New Chiral Zwitterionic λ^5*Si*-Silicates with an SiO_5 or SiO_4C Framework: Syntheses, Crystal Structures, and Properties

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

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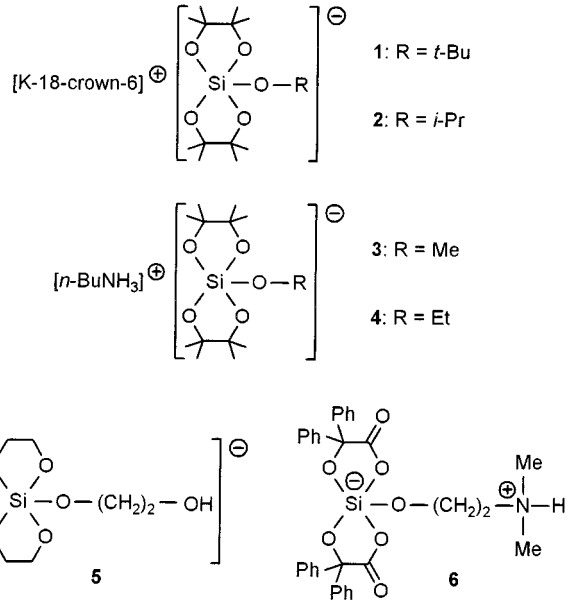
The syntheses of the zwitterionic (molecular) spirocyclic λ^5*Si*-silicates **7** and **8** (SiO_5 skeletons) and **10**–**12** (SiO_4C skeletons) are described. These chiral compounds contain a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom. The pairs **7**/**11** and **8**/**12** are isoelectronic O/CH_2 analogues and **10**–**12** represent a series of homologous compounds containing different alkylene spacers that connect the *ate* and *onium* center of these zwitterions. Compound **7**, **8**, and **10**–**12** were studied by single-crystal X-ray diffraction, solution-state (^{1}H, ^{13}C, ^{29}Si) and solid-state (^{29}Si CP/MAS) NMR spectroscopy, and VT ^{1}H-NMR spectroscopy. The experimental investigations were completed by ab initio studies of the related anionic λ^5*Si*-silicate **13**.

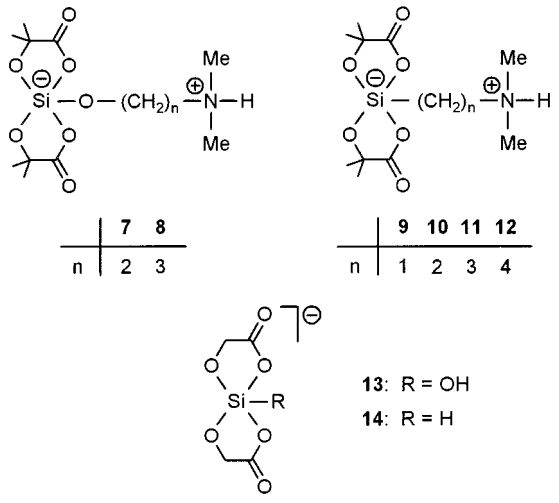
Introduction

Numerous pentacoordinate silicon compounds have been described in the literature over the past thirty years.[1] Surprisingly, only a few examples with an SiO_5 skeleton have been reported. To the best of our knowledge, the ionic λ^5*Si*-silicates **1**,[2a] **2**,[2b] **3**·MeOH,[2a] **4**,[2a] and **5**[2c] as well as the zwitterionic λ^5*Si*-silicate **6**·DMF[2d] are the only examples of this particular type of compound that have been structurally characterized by single-crystal X-ray diffraction.[2]



The spirocyclic anions of **1**−**5** contain two bidentate ligands of the ethane-1,2-diolato(2−) type, whereas the spirocyclic zwitterion **6** contains two bidentate benzilato(2−)-O^1,O^2 ligands.

Here we report on the syntheses, crystal structure analyses, and properties of two further zwitterionic λ^5*Si*-silicates with an SiO_5 framework, compounds **7** and **8**.[3] These spirocyclic zwitterions contain two bidentate 2-methyllactato(2−)-O^1,O^2 ligands. In addition, the syntheses, crystal structures, and properties of the related zwitterionic λ^5*Si*-silicates **10**−**12** (SiO_4C skeletons) are described.[3] The zwitterions **11** and **12** formally derive from compounds **7** and **8** by replacement of an oxygen atom by a methylene group. Furthermore, the zwitterions **10**−**12** can be regarded as homologs of compound **9** which has recently been described in the literature.[4] The zwitterionic λ^5*Si*-silicates **9**−**12** differ in their alkylene spacers that connect the *ate* and *onium* centers of these molecules. The experimental investigations



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concerning compounds **7** and **8** (SiO_5 skeletons) were completed by ab initio studies of the related anionic λ^5*Si*-silicate **13** (for ab initio investigations of the anion **14**, see ref.[4]).

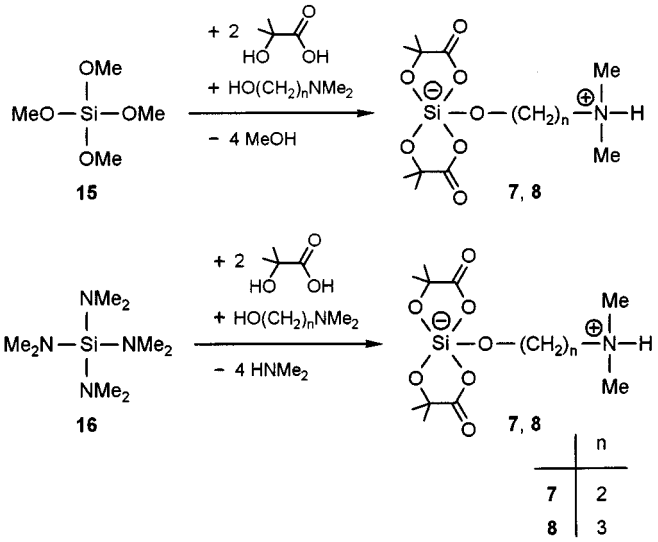
The main goal of the experimental and computational studies presented here was to contribute to the chemistry of pentacoordinate silicon compounds with an SiO_5 framework. These investigations were carried out with a special emphasis on the comparison of the structures and properties of the O/CH_2 analogues **7/11** and **8/12**. A further concern was to study the influence of the alkylene spacer on the structures and properties of the homologs **9**−**12**.

Results and Discussion

Syntheses

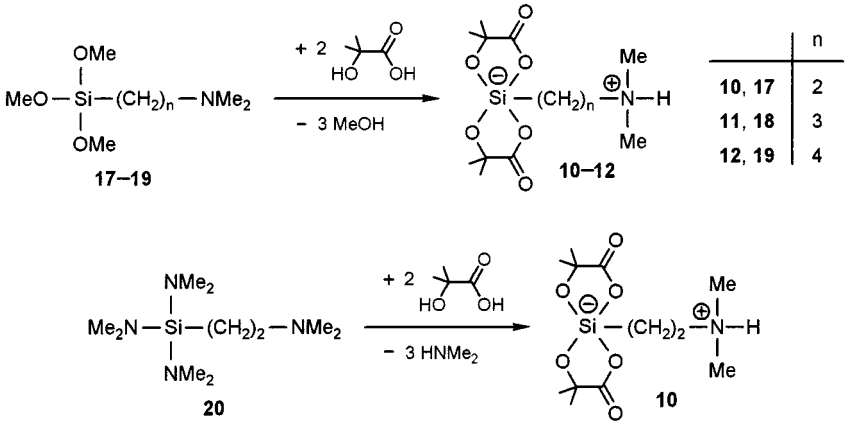
The zwitterionic λ^5*Si*-silicates **7** and **8** were prepared according to Scheme 1 using two different synthetic methods each. The first method implies reaction of tetramethoxysilane (**15**) with two mol equivalents of 2-methyllactic acid and one mol equivalent of 2-(dimethylamino)ethanol and 3-(dimethylamino)propanol, respectively. The reactions were carried out in boiling acetonitrile and the resulting methanol, along with part of the solvent, was removed by distillation. After the reaction mixtures were cooled to room temperature, the products precipitated. Compounds **7** and **8** were isolated, after recrystallization from acetonitrile, in 73% (**7**) and 71% yield (**8**). The second method is based on treatment of tetrakis(dimethylamino)silane[5] (**16**) with one mol equivalent of the respective aminoalcohol, followed by treatment with two mol equivalents of 2-methyllactic acid. The syntheses were again carried out in boiling acetonitrile and compounds **7** and **8** were isolated, after recrystallization from acetonitrile, in 62% (**7**) and 53% yield (**8**).

The zwitterionic λ^5*Si*-silicates **10**−**12** were synthesized according to Scheme 2 by reaction of the respective [(dimethylamino)alkyl]trimethoxysilanes **17**−**19** with 2-methyllactic acid (molar ratio 1:2) in acetonitrile at room temperature. Compounds **10**−**12** were isolated, after recrystallization from acetonitrile, in 78% (**10**), 88% (**11**), and 90% yield (**12**). Alternatively, compound **10** was synthesized according to Scheme 2 by treatment of tris(dimethylamino)[2-(dimethylamino)ethyl]silane[6] (**20**) with two mol equivalents of 2-methyllactic acid in acetonitrile and isolated, after recrystallization from acetonitrile, in 82% yield.

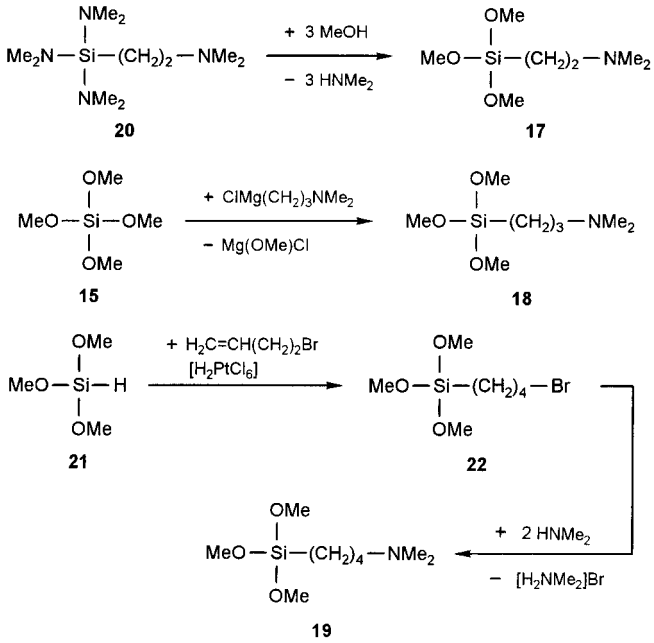


Scheme 1. Syntheses of compounds **7** and **8**

The [(dimethylamino)alkyl]trimethoxysilanes **17**−**19** used for the syntheses of **10**−**12** were prepared according to Scheme 3. [2-(Dimethylamino)ethyl]trimethoxysilane (**17**) was synthesized by methanolysis of the corresponding tris(dimethylamino)silane **20** (yield 84%). [3-(Dimethylamino)propyl]trimethoxysilane (**18**) was obtained by reaction of tetramethoxysilane (**15**) with 3-(dimethylamino)prop-1-ylmagnesium chloride in tetrahydrofuran (yield 71%). [4-(Dimethylamino)butyl]trimethoxysilane (**19**) was prepared by a two-step synthesis starting from trimethoxysilane (**21**). Hydrosilylation of 4-bromo-1-butene with **21** in an autoclave (H_2PtCl_6 as catalyst) gave (4-bromobutyl)trimethoxysilane (**22**) (yield 71%) which upon reaction with dimethylamine in an autoclave yielded the corresponding [4-(dimethylamino)butyl]silane **19** (yield 82%). The silanes **17**−**19** and **22** were isolated as colorless liquids. Their identity was established by elemental analyses, NMR studies (^{1}H, ^{13}C, ^{29}Si), and mass-spectrometric investigations (EI MS).



Scheme 2. Syntheses of compounds **10**−**12**



Scheme 3. Syntheses of compounds **17**−**19**

The title compounds **7**, **8**, and **10**−**12** are colorless crystalline solids with melting points in the temperature range between 162°C (**10**) and 298°C (**12**, dec). They are almost insoluble in nonpolar organic solvents and also exhibit a poor solubility in polar organic solvents. The identity of **7**, **8**, and **10**−**12** was established by elemental analyses (C, H, N), solution-state (^{1}H, ^{13}C, ^{29}Si) and solid-state (^{29}Si CP/MAS) NMR studies, and mass-spectrometric investigations (FAB MS). In addition, all compounds were studied by VT ^{1}H-NMR experiments and were structurally characterized by single-crystal X-ray diffraction. All these studies unequivocally established the zwitterionic structure of **7**, **8**, and **10**−**12** in the solid state and in solution.

Crystal Structure Analyses

Compounds **7**, **8**, and **10**−**12** were studied by single-crystal X-ray diffraction. They crystallize in the space group $P2_1/n$ (**11**), $P2_1/c$ (**7**, **8**, **12**), or $P\bar{1}$ (**10**). All crystals are built up by pairs of Λ- and Δ-enantiomers. There are two crystallographically independent zwitterions each in the crystal lattice of **8**, **10**, and **12**. The structures of compounds **7**, **8**, and **10**−**12** in the crystal are depicted in Figures 1−5. The crystal data and the experimental parameters used for these experiments are summarized in Table 7. Selected interatomic distances and angles are listed in Tables 1 and 2. For reasons of comparison, the respective data for compound **9**·H_2O[4] are included in Table 2.

The coordination polyhedra around the silicon atoms of **7**, **8**, and **10**−**12** can be described as distorted trigonal bipyramids, each bidentate 2-methyllactato(2−)-O^1,O^2 ligand spanning one axial (O1, O3) and one equatorial site (O2, O4). In all compounds, the axial sites are occupied by the carboxylate oxygen atoms. In terms of the Berry pseudorotation coordinate, the geometry of the coordination polyhedra is displaced by 6.1% (**7**), 19.4% (**8**, *molecule A*), 19.2% (**8**, *molecule B*), 32.6% (**10**, *molecule A*), 10.2% (**10**, *molecule B*), 9.2% (**11**), 17.2% (**12**, *molecule A*), and 19.6% (**12**, *molecule B*).[7] The atoms O5 (O5′) and C1 (C1′), respectively, are the pivot atoms that best fit to the Berry pseudorotation coordinate. For compound **9**·H_2O a similar structure was determined, the Berry distortion amounting to 8.9%.[4]

The axial Si−O distances in the SiO_5 skeletons of **7** and **8** [1.773(2)−1.810(2) Å] are significantly longer than the

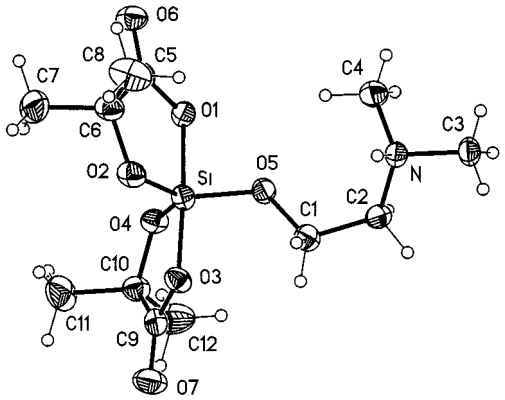


Figure 1. Molecular structure of **7** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

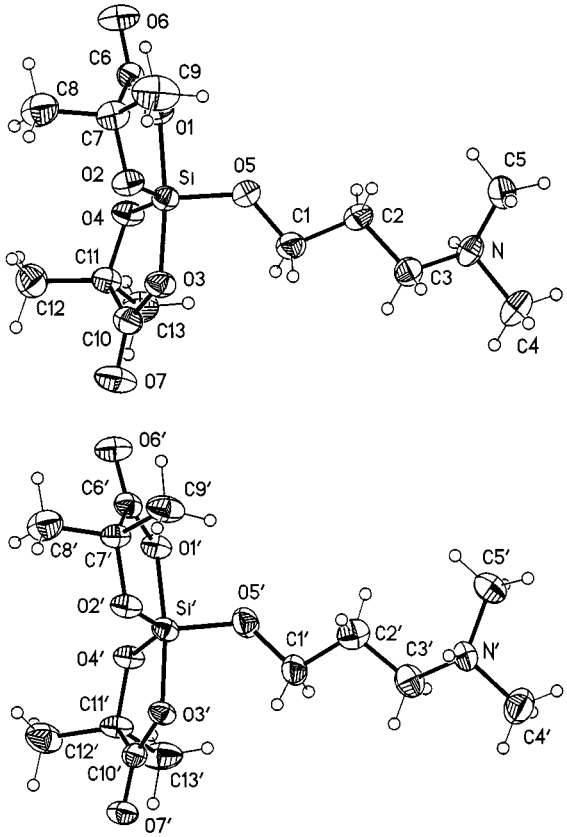


Figure 2. Molecular structures of the two crystallographically independent zwitterions (*molecule A*, above; *molecule B*, below) in the crystal of **8** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

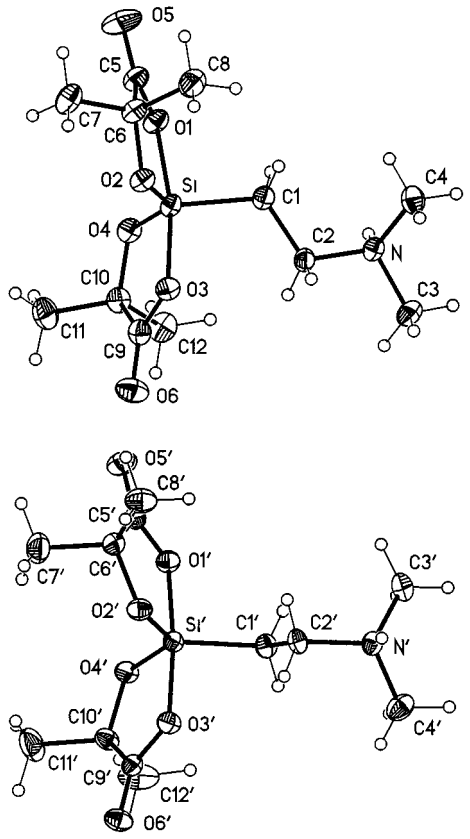


Figure 3. Molecular structures of the two crystallographically independent zwitterions (*molecule A*, above; *molecule B*, below) in the crystal of **10** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

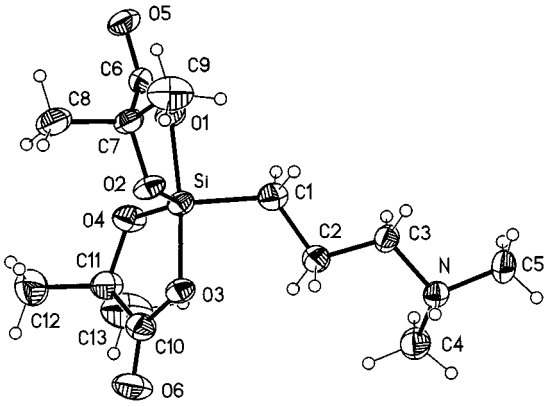


Figure 4. Molecular structure of **11** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

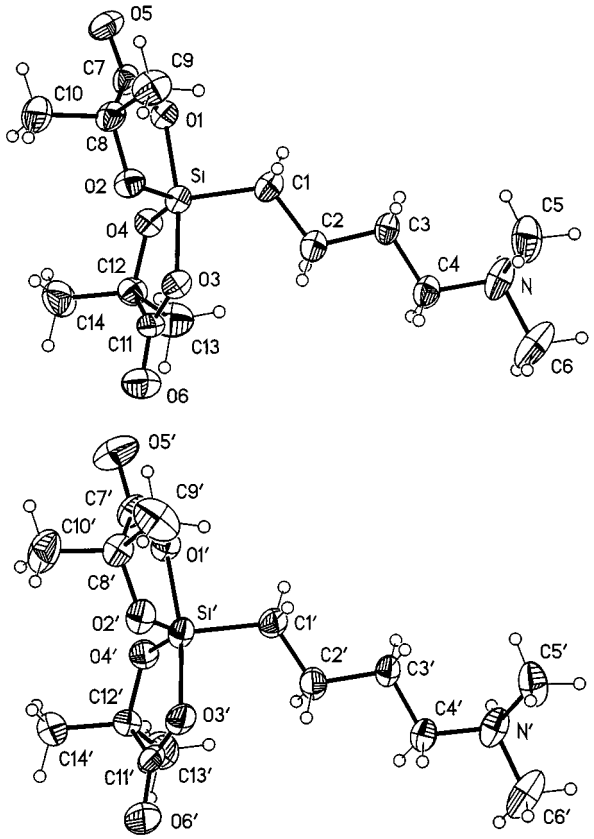


Figure 5. Molecular structures of the two crystallographically independent zwitterions (*molecule A*, above; *molecule B*, below) in the crystal of **12** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

Table 1. Selected interatomic distances [Å] and angles [°] for **7** and **8**

	7	**8**	
		molecule A	*molecule B*
Si−O1	1.798(2)	1.804(2)	1.785(2)
Si−O2	1.659(2)	1.665(2)	1.662(2)
Si−O3	1.773(2)	1.785(2)	1.810(2)
Si−O4	1.653(2)	1.660(2)	1.668(2)
Si−O5	1.643(2)	1.633(2)	1.634(2)
O1−Si−O2	88.68(8)	88.41(11)	89.40(12)
O1−Si−O3	176.83(8)	172.68(12)	172.02(12)
O1−Si−O4	88.61(8)	87.50(11)	87.92(11)
O1−Si−O5	88.03(8)	90.81(11)	91.24(12)
O2−Si−O3	89.82(8)	88.14(11)	86.97(12)
O2−Si−O4	121.01(9)	125.98(13)	125.36(13)
O2−Si−O5	119.97(9)	116.63(13)	117.58(13)
O3−Si−O4	89.77(8)	89.32(11)	88.39(11)
O3−Si−O5	95.14(8)	96.50(12)	96.74(11)
O4−Si−O5	118.80(9)	117.26(13)	117.03(13)

equatorial ones [1.633(2)−1.668(2) Å]. The same holds true for the axial [1.786(3)−1.841(3) Å] and equatorial Si−O distances [1.663(3)−1.685(3) Å] in the *Si*O_4C frameworks of **10**−**12**. Generally, in the case of those oxygen atoms that are involved as acceptor atoms in N−H···O hydrogen bonds (see below), significantly elongated Si−O distances were observed. The Si−C distances for **10**−**12** are very similar [1.868(4)−1.884(2) Å]. Both replacement of oxygen atoms by methylene groups (**7** → **11**; **8** → **12**) and elongation of the $SiO(CH_2)_nN$ and $Si(CH_2)_nN$ chains (**7** → **8**; **9** → **10** → **11** → **12**) do not affect the geometry of the *Si*-coordination polyhedra in a systematic manner. It rather appears that the distortion of the trigonal-bipyramidal coordination polyhedra of the title compounds is mainly influenced by the crystal packing, including hydrogen-bonding interactions between the zwitterions (see below). This is best reflected by the quite different Berry distortions observed for the two crystallographically independent zwitterions in the crystal of **10** (*molecule A*, 32.6%; *molecule B*, 10.2%).

Table 2. Selected interatomic distances [Å] and angles [°] for **9**·H_2O and **10**−**12**

	9·H_2O[a]	**10**		**11**	**12**	
		molecule A	*molecule B*		*molecule A*	*molecule B*
Si−O1	1.8003(8)	1.8334(12)	1.8004(12)	1.832(2)	1.841(3)	1.836(4)
Si−O2	1.6636(8)	1.6669(12)	1.6670(13)	1.672(2)	1.663(3)	1.665(4)
Si−O3	1.8029(8)	1.7907(12)	1.8371(12)	1.804(2)	1.786(3)	1.810(4)
Si−O4	1.6764(8)	1.6771(13)	1.6687(11)	1.670(2)	1.685(3)	1.671(3)
Si−C1	1.8915(11)	1.884(2)	1.884(2)	1.871(4)	1.874(4)	1.868(4)
O1−Si−O2	89.45(4)	87.55(6)	89.22(6)	87.71(10)	87.8(2)	87.9(2)
O1−Si−O3	176.06(4)	168.64(6)	173.70(5)	173.40(11)	170.1(2)	169.82(14)
O1−Si−O4	88.28(4)	85.66(6)	88.49(6)	87.26(9)	86.3(2)	86.3(2)
O1−Si−C1	95.43(4)	92.89(7)	94.40(7)	90.46(13)	92.9(2)	93.9(2)
O2−Si−O3	89.58(4)	88.58(5)	88.27(6)	89.29(10)	88.0(2)	87.4(2)
O2−Si−O4	122.20(4)	130.22(6)	121.50(6)	120.52(12)	122.9(2)	124.0(2)
O2−Si−C1	120.82(5)	114.38(7)	118.74(7)	120.61(14)	118.5(2)	118.7(2)
O3−Si−O4	89.01(4)	88.70(6)	87.90(6)	89.21(10)	88.5(2)	88.9(2)
O3−Si−C1	88.34(4)	98.43(7)	91.87(7)	96.14(13)	97.0(2)	96.3(2)
O4−Si−C1	116.88(5)	115.18(7)	119.72(7)	118.7(2)	118.5(2)	117.2(2)

[a] Data taken from ref.[4]

As expected from the presence of their potential NH donor functions and potential oxygen acceptor atoms, all title compounds form N−H···O hydrogen bonds in the crystal. The relevant geometric data for the respective hydrogen-bonding systems are summarized in Table 3.

Table 3. Geometric data for the N−H···O hydrogen bonds in the crystal of **7**, **8**, and **10**−**12**

compd	N−H···O	N···O [Å]	N−H [Å]	H···O [Å]	N−H···O [°]
7[a]	N−H···O1	3.041(3)	0.90(3)	2.48(3)	120(2)
	N−H···O6	2.803(3)	0.90(3)	1.90(3)	178(3)
8[b]	N−H···O1	3.021(4)	0.97(3)	2.24(3)	137(3)
	N−H···O6	2.895(4)	0.97(3)	1.98(3)	157(3)
	N′−H′···O3′	3.246(4)	0.98(3)	2.55(4)	129(3)
	N′−H′···O7′	2.787(4)	0.98(3)	1.82(3)	169(3)
10[c]	N−H···O1	2.8934(18)	0.86(2)	2.08(2)	157(2)
	N−H···O4	3.2833(18)	0.86(2)	2.58(2)	139(2)
	N′−H′···O3′	3.147(2)	0.91(2)	2.60(2)	119.3(18)
	N′−H′···O6′	2.8146(18)	0.91(2)	1.90(2)	176(2)
11[d]	N−H···O1	2.956(3)	0.86(4)	2.30(4)	133(3)
	N−H···O5	3.015(3)	0.86(4)	2.17(4)	167(3)
12[e]	N−H···O1	2.841(6)	1.00(7)	1.88(7)	162(6)
	N−H···O4	3.270(6)	1.00(7)	2.52(7)	132(5)
	N′−H′···O1′	2.847(6)	0.89(6)	1.98(6)	163(4)

[a] O1···H···O6, 59.0(7)°. − [b] O1···H···O6, 62.9(10)°; O3′···H′···O7′, 58.4(10)°. − [c] O1···H···O4, 60.4(6)°; O3′···H′···O6′, 56.8(6)°. − [d] O1···H···O5, 59.4(10)°. − [e] O1···H···O4, 65(2)°.

For compounds **7**, **8**, and **11**, intermolecular bifurcate N−H···O/O hydrogen bonds were observed leading to the formation of infinite chains in the crystal. These chains each are built up by zwitterions with the same (**7**, **8**) or alternating (**11**) absolute configuration. In the case of compound **8**, these chains each contain crystallographically identical molecules. In the crystal of **10** and **12**, centrosymmetric dimers were observed containing zwitterions with opposite absolute configuration. These dimers are built up by intermolecular bifurcate N−H···O/O hydrogen bonds (**10**, *molecules A* and *B*; **12**, *molecule A*) or intermolecular non-furcate N−H···O hydrogen bonds (**12**, *molecule B*). Both axial (**7**, **8**, **10**−**12**) and equatorial oxygen atoms (**10**, **12**) in the *Si*-coordination polyhedra were found to act as acceptor atoms in the above-mentioned hydrogen-bonding systems. In all cases, these intermolecular N−H···O interactions lead to a significant elongation of the respective Si−O distances compared to those of the chemically equivalent SiO moieties that are not involved in hydrogen bonding. Interestingly, the equatorial O5 oxygen atoms of **7** and **8** do not participate in any hydrogen bonding.

NMR Studies

Compounds **7**, **8**, and **10**−**12** were studied by ^{29}Si CP/MAS NMR experiments in the solid state and by ^{1}H-, ^{13}C-, and ^{29}Si-NMR experiments in solution ([D_6]DMSO). All these investigations were performed at room temperature (for VT ^{1}H-NMR studies, see next chapter).

The isotropic ^{29}Si-NMR chemical shifts obtained in the solid-state NMR studies (Table 4) clearly characterize these ^{29}Si resonances as arising from pentacoordinate silicon atoms. For compounds **8** and **10** separated resonance signals for the two crystallographically independent molecules were detected. Replacement of an oxygen ligand atom by a methylene group in **7** (→ **11**) and **8** (→ **12**) leads to a significant change in the isotropic ^{29}Si chemical shift by 24.9 ppm and 27.3 ppm, respectively. In contrast, the length of the spacers between the *ate* and *onium* centers of the zwitterions (comparison of **7**/**8** and **9**/**10**/**11**/**12**) does not significantly affect the ^{29}Si chemical shift.

As the isotropic ^{29}Si chemical shifts for **7**, **8**, and **10**−**12** are very similar to those observed for these compounds in solution [maximum deviation 4.1 ppm (**10**)] (Table 4), it is concluded that pentacoordination is present in solution as well. In addition, the ^{1}H chemical shifts observed for the NCH_3 (δ = 2.71 to 2.78) and NH moieties (δ = 8.7 to 9.2) clearly indicate the presence of ammonium groups in solution. Thus, the NMR experiments unequivocally demonstrate that the zwitterions **7**, **8**, and **10**−**12** also exist in solution.

Table 4. ^{29}Si NMR data for **7**−**12** in the crystal and in solution[a]

compound	δ^{29}Si (crystal)[b]	δ^{29}Si (solution)[c]
7	−115.4	−111.6
8	−115.2/−116.2	−114.8
9[d]	−98.4	−100.5
10	−89.5/−95.2	−93.6
11	−90.5	−90.3
12	−88.4	−89.4

[a] Spectra recorded at room temperature. − [b] Isotropic chemical shifts, ppm values. − [c] Chemical shifts obtained in [D$_6$]DMSO, ppm values. − [d] ^{29}Si CP/MAS NMR studies were performed with **9**·H$_2$O[4].

In all cases the solution-state NMR data are compatible with the presence of one particular species or with a rapid low-energy interconversion of different isomers (in this context, see ab initio Studies). The results of both the crystal structure analyses and the ab initio studies suggest that the trigonal-bipyramidal structure, with the carboxylate oxygen atoms in the axial positions (the energetically most stable structure), dominates in solution. The diastereotopism observed for the two methyl groups of the 2-methyllactato(2−) ligands (two separated singlets in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra) is in accordance with the chiral nature of the respective λ^5*Si*-silicate skeletons of **7**, **8**, and **10**−**12**. In addition, the NMR data obtained indicate that the Λ- and Δ-enantiomers of these species are configurationally stable on the NMR time scale at room temperature.

VT ^{1}H-NMR Studies

Compounds **7**, **8**, and **10**−**12** were investigated by VT ^{1}H-NMR studies at 300.1 MHz in the temperature ranges of 27−116°C (**7**, **10**), 27−124°C (**8**), and 27−128°C (**11**, **12**) (solvent [D$_6$]DMSO). For all solutions studied two separated singlets for the diastereotopic methyl groups of the 2-methyllactato(2−) ligands were observed, indicating that the respective Λ- and Δ-enantiomers of these λ^5*Si*-silicates are configurationally stable on the NMR time scale under these conditions. Upon heating coalescence of the two singlets was observed in all cases, the temperature dependence of the ^{1}H-NMR spectra being completely reversible on subsequent cooling. These results can be interpreted in terms of an intramolecular isomerization process that leads to a conversion of the respective Λ- and Δ-enantiomers into each other (in this context, see ref.[4]). As determined by line-shape analyses, the activation free enthalpies for this process amount to 79.7(4) kJ mol^{-1} (**7**) to 89(2) kJ mol^{-1} (**12**) (Table 5). According to these results, both the O/CH$_2$ exchange (**7** → **11**; **8** → **12**) and the elongation of the SiO(CH$_2$)$_n$N and Si(CH$_2$)$_n$N chains (**7** → **8**; **9** → **10** → **11** → **12**) lead to an increase of the respective $\Delta G^{\neq}$ values for the Λ/Δ-isomerization. The experimentally established activation free enthalpies are comparable with the respective energy barriers calculated for the anionic model species

Table 5. Activation free enthalpies $\Delta G^{\neq}$ for the Λ/Δ-isomerization of **7**−**12** in [D$_6$]DMSO as determined by VT ^{1}H-NMR spectroscopy

compound	$\Delta G^{\neq}$ [kJ mol^{-1}]	compound	$\Delta G^{\neq}$ [kJ mol^{-1}]
7	79.7(4)	**10**	84.6(4)
8	84.6(6)	**11**	88.5(7)
9[a]	76(1)	**12**	89(2)

[a] Data taken from ref.[4]

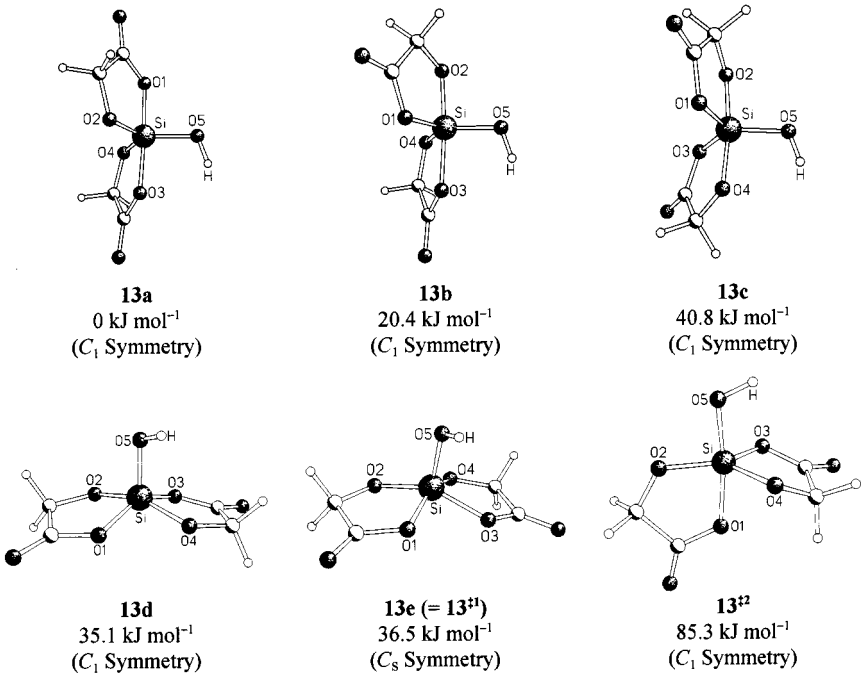


Figure 6. Calculated structures and relative energies of the local minima **13a**−**13c** and the transition states **13d**, **13e** (= 13$^{\neq 1}$), and **13**$^{\neq 2}$

13 (85.3 kJ mol^{-1}; see next chapter) and **14** (70.8 kJ mol^{-1}; see ref.[4]).

ab initio Studies

The structure and dynamic behavior of compounds **7** and **8** (SiO_5 skeletons) were studied by quantum-chemical methods using the anionic λ^5*Si*-silicate bis[glycolato(2−)-O^1,O^2]hydroxosilicate(1−) (**13**) as a model species. The computational methods used are described in the Experimental Section.

Five different idealized geometries (**13a**−**13e**, Figure 6) for the anion **13** were considered in this study. For energetic reasons, trigonal bipyramids with the hydroxo ligand in an axial site and square pyramids with the hydroxo group in a basal position were excluded. Calculations of the vibrational frequencies demonstrated that the chiral trigonal-bipyramidal isomers **13a**−**13c** represent local minima, whereas the square-pyramidal species **13d** (chiral) and **13e** (**13**$^{\neq 1}$) (achiral) are transition states (for selected geometric parameters of **13a**−**13e**, see Table 6).[8] Isomer **13a**, with the two carboxylate oxygen atoms in the axial sites, was found to be the energetically most favorable one. This is in agreement with the experimentally established crystal structures of **7** and **8**.

Table 6. Calculated interatomic distances [Å] and angles [°] for the local minima **13a**−**13c** and the transition states **13d**, **13e** (= **13**$^{\neq 1}$), and **13**$^{\neq 2}$ as obtained by SCF/SVP geometry optimizations

	13a	**13b**	**13c**	**13d**	**13e**	**13**$^{\neq 2}$
Si−O1	1.772	1.720	1.731	1.764	1.771	1.873
Si−O2	1.664	1.704	1.701	1.687	1.687	1.661
Si−O3	1.812	1.826	1.731	1.759	1.771	1.726
Si−O4	1.665	1.666	1.735	1.704	1.687	1.676
Si−O5	1.650	1.651	1.654	1.653	1.654	1.673
O1−Si−O2	88.6	88.6	87.6	86.8	86.7	83.8
O1−Si−O3	177.0	87.0	124.0	146.2	83.7	86.2
O1−Si−O4	91.0	120.5	89.4	86.3	151.3	88.1
O1−Si−O5	92.0	117.1	115.8	105.8	101.4	172.7
O2−Si−O3	90.3	174.6	88.8	86.6	151.3	130.7
O2−Si−O4	119.9	93.2	171.9	156.2	89.1	134.1
O2−Si−O5	119.0	95.0	94.8	102.1	107.0	89.2
O3−Si−O4	87.2	86.3	86.7	86.5	86.7	93.5
O3−Si−O5	91.0	89.8	120.2	108.0	101.4	97.0
O4−Si−O5	121.1	122.0	93.2	101.7	107.0	98.3

As shown by further ab initio studies, the enantiomers Λ-**13a** and Δ-**13a** can be converted into each other by an intramolecular isomerization process along the reaction path Λ-**13a** ⇌ Δ-**13c** ⇌ **13**$^{\neq 2}$ ⇌ Λ-**13b** ⇌ **13**$^{\neq 1}$ ⇌ Δ-**13b** ⇌ **13**$^{\neq 2'}$ ⇌ Λ-**13c** ⇌ Δ-**13a** (**13**$^{\neq 1}$ and **13e** are identical; **13**$^{\neq 2'}$ is the antipode of **13**$^{\neq 2}$) (Figure 7).[9−11] The structure of the trigonal-bipyramidal transition state **13**$^{\neq 2}$ is also depicted in Figure 6. The hydroxo groups in the transition states occupy an apical (**13**$^{\neq 1}$) or axial position (**13**$^{\neq 2}$). The species **13**$^{\neq 1}$ can be regarded as a transition state of a Berry-type conversion (OH as pivot ligand), whereas **13**$^{\neq 2}$ (**13**$^{\neq 2'}$) represents the transition state of a "twist-type" mechanism (in this context, see ref.[4]). The highest relative energy was calculated for **13**$^{\neq 2}$ (**13**$^{\neq 2'}$) (85.3 kJ mol^{-1}), the energy being very similar to the experimentally established activation free enthalpies for the isomerization processes Λ-**7** ⇌ Δ-**7** and Λ-**8** ⇌ Δ-**8** (see VT ^{1}H-NMR Studies).

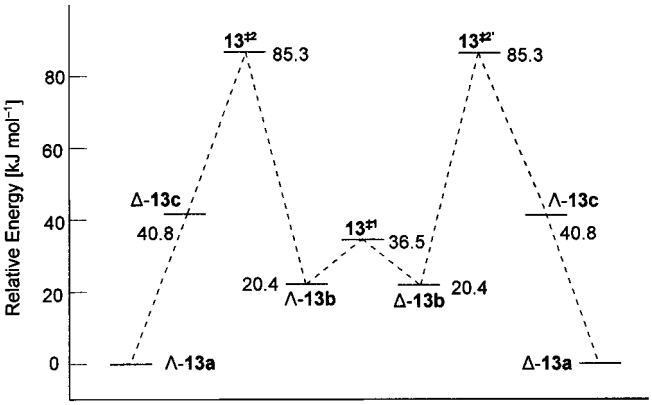


Figure 7. Calculated intramolecular reaction path for the isomerization of **13a** (Λ-**13a** ⇌ Δ-**13a**), showing the relative energies of the local minima **13a**−**13c** and of the transition states **13**$^{\neq 1}$ (= **13e**) and **13**$^{\neq 2}$ (**13**$^{\neq 2'}$)

Experimental Section

General: 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 Büchi Melting Point apparatus, type B-540. − The ^{1}H, ^{13}C, and ^{29}Si solution-state NMR spectra were recorded at room temperature on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 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), and external TMS (^{29}Si, δ = 0; $CDCl_3$, [D_6]DMSO). Assignment of the ^{13}C-NMR data was supported by DEPT 135 experiments. ^{29}Si CP/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. 200 mg of sample [79.5 MHz, TMS as external standard (δ = 0), spinning rate 5000 Hz, contact time 5 ms, 90° ^{1}H transmitter pulse length 3.6 μs, repetition time 4 s]. − Mass spectra were obtained with a Finnigan MAT-8200 or Finnigan MAT-8430 mass spectrometer (FAB MS, 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source) and with a Trio-1000 mass spectrometer (ThermoQuest; EI MS, 70 eV). The selected *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{28}Si, and ^{79}Br. − Compounds **15** and **21** were purchased from Aldrich, **16**[5] and **20**[6] were prepared as described in the literature.

[2-(Dimethylammonio)ethoxy]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate (7) and [3-(Dimethylammonio)propoxy]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate (8):

Preparation from 15: A solution of **15** (2.04 g, 13.4 mmol) in acetonitrile (20 mL) was added dropwise within 10 min to a stirred boiling solution of 2-methyllactic acid (2.79 g, 26.8 mmol) and the respective aminoalcohol (13.4 mmol) in acetonitrile (35 mL). Subsequently, part of the solvent (30−40 mL) was removed by distillation (760 Torr) and the residue allowed to cool to room temperature (formation of a precipitate after ca. 6 h). The precipitate was filtered off, recrystallized from acetonitrile (slow cooling of a saturated boiling solution to room temperature), and dried in vacuo

(0.01 Torr, 6 h) to give a colorless crystalline product [**7**, 3.14 g (yield 73%); **8**, 3.21 g (yield 71%)].

Preparation from 16: A solution of the respective aminoalcohol (4.80 mmol) in acetonitrile (30 mL) was added within 30 min to a boiling solution of **16** (981 mg, 4.80 mmol) in acetonitrile (50 mL). Subsequently, a solution of 2-methyllactic acid (999 mg, 9.60 mmol) in acetonitrile (50 mL) was added dropwise to this mixture within 2 h and part of the solvent was removed slowly by distillation at the same time. The distillation was continued for a further 2 h until ca. 80 mL of the solvent were removed. The reaction mixture was then kept at 20°C for 24 h (**7**) or at −20°C for 72 h (**8**), and the resulting precipitate was filtered off and dried in vacuo (0.01 Torr, 6 h) to give a colorless crystalline product [**7**, 950 mg (yield 62%); **8**, 860 mg (yield 53%)].

Data for 7: Mp 243°C (dec). − ^{1}H NMR ([D$_6$]DMSO): δ = 1.17 (s, 6 H, CCH$_3$), 1.20 (s, 6 H, CCH$_3$), 2.78 (s, 6 H, NCH$_3$), 3.12−3.14 (m, 2 H, CCH$_2$N), 3.70−3.87 (m, 2 H, CCH$_2$O), 9.2 (broad s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 27.2 (C*C*H$_3$), 27.5 (C*C*H$_3$), 42.8 (NCH$_3$), 57.9 and 58.2 (C*C*H$_2$N, O*C*H$_2$C), 73.5 (O*C*C$_3$), 178.4 (C=O). − ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ = −111.6. − ^{29}Si CP/MAS NMR (359 transients): δ = −115.4. − FAB MS (positive ions): *m*/*z* 322 (1) [*M* + H$^+$], 90 (100) [HO(CH$_2$)$_2$NH(CH$_3$)$_2^+$]. − FAB MS (negative ions): *m*/*z* 320 (1) [*M* − H$^+$], 249 (100) [{OCMe$_2$C(O)O}$_2$SiOH$^-$]. − $C_{12}H_{23}NO_7Si$ (321.4): calcd C 44.84, H 7.21, N 4.36; found C 44.5, H 7.3, N 4.4.

Data for 8: Mp 162 (dec). − ^{1}H NMR ([D$_6$]DMSO): δ = 1.16 (s, 6 H, CCH$_3$), 1.19 (s, 6 H, CCH$_3$), 1.72−1.79 (m, 2 H, CCH$_2$C), 2.76 (s, 6 H, NCH$_3$), 3.04−3.08 (m, 2 H, CCH$_2$N), 3.45−3.64 (m, 2 H, CCH$_2$O), 9.1 (broad s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 27.2 (C*C*H$_2$C), 27.2 (C*C*H$_3$), 27.3 (C*C*H$_3$), 42.4 (NCH$_3$), 55.0 and 59.7 (C*C*H$_2$N, O*C*H$_2$C), 73.2 (O*C*C$_3$), 178.9 (C=O). − ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ = −114.8. − ^{29}Si CP/MAS NMR (1661 transients): δ = −115.2, −116.2. − FAB MS (positive ions): *m*/*z* 336 (1) [*M* + H$^+$], 104 (100) [HO(CH$_2$)$_3$NH(CH$_3$)$_2^+$]. − FAB MS (negative ions): *m*/*z* 334 (1) [*M* − H$^+$], 249 (100) [{OCMe$_2$C(O)O}$_2$SiOH$^-$]. − $C_{13}H_{25}NO_7Si$ (335.4): calcd C 46.55, H 7.51, N 4.18; found C 46.7, H 7.5, N 4.3.

[2-(Dimethylammonio)ethyl]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate (**10**):

Preparation from 17: Compound **17** (622 mg, 3.22 mmol) was added to a stirred solution of 2-methyllactic acid (671 mg, 6.44 mmol) in acetonitrile (10 mL) and the reaction mixture kept at room temperature for 4 h. After part of the solvent (ca. 6 mL) was removed by distillation (760 Torr), the boiling solution was cooled slowly to room temperature (formation of a crystalline solid after ca. 3 h). After 24 h the precipitate was filtered off, recrystallized from acetonitrile (slow cooling of a saturated boiling solution to room temperature), and dried in vacuo (0.02 Torr, 6 h) to give 770 mg (yield 78%) of a colorless crystalline product.

Preparation from 20: A solution of **20** (2.00 g, 8.60 mmol) in acetonitrile (30 mL) was added to a stirred solution of 2-methyllactic acid (1.79 g, 17.2 mmol) in acetonitrile (40 mL) and the reaction mixture kept at room temperature for 4 h. After part of the solvent (ca. 40 mL) was removed by distillation (760 Torr), the boiling solution was cooled slowly to room temperature (formation of a crystalline solid after ca. 2 h). After 24 h the precipitate was filtered off, recrystallized from acetonitrile (cooling of a saturated boiling solution to room temperature), and dried in vacuo (0.02 Torr, 6 h) to give 2.15 g (yield 82%) of a colorless crystalline product.

Data for 10: Mp 287°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 0.81−0.98 (m, 2 H, SiCH$_2$C), 1.17 (s, 6 H, CCH$_3$), 1.20 (s, 6 H, CCH$_3$), 2.71 (s, 6 H, NCH$_3$), 2.84−3.04 (m, 2 H, CCH$_2$N), 8.7 (broad s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 14.4 (Si*C*H$_2$C), 27.1 (C*C*H$_3$), 27.7 (C*C*H$_3$), 41.2 (NCH$_3$), 55.8 (C*C*H$_2$N), 73.3 (O*C*C$_3$), 178.7 (C=O). − ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ = −93.6. − ^{29}Si CP/MAS NMR (109 transients): δ = −89.5, −95.2. − FAB MS (positive ions): *m*/*z* 306 (100) [*M* + H$^+$]. − FAB MS (negative ions): *m*/*z* 304 (100) [*M* − H$^+$]. − $C_{12}H_{23}NO_6Si$ (305.4): calcd C 47.19, H 7.59, N 4.59; found C 46.8, H 7.6, N 4.6.

[3-(Dimethylammonio)propyl]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate (**11**) **and [4-(Dimethylammonio)butyl]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate** (**12**): The respective silane (**18**, **19**; 7.62 mmol) was added dropwise within 2 min to a stirred solution of 2-methyllactic acid (1.58 g, 15.2 mmol) in acetonitrile (40 mL) (formation of a precipitate after ca. 10 min). After 48 h the precipitate was filtered off, recrystallized from acetonitrile (slow cooling of a saturated boiling solution to room temperature), and dried in vacuo (0.02 Torr, 6 h) to give a colorless crystalline product [**11**, 2.13 g (yield 88%); **12**, 2.15 (yield 90%)].

Data for 11: Mp 292°C (dec). − ^{1}H NMR ([D$_6$]DMSO): δ = 0.42−0.47 (m, 2 H, SiCH$_2$C), 1.16 (s, 6 H, CCH$_3$), 1.18 (s, 6 H, CCH$_3$), 1.50−1.61 (m, 2 H, CCH$_2$C), 2.71 (s, 6 H, NCH$_3$), 2.90−3.00 (m, 2 H, CCH$_2$N), 9.0 (broad s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 15.0 (Si*C*H$_2$C), 20.1 (C*C*H$_2$C), 27.1 (C*C*H$_3$), 27.8 (C*C*H$_3$), 42.2 (NCH$_3$), 59.7 (C*C*H$_2$N), 73.2 (O*C*C$_3$), 178.9 (C=O). − ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ = −90.3. − ^{29}Si CP/MAS NMR (253 transients): δ = −90.5. − FAB MS (positive ions): *m*/*z* 320 (100) [*M* + H$^+$]. − FAB MS (negative ions): *m*/*z* 318 (100) [*M* − H$^+$]. − $C_{13}H_{25}NO_6Si$ (319.4): calcd C 48.88, H 7.89, N 4.38; found C 48.8, H 7.7, N 4.4.

Data for 12: Mp 298°C (dec). − ^{1}H NMR ([D$_6$]DMSO): δ = 0.44−0.55 (m, 2 H, SiCH$_2$C), 1.15 (s, 6 H, CCH$_3$), 1.16 (s, 6 H, CCH$_3$), 1.21−1.31 (m, 2 H, SiCCH$_2$C), 1.50−1.61 (m, 2 H, CCH$_2$CN), 2.72 (s, 6 H, NCH$_3$), 2.95−3.00 (m, 2 H, CCH$_2$N), 9.1 (broad s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 18.3 (Si*C*H$_2$C), 21.9 (C*C*H$_2$C), 27.2 (C*C*H$_3$), 27.3 (C*C*H$_2$C), 27.9 (C*C*H$_3$), 42.2 (NCH$_3$), 56.8 (C*C*H$_2$N), 73.1 (O*C*C$_3$), 179.0 (C=O). − ^{29}Si{^{1}H} NMR ([D$_6$]DMSO): δ = −89.4. − ^{29}Si CP/MAS NMR (97 transients): δ = −88.4. − FAB MS (positive ions): *m*/*z* 334 (100) [*M* + H$^+$]. − FAB MS (negative ions): *m*/*z* 332 (100) [*M* − H$^+$]. − $C_{14}H_{27}NO_6Si$ (333.5): calcd C 50.43, H 8.16, N 4.20; found C 50.1, H 8.1, N 4.2.

[2-(Dimethylamino)ethyl]trimethoxysilane (**17**): Compound **20** (17.2 g, 74.0 mmol) was added dropwise at 0°C within 20 min to a stirred solution of methanol (14.2 g, 443 mmol). The solution was warmed to room temperature within 30 min and then heated under reflux for 1 h. The volatile components of the reaction mixture were removed under reduced pressure (ca. 100 Torr), and the residue was distilled over a Vigreux column to give 12.0 g (yield 84%) of a colorless liquid. Bp 162°C/760 Torr. − ^{1}H NMR (CDCl$_3$): δ = 0.46−0.52 (m, 2 H, SiCH$_2$C), 2.03 (s, 6 H, NCH$_3$), 2.19−2.24 (m, 2 H, CCH$_2$N), 3.39 (s, 9 H, OCH$_3$). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 8.6 (Si*C*H$_2$C), 44.8 (OCH$_3$), 50.5 (NCH$_3$), 53.7 (C*C*H$_2$N). − ^{29}Si{^{1}H} NMR (CDCl$_3$): δ = −42.4. − EI MS: *m*/*z* 193 (24) [*M*$^+$], 162 (4) [*M*$^+$ − OCH$_3$], 121 (51) [*M*$^+$ − (CH$_2$)$_2$N(CH$_3$)$_2$], 58 (100) [H$_2$C=N(CH$_3$)$_2^+$]. − $C_7H_{19}NO_3Si$ (193.3): calcd C 43.49, H 9.91, N 7.25; found C 43.7, H 10.0, N 7.2.

[3-(Dimethylamino)propyl]trimethoxysilane (**18**): A Grignard reagent, prepared from 1-chloro-3-(dimethylamino)propane (24.3 g, 200 mmol) and magnesium (5.10 g, 210 mmol) in THF (150 mL), was added dropwise at 0°C within 1 h to a solution of **15** (25.9 g, 170 mmol) in THF (160 mL). The mixture was heated under reflux for 4 h and then stirred at room temperature for a further 18 h.

Table 7. Crystal data and experimental parameters for the crystal structure analyses of **7**, **8**, and **10**−**12**

compound	**7**	**8**	**10**	**11**	**12**
empirical formula	$C_{12}H_{23}NO_7Si$	$C_{13}H_{25}NO_7Si$	$C_{12}H_{23}NO_6Si$	$C_{13}H_{25}NO_6Si$	$C_{14}H_{27}NO_6Si$
formula mass [g mol^{-1}]	321.40	335.43	305.40	319.43	333.46
collection T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
λ(Mo-$K\alpha$) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/c$ (14)
a [Å]	6.611(2)	16.307(4)	11.151(2)	8.232(2)	10.4880(12)
b [Å]	18.633(4)	11.553(2)	11.659(2)	16.583(3)	24.640(3)
c [Å]	14.328(4)	19.072(5)	13.969(3)	13.133(3)	14.1119(13)
α [deg]	90	90	85.31(3)	90	90
β [deg]	103.04(3)	106.53(6)	76.50(3)	99.89(3)	95.908(13)
γ [deg]	90	90	62.07(3)	90	90
V [Å^3]	1719.6(8)	3444.4(14)	1559.4(5)	1766.0(6)	3627.4(7)
Z	4	8	4	4	8
D(calcd) [g cm^{-3}]	1.241	1.294	1.301	1.201	1.221
μ [mm^{-1}]	0.165	0.168	0.174	0.156	0.155
F(000)	688	1440	656	688	1440
cryst dimens [mm]	0.4×0.3×0.2	0.4×0.4×0.2	0.8×0.6×0.3	0.4×0.3×0.2	0.5×0.02×0.01
2θ range [deg]	5.26−45.98	4.18−46.52	4.24−52.24	4.92−46.52	4.40−46.62
index ranges	$-7 \le h \le 3$, $0 \le k \le 20$, $-15 \le l \le 15$	$-18 \le h \le 17$, $0 \le k \le 12$, $0 \le l \le 21$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-8 \le h \le 8$, $-18 \le k \le 18$, $-14 \le l \le 14$	$-7 \le h \le 11$, $-27 \le k \le 27$, $-15 \le l \le 13$
no. of coll reflns	3792	4943	14753	12204	10717
no. of indep reflns	2392	4943	5664	2426	4726
R_{int}	0.0247	−	0.0592	0.0980	0.0756
no. of reflns used	2392	4943	5664	2426	4726
no. of params	200	418	545	290	417
S[a]	1.015	1.015	1.015	0.918	0.865
weight params a/b[b]	0.0372/0.2836	0.0345/2.7399	0.0464/0.3261	0.0672/0	0.0894/0
$R1$[c] [$I > 2\sigma(I)$]	0.0374	0.0491	0.0373	0.0448	0.0585
$wR2$[d] (all data)	0.0839	0.1043	0.0861	0.1104	0.1566
extinction coeff	−	0.0018(2)	−	−	−
max/min res electron dens [e Å^{-3}]	+0.163/−0.233	+0.453/−0.257	+0.314/−0.224	+0.492/−0.331	+1.447/−0.303

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. − [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (F_o^2 + 2F_c^2)/3$. − [c] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. − [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

The precipitate was filtered off, the solvent removed under reduced pressure, and the residue distilled in vacuo to give 24.9 g (yield 71%) of a colorless liquid. Bp 42°C/0.05 Torr. − ^{1}H NMR ($CDCl_3$): δ = 0.46−0.52 (m, 2 H, $SiCH_2C$), 1.37−1.48 (m, 2 H, CCH_2C), 2.07 (s, 6 H, NCH_3), 2.08−2.13 (m, 2 H, CCH_2N), 3.42 (s, 9 H, OCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 6.9 ($SiCH_2C$), 21.0 (CCH_2C), 45.7 (OCH_3), 50.7 (NCH_3), 62.9 (CCH_2N). − $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ = −41.5. − EI MS: *m*/*z* 207 (16) [M^+], 176 (6) [$M^+ - OCH_3$], 121 (51) [$M^+ - (CH_2)_3N(CH_3)_2$], 58 (100) [$H_2C{=}N(CH_3)_2^+$]. − $C_8H_{21}NO_3Si$ (207.3): calcd C 46.34, H 10.21, N 6.76; found C 46.3, H 10.2, N 6.8.

[4-(Dimethylamino)butyl]trimethoxysilane (**19**): A mixture of **22** (4.00 g, 15.6 mmol) and dimethylamine (2.16 g, 47.9 mmol) was heated in an autoclave at 60°C/10 bar for 4 h. After the mixture was cooled to room temperature, the excess amine was evaporated and *n*-pentane (25 ml) added to the residue. The precipitate was filtered off, the solvent removed under reduced pressure, and the residue distilled in vacuo to give 2.83 g (yield 82%) of a colorless liquid. Bp 92°C/11 Torr. − ^{1}H NMR ($CDCl_3$): δ = 0.54−0.60 (m, 2 H, $SiCH_2C$), 1.30−1.44 (m, 4 H, CCH_2C), 2.11 (s, 6 H, NCH_3), 2.12−2.17 (m, 2 H, CCH_2N), 3.47 (s, 9 H, OCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.5 ($SiCH_2C$), 21.0 (CCH_2C), 31.5 (CCH_2C), 45.9 (OCH_3), 50.8 (NCH_3), 59.9 (CCH_2N). − $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ = −41.8. − EI MS: *m*/*z* 221 (15) [M^+], 190 (2) [$M^+ - OCH_3$], 121 (34) [$M^+ - (CH_2)_4N(CH_3)_2$], 58 (100) [$H_2C{=}N(CH_3)_2^+$]. − $C_9H_{23}NO_3Si$ (221.4): calcd C 48.83, H 10.47, N 6.33; found C 48.7, H 10.5, N 6.3.

(4-Bromobutyl)trimethoxysilane (**22**): A mixture of 4-bromo-1-butene (5.00 g, 37.0 mmol), **21** (6.78 g, 55.5 mmol), hexachloroplatinic acid hexahydrate (20 mg, 39 μmol), and 2-propanol (0.2 mL) was heated in an autoclave at 140°C/2 bar for 8 h. After the mixture was cooled to room temperature, the solid particles were removed by filtration, and the filtrate was distilled in vacuo to give 6.72 g (yield 71%) of a colorless liquid. Bp 49°C/2 Torr. − ^{1}H NMR ($CDCl_3$): δ = 0.52−0.58 (m, 2 H, $SiCH_2C$), 1.39−1.53 (m, 2 H, CCH_2C), 1.72−1.83 (m, 2 H, CCH_2C), 3.29−3.33 (m, 2 H, CCH_2Br), 3.48 (s, 9 H, OCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.2 ($SiCH_2C$), 21.6 (CCH_2C), 33.7 (CCH_2C), 36.1 (CCH_2Br), 50.7 (OCH_3). − $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ = −42.2. − EI MS: *m*/*z* 256 (1) [M^+], 121 (100) [$M^+ - C_4H_8Br$]. − $C_7H_{17}BrO_3Si$ (257.2): calcd C 32.69, H 6.66; found C 32.2, H 6.7.

Crystal Structure Analyses: Suitable single crystals of **7**, **8**, and **10**−**12** were obtained by crystallization from acetonitrile (slow cooling of saturated boiling solutions to room temperature). The crystals were mounted in inert oil (RS 3000, Riedel-de Haën) on a glass fiber and then transferred to the cold gas stream of the diffractometer [**7**, **8**: Enraf-Nonius CAD4; **10**−**12**: Stoe IPDS; graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å)]. The structures were solved by direct methods.[12] All non-hydrogen atoms were refined anisotropically.[13] The positions of the NH hydrogen atoms were localized in difference Fourier syntheses and refined freely (**8**: with one distance restraint). The CH hydrogen atoms were refined freely (**10**, **11**) or a riding model was employed in the refinement of the CH hydrogen atom positions (**7**, **8**, and

12). The maximum residual electron density of 1.447 e $Å^{-3}$ in the crystal of **12** corresponds to a single peak which could be refined to a (hydrogen bonded) oxygen atom (occupation 0.3), but neither the ^{1}H-NMR data nor the elemental analyses confirm any content of water in the crystal of **12** (second residual electron density peak: 0.21 e $Å^{-3}$).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102600 (**7**), CCDC-102601 (**8**), CCDC-102602 (**10**), CCDC-102603 (**11**), and CCDC-102604 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223/ 336-033; e-mail: deposit@ccdc.cam.ac.uk].

VT ^{1}H-NMR Studies: The experiments were carried out analogously to the standard ^{1}H-NMR measurements using a Bruker DRX-300 spectrometer. [D_6]DMSO was used as solvent. The thermocouple used with the probe was calibrated for high temperatures according to ref.[14] using a 80% solution of 1,2-ethanediol in [D_6]DMSO. Spectra were recorded in the temperature ranges of 27−116°C (**7**, **10**), 27−124°C (**8**), and 27−128°C (**11**, **12**). The time required for temperature equilibration was 15 min. The data obtained were fitted and simulated by using the Bruker software program WinDyna 1.0b (line-shape analysis). From the simulated spectra the coalescence temperatures T_C and the exchange rates k_C at the coalescence points were extracted, and the respective values for the activation free enthalpy $\Delta G^{\neq}$ for the exchange process were calculated by using the Eyring equation: $\Delta G^{\neq} = 19.14 \cdot T_C \cdot [10.32 + \log (T_C/k_C)]$ [J mol^{-1}].[15]

Computational Methods: Geometry optimizations at the SCF/SVP level for the anionic model species **13** were performed using the TURBOMOLE program system.[16] Stationary geometries and transition states were characterized as local minima (zero imaginary frequencies) and saddle points (one imaginary frequency), respectively, by calculation of the vibrational frequencies. The energies given for **13** include the single point MP2 energy (SVP basis set) and the zero point vibrational energy.

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[8] Calculated energies (SCF + single point MP2 + E(vib0) energies [Hartree]): **13a**, −968.7280119 (C_1 symmetry); **13b**, −968.7202435 (C_1 symmetry); **13c**, −968.7124818 (C_1 symmetry); **13d**, −968.7145996 (C_1 symmetry); **13e**, −968.7141209 (C_S symmetry).

[9] Calculated energy (SCF + single point MP2 + E(vib0) energies [Hartree]): $\mathbf{13}^{\neq 2}$, −968.6955135 (C_1 symmetry).

[10] As the equipotential surface around the local minimum **13c** is quite flat, further calculations with a larger basis set have to be performed to determine the Berry-type transition state which is expected to connect the two minima **13a** and **13c**. In the case of the anionic model species **14**, a related transition state could be found (see ref.[4]).

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