic spirocyclic λ^5*Si*-silicates **9-I** (major isomer) and **9-II** (minor isomer) was prepared on a preparative scale according to Scheme 4 by treatment of **7** with 2 molar equiv of **2** in boiling $CHCl_3$. The

Scheme 1



R = Me (**a**), *i*-Pr (**b**), *t*-Bu (**c**)

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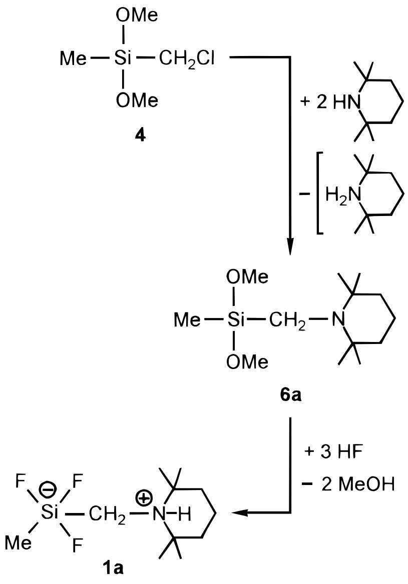
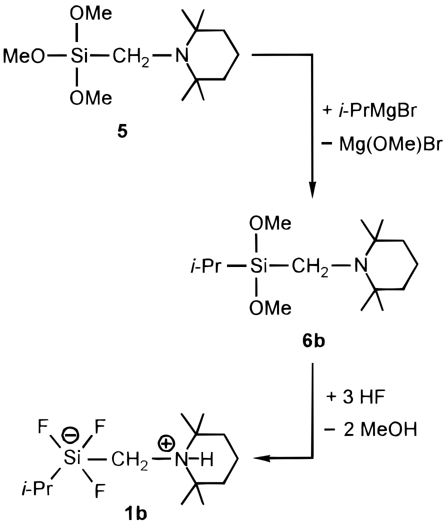
Scheme 2



Scheme 3

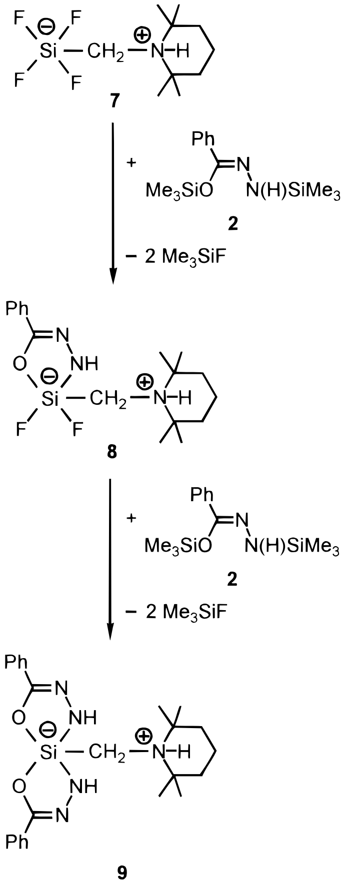


mixture was isolated in moderate yield (57%) as a solid product.[51] Attempts to separate the isomers **9-I** and **9-II** as pure crystalline phases on a preparative scale failed. However, a few single crystals of the solvate **9-I**·$CHCl_3$ could be obtained by recrystallization of **9-I**/**9-II** from $CHCl_3$/*n*-hexane. An alternative synthesis of **9-I** in boiling CH_3CN and subsequent recrystallization of the product from CH_3CN gave the crystalline diastereomerically pure solvate **9-I**·CH_3CN (yield 43%).

The identities of the crystalline compounds **1a**, **1b**, **3a**, **3c**, **8**, and **9-I**·CH_3CN were established by elemental analyses (C, H, N) and solution NMR studies (^{1}H, ^{13}C, ^{19}F, ^{29}Si) and solid-state NMR experiments (^{15}N, ^{29}Si). Furthermore, compounds **1a**, **3a**, **8**, **9-I**·$CHCl_3$, and **9-I**·CH_3CN were structurally characterized by single-crystal X-ray diffraction. The identities of **3b** and **9-II** were established by multinuclear solution NMR studies (^{1}H, ^{13}C, ^{29}Si).

Crystal Structure Analyses. The crystal structures of compounds **1a**, **3a**, **8**, **9-I**·$CHCl_3$, and **9-I**·CH_3CN were determined by single-crystal X-ray diffraction. The molecular structures of the zwitterions in the crystal are depicted in Figures 1−5. The crystal data and the experimental parameters used for the crystal structure analyses are summarized in Table 1. Selected interatomic distances and angles are listed in Tables 2−5.

Scheme 4



As can be seen from Figure 1 and Table 2, the Si-coordination polyhedron of **1a** is a distorted trigonal bipyramid (TBP), with fluorine atoms in both axial positions. The sum of the equatorial bond angles is 360°, indicating that the silicon atom lies in the plane generated by the three equatorial ligand atoms. On the basis of the relevant geometric data, the existence of bifurcate N−H···F2/F2A hydrogen bonds can be assumed [N−H, 0.881(15) Å; H···F2, 2.180(14) Å; N···F2, 2.7751(13) Å; N−H···F2, 124.4(11)°].[52] This particular hydrogen-bonding interaction leads to the formation of centrosymmetric dimers in the crystal.

The coordination polyhedron around the silicon atom of **3a** is also a distorted TBP, the axial positions being occupied by the fluorine atom and oxygen atom (Figure 2 and Table 3). The sum of the three equatorial bond angles amounts to 360°. The Si−N1 distance is very similar to those observed for zwitterionic spirocyclic λ^5*Si*-silicates with an SiO_2N_2C skeleton,[14,39] and the Si−O, Si−F, Si−C1, and Si−C2 distances are within the range reported for related zwitterionic monocyclic λ^5*Si*-silicates with an SiO_2FC_2 framework.[14] The oxygen atom and the nitrogen atom N3 are in cis position to

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[51] As this product was not homogeneous, elemental analyses were not performed.

[52] Hydrogen-bonding system analyzed by using the program PLATON: Spek, A. L. *PLATON*; University of Utrecht, The Netherlands, 1998.

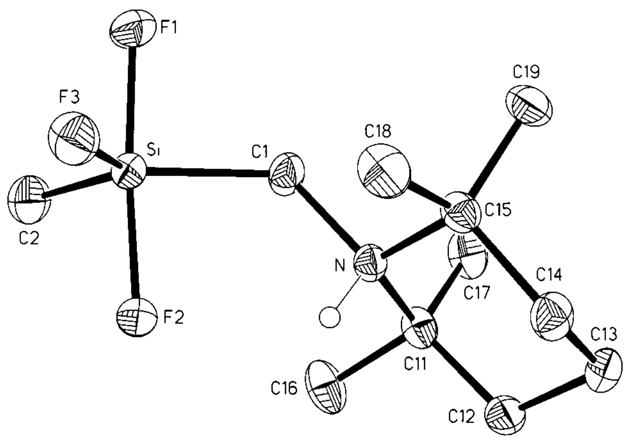

Figure 1. Molecular structure of **1a** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. Hydrogen atoms (except for N-*H*) are omitted for clarity. For selected geometric parameters, see Table 2.

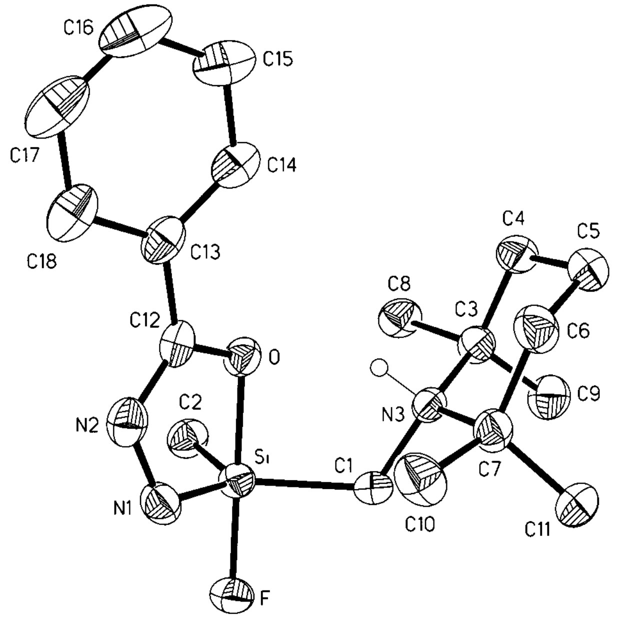

Figure 2. Molecular structure of **3a** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. Hydrogen atoms (except for N3-*H*) are omitted for clarity. For selected geometric parameters, see Table 3.

each other, and the distance between them suggests the presence of an intramolecular N3−H···O hydrogen bond, which determines the present conformation in the solid state [N3−H, 0.91(3) Å; H···O, 1.89(2) Å; N3···O, 2.667(2) Å; N3−H···O, 142(2)°].[52]

As can be seen from Figure 3 and Table 4, the Si-coordination polyhedron of **8** is a distorted TBP, with a fluorine atom and the oxygen atom in the axial positions. The sum of the three equatorial bond angles is 360°. The Si−N1 distance is very similar to those observed for zwitterionic spirocyclic λ^5*Si*-silicates with an SiO_2N_2C skeleton,[14,39] and the Si−O, Si−F1, and Si−C1 distances are within the range reported for related zwitterionic monocyclic λ^5*Si*-silicates with an SiO_2FC_2 framework.[14] As in **3a**, the oxygen atom and the nitrogen atom N3 are in cis position to each other, and the N3···O distance is indicative of the presence of an intramolecular N3−H···O hydrogen bond [N3−H, 0.85(3) Å; H···O, 1.96(3) Å; N3···O, 2.681(3) Å; N3−H···O, 142(3)°].[52]

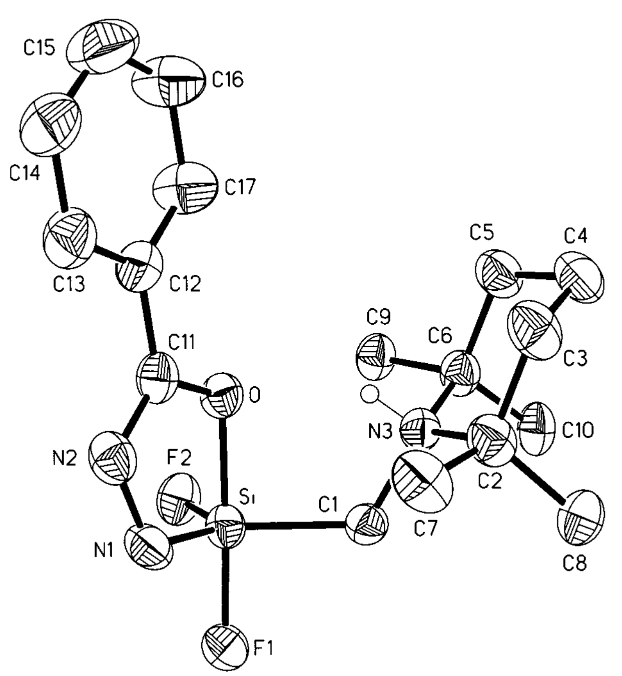

Figure 3. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. Hydrogen atoms (except for N3-*H*) are omitted for clarity. For selected geometric parameters, see Table 4.

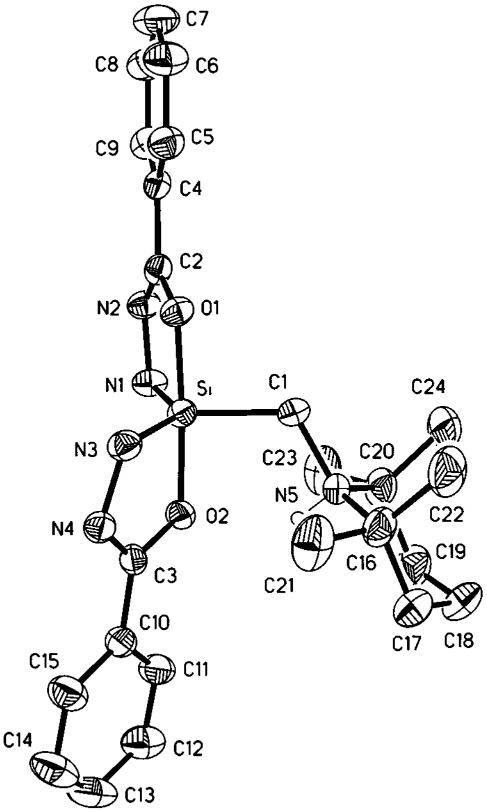

Figure 4. Molecular structure of **9-I** in the crystal of **9-I**·$CHCl_3$ (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. Hydrogen atoms (except for N5-*H*) are omitted for clarity. For selected geometric parameters, see Table 5.

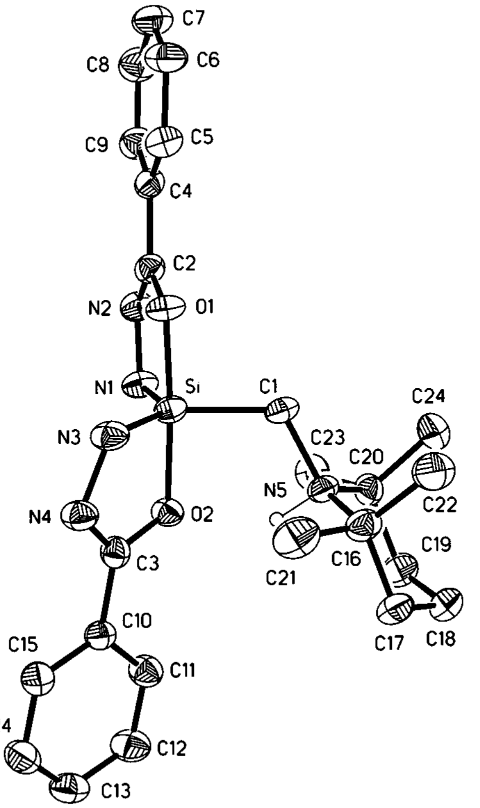

Figure 5. Molecular structure of **9-I** in the crystal of **9-I**·CH_3CN (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. Hydrogen atoms (except for N5-*H*) are omitted for clarity. For selected geometric parameters, see Table 5.

The structures of the zwitterions in the crystal lattices of the two solvates **9-I**·$CHCl_3$ and **9-I**·CH_3CN are very similar. The Si-coordination polyhedra are distorted TBPs, the axial positions being occupied by the two oxygen atoms. The sum of the equatorial bond angles is 360° in both cases. The Si−N, Si−O, and Si−C distances are very similar to those observed for other spirocyclic λ^5Si-silicates with an SiO_2N_2C skeleton.[14,39] The oxygen atom O2 and the nitrogen atom N5 of both compounds are in cis position to each other, and the N5···O2 distances suggest the existence of intramolecular N5−H···O2 hydrogen bonds [**9-I**·$CHCl_3$/**9-I**·CH_3CN: N5−H, 0.85(3)/0.98(3) Å; H···O2, 2.04(3)/1.89(3) Å; N5···O2, 2.749(2)/2.726(3) Å; N5−H···O2, 141(2)/142(3)°].[52] In addition, the presence of N1−H1···N2A and N3−H3···N4B hydrogen bonds can be assumed.[53] These particular hydrogen-bonding interactions lead to the formation of infinite chains along the [1 0 0] axis in the crystals of **9-I**·$CHCl_3$ and **9-I**·CH_3CN.

NMR Studies. The structures of **3a**−**c** in solution can be correlated with the crystal structure of **3a**: The ^{29}Si NMR spectra for **3a**−**c** (Table 6) feature chemical shifts typical of pentacoordinate silicon atoms, with doublets due to a single adjacent fluoro ligand in each case. The ^{29}Si chemical shifts of **3a**−**c** in solution are very similar to the isotropic chemical shifts in the solid state (^{29}Si VACP/MAS NMR experiments; see Experimental Section). The zwitterions **3a**−**c** are chiral (C_1 symmetry), as is evident from the nonequivalence of signal pairs in the ^1H and ^{13}C NMR spectra of the four (five in **3b**) well-resolved prochiral groups present, excluding the piperidinium-CH_2 groups: $SiCH_2N$ moiety, piperidinium group (including the C2/C6 and C3/C5 resonance pairs in the ^{13}C NMR spectra), and two diastereotopic CMe_2 groups, and an additional isopropyl moiety in **3b** (Tables 6 and 7; note that the numbering scheme for the piperidinium-carbon atoms differs from that used for the crystal structures in this paper).

The NMR spectra of **8** (solvent CD_2Cl_2) verify its structural assignment: At room temperature the ^{29}Si NMR spectrum features a triplet ($\delta = -106.6$ ppm, $^1J_{SiF} = 224.9$ Hz), corresponding to two equivalent fluoro ligands coupled to a pentacoordinate silicon atom (Table 8). The question arises whether the fluorine atoms are indeed stereochemically equivalent (both in axial or equatorial positions), or just rapidly equilibrate. At lower temperatures the triplet splits into a doublet of doublets, when the exchange of the two fluoro ligands becomes slow on the NMR time scale, and the resulting coupling constants are typical[54] of one equatorial and one axial fluoro ligand: $^1J_{SiF(eq)} = 215.7$ Hz, $^1J_{SiF(ax)} = 231.5$ Hz.

A similar picture arises from the ^1H NMR spectra (Table 8): At 297 K the four piperidinium C-methyl groups appear as two singlets (cis−trans), which, upon cooling to 220 K, split to four singlets, as stereomutation at the silicon atom is “frozen”, resulting in a chiral arrangement of the five ligand atoms. Likewise, at low temperature the signal of the initially equivalent $SiCH_2N$ protons splits to an AB system typical of a chiral environment.

This assignment is further confirmed by the ^{13}C NMR spectra, in which the $SiCH_2N$ signal is split at room temperature to a triplet, and to a doublet of doublets at lower temperature (200 K) due to coupling with the nonequivalent fluoro ligands (Table 9).

When the zwitterionic λ^5Si-tetrafluorosilicate **7** is heated for several hours in $CHCl_3$ or $PhNO_2$ solution with 2 molar equiv of **2**, monitoring by NMR spectroscopy shows that the monocyclic λ^5Si-silicate **8** is initially formed as an intermediate, followed by further conversion to the zwitterionic spirocyclic λ^5Si-silicate **9** (Scheme 4). This is evident from the ^{29}Si NMR spectrum, in which the multiplet due to coupling with the fluoro ligands has changed to a singlet, indicating that no fluorine atoms are attached to the silicon atom. This is supported by the ^1H NMR spectrum, in which two chelate ligands are present for each piperidinium ring. Product **9** is formed as a mixture of two diastereomers, **9-I** and **9-II**, which differ by the arrangement of their chelate rings (Figure 6, Tables 8 and 9): A single ^{13}C resonance signal for the two chelate-ring carbon atoms in **9-I** is evidence that these chelate rings are stereochemically equivalent and hence must have the two

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(53) Additional geometric data for the hydrogen-bonding system in the crystal of **9-I**·$CHCl_3$: N1−H1, 0.84(2) Å; H1···N2A, 2.39(2) Å; N1···N2A, 3.114(2) Å; N1−H1···N2A, 145(2)°; N3−H3, 0.85(2) Å; H3···N4B, 2.34(2) Å; N3···N4B, 3.114(2) Å; N3−H3···N4B, 152(2)°. Additional geometric data for the hydrogen-bonding system in the crystal of **9-I**·CH_3CN: N1−H1, 0.89(3) Å; H1···N2A, 2.32(3) Å; N1···N2A, 3.143(4) Å; N1−H1···N2A, 155(3)°; N3−H3, 0.72(3) Å; H3···N4B, 2.40(3) Å; N3···N4B, 3.056(4) Å; N3−H3···N4B, 153(3)°.

(54) (a) Pestunovich, V. A.; Larin, M. F.; Sorokin, M. S.; Albanov, A. I.; Voronkov, M. G. *J. Organomet. Chem.* **1985**, *280*, C17−C20. (b) Johnson, S. E.; Payne, J. S.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1989**, *28*, 3190−3198.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 1a, 3a, 8, 9-I·CHCl$_3$, and 9-I·CH$_3$CN

	1a	**3a**	**8**	**9-I**·CHCl$_3$	**9-I**·CH$_3$CN
empirical formula	$C_{11}H_{24}F_3NSi$	$C_{18}H_{30}FN_3OSi$	$C_{17}H_{27}F_2N_3OSi$	$C_{25}H_{34}Cl_3N_5O_2Si$	$C_{26}H_{36}N_6O_2Si$
formula mass, g mol^{-1}	255.40	351.54	355.51	571.01	492.70
collection T, K	173(2)	173(2)	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$C2/c$ (15)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a, Å	9.6154(19)	17.676(4)	15.443(3)	12.3879(19)	9.910(2)
b, Å	10.726(2)	8.1451(16)	8.5250(17)	8.8152(9)	11.823(2)
c, Å	13.124(3)	14.657(3)	28.833(6)	25.669(4)	11.968(2)
α, deg	90	90	90	90	83.90(3)
β, deg	108.22(3)	114.31(3)	101.56(3)	94.670(18)	87.95(3)
γ, deg	90	90	90	90	69.36(3)
V, Å^3	1285.8(4)	1923.2(7)	3718.9(13)	2793.8(7)	1304.9(5)
Z	4	4	8	4	2
D(calcd), g cm^{-3}	1.319	1.214	1.270	1.358	1.254
μ, mm^{-1}	0.195	0.141	0.154	0.403	0.125
F(000)	552	760	1520	1200	528
cryst dimens, mm	0.5 × 0.4 × 0.3	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.1	0.3 × 0.2 × 0.2	0.3 × 0.1 × 0.1
2θ range, deg	4.46−56.04	5.60−46.50	5.38−49.42	4.40−47.62	4.64−49.42
index ranges	$-12 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 17$	$-19 \le h \le 17$, $0 \le k \le 9$, $0 \le l \le 16$	$-18 \le h \le 17$, $0 \le k \le 10$, $0 \le l \le 33$	$-14 \le h \le 14$, $-9 \le k \le 9$, $-29 \le l \le 29$	$-11 \le h \le 11$, $-13 \le k \le 13$, $0 \le l \le 14$
no. of coll reflns	18 790	22 807	11 129	20 573	11 942
no. of indep reflns	3084	2742	3061	4186	4176
R_{int}	0.0490	0.0537	0.0805	0.0371	0.0577
max/min transmission		0.4389/0.1639			
no. of reflns used	3084	2742	3061	4186	4176
no. of params	218	228	322	365	416
no. of restraints	0	0	176	66	0
S^a	1.038	0.988	0.927	1.015	0.821
weight params a/b^b	0.0630/0.1972	0.0994/0.0000	0.0829/0.0000	0.0548/0.0000	0.0392/0.0000
$R1^c$ [$I > 2\sigma(I)$]	0.0330	0.0477	0.0473	0.0325	0.0420
$wR2^d$ (all data)	0.0945	0.1278	0.1234	0.0869	0.0951
max/min res electron dens, e Å^{-3}	+0.334/−0.244	+0.251/−0.337	+0.351/−0.210	0.345/−0.336	0.228/−0.245

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. 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] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 1a

Si−F1	1.6999(8)	Si−C1	1.9098(12)
Si−F2	1.7257(7)	Si−C2	1.8639(13)
Si−F3	1.6212(8)		
F1−Si−F2	173.51(4)	F2−Si−C1	89.75(5)
F1−Si−F3	89.26(5)	F2−Si−C2	93.13(5)
F1−Si−C1	86.71(5)	F3−Si−C1	123.60(5)
F1−Si−C2	93.33(5)	F3−Si−C2	118.64(6)
F2−Si−F3	88.17(5)	C1−Si−C2	117.75(6)

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 3a

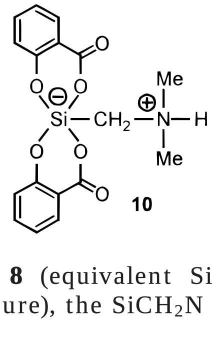
Si−F	1.6868(14)	Si−C1	1.927(2)
Si−O	1.8713(16)	Si−C2	1.869(2)
Si−N1	1.740(2)		
F−Si−O	169.83(8)	O−Si−C1	90.56(8)
F−Si−N1	90.34(9)	O−Si−C2	93.79(9)
F−Si−C1	89.24(8)	N1−Si−C1	124.68(10)
F−Si−C2	95.56(9)	N1−Si−C2	120.82(11)
O−Si−N1	81.42(8)	C1−Si−C2	114.26(11)

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for 8

Si−F1	1.6676(16)	Si−N1	1.722(2)
Si−F2	1.6106(16)	Si−C1	1.906(2)
Si−O	1.8142(19)		
F1−Si−F2	92.95(9)	F2−Si−N1	121.31(10)
F1−Si−O	174.05(8)	F2−Si−C1	110.86(11)
F1−Si−N1	91.31(11)	O−Si−N1	83.01(10)
F1−Si−C1	90.29(10)	O−Si−C1	91.76(10)
F2−Si−O	91.54(9)	N1−Si−C1	127.63(13)

oxygen atoms in the axial and the two nitrogen atoms in equatorial positions of the Si-coordination polyhedron (or vice versa; however, it is less likely that the less electronegative nitrogen atoms would occupy both axial positions). This interpretation is corroborated by the crystal structures of **9-I**·CHCl$_3$ and **9-I**·CH$_3$CN. By contrast, isomer **9-II** displays two ^{13}C resonance signals, one for each of the chelate ring carbon nuclei, in agreement with the asymmetry associated with the structure assigned to **9-II**.

Very recently, a related example of this particular type of isomerism has been observed for another zwitterionic spirocyclic λ^5Si-silicate, compound **10**: Its isomers **10-I** (both carboxylate oxygen atoms in the axial sites of the trigonal-bipyramidal Si-coordination polyhedron) and **10-II** (one carboxylate oxygen atom and one alcoholate oxygen atom in the axial positions) were structurally characterized by single-crystal X-ray diffraction.[55]



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In contrast to **8** (equivalent SiCH$_2$N protons at ambient temperature), the SiCH$_2$N protons in **9-I** and

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for 9-I·$CHCl_3$ and 9-I·CH_3CN

	9-I·$CHCl_3$	**9-I**·CH_3CN		**9-I**·$CHCl_3$	**9-I**·CH_3CN
Si−O1	1.7827(14)	1.7609(18)	Si−N3	1.7282(18)	1.728(2)
Si−O2	1.8174(14)	1.8098(18)	Si−C1	1.910(2)	1.907(3)
Si−N1	1.7308(18)	1.718(3)			
O1−Si−O2	176.52(7)	175.63(10)	O2−Si−N3	84.44(8)	84.03(10)
O1−Si−N1	85.59(8)	86.09(11)	O2−Si−C1	93.35(8)	92.76(11)
O1−Si−N3	93.62(8)	92.73(10)	N1−Si−N3	127.76(10)	126.61(13)
O1−Si−C1	90.10(8)	91.35(11)	N1−Si−C1	116.17(9)	115.49(13)
O2−Si−N1	93.31(8)	93.47(11)	N3−Si−C1	116.06(9)	117.90(14)

Table 6. ^1H and ^{29}Si NMR Data for Compounds 3a−c [$CDCl_3$ Solutions at 300 and 335 K: δ ppm, Multiplicity, (J, Hz)]

		^1H						
compd	T, K	$SiR^{a,b}$	Me_A	Me_B	$Me_{B'}$	$Me_{A'}$	$SiCH_2N^c$	^{29}Si
3a	300	0.12 d (4.2)	1.52 s	1.26 s	1.17 s	1.01 s	2.44, 2.35 (16.4, 0, 0)	−83.3 d (248.1)
3a	335	0.12 d (4.2)	1.50 br s	1.25 br s	1.17 br s	0.92 br s	2.44, 2.35 (16.4, 1.7, 0)	−83.2 d (248.1)
3b	300	0.91 d, 0.85 d 0.76 sp (7.0)	1.56 s	1.28 s	1.18 s	1.03 s	2.47, 2.27 (16.5, 2.5, 1.0)	−83.5 d (261.2)
3b	335	0.91 d, 0.85 d 0.76 sp (7.0)	1.56 br s	1.28 br s	1.18 br s	1.03 br s	2.47, 2.27 (16.5, 2.5, 1.0)	−83.3 (260.9)
3c	300	0.87 s	1.63 s	1.26 s	1.15 s	1.03 s	2.58, 2.33 (16.3, 1.3, 3.0)	−84.7 d (266.0)
3c	335	0.87 s	1.63 br s	1.26 br s	1.15 br s	1.03 br s	2.58, 2.33 (16.3, 1.3, 3.0)	−85.0 (260.3)

[a] R = Me for **3a**, *i*-Pr for **3b**, and *t*-Bu for **3c**. [b] Resonance signals of the α-protons are split by the fluoro ligand. [c] AB part of an ABX system, X = F: δ_A, δ_B (J_{AB}, J_{AX}, J_{BX}).

Table 7. ^{13}C NMR Data for Compounds 3a−c [$CDCl_3$ Solutions at 300 and 335 K: δ ppm, Multiplicity, (J, Hz)]

compd	T, K	$SiR^{a,b}$	Me_A	Me_B	$Me_{B'}$	$Me_{A'}$	$SiCH_2N^b$	C2	C6	C3	C5	C4
3a	300	4.51 d (41.5)	30.62 s	20.26 s	19.96 s	28.68 s	39.90 d (59.0)	63.20 s	63.04 s	39.41 s	39.25 s	15.74 s
3a	335	4.51 d (41.5)	30.62 br s	20.31 br s	20.04 br s	28.79 br s	40.00 d (59.0)	63.15 s		39.29 s		15.78 s
3b	300	19.00 d (28.6) 18.09 s, 18.89 s	30.35 s	20.32 s	19.99 s	28.60 s	37.80 d (59.6)	63.27 s	63.05 s	39.29 s	39.22 s	15.72 s
3b	335	19.00 d (27.7) 19.1 s, 18.1 s	30.37 br s	20.36 br s	20.05 br s	28.68 br s	38.00 d (59.5)	63.15 s		39.33 s		15.72 s
3c	300	22.25 d (25.9) 29.30 s	31.54 s	20.59 s	20.17 s	28.75 s	37.89 d (64.1)	63.79 s	63.24 s	39.50 s	39.42 s	15.83 s
3c	335	22.25 d (25.9) 29.30 s	31.41 br s	20.59 br s	20.29 br s	26.63 br s	38.24 d (63.7)	63.50 s		39.50 s		15.83 s

[a] R = Me for **3a**, *i*-Pr for **3b**, and *t*-Bu for **3c**. [b] Resonance signals of the α-carbon atoms are split by the fluoro ligand.

Table 8. ^1H and ^{29}Si NMR Data for Compound 8 (CD_2Cl_2 Solutions at 220 and 297 K) and Compound 9 (Isomers 9-I and 9-II; $CDCl_3$ Solutions at 300 K) [δ ppm, Multiplicity, (J, Hz)]

		^1H							
compd	T, K	Me_A	$Me_{A'}$	Me_B	$Me_{B'}$	$SiCH_2N^a$	N^+H	NH	^{29}Si
8	220	1.59 s	0.95 s	1.30 s	1.20 s	2.67, 2.54 (16.3, 0, 0)	6.92 br s	5.53 s	−106.6 dd (215.7, 231.5)
8	297	1.37 s^b		1.34 s^c		2.62, 2.62 $(0, 3.2, 3.2)^c$	7.03 br s	5.44 s	−106.6 t $(224.9)^d$
9-I	300	1.59 s	1.13 s	1.24 s	1.22 s	2.58, 2.51 (16.3, 3.0, 3.5)	6.49 br s	5.00 s	−95.6 s
9-II	300	1.57 s	1.09 s	1.22 s	0.96 s	2.49, 2.48 (16.3, 2.3, 0)	6.96 br s	5.30 s	−92.0 s

[a] AB part of an ABX system, X = N*H* (confirmed by a 2D-COSY spectrum): δ_A, δ_B (J_{AB}, J_{AX}, J_{BX}). [b] T_{coal} = 260 K. [c] T_{coal} = 240 K. [d] T_{coal} = 230 K.

9-II are nonequivalent due to the chiral nature of the λ^5Si-silicate skeleton and appear as the AB part of an ABX system, in which X is the vicinal NH proton. Lack of symmetry in **9-I** and **9-II** is also apparent in the nonequivalence of all four C-methyl groups (Table 8).

NMR experiments showed that the diastereomers **9-I** and **9-II** are formed in unequal populations. The molar ratio of the isomers depends on the reaction conditions: solvent and temperature. The predominant isomer is **9-I**, which is formed exclusively in CH_2Cl_2 at ambient temperature after 14 days. However, in $PhNO_2$ solution under similar conditions the ratio of the isomers was ca. 1:1. Treatment of **7** with 2 molar equiv of **2** in the same solvent at 100 °C for 5 h resulted in a ratio of 3:2. A ratio of 9:1 was obtained in boiling $CHCl_3$ after 10 h.

^1H and ^{13}C NMR studies of a solution of the diastereomerically pure isomer **9-I** (see below) in $CDCl_3$

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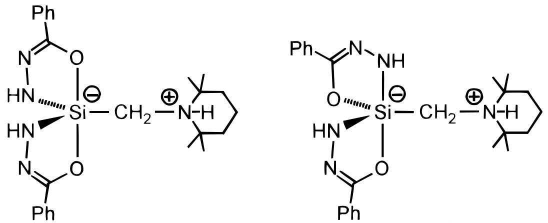
(55) Pülm, M.; Willeke, R.; Tacke, R. In *Organosilicon Chemistry IV—From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2000; pp 478−488.

Table 9. ^{13}C NMR Data for Compound 8 (CD_2Cl_2 Solutions at 215 and 300 K) and Compound 9 (Isomers 9-I and 9-II; $PhNO_2$-d_5 Solutions at 300 K) [δ ppm, Multiplicity, (J, Hz)]

compd	T, K	C=N	Me_A	$Me_{A'}$	Me_B	$Me_{B'}$	$SiCH_2N$	C2, C6		C3, C5		C4
8	215	152.33 s	30.69 s	28.61 s	19.90 s	19.48 s	35.90 dd (71.1, 26.0)[a]	64.19 s	63.90 s	39.19 s	39.06 s	15.60 s
8	300	152.42 s	29.01 s[b]		19.82 s[c]		36.66 t (49.1)[c]	64.05 s[d]		39.39 s[e]		15.72 s
9-I	300	152.98 s	30.21 s	28.51 s	19.10 s	18.89 s	38.94 s	63.59 s	63.20 s	39.13 s	39.03 s	15.38 s
9-II	300	153.30 s 153.91 s	30.29 s	28.67 s	19.13 s	18.99 s	39.00 s	63.59 s	63.04 s	39.18 s	39.13 s	15.41 s

[a] Resonance signal of the α-carbon atom is split by one axial and one equatorial fluoro ligand. [b] T_{coal} = 260 K. [c] T_{coal} = 245 K. [d] T_{coal} = 235 K. [e] T_{coal} = 230 K.



9-I **9-II**

Figure 6. Structures of the diastereomers **9-I** and **9-II** [the (Λ)-enantiomers are shown].

demonstrated its configurational stability: Over a period of 4 days no isomerization (formation of **9-II**) was observed at ambient temperature.

Stereodynamics of 3a–c: Evidence for Two Exchange Processes, "Ammonium–Nitrogen Inversion" and Inversion of Configuration at Silicon. An unusual sequence of stereomutations is observed in the NMR spectra of **3a–c**. Upon warming of $CDCl_3$ solutions of each of these compounds, line broadening (^1H and ^{13}C NMR spectra) and eventual coalescence of signals (^{13}C NMR spectra) of the diastereotopic groups in the piperidinium ring are observed (Tables 6 and 7). Thus, coalescence of the signal pairs of C2/C6 and C3/C5 (T_{coal} = 330 and 333 K, respectively, and $\Delta G^{\ddagger} = 17.0 \pm 0.3$ kcal mol^{-1}) and line broadening of the four ring C-methyl singlets are observed. However, throughout this process the $SiCH_2N$ protons and the two methyl groups of the isopropyl moiety (in **3b**) remain nonequivalent and display sharp signals in the NMR spectra. The only prochiral group that becomes equivalent on the NMR time scale at temperatures near 333 K, and no longer "senses" chirality, is the ammonium moiety.

It follows that no change in the configuration of ligands around the silicon atom takes place, and hence the λ^5Si-silicate moiety retains its chirality; it is the ammonium group that appears to lose its prochiral property, suggesting that inversion of configuration at the nitrogen atom takes place. This process is most likely due to NH proton transfer, which can be effected by any basic moiety: the fluorine, oxygen, or nitrogen ligand atoms at the adjacent silicon atom may deprotonate the ammonium group, or the solvent or traces of impurities may have the same effect. Deprotonation of the ammonium-nitrogen atom results in a transient tricoordinate piperidine-nitrogen atom that rapidly inverts and is protonated again on the opposite side, rendering the two ring parts equivalent and resulting in loss of prochirality. All other prochiral groups in the molecule remain unaffected and sense the persistent chirality of the λ^5Si-silicate skeleton.

To establish how proton abstraction is effected in compounds **3a–c**, and whether it is intra- or intermolecular, the influence of added base and acid on the exchange rate was determined. Varying amounts of dry pyridine, ranging between 0.1 and 1 molar equiv, were added to a solution of **3c** in predistilled and dried $CDCl_3$. The coalescence temperatures of various pairs of exchanging nuclei were measured and were found essentially unaffected relative to the pyridine-free solution. Likewise, the effect of added dry *p*-nitrobenzoic acid on the barrier was measured. It was found that the coalescence temperatures remained unchanged with added 0.1 molar equiv of acid. With higher acid concentrations, significant decomposition of **3c** was observed.

It may be concluded from these experiments that deprotonation of the ammonium proton occurs by an *intra*molecular process and is unaffected by relatively weak external acid or base. Thus, one of the electronegative atoms present in the vicinity of the ammonium group (O, N, or F) forms a hydrogen bond with the ammonium proton (in this context, see the crystal structure of **3a**) and eventually catalyzes its removal and enables nitrogen inversion.

A detailed analysis of the NH-deprotonation/reprotonation process (Figure 7) reveals that a true topomerization (i.e., an intramolecular ligand exchange within identical species) requires the exchange of a cis methyl group on one side of the piperidinium ring with a trans methyl moiety on the opposite side (cis/trans position relative to the CH_2SiR_4 moiety): A ⇄ B′ and B ⇄ A′. Note that no coalescence of the signals for the geminal methyl groups takes place by this process, so that each of the prochiral CMe_2 groups continues to respond to the chiral nature of the λ^5Si-silicate framework.

To verify this exchange mechanism, it was necessary to obtain information on the exchange of the C-methyl groups. This was accomplished by a 2D-ROESY spectrum of **3a** in $CDCl_3$ solution at 315 K: pairwise exchange between a cis and a trans methyl group, and between the second pair of cis–trans methyl groups, as required by the "ammonium-nitrogen inversion", is indicated by corresponding strong cross-peaks (Figure 8). This information is corroborated by a C,H correlation spectrum of **3a**, which provided identification of the cis (A, A′) and trans (B, B′) methyl groups, as indicated in Figure 8. The ROESY experiment clearly excludes a single simultaneous exchange of all four methyl groups, as well as interchange of geminal C-methyl groups, which would result from an inversion of configuration of the chiral λ^5Si-silicate skeleton.

Enantiomerization at the silicon atom, which might be observed by coalescence of the $SiCH_2N$ AB systems in the ^1H NMR spectra of **3a–c**, was not observed up

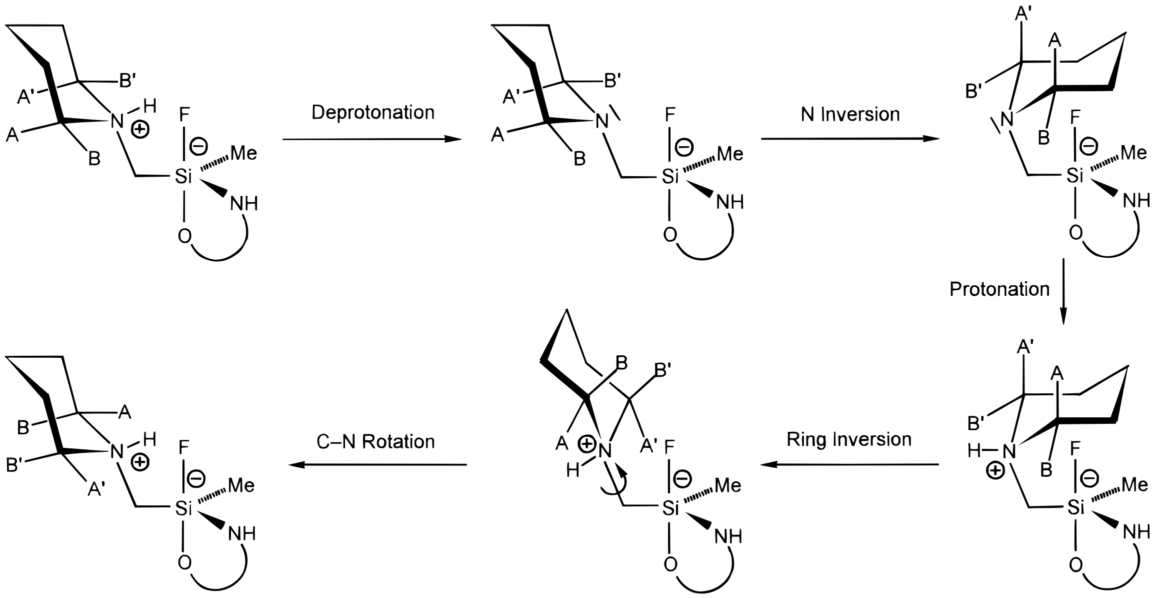


Figure 7. Schematic representation of the topomerization of **3a** via deprotonation at the ammonium-nitrogen atom followed by nitrogen inversion and reprotonation, resulting in the interchange A ⇄ B′ and B ⇄ A′.

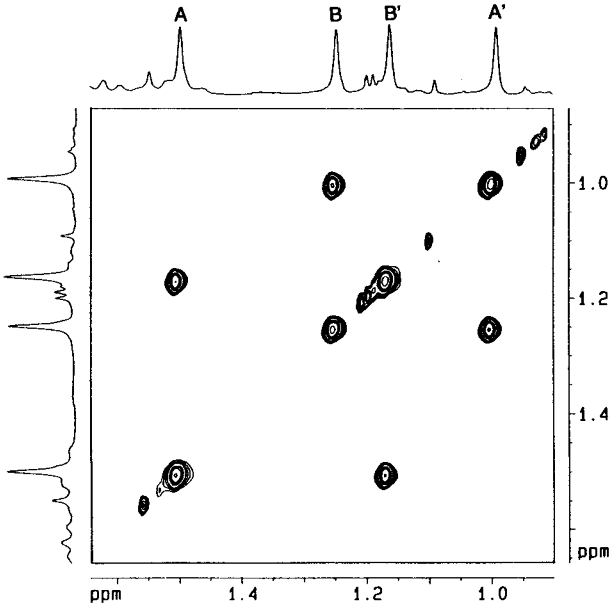


Figure 8. 500 MHz 2D-ROESY spectrum of **3a** in $CDCl_3$ solution at 315 K, C-Me region (spin-lock mixing time 200 ms). Positive cross signals represent exchange between corresponding methyl groups.

to 370 K, nor was any significant line broadening observed at this temperature (solvent $PhNO_2$-d_5). This is not surprising in view of reports that in chiral pentacoordinate silicon complexes bearing only one highly electronegative ligand the barrier for pseudorotation is either very high[46] or cannot be observed at all.[56] However, the temperature range for observation of kinetic processes by NMR spectroscopy can be significantly extended by using the selective inversion recovery (SIR) technique.[57,58] We have applied the latter for the study of exchange between the $SiCH_2N$ protons, as manifested in the spectral changes of the corresponding pair of doublets in **3c**. With this method, the presence of an exchange process between these protons is immediately evident from the line shape of the relaxation spectra: The initial decrease of intensity of signal B, which was not inverted (Figure 9), is due to magnetization transfer from the selectively inverted signal by an exchange process.

The first-order rate constant for enantiomerization at the silicon center was determined at 350 K by linear fitting of the spectral data to eq 1[57,59] (Figure 9). In this equation, I_A and I_B are the intensities of the corresponding signals in arbitrary units, and I_A^0, I_B^0, I_A^∞, and I_B^∞ are the corresponding intensities at times zero and infinity (in practice: 0.001 and 10 s, respectively). The rate constant k for the $SiCH_2N$ proton exchange was calculated from the slope of the linear correlation (correlation coefficient = 0.999) and found to equal 0.84 s^{-1}, corresponding to a free energy of activation for enantiomerization $\Delta G^\ddagger = 20.7 \pm 0.3$ kcal mol^{-1}.

$$\ln\left(1-\frac{I_A+I_B}{I_A^\infty+I_B^\infty}\right)-\ln\frac{I_B-I_A}{I_B^0-I_A^0}=2k\tau \qquad (1)$$

Stereodynamics of 8. All of the spectral changes described for **8** in the section NMR Studies, which are associated with a single topomerization, are the result of an inversion of absolute configuration of the initially chiral λ^5Si-silicate moiety. Enantiomerization at the silicon atom of **8** most likely takes place through a Berry-type pseudorotation, rendering both fluoro ligands equivalent on the NMR time scale and resulting in coalescence of all the signal pairs due to prochiral groups. Observation of coalescence spectra for several of the exchanging signal pairs (C2/C6 and C3/C5 in the ^{13}C NMR spectra; $SiCH_2N$ in the ^1H NMR spectra) provided rate constants (80 s^{-1} at 237 K and 140 s^{-1} at

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[56] Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; de Saxcé, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1–26.

[57] Blanca, B.-D. M.; Maimon, E.; Kost, D. *Angew. Chem.* **1997**, *109*, 2294–2297; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2216–2219.

[58] Orrell, K. G.; Sik, V. *Annu. Rep. NMR Spectrosc.* **1993**, *27*, 103–171.

[59] The two equations, 5 and 6, from ref 57, were substituted by eq 1 by addition.

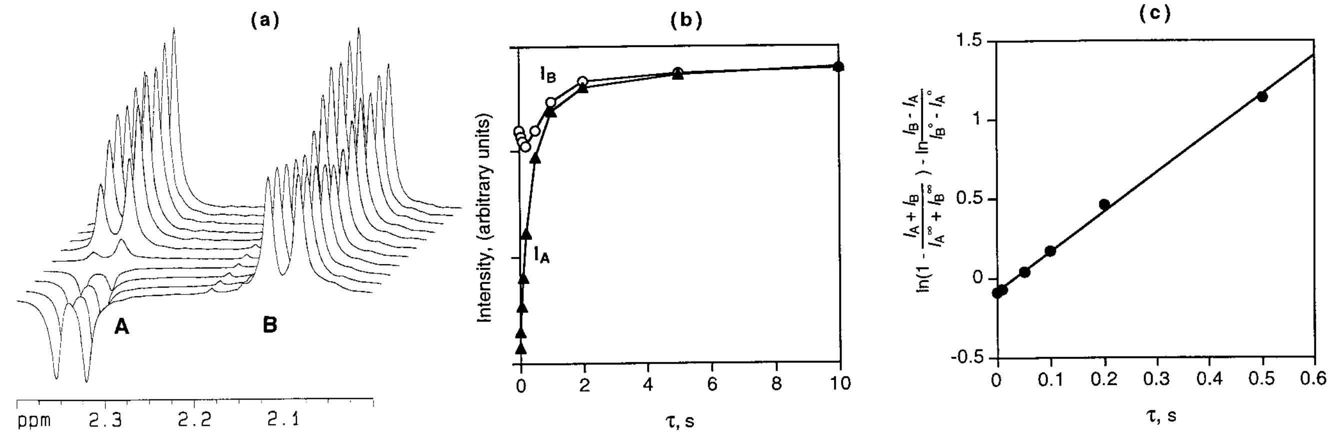

Figure 9. ^{1}H NMR selective inversion recovery experiment for the exchange of the $SiCH_2N$ protons of **3c** in $PhNO_2$-d_5 solution at 350 K. (a) Stack plot of spectra, $SiCH_2N$ region. (b) Plot of the $SiCH_2N$ signal intensities as a function of the variable delay τ (delays used: 0.001, 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10 s). (c) Linear plot of eq 1.

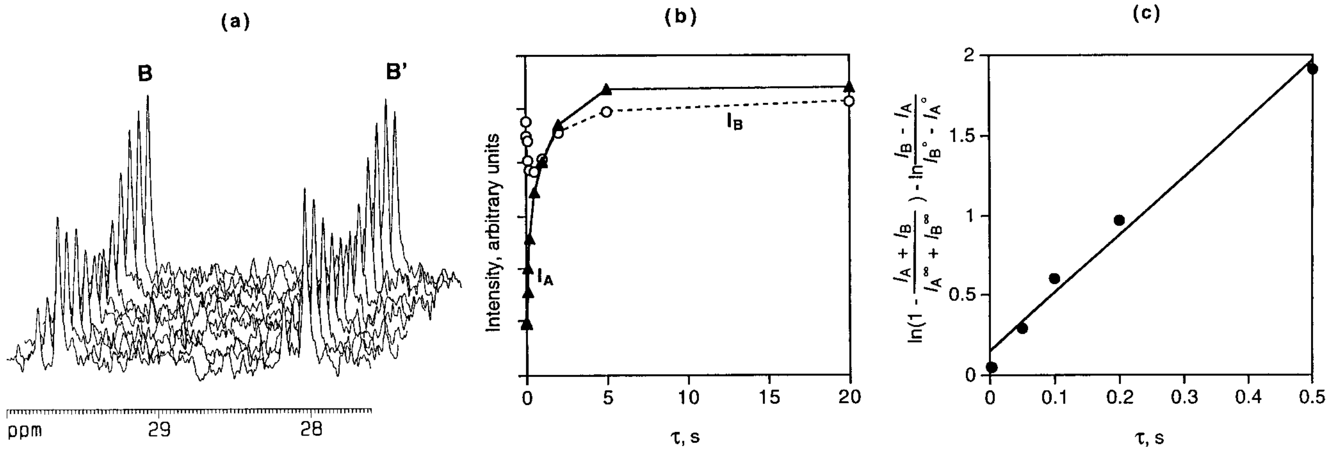

Figure 10. ^{13}C NMR selective inversion recovery experiment for the exchange of the C-methyl groups in **9-I** (the major diastereomer of **9**) in $PhNO_2$-d_5 solution at 360 K. (a) Stack plot of spectra, showing only the signals B and B′; the signals due to **9-II** can be seen to the left of each signal. (b) Plot of the C-methyl signal intensities as a function of the variable delay τ (delays used: 0.001, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 20 s). (c) Linear plot of eq 1.

240 K, respectively) and a free energy of activation for the process $\Delta G^{\ddagger} = 11.7 \pm 0.3$ kcal mol^{-1}. This relatively low barrier for stereomutation is typical of pentacoordinate silicon complexes with two fluoro ligands.[60]

It was of great interest to study whether the "ammonium-nitrogen inversion", first observed for **3a**, could also be observed for **8**. For this purpose a $PhNO_2$-d_5 solution of **8** was heated and the NMR spectra at high temperatures were studied. No significant spectral changes, which might indicate nitrogen inversion, were apparent up to 360 K. However, application of the ^{1}H SIR method facilitated the measurement of the exchange rate between the pairs of cis–trans C-methyl groups. The first-order rate constant for exchange was determined at 360 K as detailed above, resulting in $k = 1.78$ s^{-1}, corresponding to a free energy of activation $\Delta G^{\ddagger} = 20.8 \pm 0.3$ kcal mol^{-1}.

This high-temperature process renders the cis and trans C-methyl groups equivalent and must result from an inversion of the ammonium-nitrogen configuration. The only plausible mechanism for this nitrogen inversion, as suggested above, is deprotonation, which may be effected by any basic moiety present in solution, followed by nitrogen inversion and reprotonation.

Stereodynamics of 9-I and 9-II. High-temperature NMR measurements of mixtures of the diastereomers **9-I** and **9-II** in $PhNO_2$-d_5 solution did not indicate any line broadening or exchange phenomena. Application of the SIR method to the $SiCH_2N$ doublets (up to 360 K) also did not reveal any exchange between the diastereotopic protons, indicating that no enantiomerization takes place at the silicon atom under these conditions. However, in view of the "ammonium-nitrogen inversion" found for **3a**–**c** and **8**, it was of interest to measure possible exchange between the C-methyl and other diastereotopic nuclei in the piperidinium ring, even in the absence of exchange of the $SiCH_2N$ protons. This was accomplished by a ^{13}C SIR measurement of the exchange between the C-methyl groups of the major isomer **9-I** (Figure 10).[61] Partial overlap of signals of **9-I** and **9-II** prevented SIR measurement of the minor isomer **9-II**. The resulting free energy of activation for

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(60) (a) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Corey, J. Y. *J. Organomet. Chem.* **1984**, *277*, C25–C30. (b) Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C.; Belin, C. *J. Organomet. Chem.* **1994**, *470*, 43–57.

(61) The choice of ^{13}C NMR was dictated by the fact that neither a reliable DNMR, nor a SIR measurement of the ^{1}H NMR spectra of the ring-methyl signals was practical, due to low resolution and partial overlap with other ring signals.

exchange in **9-I** was $\Delta G^{\ddagger} = 20.8 \pm 0.3$ kcal mol^{-1}. The exchange between the diastereotopic groups of the piperidinium ring, while no exchange of the $SiCH_2N$ protons can be found, indicates that the "ammonium-nitrogen inversion" observed for **3a** and **8** also takes place in **9-I**, and by analogy possibly also in **9-II**.

Conclusion

(1) Three new types of zwitterionic λ^5Si-silicates, with $SiONFC_2$, $SiONF_2C$, and SiO_2N_2C frameworks (compounds **3a**−**c**, **8**, and **9-I**/**9-II**), were obtained from the reaction of (*Z*)-$Me_3SiO(Ph)C{=}NN(H)SiMe_3$ (**2**) with the zwitterionic λ^5Si-trifluorosilicates **1a**−**c** (→ **3a**−**c**) and the λ^5Si-tetrafluorosilicate **7** (→ **8**, **9-I**/**9-II**), respectively.

(2) The pentacoordinate silicon compounds undergo two types of exchange processes (only one process observed for **9-I** and **9-II**), which have been monitored and measured using ^1H, ^{13}C, and ^{29}Si variable-temperature and selective inversion recovery NMR techniques.

(3) One of the exchange processes is an inversion of absolute configuration at the silicon atom of the chiral λ^5Si-silicate skeleton, with an activation barrier ranging between 11.7 and 20.7 kcal mol^{-1}, depending on the number of fluoro ligands (no enantiomerization observed for **9-I** and **9-II**). This large barrier variation is in agreement with previously reported pseudorotation barriers in monocyclic pentacoordinate silicon complexes with one or two Si−F bonds.

(4) The pentacoordinate silicon complexes **3a**−**c**, **8**, and **9-I** undergo deprotonation at the ammonium-nitrogen atom, followed by nitrogen inversion and reprotonation, in an exchange process not previously reported, with an activation barrier ranging from 17.0 to 20.8 kcal mol^{-1}.

Experimental Section

General Procedures. Except for the reactions with hydrofluoric acid, all syntheses were carried out under dry nitrogen or argon. The solvents used were dried and purified 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 Büchi Melting Point B-540 apparatus using samples in sealed capillaries. ^1H, ^{13}C, ^{19}F, and ^{29}Si solution NMR spectra were recorded at room temperature on a Bruker DRX-300 NMR spectrometer (^1H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{19}F, 282.4 MHz; ^{29}Si, 59.6 MHz) or a Bruker DMX-500 NMR spectrometer (^1H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). Variable-temperature and SIR NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer. Chemical shifts (ppm) were determined relative to internal $CDHCl_2$ (^1H, δ 5.32; CD_2Cl_2), $CHCl_3$ (^1H, δ 7.24; $CDCl_3$), $PhNO_2$-d_4 (^1H, δ 8.11; $PhNO_2$-d_5), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), and $PhNO_2$-d_5 (^{13}C, δ 148.6; $PhNO_2$-d_5), and relative to external TMS (^{29}Si, δ 0) and $CFCl_3$ (^{19}F, δ 0). Analyses and assignment of the ^1H NMR spectra were supported by ^1H,^1H, ^{13}C,^1H, and ^{19}F,^1H correlation experiments, and some of the ^1H spin systems were analyzed by using the program WIN-DAISY.[62] Assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C,^1H correlation experiments. Solid-state ^{15}N and ^{29}Si VACP/MAS NMR spectra were recorded at room temperature on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 7 mm), containing ca. 300 mg of sample [^{29}Si, 79.5 MHz, external standard TMS (δ 0); ^{15}N, 40.6 MHz, external standard glycine (δ −342.0); spinning rate 5 kHz (^{15}N) and 5−7 kHz (^{29}Si), contact time 5 ms, 90° ^1H transmitter pulse length 3.6 μs, repetition time 4 s].

Preparation of Trifluoro(methyl)[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (1a). Hydrofluoric acid (48%, 4.39 g, 105 mmol HF) was added dropwise at −30 °C within 3 min to a stirred solution of **6a** (6.80 g, 26.2 mmol) in ethanol (100 mL) (formation of a precipitate after a few minutes). The precipitate was filtered off, and part of the solvent of the filtrate was removed under reduced pressure (again formation of a precipitate). The precipitate was isolated by filtration, and the combined solid crude products were recrystallized from acetonitrile (cooling of a saturated solution from room temperature to −20 °C) to give **1a** in 93% yield as a colorless crystalline product (6.20 g, 24.3 mmol); mp 120 °C (dec). ^1H NMR (CD_2Cl_2, 300.1 MHz, 295 K): δ 0.06 (q, $^3J_{HF} = 6.8$ Hz, 3 H, $SiCH_3$), 1.33 (s, 6 H, $NCCH_3$), 1.40 (s, 6 H, $NCCH_3$), 1.57−1.92 (m, 6 H, CCH_2C), 2.44 (d, $^3J_{HH} = 3.6$ Hz, 2 H, $SiCH_2N$), 6.6 (br t, J_{HF} = ca. 40 Hz, 1 H, NH). ^1H NMR (CD_2Cl_2, 300.1 MHz, 169 K): δ −0.01 (t, $^3J_{HF} = 9.1$ Hz, 3 H, $SiCH_3$), 1.23 (s, 6 H, $NCCH_3$), 1.28 (s, 3 H, $NCCH_3$), 1.29 (s, 3 H, $NCCH_3$), 1.46−1.84 (m, 6 H, CCH_2C), 2.40 (s, 2 H, $SiCH_2N$), 6.23 (br d, $J_{HF(ax)} = 30$ Hz, 1 H, NH). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, 295 K): δ 1.1 (q, $^2J_{CF} = 34.5$ Hz, $SiCH_3$), 16.2 (s, $NCC\mathit{C}H_2C$), 20.2 (s, $NC\mathit{C}H_3$), 30.4 (s, $NC\mathit{C}H_3$), 38.7 (q, $^2J_{CF} = 41.2$ Hz, $SiCH_2N$), 39.3 (s, $NC\mathit{C}H_2C$), 64.1 (s, $N\mathit{C}CH_3$). ^{19}F NMR (CD_2Cl_2, 295 K): δ −90 (br s). ^{19}F NMR (CD_2Cl_2, 169 K): δ −142.2 (d, $^2J_{F(eq)F(ax)} = 6.4$ Hz, $^1J_{SiF} = 221.1$ Hz, 1 F, F(eq)), −88.6 (dd, $^2J_{F(ax)F(ax)} = 33.6$ Hz, $^2J_{F(eq)F(ax)} = 6.4$ Hz, $^1J_{SiF} = 252.8$ Hz, 1 F, F(ax)), −87.9 (d, $^2J_{F(ax)F(ax)} = 33.6$ Hz, $^1J_{SiF} = 251.1$ Hz, 1 F, F(ax)). ^{29}Si NMR (CD_2Cl_2, 59.6 MHz, 295 K): δ −87.1 (q, $^1J_{SiF} = 243.5$ Hz). ^{15}N VACP/MAS NMR (17435 accumulated spectra): δ −297.8 (s). ^{29}Si VACP/MAS NMR (ν_{rot} = 5 kHz, 1291 accumulated spectra): δ −96.2 to −85.9 (m). Anal. Calcd for $C_{11}H_{24}F_3NSi$: C, 51.73; H, 9.47; N, 5.48. Found: C, 51.9; H, 9.5; N, 5.4.

Preparation of Trifluoro(isopropyl)[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (1b). Compound **1b** was prepared in analogy with the synthesis of **1a** [**6b** (4.00 g, 13.9 mmol), hydrofluoric acid (48%, 2.32 g, 55.7 mmol HF), ethanol (50 mL)] and isolated in 89% yield as a colorless crystalline solid (3.50 g, 12.3 mmol); mp 143 °C (dec). ^1H NMR (CD_2Cl_2, 300.1 MHz, 295 K): δ 0.75−0.95 (m, 1 H, $SiCHC_2$), 0.98 (d, $^3J_{HH} = 6.2$ Hz, 6 H, $SiCCH_3$), 1.34 (s, 6 H, $NCCH_3$), 1.41 (s, 6 H, $NCCH_3$), 1.57−1.92 (m, 6 H, CCH_2C), 2.43 (d, $^3J_{HH} = 3.6$ Hz, 2 H, $SiCH_2N$), 6.6 (br t, J_{HF} = ca. 38 Hz, 1 H, NH). ^1H NMR (CD_2Cl_2, 300.1 MHz, 178 K): δ 0.68−0.85 (m, 1 H, $SiCHC_2$), 0.87 (d, $^3J_{HH} = 5.7$ Hz, 3 H, $SiCCH_3$), 0.92 (d, $^3J_{HH} = 6.2$ Hz, 3 H, $SiCCH_3$), 1.25 (s, 6 H, $NCCH_3$), 1.30 (s, 3 H, $NCCH_3$), 1.31 (s, 3 H, $NCCH_3$), 1.47−1.85 (m, 6 H, CCH_2C), 2.35 and 2.41 (AB system, $^2J_{AB} = 18.6$ Hz, 2 H, $SiCH_2N$), 6.26 (br d, $J_{HF(ax)} = 30$ Hz, 1 H, NH). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, 295 K): δ 16.2 (s, $NCC\mathit{C}H_2C$), 18.1 (br s, $Si\mathit{C}HC_2$), 19.3 (s, $CH\mathit{C}H_3$), 20.3 (s, $NC\mathit{C}H_3$), 30.5 (s, $NC\mathit{C}H_3$), 38.1 (br s, $SiCH_2N$), 39.4 (s, $NC\mathit{C}H_2C$), 64.2 (s, $N\mathit{C}CH_3$). ^{19}F NMR (CD_2Cl_2, 295 K): δ −104 (br s). ^{19}F NMR (CD_2Cl_2, 178 K): δ −147.2 (d, $^2J_{F(eq)F(ax)} = 7.1$ Hz, $^1J_{SiF} = 229.5$ Hz, 1 F, F(eq)), −106.1 (dd, $^2J_{F(ax)F(ax)} = 35.6$ Hz, $^2J_{F(eq)F(ax)} = 7.1$ Hz, $^1J_{SiF} = 269.0$ Hz, 1 F, F(ax)), −99.4 (d, $^2J_{F(ax)F(ax)} = 35.6$ Hz, $^1J_{SiF} = 267.7$ Hz, 1 F, F(ax)). ^{29}Si NMR ($CDCl_3$, 59.6 MHz, 295 K): δ −90.7 (q, $^1J_{SiF} = 258.3$ Hz). ^{15}N VACP/MAS NMR (41150 accumulated spectra): δ −296.5 (s). ^{29}Si VACP/MAS NMR (ν_{rot} = 6 kHz, 15239 accumulated spectra): δ −97.1 to −87.6 (m). Anal. Calcd for $C_{13}H_{28}F_3NSi$: C, 55.09; H, 9.96; N, 4.94. Found: C, 55.1; H, 10.0; N, 5.0.

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[62] 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.

Preparation of *tert*-Butyltrifluoro[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (1c). Synthesis according to ref 36.

Preparation of (*Z*)-*N*-(Trimethylsilyl)benzohydrazonic Acid Trimethylsilyl Ester (2). Hexamethyldisilazane (23.7 g, 147 mmol) followed by chlorotrimethylsilane (15.9 g, 146 mmol) were added at room temperature to a stirred suspension of benzhydrazide (20.0 g, 147 mmol) in *n*-pentane (500 mL), and the resulting mixture was stirred for 3 days at room temperature. The precipitate was filtered off, the solvent of the filtrate removed under reduced pressure, and the residue distilled in vacuo to give compound **2** in 95% yield as a colorless liquid (39.1 g, 139 mmol); bp 65 °C/0.05 Torr. ^{1}H NMR (CDCl$_3$, 300.1 MHz, 295 K): δ 0.07 (s, 9 H, SiCH$_3$), 0.10 (s, 9 H, SiCH$_3$), 5.27 (br s, 1 H, NH), 6.96−7.64 (m, 5 H, C$_6$H$_5$). The (*Z*)-configuration of **2** was established by a crystal structure analysis and a 2D-NOESY NMR experiment, which showed proximity of the N*H* proton to *both* TMS groups. ^{13}C NMR (CDCl$_3$, 75.5 MHz, 295 K): δ −0.7 (s, SiCH$_3$), 0.7 (s, SiCH$_3$), 125.4 (s, C3/C5, C$_6$H$_5$), 127.8 (s, C4, C$_6$H$_5$), 127.9 (s, C2/C6, C$_6$H$_5$), 135.1 (s, C1, C$_6$H$_5$), 142.6 (s, C=N). ^{29}Si NMR (CDCl$_3$, 59.6 MHz, 295 K): δ 6.8 (s, Me$_3$SiN), 22.0 (s, Me$_3$SiO). Anal. Calcd for C$_{13}$H$_{24}$N$_2$OSi$_2$: C, 55.66; H, 8.62; N, 9.99. Found: C, 55.7; H, 8.3; N, 10.2.

Preparation of [Benzohydrazonato(2−)]fluoro(methyl)-[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (3a). Compound **2** (549 mg, 1.96 mmol) was added at room temperature to a stirred solution of **1a** (500 mg, 1.96 mmol) in acetonitrile (20 mL), and the resulting mixture was stirred for 3 days at room temperature. The solvent was removed under reduced pressure and the solid crude product recrystallized from acetonitrile (cooling of a saturated solution from room temperature to −20 °C) to give **3a** in 70% yield as a colorless crystalline product (480 mg, 1.37 mmol); mp 106 °C (dec). ^{1}H NMR (CDCl$_3$, 500.1 MHz, 300 K): δ 0.12 (d, $^3J_{\rm HF}$ = 4.2 Hz, 3 H, SiCH$_3$), 1.01 (s, 3 H, NCCH$_3$), 1.17 (s, 3 H, NCCH$_3$), 1.26 (s, 3 H, NCCH$_3$), 1.52 (s, 3 H, NCCH$_3$), 1.07−1.81 (m, 6 H, CCH$_2$C), 2.35 and 2.44 (AB system, $^2J_{\rm AB}$ = 16.4 Hz, 2 H, SiCH$_2$N), 4.75 (s, 1 H, NH), 7.40 (s, 1 H, N$^+$H), 7.14−7.67 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 125.8 MHz, 300 K): δ 4.51 (d, $^2J_{\rm CF}$ = 41.5 Hz, SiCH$_3$), 15.74 (s, NCCC*H*$_2$C), 19.96 (s, NCCH$_3$), 20.26 (s, NC*C*H$_3$), 28.68 (s, NC*C*H$_3$), 30.62 (s, NC*C*H$_3$), 39.25 (s, NC*C*H$_2$C), 39.41 (s, NC*C*H$_2$C), 39.90 (d, $^2J_{\rm CF}$ = 59.0 Hz, SiCH$_2$N), 63.04 (s, N*C*C$_3$), 63.20 (s, N*C*C$_3$), 123.86 (s, C3/C5, C$_6$H$_5$), 127.34 (s, C2/C6, C$_6$H$_5$), 128.15 (s, C4, C$_6$H$_5$), 133.02 (s, C1, C$_6$H$_5$), 153.35 (s, C=N). ^{19}F NMR (CDCl$_3$, 295 K): δ −100.5 (s, $^1J_{\rm SiF}$ = 246.3 Hz). ^{29}Si NMR (CDCl$_3$, 99.4 MHz, 300 K): δ −83.3 (d, $^1J_{\rm SiF}$ = 248.1 Hz). ^{29}Si VACP/MAS NMR ($\nu_{\rm rot}$ = 7 kHz, 1885 accumulated spectra): δ −82.4 (d, $^1J_{\rm SiF}$ = 201.2 Hz). ^{15}N VACP/MAS NMR (20456 accumulated spectra): δ −115.0 (s, C=N), −266.1 (s, SiN), −293.6 (s, N$^+$). Anal. Calcd for C$_{18}$H$_{30}$FN$_3$OSi: C, 61.50; H, 8.60; N, 11.95. Found: C, 60.9; H, 8.9; N, 11.7.

Preparation of [Benzohydrazonato(2−)]fluoro(isopropyl[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (3b). This compound was prepared on an analytical scale in an NMR tube as follows: Compound **1b** (25.7 mg, 90.7 μmol) was added to a solution of **2** (25.4 mg, 90.5 μmol) in dry CDCl$_3$ (0.5 mL) in an NMR tube (diameter 5 mm). The tube was placed for 40 min in an oil bath at 65 °C, followed by cooling and evaporation of solvent and volatile products under reduced pressure. Dry CDCl$_3$ was added to the residue, and the sample was degassed and sealed in vacuo. ^{1}H NMR (CDCl$_3$, 500.1 MHz, 300 K): δ 0.76 (sp, $^3J_{\rm HH}$ = 7.0 Hz, 1 H, SiCHC$_2$), 0.85 (d, $^3J_{\rm HH}$ = 7.0 Hz, 3 H, SiCCH$_3$), 0.91 (d, $^3J_{\rm HH}$ = 7.0 Hz, 3 H, SiCCH$_3$), 1.03 (s, 3 H, NCCH$_3$), 1.18 (s, 3 H, NCCH$_3$), 1.28 (s, 3 H, NCCH$_3$), 1.56 (s, 3 H, NCCH$_3$), 1.07−1.81 (m, 6 H, CCH$_2$C), 2.27 and 2.47 (AB part of an ABX system with F as the X nucleus, $^2J_{\rm AB}$ = 16.4 Hz, $^3J_{\rm AX}$ = 2.5 Hz, $^3J_{\rm BX}$ = 1.0 Hz, 2 H, SiCH$_2$N), 4.72 (s, 1 H, NH), 7.35 (s, 1 H, N$^+$H), 7.14−7.67 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 125.8 MHz, 300 K): δ 15.72 (s, NCC*C*H$_2$C), 18.09 (s, SiC*C*H$_3$), 18.89 (s, SiC*C*H$_3$), 19.00 (d, $^2J_{\rm CF}$ = 28.6 Hz, Si*C*HC$_2$), 19.99 (s, NC*C*H$_3$), 20.32 (s, NC*C*H$_3$), 28.60 (s, NC*C*H$_3$), 30.35 (s, NC*C*H$_3$), 37.80 (d, $^2J_{\rm CF}$ = 59.6 Hz, SiCH$_2$N), 39.22 (s, NC*C*H$_2$C), 39.29 (s, NC*C*H$_2$C), 63.05 (s, N*C*C$_3$), 63.27 (s, N*C*C$_3$), 123.82 (s, C3/C5, C$_6$H$_5$), 127.25 (s, C2/C6, C$_6$H$_5$), 128.04 (s, C4, C$_6$H$_5$), 133.02 (s, C1, C$_6$H$_5$), 153.56 (s, C=N). ^{29}Si (CDCl$_3$, 99.4 MHz, 300 K): δ −83.5 (d, $^1J_{\rm SiF}$ = 261.2 Hz).

Preparation of [Benzohydrazonato(2−)]*tert*-butylfluoro[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (3c). Compound **2** (472 mg, 1.68 mmol) was added at room temperature to a stirred solution of **1c** (500 mg, 1.68 mmol) in acetonitrile (20 mL), and the resulting mixture was stirred for 3 days at room temperature. The solvent was removed under reduced pressure and the solid crude product recrystallized from acetonitrile (cooling of a saturated solution from room temperature to −30 °C) to give **3c** in 54% yield as a colorless crystalline product (357 mg, 907 μmol); mp 124 °C (dec). ^{1}H NMR (CDCl$_3$, 500.1 MHz, 300 K): δ 0.87 (s, 9 H, SiCCH$_3$), 1.03 (s, 3 H, NCCH$_3$), 1.15 (s, 3 H, NCCH$_3$), 1.26 (s, 3 H, NCCH$_3$), 1.63 (s, 3 H, NCCH$_3$), 1.07−1.80 (m, 6 H, CCH$_2$C), 2.33 and 2.58 (AB part of an ABX system with F as the X nucleus, $^2J_{\rm AB}$ = 16.3 Hz, $^3J_{\rm AX}$ = 1.3 Hz, $^3J_{\rm BX}$ = 3.0 Hz, 2 H, SiCH$_2$N), 4.90 (s, 1 H, NH), 7.20 (s, 1 H, N$^+$H), 7.14−7.67 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 125.8 MHz, 300 K): δ 15.83 (s, NCC*C*H$_2$C), 20.17 (s, NC*C*H$_3$), 20.59 (s, NC*C*H$_3$), 22.25 (d, $^2J_{\rm CF}$ = 25.9 Hz, Si*C*C$_3$) 28.75 (s, NC*C*H$_3$), 29.30 (s, SiC*C*H$_3$), 31.54 (s, NC*C*H$_3$), 37.89 (d, $^2J_{\rm CF}$ = 64.1 Hz, SiCH$_2$N), 39.42 (s, NC*C*H$_2$C), 39.50 (s, NC*C*H$_2$C), 63.24 (s, N*C*C$_3$), 63.79 (s, N*C*C$_3$), 123.88 (s, C3/C5, C$_6$H$_5$), 127.25 (s, C2/C6, C$_6$H$_5$), 128.14 (s, C4, C$_6$H$_5$), 133.02 (s, C1, C$_6$H$_5$), 153.56 (s, C=N). ^{19}F NMR (CDCl$_3$, 295 K): δ −113.0 (s, $^1J_{\rm SiF}$ = 263.5 Hz). ^{29}Si (CDCl$_3$, 99.4 MHz, 300 K): δ −84.7 (d, $^1J_{\rm SiF}$ = 266.0 Hz). ^{29}Si VACP/MAS NMR ($\nu_{\rm rot}$ = 5 kHz, 836 accumulated spectra): δ −84.9 (d, $^1J_{\rm SiF}$ = 271.3 Hz). ^{15}N VACP/MAS NMR (15491 accumulated spectra): δ −110.6 (s, C=N), −268.1 (s, SiN), −293.8 (s, N$^+$). Anal. Calcd for C$_{21}$H$_{36}$FN$_3$OSi: C, 64.08; H, 9.22; N, 10.68. Found: C, 63.9; H, 9.5; N, 10.5.

Preparation of Dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane (6a). A mixture of **4** (18.3 g, 118 mmol) and 2,2,6,6-tetramethylpiperidine (50.0 g, 354 mmol) was stirred under reflux for 8 h. Then *n*-pentane (50 mL) was added at room temperature and the mixture stirred for an additional 3 h. The precipitate was filtered off, the solvent of the filtrate removed under reduced pressure, and the residue distilled in vacuo to give compound **6a** in 60% yield as a colorless liquid (18.3 g, 70.5 mmol); bp 77 °C/0.04 Torr. ^{1}H NMR (CDCl$_3$, 300.1 MHz, 295 K): δ 0.17 (s, 3 H, SiCH$_3$), 0.94 (s, 12 H, NCCH$_3$), 1.36−1.47 (m, 6 H, CCH$_2$C), 1.88 (s, 2 H, SiCH$_2$N), 3.49 (s, 6 H, OCH$_3$). ^{13}C NMR (CDCl$_3$, 75.5 MHz, 295 K): δ −6.1 (s, SiCH$_3$), 17.8 (s, NCC*C*H$_2$C), 26.5 (s, NC*C*H$_3$), 30.8 (s, SiCH$_2$N), 41.3 (s, NC*C*H$_2$C), 50.3 (s, OCH$_3$), 54.7 (s, N*C*C$_3$). ^{29}Si NMR (CDCl$_3$, 59.6 MHz, 295 K): δ −2.5 (s). Anal. Calcd for C$_{13}$H$_{29}$NO$_2$Si: C, 60.18; H, 11.27; N, 5.40. Found: C, 60.0; H, 11.2; N, 5.5.

Preparation of Isopropyldimethoxy[(2,2,6,6-tetramethylpiperidino)methyl]silane (6b). A solution of isopropylmagnesium chloride (55.5 mmol) in diethyl ether (20 mL) was added dropwise at 0 °C within 30 min to a stirred solution of **5** (15.3 g, 55.5 mmol) in *n*-pentane (100 mL), and the resulting mixture was stirred for 24 h at room temperature. The precipitate was filtered off and washed with *n*-pentane (20 mL). Filtrate and washings were combined, the solvent removed under reduced pressure, and the residue distilled in vacuo to give compound **6b** in 85% yield as a colorless liquid (13.5 g, 47.0 mmol); bp 84 °C/0.4 Torr. ^{1}H NMR (CDCl$_3$, 300.1 MHz, 295 K): δ 0.95−1.12 (m, 7 H, SiCH(CH$_3$)$_2$), 0.98 (s, 12 H, NCCH$_3$), 1.36−1.53 (m, 6 H, CCH$_2$C), 2.00 (s, 2 H, SiCH$_2$N), 3.61 (s, 6 H, OCH$_3$). ^{13}C NMR (CDCl$_3$, 75.5 MHz, 295 K): δ 12.9 (s, Si*C*HC$_2$), 17.4 (s, SiC*C*H$_3$), 17.9 (s, NCC*C*H$_2$C), 26.5 (s, NC*C*H$_3$), 29.6 (s, SiCH$_2$N), 41.3 (s, NC*C*H$_2$C), 51.1 (s, OCH$_3$), 54.9 (s, N*C*CH$_3$). ^{29}Si NMR (CDCl$_3$, 59.6 MHz, 295 K): δ −12.3

(s). Anal. Calcd for $C_{15}H_{33}NO_2Si$: C, 62.66; H, 11.57; N, 4.87. Found: C, 62.6; H, 11.6; N, 4.5.

Preparation of Tetrafluoro[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (7). Synthesis according to ref 36.

Preparation of [Benzohydrazonato(2−)]difluoro[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (8). Compound **2** (541 mg, 1.93 mmol) was added at room temperature to a stirred solution of **7** (500 mg, 1.93 mmol) in acetonitrile (25 mL), and the resulting mixture was stirred under reflux for 24 h. The solvent was removed under reduced pressure and the solid crude product recrystallized from acetonitrile (cooling of a saturated solution from room temperature to −30 °C) to give **8** in 58% yield as a colorless crystalline product (398 mg, 1.12 mmol); mp 153 °C (dec). ^{1}H NMR (CD_2Cl_2, 500.1 MHz, 297 K): δ 1.34 (s, 6 H, NCCH$_3$), 1.37 (s, 6 H, NCCH$_3$), 1.03−1.84 (m, 6 H, CCH$_2$C), 2.62 (d, $^3J_{H,(N)H}$ = 3.2 Hz, 2 H, SiCH$_2$N), 5.44 (s, 1 H, NH), 7.03 (br s, 1 H, N$^+$H), 7.30−7.79 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CD_2Cl_2, 125.8 MHz, 300 K): δ 15.72 (s, NCC*C*H$_2$C), 19.82 (s, NC*C*H$_3$), 29.01 (s, NC*C*H$_3$), 36.66 (t, $^2J_{CF}$ = 49.1 Hz, SiCH$_2$N), 39.39 (s, NC*C*H$_2$C), 64.05 (s, N*C*C$_3$), 123.88 (s, C3/C5, C$_6$H$_5$), 127.25 (s, C2/C6, C$_6$H$_5$), 128.14 (s, C4, C$_6$H$_5$), 133.02 (s, C1, C$_6$H$_5$), 153.17 (s, C═N). ^{19}F NMR (CDCl$_3$, 295 K): δ −115.0 (br s). ^{29}Si NMR (CD_2Cl_2, 99.4 MHz, 300 K): δ −106.6 (t, $^1J_{SiF}$ = 224.9 Hz). ^{29}Si VACP/MAS NMR (ν_{rot} = 7 kHz, 852 accumulated spectra): δ −99.0 to −112.3 (m). ^{15}N VACP/MAS NMR (15982 accumulated spectra): δ −118.8 (s, C═N), −256.4 (s, SiN), −291.7 (s, N$^+$). Anal. Calcd for $C_{17}H_{27}F_2N_3OSi$: C, 57.44; H, 7.66; N, 11.82. Found: C, 57.8; H, 7.8; N, 11.9.

Preparation of Bis[benzohydrazonato(2−)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate, Mixture of Diastereomers 9-I and 9-II. Compound **2** (1.08 g, 3.85 mmol) was added at room temperature to a stirred solution of **7** (500 mg, 1.93 mmol) in trichloromethane (20 mL), and the resulting mixture was stirred under reflux for 24 h. The solvent was removed under reduced pressure and the solid crude product recrystallized from a trichloromethane/*n*-hexane (1:1) mixture (cooling of a saturated solution from room temperature to −20 °C) to give 500 mg (1.11 mmol, yield 57%) of a solid product consisting of **9-I** and **9-II**.[51]

NMR Data of Isomer 9-I. ^{1}H NMR (CDCl$_3$, 500.1 MHz, 300 K): δ 1.13 (s, 3 H, NCCH$_3$), 1.22 (s, 3 H, NCCH$_3$), 1.24 (s, 3 H, NCCH$_3$), 1.59 (s, 3 H, NCCH$_3$), 0.97−1.84 (m, 6 H, CCH$_2$C), 2.51 and 2.58 (AB part of an ABX system with N*H* as the X nucleus, $^2J_{AB}$ = 16.3 Hz, $^3J_{AX}$ = 3.0 Hz, $^3J_{BX}$ = 3.5 Hz, 2 H, SiCH$_2$N), 5.00 (s, 2 H, NH), 6.49 (br s, 1 H, N$^+$H), 7.21−7.76 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 125.8 MHz, 300 K): δ 15.64 (s, NCC*C*H$_2$C), 19.81 (s, NC*C*H$_3$), 20.02 (s, NC*C*H$_3$), 29.07 (s, NC*C*H$_3$), 30.87 (s, NC*C*H$_3$), 39.12 (s, SiCH$_2$N), 39.40 (s, NC*C*H$_2$C), 39.62 (s, NC*C*H$_2$C), 63.45 (s, N*C*C$_3$), 63.81 (s, N*C*C$_3$), 124.16 (s, C3/C5, C$_6$H$_5$), 127.50 (s, C4, C$_6$H$_5$), 127.93 (s, C2/C6, C$_6$H$_5$), 132.63 (s, C1, C$_6$H$_5$), 153.55 (s, C═N). ^{29}Si NMR (CDCl$_3$, 99.4 MHz, 300 K): δ −95.6 (s).

NMR Data of Isomer 9-II. ^{1}H NMR (CDCl$_3$, 500.1 MHz, 300 K): δ 0.96 (s, 3 H, NCCH$_3$), 1.09 (s, 3 H, NCCH$_3$), 1.22 (s, 3 H, NCCH$_3$), 1.57 (s, 3 H, NCCH$_3$), 0.97−1.84 (m, 6 H, CCH$_2$C), 2.48 and 2.49 (AB part of an ABX system with N*H* as the X nucleus, $^2J_{AB}$ = 16.3 Hz, $^3J_{AX}$ = 2.3 Hz, $^3J_{BX}$ = 0 Hz, 2 H, SiCH$_2$N), 5.30 (s, 2 H, NH), 6.96 (br s, 1 H, N$^+$H), 7.21−7.76 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 125.8 MHz, 300 K): δ 15.67 (s, NCC*C*H$_2$C), 19.92 (s, NC*C*H$_3$), 20.06 (s, NC*C*H$_3$), 29.13 (s, NC*C*H$_3$), 30.97 (s, NC*C*H$_3$), 39.12 (s, SiCH$_2$N), 39.40 (s, NC*C*H$_2$C), 39.62 (s, NC*C*H$_2$C), 63.11 (s, N*C*C$_3$), 63.69 (s, N*C*C$_3$), 124.28 (s, C3/C5, C$_6$H$_5$), 124.40 (s, C3/C5, C$_6$H$_5$), 127.21 (s, C4, C$_6$H$_5$), 127.93 (s, C2/C6, C$_6$H$_5$), 132.65 (s, C1, C$_6$H$_5$), 132.70 (s, C1, C$_6$H$_5$), 153.94 (s, C═N), 154.11 (s, C═N). ^{29}Si NMR (CDCl$_3$, 99.4 MHz, 300 K): δ −92.0 (s).

Preparation of Bis[benzohydrazonato(2−)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate−Acetonitrile (9-I·CH$_3$CN). Compound **2** (1.08 g, 3.85 mmol) was added at room temperature to a stirred solution of **7** (500 mg, 1.93 mmol) in acetonitrile (20 mL), and the resulting mixture was stirred under reflux for 24 h. The solvent was removed under reduced pressure and the solid crude product recrystallized from acetonitrile (cooling of a saturated solution from room temperature to −30 °C) to give **9-I**·CH$_3$CN in 43% yield as a colorless crystalline product (406 mg, 824 μmol); mp 192−193 °C (dec). ^{1}H NMR (CDCl$_3$, 300.1 MHz, 295 K): δ 1.12 (s, 3 H, NCCH$_3$), 1.22 (s, 3 H, NCCH$_3$), 1.26 (s, 3 H, NCCH$_3$), 1.58 (s, 3 H, NCCH$_3$), 0.95−1.83 (m, 6 H, CCH$_2$C), 1.96 (s, 3 H, CH$_3$CN), 2.56 and 2.62 (AB part of an ABX system with N*H* as the X nucleus, $^2J_{AB}$ = 16.4 Hz, $^3J_{AX}$ = 3.8 Hz, $^3J_{BX}$ = 3.2 Hz, 2 H, SiCH$_2$N), 4.92 (s, 2 H, NH), 6.33 (s, 1 H, N$^+$H), 7.23−7.73 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 75.5 MHz, 295 K): δ 1.8 (s, *C*H$_3$CN) 15.9 (s, NCC*C*H$_2$C), 20.0 (s, NC*C*H$_3$), 20.3 (s, NC*C*H$_3$), 29.1 (s, NC*C*H$_3$), 30.9 (s, NC*C*H$_3$), 39.2 (s, SiCH$_2$N), 39.7 (s, NC*C*H$_2$C), 39.8 (s, NC*C*H$_2$C), 63.7 (s, N*C*C$_3$), 64.1 (s, N*C*C$_3$), 116.8 (s, (CH$_3$*C*N), 124.4 (s, C3/C5, C$_6$H$_5$), 127.6 (s, C2/C6, C$_6$H$_5$), 128.2 (s, C4, C$_6$H$_5$), 133.1 (s, C1, C$_6$H$_5$), 153.4 (s, C═N). ^{29}Si NMR (CDCl$_3$, 59.6 MHz, 295 K): δ −95.2 (s). ^{29}Si VACP/MAS NMR (ν_{rot} = 7 kHz, 689 accumulated spectra): δ −94.4. ^{15}N VACP/MAS NMR (12664 accumulated spectra): δ −114.5 (s, C═N), −117.8 (s, C═N), −128.8 (CH$_3$CN), −261.7 (s, SiN), −265.2 (s, SiN), −290.9 (s, N$^+$). Anal. Calcd for $C_{26}H_{36}N_6O_2Si$: C, 63.38; H, 7.36; N, 17.06. Found: C, 62.9; H, 7.3; N, 16.9.

Crystal Structure Analyses of 1a, 3a, 8, 9-I·CHCl$_3$, and 9-I·CH$_3$CN. Suitable single crystals of **1a**, **3a**, **8**, and **9-I**·CH$_3$CN were obtained by cooling saturated solutions of these compounds in acetonitrile from room temperature to −20 °C. A suitable single crystal of **9-I**·CHCl$_3$ was obtained by cooling a saturated solution of **9-I**/**9-II** (see synthesis) in trichloromethane/*n*-hexane (2:3) from room temperature to 0 °C. The crystals were mounted in inert oil on a glass fiber and then transferred to the cold gas stream of the diffractometer [Stoe IPDS diffractometer; graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)]. For **3a** a semiempirical absorption correction was applied. All structures were solved by direct methods.[63] All non-hydrogen atoms were refined anisotropically.[64] The positions of all hydrogen atoms of **1a**, **8**, and **9-I**·CH$_3$CN were localized in difference Fourier syntheses and refined freely. A riding model was employed in the refinement of the CH hydrogen atoms of **3a** and **9-I**·CHCl$_3$. The phenyl ring in **8** showed a rotation disorder, which was refined to an occupancy of 0.66:0.34. The trichloromethane molecule in **9-I**·CHCl$_3$ showed a disorder over two positions, which were refined to an occupancy of 0.7:0.3. The positions of the NH hydrogen atoms of **3a** and **9-I**·CHCl$_3$ were localized in difference Fourier syntheses and refined freely.

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Supporting Information Available: Tables of anisotropic thermal parameters, atomic coordinates, and additional interatomic distances and angles for **1a**, **3a**, **8**, **9-I**·CHCl$_3$, and **9-I**·CH$_3$CN, and figures showing the hydrogen-bonding systems in the crystals of **1a** and **9-I**·CHCl$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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