Syntheses, Stereochemistry, and Dynamic Behavior of Chiral Zwitterionic (Ammoniomethyl)bis[glycolato(2–)-O^1,O^2]silicates

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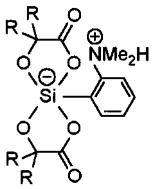
Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

Keywords: Ab initio studies / Chirality / Pentacoordinate silicon / Stereochemistry / Zwitterionic λ^5*Si*-silicates

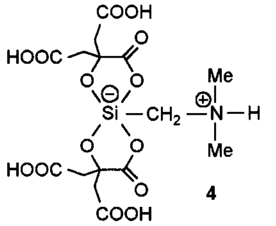
The syntheses of the zwitterionic (molecular) spirocyclic λ^5*Si*-silicates **5**–**9** are described. These chiral compounds contain a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom. The stereochemistry and dynamic behavior of **5**–**9** were investigated. For this purpose, compounds **5**–**9** were studied by solution-state NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si; including VT ^{1}H-NMR studies of **9**) and solid-state NMR spectroscopy (^{13}C CP/MAS, ^{29}Si CP/MAS). In addition, compounds **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$ were structurally characterized by single-crystal X-ray diffraction, and ab initio investigations of the zwitterion **8** and the related anionic model species **10** were carried out.

Introduction

The study of compounds with higher coordinate silicon atoms currently represents one of the main areas of research in silicon chemistry.[1] In context with our systematic investigations on zwitterionic λ^5*Si*-silicates,[1f,1h,1i,2] we have recently reported on the syntheses and crystal structure analyses of the spirocyclic compounds **1**−**3**[2e] and **4**·H_2O[2g]. These molecular pentacoordinate silicon compounds each contain two identical bidentate diolato(2−) ligands that derive from α-hydroxycarboxylic acids. λ^5*Si*-silicates of this particular formula type offer a variety of interesting stereochemical features. In this paper, the results of experimental and theoretical studies concerning the stereochemistry and dynamic behavior of such compounds are described. We report here on the syntheses and characterization of the zwitterionic λ^5*Si*-silicates **5**−**9**, including (i) the crystal structure analyses of **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$, (ii) VT ^{1}H-NMR studies of **9**, and (iii) ab initio investigations of **8** and **10**.[3]



	R
1	H
2	Me
3	Ph



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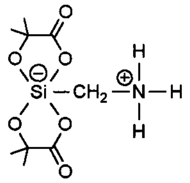

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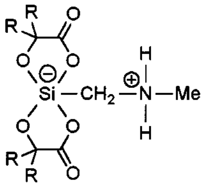
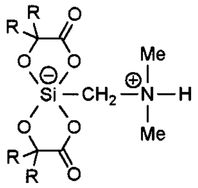
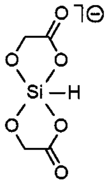


6: R = H
7: R = Me



8: R = H
9: R = Me



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Results and Discussion

Syntheses

The zwitterionic λ^5*Si*-silicates **5**−**9** were prepared according to Scheme 1, starting from the trialkoxy(aminomethyl)silanes $(EtO)_3SiCH_2NH_2$ (**11**), $(MeO)_3SiCH_2N(H)Me$ (**12**), and $(MeO)_3SiCH_2NMe_2$ (**13**). Compounds **8** and **9** were synthesized alternatively according to Scheme 2 and 3, starting from the dialkoxy(phenyl)(aminomethyl)silane $Ph(MeO)_2SiCH_2NMe_2$ (**14**) and from the (ammoniomethyl)tetrafluorosilicate $F_4SiCH_2NMe_2H$ (**15**), respectively.

Following the strategy described for the synthesis of **1**−**4**,[2e,2g] compounds **5**−**9** were prepared according to *method a* by reaction of the respective silanes **11**−**13** with two mol equivalents of glycolic acid and 2-methyllactic acid, respectively (Scheme 1). The reactions were performed in acetonitrile at room temperature and the products **5**−**9** were formed spontaneously in precipitation reactions. Com-

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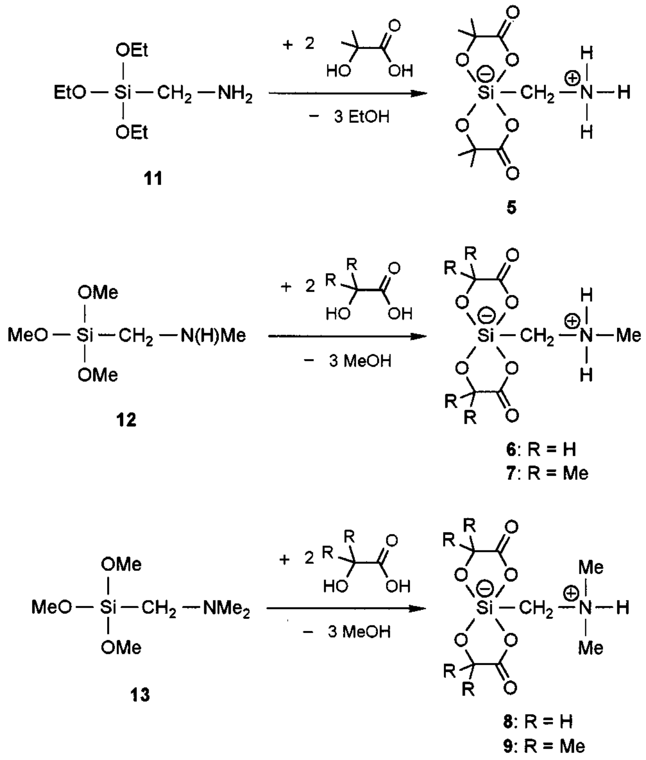
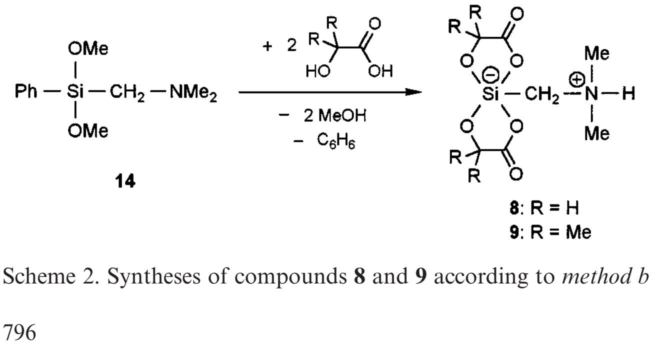


Scheme 1. Syntheses of compounds **5**−**9** according to *method a*

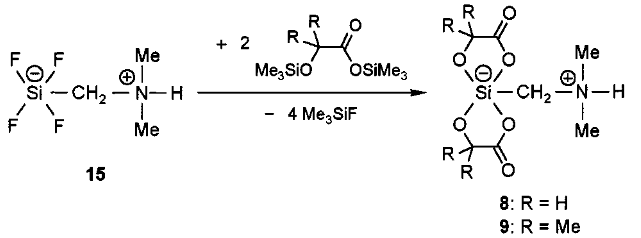
pounds **6**−**9** were isolated, after recrystallization from acetonitrile and drying in vacuo, as colorless crystalline solids (yields: **6**, 77%; **7**, 73%; **8**, 88%; **9**, 79%), whereas compound **5** was obtained as the crystalline hydrate **5**·H_2O (recrystallization from water; yield 78%). Recrystallization of **9** from water also yielded the corresponding hydrate **9**·H_2O which was isolated in almost quantitative yield as a colorless crystalline solid.

Compounds **8** and **9** were synthesized alternatively according to *method b* by reaction of the silane **14** with two mol equivalents of glycolic acid and 2-methyllactic acid, respectively, in acetonitrile at room temperature (Scheme 2). As these syntheses involve a relatively slow Si−C cleavage reaction as rate-determining step, product formation (first crystals formed after several hours) was significantly slower than that observed for *method a*. The syntheses according to *method b* generally yielded directly well-crystallized products which did not need further purification by recrystallization (yields after drying in vacuo: **8**, 98%; **9**, 88%). Crystals of **9**·$2CH_3CN$ (no drying in vacuo) were isolated directly from the reaction mixture.



Scheme 2. Syntheses of compounds **8** and **9** according to *method b*

The third strategy *(method c)* for the preparation of compounds **8** and **9** is based on the reaction of the zwitterionic λ^5*Si*-tetrafluorosilicate **15** with two mol equivalents of $Me_3SiOCH_2C(O)OSiMe_3$ (**16**) and $Me_3SiOCMe_2C(O)OSiMe_3$ (**17**), respectively (Scheme 3). These syntheses were also carried out in acetonitrile at room temperature (first crystals formed after ca. 30 minutes) and the products **8** and **9** were isolated, after recrystallization from acetonitrile and drying in vacuo, as colorless crystalline solids (yields: **8**, 91%; **9**, 79%).



Scheme 3. Syntheses of compounds **8** and **9** according to *method c*

Because of their zwitterionic nature, the high-melting compounds **5**·H_2O, **6**−**9**, **9**·H_2O, and **9**·$2CH_3CN$ are almost insoluble in unpolar organic solvents and also exhibit a very poor solubility in most polar organic solvents. The identity of **5**·H_2O, **6**−**9**, and **9**·H_2O was established by elemental analyses (C, H, N) and solution-state (^1H, ^{13}C, ^{29}Si) and solid-state (^{13}C and ^{29}Si CP/MAS) NMR studies. In addition, the zwitterions **6**−**9** were characterized by mass-spectrometric investigations (FAB MS). Furthermore, crystal structure analyses of compounds **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$ were performed.

Crystal Structure Analyses

Compounds **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$ were structurally characterized by single-crystal X-ray diffraction. The structures of the chiral zwitterions **5** and **7**−**9** in the crystal are depicted in Figures 1−5. In all cases the crystals were found to be built up by pairs of Λ- and Δ-enantiomers. The crystal data and the experimental parameters used for these experiments are summarized in Table 6; selected interatomic distances and angles are listed in Table 1.

The *Si*-coordination polyhedra of the zwitterions **5** and **7**−**9** can be described as somewhat distorted trigonal bipyramids, in which each of the axial positions is occupied by the carboxylate oxygen atoms (transition trigonal bipyramid → square pyramid: **5**·H_2O, 4.4%; **7**, 5.4%; **8**, 14.6%; **9**·H_2O, 8.9%; **9**·$2CH_3CN$, 5.1%; pivot atom C1).[4] In all structures the axial Si−O distances [1.7930(12)−1.822(2) Å] are significantly longer than the equatorial ones [1.656(2)−1.6764(8) Å]. The Si−C distances amount to 1.883(2)−1.896(2) Å. Generally, the structural data obtained for the *Si*-coordination polyhedra of the zwitterions **5** and **7**−**9** are very similar to those calculated for **8** and **10** (see ab initio Studies).

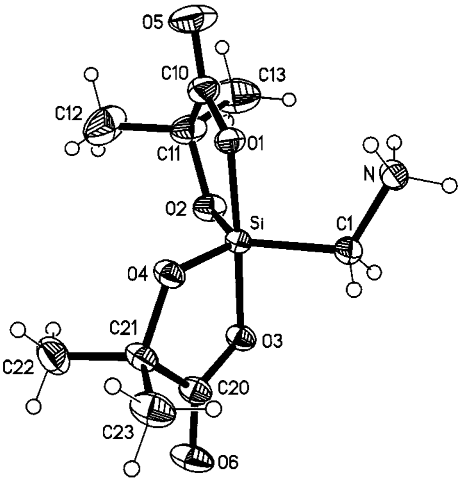


Figure 1. Molecular structure of **5** in the crystal of **5**·H_2O (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

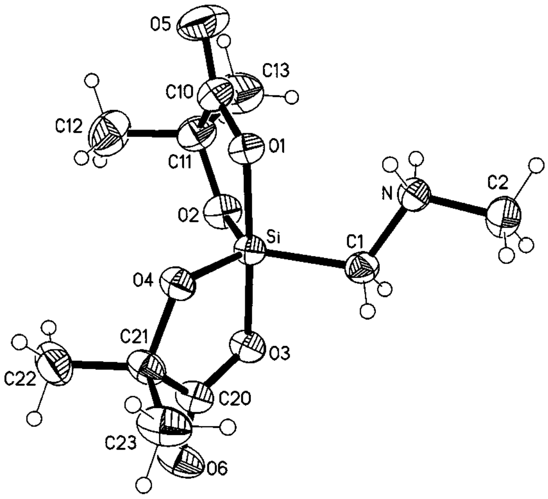


Figure 2. Molecular structure of **7** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

As would be expected from the presence of the potential NH donor functions and potential oxygen acceptor atoms, intra- and intermolecular N−H···O hydrogen bonds between the zwitterions exist in the crystal of **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$. For the hydrates additional intermolecular O−H···O (**5**·H_2O, **9**·H_2O) and N−H···O (**5**·H_2O) hydrogen bonds between the water molecules and the zwitterions were observed. Based on the relevant geometric data, the existence of the hydrogen bonds listed in Table 2 can be assumed.

A bifurcate hydrogen bond [N−H···O1 (intra), N−H···O5 (inter)] leads to the formation of centrosymmetric dimers in the crystal of **8** (Figure 6). These dimers are built up by pairs of enantiomers. The crystal lattices of all the other compounds are characterized by a more complex hydrogen bonding system (Table 2). Although **5**·H_2O, **7**, **9**·H_2O, and **9**·$2CH_3CN$ differ significantly in their hydrogen bonding network, there is at least one common structural feature: in all cases trifurcate hydrogen bonds were observed, each consisting of an intramolecular N−H···O1 interaction and intermolecular N−H···O1 and N−H···O4 interactions.

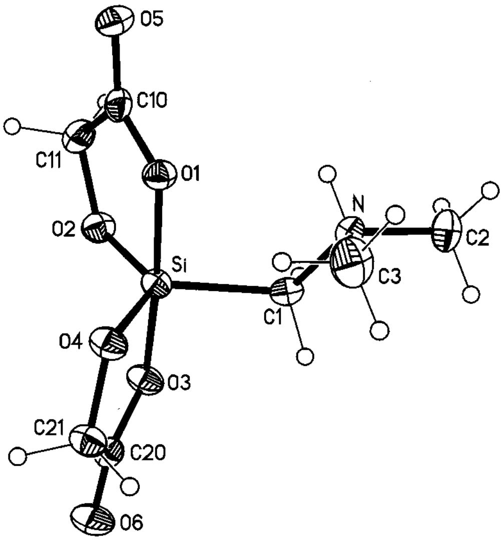


Figure 3. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

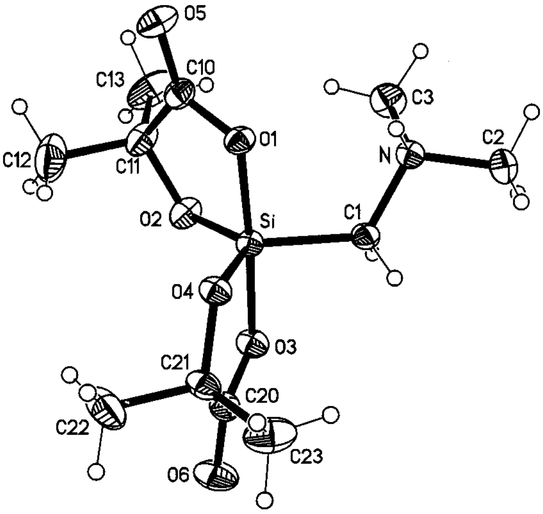


Figure 4. Molecular structure of **9** in the crystal of **9**·H_2O (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

ab initio Studies

The structure and dynamic behavior of the title compounds were investigated by quantum-chemical methods. For this purpose, computational studies of the anionic model species **10** and the zwitterion **8** were performed. The computational methods used are described in the Experimental Section.

As demonstrated for the model species bis[glycolato(2−)-O^1,O^2]hydridosilicate(1−) (**10**), five different idealized geometries (**10a**−**10e**, Figure 7) have to be considered for the

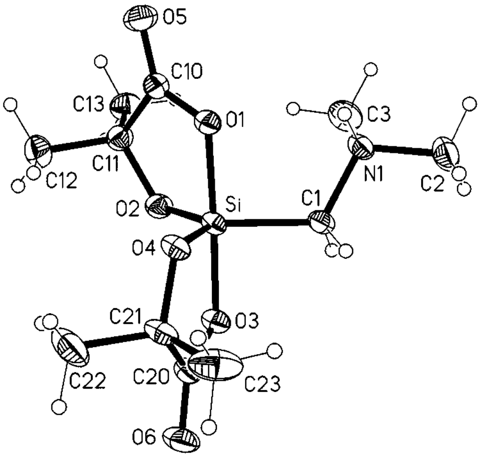


Figure 5. Molecular structure of **9** in the crystal of **9**·$2CH_3CN$ (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

Table 1. Selected interatomic distances [Å] and angles [°] for **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$

	5·H_2O	**7**	**8**	**9**·H_2O	**9**·$2CH_3CN$
Si−O1	1.7943(12)	1.7941(14)	1.822(2)	1.8003(8)	1.8060(12)
Si−O2	1.6623(12)	1.656(2)	1.666(2)	1.6636(8)	1.6656(12)
Si−O3	1.7974(12)	1.8132(14)	1.795(2)	1.8029(8)	1.7930(12)
Si−O4	1.6601(12)	1.6733(14)	1.656(2)	1.6764(8)	1.6751(13)
Si−C1	1.883(2)	1.889(2)	1.893(2)	1.8915(11)	1.896(2)
O1−Si−O2	89.13(6)	89.92(6)	88.50(7)	89.45(4)	89.03(6)
O1−Si−O3	177.17(5)	176.98(5)	175.46(7)	176.06(4)	177.51(6)
O1−Si−O4	89.05(6)	89.20(7)	89.37(7)	88.28(4)	88.59(6)
O1−Si−C1	93.52(6)	94.33(7)	93.96(8)	95.43(4)	93.92(6)
O2−Si−O3	89.94(6)	89.08(6)	87.74(7)	89.58(4)	90.63(6)
O2−Si−O4	120.30(6)	120.59(7)	125.51(8)	122.20(4)	120.98(6)
O2−Si−C1	121.84(7)	121.91(8)	119.93(9)	120.82(5)	122.26(7)
O3−Si−O4	89.11(5)	88.85(6)	90.74(7)	89.01(4)	89.47(6)
O3−Si−C1	89.25(6)	88.62(7)	90.13(8)	88.34(4)	88.34(6)
O4−Si−C1	117.83(7)	117.38(8)	114.54(9)	116.88(5)	116.74(7)

title compounds. For energetic reasons, trigonal bipyramids with the hydrogen (carbon) atom in an axial site and square pyramids with the hydrogen (carbon) atom in a basal position can be excluded. The trigonal-bipyramidal isomers **10a**−**10c** and the square-pyramidal species **10d** are chiral and therefore exist as pairs of Λ- and Δ-enantiomers, whereas the square-pyramidal species **10e** is achiral. Calculations of the vibrational frequencies for **10a**−**10e** have demonstrated that only the isomers **10a**−**10c** represent local minima, the isomer **10a** being the energetically most favorable one (for selected geometric parameters of **10a**−**10e**, see Table 3).[5] This result is in agreement with the experimentally established crystal structures of **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$, indicating that the trigonal-bipyramidal geometry, with the carboxylate oxygen atoms in the axial sites, is indeed the energetically most favorable one. Based on this particular structure, geometry optimizations at the SCF/SVP level were carried out for the zwitterionic λ^5*Si*-silicate **8** (Figure 8).[6] As can be seen from Table 4, the calculated interatomic distances and angles for the *Si*O_4C framework of **8** are in good agreement with the experimentally established values for **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$.

These results suggest that the energetically preferred trigonal-bipyramidal *Si*-coordination polyhedra of **5**−**9**, with the carboxylate oxygen atoms in the axial sites, also play the major role in solution, all compounds being expected to exist as pairs of enantiomers. As demonstrated for the model species **10**, an intramolecular isomerization of the antipodes of **5**−**9** should be possible leading to an inversion of absolute configuration of their chiral trigonal-bipyramidal λ^5*Si*-silicate skeletons (Figure 9). According to the results of ab initio studies, the enantiomers **Λ-10a** and **Δ-10a** can be converted into each other along the reaction coordinate **Λ-10a** $\rightleftharpoons$ $\mathbf{10}^{\neq 2}$ $\rightleftharpoons$ **Δ-10c** $\rightleftharpoons$ $\mathbf{10}^{\neq 3}$ $\rightleftharpoons$ **Λ-10b** $\rightleftharpoons$ $\mathbf{10}^{\neq 1}$ $\rightleftharpoons$ **Δ-10b** $\rightleftharpoons$ $\mathbf{10}^{\neq 3'}$ $\rightleftharpoons$ **Λ-10c** $\rightleftharpoons$ $\mathbf{10}^{\neq 2'}$ $\rightleftharpoons$ **Δ-10a** ($\mathbf{10}^{\neq 1}$ = **10e**; the pairs $\mathbf{10}^{\neq 2}$/$\mathbf{10}^{\neq 2'}$ and $\mathbf{10}^{\neq 3}$/$\mathbf{10}^{\neq 3'}$ are antipodes) (Figure 9).[7,8] The square-pyramidal species $\mathbf{10}^{\neq 1}$ and the trigonal-bipyramidal species $\mathbf{10}^{\neq 2}$ and $\mathbf{10}^{\neq 3}$ are transition states in this isomerization process.[9] Their relative energies amount to 31.4 kJ mol^{-1} ($\mathbf{10}^{\neq 1}$), 47.1 kJ mol^{-1} ($\mathbf{10}^{\neq 2}$), and 70.8 kJ mol^{-1} ($\mathbf{10}^{\neq 3}$). The hydrogen atoms in these transition states occupy an apical ($\mathbf{10}^{\neq 1}$), equatorial ($\mathbf{10}^{\neq 2}$), or axial ($\mathbf{10}^{\neq 3}$) position (for selected geometric data, see Table 3). The conversions **Λ-10b** $\rightleftharpoons$ $\mathbf{10}^{\neq 1}$ $\rightleftharpoons$ **Δ-10b** and the conversions **Λ-10a** $\rightleftharpoons$ $\mathbf{10}^{\neq 2}$ $\rightleftharpoons$ **Δ-10c** (**Δ-10a** $\rightleftharpoons$ $\mathbf{10}^{\neq 2'}$ $\rightleftharpoons$ **Λ-10c**) can be described in terms of a Berry-type mechanism, with the hydrogen atom as the pivot ligand. In contrast, the conversions **Δ-10c** $\rightleftharpoons$ $\mathbf{10}^{\neq 3}$ $\rightleftharpoons$ **Λ-10b** (**Λ-10c** $\rightleftharpoons$ $\mathbf{10}^{\neq 3'}$ $\rightleftharpoons$ **Δ-10b**) differ significantly from a Berry-type mechanism, the transition state being characterized by a distorted trigonal-bipyramidal *Si*-coordination polyhedron with the hydrogen atom in an axial position. As the structure of this transition state is rather twisted [one of the diolato(2−) ligands occupies two equatorial positions], the term "twist mechanism" is suggested for this particular intramolecular isomerization process. The calculated relative energy of the corresponding transition state $\mathbf{10}^{\neq 3}$ (70.8 kJ mol^{-1}) is in good agreement with the experimentally established energy barrier for the isomerization process **Λ-9** $\rightleftharpoons$ **Δ-9** (see VT ^{1}H-NMR Studies of **9**).

NMR Studies of 5·H_2O, 6−9, and 9·H_2O

Compounds **5**·H_2O, **6**−**9**, and **9**·H_2O were studied by ^{1}H, ^{13}C, and ^{29}Si solution-state NMR experiments (solvent [D_6]DMSO) and by ^{13}C and ^{29}Si CP/MAS solid-state NMR experiments.[10] All these investigations were performed at room temperature (for VT ^{1}H-NMR studies of **9**, see next chapter).

The isotropic ^{29}Si chemical shifts obtained in the CP/MAS NMR studies of **5**·H_2O, **6**−**9**, and **9**·H_2O (Table 5) clearly characterize the ^{29}Si resonances as arising from pentacoordinate silicon atoms. In the case of **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$, pentacoordination of silicon was established independently by single-crystal X-ray diffraction (see Crystal Structure Analyses). As the ^{29}Si chemical shifts obtained in the solid-state NMR experiments are very simi-

Table 2. Hydrogen-bonding geometries for **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$ in the crystal

	Donor−H···Acceptor	D−H [Å]	H···A [Å]	D···A [Å]	D−H···A [°]
5·H_2O[a]	N−H1···O1	0.87(2)	2.39(3)	2.744(2)	104.8(18)
	N−H1···O1′	0.87(2)	2.55(2)	3.151(2)	127(2)
	N−H1···O4′	0.87(2)	2.04(2)	2.866(2)	157(2)
	N−H2···O1W	0.95(3)	1.79(3)	2.730(3)	172(2)
	N−H3···O6′	0.90(2)	2.02(2)	2.805(2)	144(2)
	O1W−H1W···O5	0.80(4)	1.97(4)	2.754(3)	167(3)
	O1W−H2W···O2	0.83(4)	2.09(4)	2.894(3)	164(4)
7[b]	N−H2···O1	0.89(2)	2.39(2)	2.786(3)	107.6(16)
	N−H2···O1′	0.89(2)	2.48(2)	3.109(3)	128.1(17)
	N−H2···O4′	0.89(2)	2.08(2)	2.901(3)	152.6(19)
	N−H1···O6′	0.945(19)	1.946(19)	2.809(3)	150.9(17)
8[c]	N−H···O1	0.89(2)	2.38(2)	2.790(2)	108.6(17)
	N−H···O5′	0.89(2)	2.05(2)	2.830(3)	146(2)
9·H_2O[d]	N−H···O1	0.871(15)	2.450(14)	2.8685(12)	110.1(11)
	N−H···O1′	0.871(15)	2.416(15)	3.0640(12)	131.6(12)
	N−H···O4′	0.871(15)	2.126(15)	2.9373(12)	154.7(13)
	O1W−H1···O6	0.92(3)	1.96(3)	2.8695(15)	168(2)
	O1W−H2···O6	0.82(2)	2.10(2)	2.9204(16)	173(3)
9·$2CH_3CN$[e]	N−H···O1	0.89(2)	2.36(2)	2.8115(19)	111.2(16)
	N−H···O1′	0.89(2)	2.43(2)	3.058(2)	128.0(16)
	N−H···O4′	0.89(2)	2.14(2)	2.949(2)	150.7(18)

[a] O1···H1···O1′ = 80.5(7)°, O1···H1···O4′ = 97.1(10)°, O1′···H1···O4′ = 62.6(6)°. − [b] O1···H2···O1′ = 81.8(7)°, O1···H2···O4′ = 98.2(8)°, O1′···H2···O4′ = 63.8(6)°. − [c] O1···H···O5′ = 90.6(8)°. − [d] O1···H···O1′ = 77.9(4)°, O1···H···O4′ = 91.6(5)°, O1′···H···O4′ = 64.1(4)°. − [e] O1···H···O1′ = 79.8(6)°, O1···H···O4′ = 96.8(8)°, O1′···H···O4′ = 64.0(6)°.

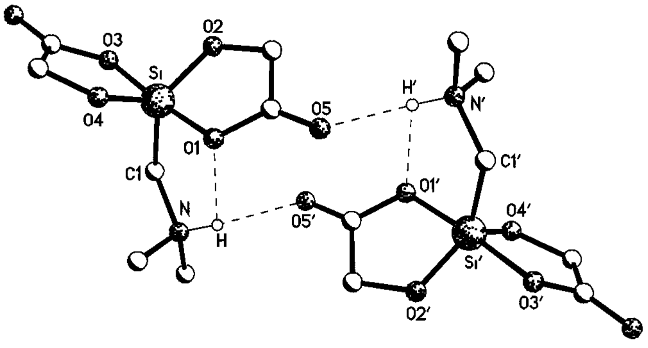
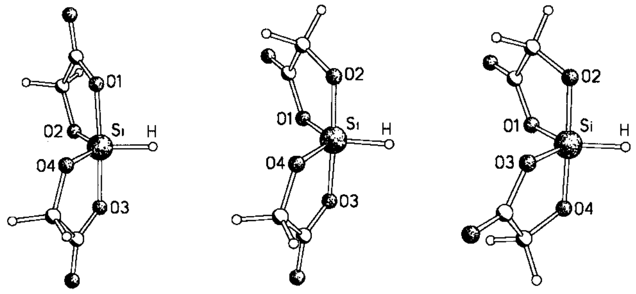


Figure 6. Structure of the centrosymmetric dimer in the crystal of **8**. The hydrogen atoms (except for N*H*) are omitted for clarity

lar to those obtained for the zwitterions **5**−**9** in $[D_6]$DMSO ($\Delta\delta^{29}Si \leq 2.1$; Table 5), it is concluded that pentacoordination of silicon is also present in solution. In addition, the ^1H chemical shifts observed for the NH protons [$\delta^1H = 7.2$ (**5**·H_2O), 7.9 (**6**), 7.8 (**7**), 8.3 (**8**), 8.4 (**9**, **9**·H_2O)] clearly indicate the presence of ammonium groups in solution. Furthermore, the ^{13}C CP/MAS NMR data of **5**·H_2O, **6**−**9**, and **9**·H_2O are very similar to those obtained for these compounds in solution. Thus, the NMR experiments unequivocally demonstrate that the zwitterions **5**−**9** also exist in $[D_6]$DMSO.

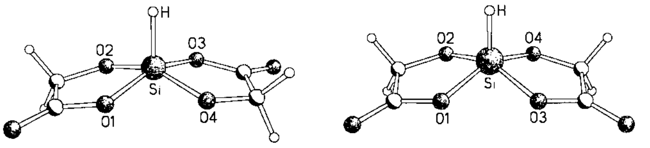
The solution-state NMR data of the zwitterions **5**−**9** are compatible with the presence of one particular species (such as the trigonal-bipyramidal isomer, with the carboxylate oxygen atoms in the axial positions) or with a rapid low-energy interconversion of different isomers (in this context, see ab initio Studies). As the trigonal-bipyramidal structure, with the carboxylate oxygen atoms in the axial sites, is the energetically most favorable one, it is likely to assume that this particular species is also dominant in solution. The chiral nature of the respective λ^5Si-silicate frameworks of **5**−**9** is reflected by the diastereotopism observed for the $SiCH_2N$ (**5**−**9**; AB systems) and $OC(CH_3)_2C$ protons (**5**, **7**, **9**; two separated singlets for the two methyl groups), indicating that the Λ- and Δ-enantiomers of **5**−**9** are configurationally



10a
0 kJ mol^{-1}
(C_2 Symmetry)

10b
22.3 kJ mol^{-1}
(C_1 Symmetry)

10c
42.6 kJ mol^{-1}
(C_2 Symmetry)



10d
29.6 kJ mol^{-1}
(C_2 Symmetry)

10e
31.4 kJ mol^{-1}
(C_S Symmetry)

Figure 7. Calculated structures and relative energies of the isomers **10a**−**10e** as obtained by SCF/SVP geometry optimizations

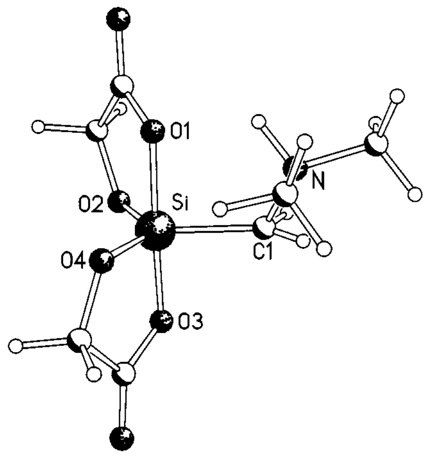


Figure 8. Calculated structure (local minimum) of **8** as obtained by SCF/SVP geometry optimizations

Table 3. Calculated interatomic distances [Å] and angles [°] for the isomers **10a**−**10e** and the transition states $\mathbf{10}^{\ddagger 1}$−$\mathbf{10}^{\ddagger 3}$ as obtained by SCF/SVP geometry optimizations[a]

	10a	**10b**	**10c**	**10d**	**10e**	$\mathbf{10}^{\ddagger 2}$	$\mathbf{10}^{\ddagger 3}$
Si−O1	1.799	1.724	1.732	1.771	1.770	1.735	1.720
Si−O2	1.666	1.722	1.727	1.690	1.697	1.727	1.682
Si−O3	1.799	1.813	1.732	1.771	1.770	1.735	1.852
Si−O4	1.666	1.670	1.727	1.690	1.697	1.727	1.678
Si−H	1.464	1.466	1.469	1.472	1.467	1.470	1.486
O1−Si−O2	87.7	87.8	87.3	87.0	86.4	86.9	94.0
O1−Si−O3	176.8	87.7	111.4	157.0	84.1	124.9	88.7
O1−Si−O4	90.7	117.2	91.5	87.5	151.1	89.0	126.2
O1−Si−H	91.6	121.3	124.3	101.5	102.0	117.6	97.7
O2−Si−O3	90.7	175.4	91.5	87.5	151.1	89.0	87.9
O2−Si−O4	120.4	94.2	177.7	152.0	89.0	171.0	138.6
O2−Si−H	119.8	93.5	91.1	104.0	106.7	94.5	96.3
O3−Si−O4	87.7	87.0	87.3	87.0	86.4	86.9	83.9
O3−Si−H	91.6	89.6	124.3	101.5	102.0	117.6	172.0
O4−Si−H	119.8	121.2	91.1	104.0	106.7	94.5	88.5

[a] The isomer **10e** and the transition state $\mathbf{10}^{\ddagger 1}$ are identical.

stable on the NMR time scale at room temperature. As demonstrated by VT ^{1}H-NMR studies of **9**, the interconversion of the Λ- and Δ-enantiomer is characterized by an energy barrier of 76(1) kJ mol^{-1} ([D$_6$]DMSO), 75(1) kJ mol^{-1} (CD$_3$CN), and 82(2) kJ mol^{-1} (CDCl$_3$) (see next chapter).

VT ^{1}H-NMR Studies of 9

Compound **9** was studied by solution-state ^{1}H-NMR spectroscopy at 300.1 MHz in the temperature range of 21−118°C ([D$_6$]DMSO), 22−94°C (CD$_3$CN), and 24−83°C (CDCl$_3$). The concentrations of **9** were 2.5 mmol L^{-1}, 25 mmol L^{-1}, and 250 mmol L^{-1} ([D$_6$]DMSO), 5.0 mmol L^{-1} (CD$_3$CN), and 2.0 mmol L^{-1} (CDCl$_3$). For all solutions studied, two separated singlets for the diastereotopic methyl groups of the 2-methyllactato(2−) ligands were observed at room temperature, indicating that **Λ-9** and **Δ-9** are configurationally stable on the NMR time scale under these conditions. Upon heating coalescence was observed, indicating a dynamic behavior of the enantiomers of **9** in solution. The temperature dependence of the ^{1}H-NMR spectra of **9** is characterized by complete reversibility (see Figure 10).

For all solutions of **9** in [D$_6$]DMSO (c = 2.5−250 mmol L^{-1}) coalescence was observed at 76°C. The calculated energy barrier (line-shape analysis) for the Λ/Δ-interconversion of the enantiomers of **9** amounts to $\Delta G^{\ddagger}$ = 76(1) kJ mol^{-1} and is independent on the concentration. The activation free enthalpy is similar in CD$_3$CN [$\Delta G^{\ddagger}$ = 75(1) kJ mol^{-1}] and somewhat higher in CDCl$_3$ [$\Delta G^{\ddagger}$ = 82(2) kJ mol^{-1}]. The coalescence temperature in CD$_3$CN was 66°C. As coalescence in CDCl$_3$ could not be observed below the boiling point of the solvent, the respective coalescence temperature could not be established directly in these experiments and therefore had to be determined by simulations (calculated coalescence temperature ca. 90°C).

As the coalescence temperature does not depend on the concentration (studies with **9** in [D$_6$]DMSO; c = 2.5−250 mmol L^{-1}), first-order kinetics for the Λ/Δ-isomerization can be assumed suggesting an intramolecular process. This is in accordance with the results obtained by the ab initio

Table 4. Selected calculated interatomic distances [Å] and angles [°] for **8** and the differences between these data and the corresponding experimental values[a] for **5**·H$_2$O, **7**, **8**, **9**·H$_2$O, and **9**·2CH$_3$CN

	8	Δ(**8**/**5**·H$_2$O)	Δ(**8**/**7**)	Δ(**8**/**8**)	Δ(**8**/**9**·H$_2$O)	Δ(**8**/**9**·2CH$_3$CN)
Si−O1	1.810	+0.016	+0.016	−0.012	+0.010	+0.004
Si−O2	1.649	−0.013	−0.007	−0.017	−0.015	−0.017
Si−O3	1.746	−0.051	−0.067	−0.049	−0.057	−0.047
Si−O4	1.653	−0.007	−0.020	−0.003	−0.023	−0.022
Si−C1	1.939	+0.056	+0.050	+0.046	+0.048	+0.043
O1−Si−O2	87.0	−2.1	−2.9	−1.5	−2.5	−2.0
O1−Si−O3	177.7	+0.5	+0.7	+2.2	+1.6	+0.2
O1−Si−O4	92.0	+3.0	+2.8	+2.6	+3.7	+3.4
O1−Si−C1	87.7	−5.8	−6.6	−6.3	−7.7	−6.2
O2−Si−O3	93.1	+3.2	+4.0	+5.4	+3.5	+2.5
O2−Si−O4	122.8	+2.5	+2.2	−2.7	+0.6	+1.8
O2−Si−C1	121.0	−0.8	−0.9	+1.1	+0.2	−1.3
O3−Si−O4	89.8	+0.7	+1.0	−0.9	+0.8	+0.3
O3−Si−C1	90.3	+1.1	+1.7	+0.2	+2.0	+2.0
O4−Si−C1	116.1	−1.7	−1.3	+1.6	−0.8	−0.6

[a] Experimental data taken from Table 2.

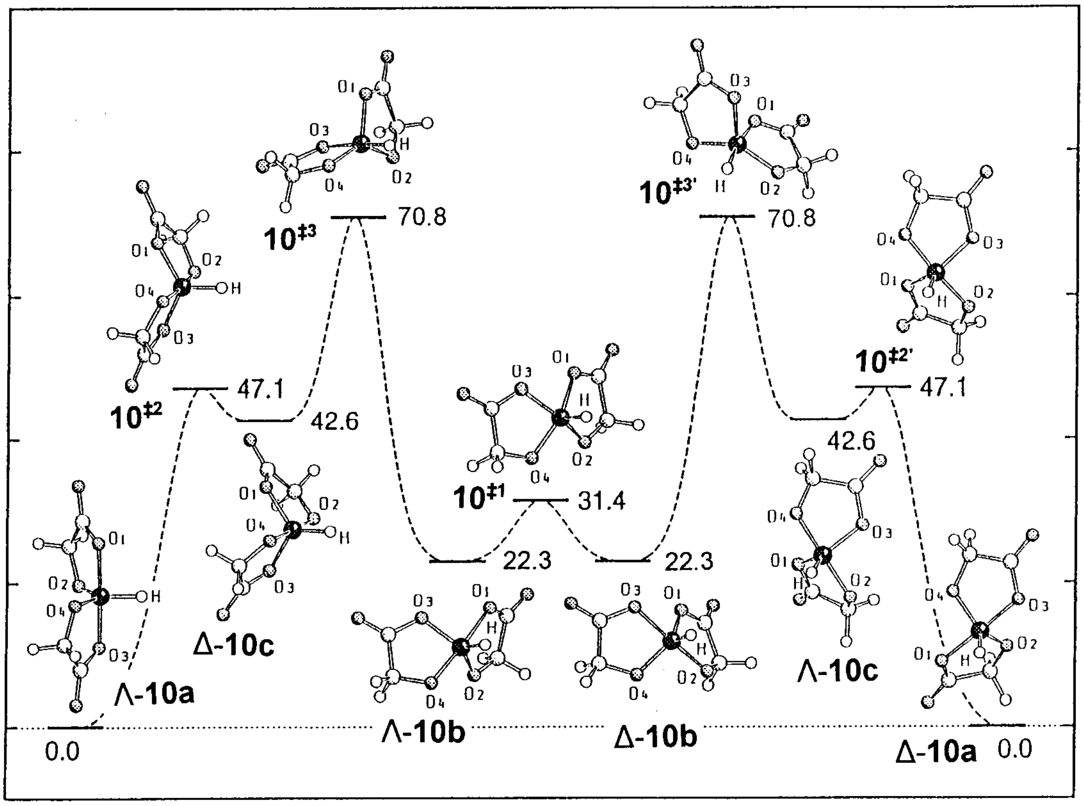


Figure 9. Calculated intramolecular reaction path for the isomerization of **10a** (Λ-**10a** ⇌ Δ-**10a**), showing the structures and relative energies of the local minima **10a**−**10c** and of the transition states $\mathbf{10}^{\ddagger1}$ (= **10e**), $\mathbf{10}^{\ddagger2}$ ($\mathbf{10}^{\ddagger2'}$), and $\mathbf{10}^{\ddagger3}$ ($\mathbf{10}^{\ddagger3'}$)

Table 5. ^{29}Si-NMR data for **5**·H_2O, **6**−**9**, and **9**·H_2O in solution ([D$_6$]DMSO) and in the crystal (chemical shifts in ppm; spectra recorded at room temperature)

Compound	δ(solution)	δ(crystal)[a]
5·H_2O	−98.0	−96.4
6	−89.2	−88.7
7	−99.2	−98.1
8	−90.3	−88.6
9	−100.5	−100.9, −100.1
9·H_2O	−100.5	−98.4

[a] Isotropic chemical shifts obtained by ^{29}Si CP/MAS NMR experiments.

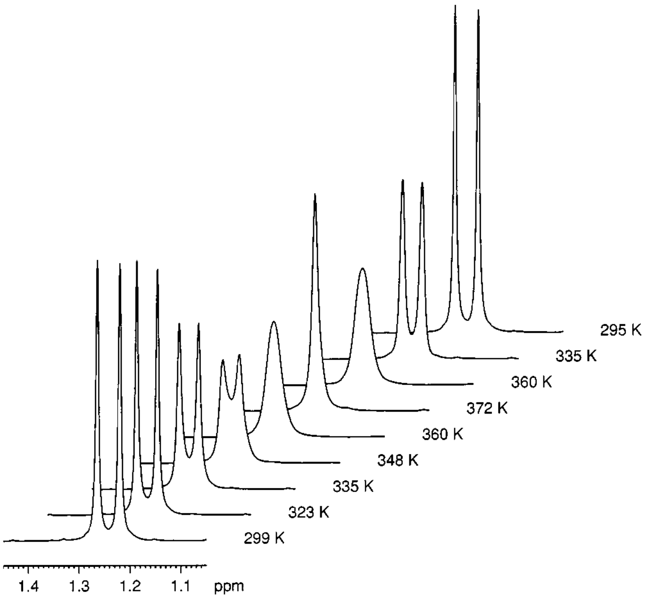


Figure 10. Temperature dependence of the ^{1}H-NMR signals for the two diastereotopic methyl groups of the 2-methyllactato(2−) ligands of **9** (solution in [D$_6$]DMSO; c = 250 mmol L^{-1}, 300.1 MHz) upon heating from 299 K to 372 K and subsequent cooling to 295 K

studies with the model species **10** (calculated energy barrier for the intramolecular Λ/Δ-isomerization: 70.8 kJ mol^{-1}).

Conclusions

The chiral title compounds exist as pairs of Λ- and Δ-enantiomers in the solid state and in solution. The trigonal-bipyramidal structure of the respective λ^5*Si*-silicate skeletons, with the carboxylate oxygen atoms in the axial sites, is the energetically most stable one. The Λ- and Δ-enantiomers of the zwitterionic λ^5*Si*-silicates **5**−**9** are configurationally stable in solution on the NMR time scale (organic solvents, room temperature) and undergo an intramolecular Λ/Δ-isomerization with an activation free enthalpy of ca. 75−80 kJ mol^{-1} (experimentally established for **9**; calculated energy barrier for **10**: 70.8 kJ mol^{-1}).

Experimental Section

General Procedures: All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. − Melting points were determined with a Leitz Biomed microscope equipped with a heater (Leitz, Model M 350). − The ^{1}H, ^{13}C, 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). $CDCl_3$, CD_3CN, C_6D_6, and $[D_6]DMSO$ were used as solvents. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, $\delta = 7.24$; $CDCl_3$), CHD_2CN (^{1}H, $\delta = 1.94$; CD_3CN), C_6HD_5 (^{1}H, $\delta = 7.28$; C_6D_6), C_6D_6 (^{13}C, $\delta = 128.0$; C_6D_6), $[D_5]DMSO$ (^{1}H, $\delta = 2.50$; $[D_6]DMSO$), $[D_6]DMSO$ (^{13}C, $\delta = 39.43$; $[D_6]DMSO$), and external TMS (^{29}Si, $\delta = 0$; C_6D_6, $[D_6]DMSO$). Assignment of the ^{13}C-NMR data was supported by DEPT 135 experiments. ^{13}C and ^{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. 20−300 mg of sample [^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz; TMS as external standard ($\delta = 0$); spinning rate 5000 Hz; contact time 5 ms; 90° ^{1}H transmitter pulse length 4.0 µs; repetition time 5 s (^{13}C) or 4 s (^{29}Si)]. − Mass spectra were obtained with a Finnigan MAT-8430 mass spectrometer (FAB MS; 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source) or 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, and ^{28}Si. − Elemental analyses were determined by Beller, Mikroanalytisches Laboratorium (Göttingen, Germany).

(Ammoniomethyl)bis[2-methyllactato(2−)-O^1,O^2]silicate Hydrate (**5**$\cdot H_2O$): A solution of **11** (967 mg, 5.00 mmol) in acetonitrile (2.5 mL) was added dropwise at room temperature within 2 min to a solution of 2-methyllactic acid (1.04 g, 9.99 mmol) in acetonitrile (22.5 mL). The reaction mixture was stirred for 1 min and then kept undisturbed at room temperature for 24 h (formation of a precipitate ca. 8 min after combining the reactants). The precipitate (compound **5**, crude product) was filtered off, washed with cold acetonitrile (3 × 5 mL), dissolved in water (40 mL), and the solution then kept undisturbed at room temperature for 6 d (slow evaporation of the water). Compound **5**$\cdot H_2O$ was isolated in 78% yield (1.10 g) as a colorless crystalline product. Mp 264°C. − ^{1}H NMR ($[D_6]DMSO$, 300.1 MHz): $\delta = 1.21$ (s, 6 H, CCH_3), 1.25 (s, 6 H, CCH_3), 2.01 and 2.19 (AB system, $J_{AB} = -16.0$ Hz, 2 H, $SiCH_2N$), 3.33 (s, 2 H, H_2O), 7.2 (broad s, 3 H, NH_3). − $^{13}C\{^{1}H\}$ NMR ($[D_6]DMSO$, 75.5 MHz): $\delta = 26.8$ ($C\mathit{C}H_3$), 27.6 ($C\mathit{C}H_3$), 28.1 ($SiCH_2N$), 73.7 ($O\mathit{C}C_3$), 178.5 (C=O). − ^{13}C CP/MAS NMR (36854 transients): $\delta = 24.7$ and 27.3 ($C\mathit{C}H_3$, $SiCH_2N$), 76.3 ($O\mathit{C}C_3$), 180.7 (C=O), 182.5 (C=O). − $^{29}Si\{^{1}H\}$ NMR ($[D_6]DMSO$, 59.6 MHz): $\delta = -98.0$. − ^{29}Si CP/MAS NMR (13168 transients): $\delta = -96.4$. − $C_9H_{19}NO_7Si$ (281.3): calcd C 38.42, H 6.81, N 4.98; found C 38.7, H 6.6, N 4.9.

Bis[glycolato(2−)-O^1,O^2][(methylammonio)methyl]silicate (**6**): The synthesis was carried out analogously to that of compound **5** by combining a solution of **12** (826 mg, 5.00 mmol) in acetonitrile (2.5 mL) with a solution of glycolic acid (761 mg, 10.0 mmol) in acetonitrile (22.5 mL) (spontaneous formation of a precipitate after combining the reactants). Compound **6** was isolated in 77% yield (852 mg) as a colorless crystalline product. Mp 165°C. − ^{1}H NMR ($[D_6]DMSO$, 300.1 MHz): $\delta = 2.27$ and 2.32 (AB system, $J_{AB} = -15.7$ Hz, 2 H, $SiCH_2N$), 2.46 (s, 3 H, NCH_3), 3.92 (s, 4 H, OCH_2C), 7.9 (broad s, 2 H, NH_2). − $^{13}C\{^{1}H\}$ NMR ($[D_6]DMSO$, 75.5 MHz): $\delta = 36.1$ (NCH_3), 39.0 ($SiCH_2N$), 62.8 ($O\mathit{C}H_2C$), 174.0 (C=O). − ^{13}C CP/MAS NMR (3540 transients): $\delta = 37.2$, 38.4, 39.5, and 41.3 (NCH_3, $SiCH_2N$), 62.6 ($O\mathit{C}H_2C$), 63.3 ($O\mathit{C}H_2C$), 64.1 ($O\mathit{C}H_2C$), 174.5 (C=O), 179.2 (C=O), 180.5 (C=O). − $^{29}Si\{^{1}H\}$ NMR ($[D_6]DMSO$, 59.6 MHz): $\delta = -89.2$. − ^{29}Si CP/MAS NMR (215 transients): $\delta = -88.7$. − FAB MS (positive ions): *m/z* (%) = 222 (32) [$M + H^+$], 154 (100) [matrix]. − $C_6H_{11}NO_6Si$ (221.2): calcd C 32.57, H 5.01, N 6.33; found C 32.5, H 5.2, N 6.2.

[(Methylammonio)methyl]bis[2-methyllactato(2−)-O^1,O^2]silicate (**7**): The synthesis was carried out analogously to that of compound **5** by combining a solution of **12** (826 mg, 5.00 mmol) in acetonitrile (2.5 mL) with a solution of 2-methyllactic acid (1.04 g, 9.99 mmol) in acetonitrile (22.5 mL) (spontaneous formation of a precipitate after combining the reactants). Compound **7** was isolated in 73% yield (1.01 g) as a colorless crystalline product. Mp 310°C (dec.) − ^{1}H NMR ($[D_6]DMSO$, 300.1 MHz): $\delta = 1.21$ (s, 6 H, CCH_3), 1.26 (s, 6 H, CCH_3), 2.18 and 2.39 (AB system, $J_{AB} = -15.9$ Hz, 2 H, $SiCH_2N$), 2.47 (s, 3 H, NCH_3), 7.8 (broad s, 2 H, NH_2). − $^{13}C\{^{1}H\}$ NMR ($[D_6]DMSO$, 75.5 MHz): $\delta = 26.7$ ($C\mathit{C}H_3$), 27.6 ($C\mathit{C}H_3$), 36.2 (NCH_3), 39.2 ($SiCH_2N$), 73.8 ($O\mathit{C}C_3$), 178.4 (C=O). − ^{13}C CP/MAS NMR (109 transients): $\delta = 25.4$ ($C\mathit{C}H_3$), 27.2 ($C\mathit{C}H_3$), 27.8 ($C\mathit{C}H_3$), 28.4 ($C\mathit{C}H_3$), 38.7 (NCH_3), 41.4 ($SiCH_2N$), 75.3 ($O\mathit{C}C_3$), 76.6 ($O\mathit{C}C_3$), 179.6 (C=O), 183.7 (C=O). − $^{29}Si\{^{1}H\}$ NMR ($[D_6]DMSO$, 59.6 MHz): $\delta = -99.2$. − ^{29}Si CP/MAS NMR (293 transients): $\delta = -98.1$. − FAB MS (positive ions): *m/z* (%) = 278 (30) [$M + H^+$], 154 (100) [matrix]. − $C_{10}H_{19}NO_6Si$ (277.3): calcd C 43.31, H 6.90, N 5.05; found C 43.4, H 6.9, N 5.1.

[(Dimethylammonio)methyl]bis[glycolato(2−)-O^1,O^2]silicate (**8**): *Method a:* The synthesis was carried out analogously to that of compound **5** by combining a solution of **13** (896 mg, 5.00 mmol) in acetonitrile (2.5 mL) with a solution of glycolic acid (761 mg, 10.0 mmol) in acetonitrile (22.5 mL) (spontaneous formation of a precipitate after combining the reactants). Compound **8** was isolated in 88% yield (1.04 g) as a colorless crystalline product. Mp 221°C (dec). − ^{1}H NMR ($[D_6]DMSO$, 300.1 MHz): $\delta = 2.51$ and 2.63 (AB system, $J_{AB} = -15.9$ Hz, 2 H, $SiCH_2N$), 2.73 (s, 6 H, NCH_3), 3.94 (s, 4 H, OCH_2C), 8.3 (broad s, 1 H, NH). − $^{13}C\{^{1}H\}$ NMR ($[D_6]DMSO$, 75.5 MHz): $\delta = 45.8$ (NCH_3), 49.3 ($SiCH_2N$), 62.7 ($O\mathit{C}H_2C$), 173.9 (C=O). − ^{13}C CP/MAS NMR (1437 transients): $\delta = 44.3$ (NCH_3), 49.0 (NCH_3), 50.8 ($SiCH_2N$), 64.0 ($O\mathit{C}H_2C$), 64.9 ($O\mathit{C}H_2C$), 176.6 (C=O), 179.9 (C=O). − $^{29}Si\{^{1}H\}$ NMR ($[D_6]DMSO$, 59.6 MHz): $\delta = -90.3$. − ^{29}Si CP/MAS NMR (20 transients): $\delta = -88.6$. − FAB MS (positive ions): *m/z* (%) = 236 (39) [$M + H^+$], 154 (100) [matrix]. − $C_7H_{13}NO_6Si$ (235.3): calcd C 35.74, H 5.57, N 5.95; found C 35.2, H 5.6, N 6.1.

Method b: A solution of **14** (1.13 g, 5.01 mmol) in acetonitrile (2.5 mL) was added at room temperature to a solution of glycolic acid (761 mg, 10.0 mmol) in acetonitrile (22.5 mL). The reaction mixture was stirred for 1 min and then kept undisturbed at room temperature for 7 d (formation of a precipitate ca. 18 h after combining the reactants). The precipitate was isolated by filtration, washed with cold acetonitrile (3 × 5 mL), and then dried in vacuo (0.01 Torr, 20°C, 12 h) to give 1.15 g (yield 98%) of colorless crystals. Mp 221°C (dec). − $C_7H_{13}NO_6Si$ (235.3): calcd C 35.74, H 5.57, N 5.95; found C 35.7, H 5.6, N 6.3. For spectroscopic data, see above.

Method c: **16** (1.36 g, 6.17 mmol) was added to a stirred solution of **15** (502 mg, 3.08 mmol) in acetonitrile (20 mL) (formation of a precipitate ca. 20 min after combining the reactants) and the reaction mixture stirred at room temperature for 24 h. The precipitate was filtered off and recrystallized from acetonitrile. The product was isolated by filtration and then dried in vacuo (0.01 Torr, 20°C, 4 h) to give 658 mg (yield 91%) of colorless crystals. Mp 221°C (dec). − $C_7H_{13}NO_6Si$ (235.3): calcd C 35.74, H 5.57, N 5.95; found C 35.8, H 5.4, N 6.1. For spectroscopic data, see above.

[(Dimethylammonio)methyl]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate (**9**): *Method a:* The synthesis was carried out analogously to that of compound **5** by combining a solution of **13** (896 mg, 5.00 mmol) in acetonitrile (2.5 mL) with a solution of 2-methyllactic acid (1.04 g, 9.99 mmol) in acetonitrile (22.5 mL) (spontaneous formation of a precipitate after combining the reactants). Compound **9** was isolated in 79% yield (1.15 g) as a colorless crystalline product. Mp 242°C. − ^1H NMR ([D_6]DMSO, 300.1 MHz): δ = 1.21 (s, 6 H, CCH_3), 1.26 (s, 6 H, CCH_3), 2.46 and 2.66 (AB system, J_{AB} = −15.9 Hz, 2 H, $SiCH_2N$), 2.75 (s, 6 H, NCH_3), 8.4 (broad s, 1 H, NH). − $^{13}C\{^1H\}$ NMR ([D_6]DMSO, 75.5 MHz): δ = 26.6 (CCH_3), 27.5 (CCH_3), 46.4 (NCH_3), 50.2 ($SiCH_2N$), 73.7 (OCC_3), 178.3 (C=O). − ^{13}C CP/MAS NMR (912 transients): δ = 24.8−29.7 (CCH_3), 47.4 (NCH_3), 48.6 (NCH_3), 51.5 ($SiCH_2N$), 52.2 ($SiCH_2N$), 75.7 (OCC_3), 76.2 (OCC_3), 177.1 (C=O), 177.7 (C=O), 178.4 (C=O), 182.0 (C=O). − $^{29}Si\{^1H\}$ NMR ([D_6]DMSO, 59.6 MHz): δ = −100.5. − ^{29}Si CP/MAS NMR (54 transients): δ = −100.9, −100.1. − FAB MS (positive ions): *m/z* (%) = 292 (100) [$M + H^+$]. − $C_{11}H_{21}NO_6Si$ (291.4): calcd C 45.34, H 7.26, N 4.81; found C 45.9, H 7.3, N 4.9.

Method b: The synthesis was carried out analogously to that of **8** *(method b)* by combining a solution of **14** (1.13 g, 5.01 mmol) in acetonitrile (2.5 mL) with a solution of 2-methyllactic acid (1.04 g, 9.99 mmol) in acetonitrile (22.5 mL) (first crystals formed ca. 40 h after combining the reactants). Compound **9** was isolated in 88% yield (1.28 g) as a colorless crystalline product. Mp 242°C. − $C_{11}H_{21}NO_6Si$ (291.4): calcd C 45.34, H 7.26, N 4.81; found C 45.1, H 7.4, N 4.9. For spectroscopic data, see above.

Method c: The synthesis was carried out analogously to that of **8** *(method c)* by combining a solution of **17** (2.51 g, 10.1 mmol) with a solution of **15** (770 mg, 4.72 mmol) in acetonitrile (20 mL) (formation of a precipitate ca. 30 min after combining the reactants). Compound **9** was isolated in 79% yield (1.09 g) as a colorless crystalline product. Mp 242°C. − $C_{11}H_{21}NO_6Si$ (291.4): calcd C 45.34, H 7.26, N 4.81; found C 45.3, H 7.1, N 4.8. For spectroscopic data, see above.

[(Dimethylammonio)methyl]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate Hydrate (**9**$\cdot H_2O$): Compound **9** (291 mg, 999 µmol) was dissolved in water (10 mL) and the solution kept undisturbed at room temperature for 6 d (slow evaporation of the water). Compound **9**$\cdot H_2O$ was isolated in 99% yield (306 mg) as a colorless crystalline product. Mp 276°C. − ^1H NMR ([D_6]DMSO, 300.1 MHz): the NMR data were identical with those of **9**, with an additional resonance signal at δ = 3.33 (s, 2 H, H_2O). − $^{13}C\{^1H\}$ NMR ([D_6]DMSO, 75.5 MHz): the NMR data were identical with those of **9**. − ^{13}C CP/MAS NMR (204 transients): δ = 26.2 (CCH_3), 27.0 (CCH_3), 28.5 (CCH_3), 30.4 (CCH_3), 47.3 (NCH_3), 49.3 (NCH_3), 51.1 ($SiCH_2N$), 75.8 (OCC_3), 76.3 (OCC_3), 181.4 (C=O). − $^{29}Si\{^1H\}$ NMR ([D_6]DMSO, 59.6 MHz): the NMR data were identical with those of **9**. − ^{29}Si CP/MAS NMR (200 transients): δ = −98.4 − $C_{11}H_{23}NO_7Si$ (309.4): calcd C 42.70, H 7.49, N 4.53; found C 42.4, H 7.4, N 4.4.

[(Dimethylammonio)methyl]bis[2-methyllactato(2−)-*O*^{1},*O*^{2}]silicate−Diacetonitrile (**9**$\cdot 2CH_3CN$): The synthesis was carried out analogously to that of **9** *(method b)*, except for the isolation by filtration and drying of the crystals formed. The crystal used for the X-ray diffraction study was taken directly from the reaction mixture. Attempts to characterize the bulk material after filtration and careful drying gave unsatisfactory results due to the loss of acetonitrile. Drying in vacuo at room temperature resulted in a complete loss of acetonitrile.

(Aminomethyl)triethoxysilane (**11**): Synthesis according to ref.[11]

Trimethoxy[(methylamino)methyl]silane (**12**): A mixture of (chloromethyl)trimethoxysilane (synthesis according to ref.[12]) (17.1 g, 100 mmol) and methylamine (15.5 g, 499 mmol) was heated in an autoclave at 120°C/20 bar for 16 h. After the reaction mixture was cooled to room temperature, the excess methylamine was evaporated and *n*-pentane (100 mL) added to the residue. The resulting precipitate was filtered off and the solvent removed from the filtrate under reduced pressure. The oily residue was distilled in vacuo over a Vigreux column to give 7.60 g (yield 46%) of a colorless liquid. Bp 40°C/6 Torr. − ^1H NMR (C_6D_6, 300.1 MHz): δ = 0.8 (broad s, 1 H, NH), 2.27 (s, 2 H, $SiCH_2N$), 2.38 (s, 3 H, NCH_3), 3.60 (s, 9 H, OCH_3). − $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ = 36.4 ($SiCH_2N$), 41.0 (NCH_3), 50.5 (OCH_3). − $^{29}Si\{^1H\}$ NMR (C_6D_6, 59.6 MHz): δ = −47.7. − EI MS: *m/z* (%) = 165 (14) [M^+], 121 (22) [$M^+ - CH_2N(H)CH_3$], 44 (100) [$CH_2{=}N(H)CH_3^+$]. − $C_5H_{15}NO_3Si$ (165.3): calcd C 36.34, H 9.15, N 8.48; found C 36.1, H 8.9, N 8.1.

[(Dimethylamino)methyl]trimethoxysilane (**13**): Synthesis according to ref.[2a]

[(Dimethylamino)methyl]dimethoxy(phenyl)silane (**14**): The synthesis was carried out analogously to that of **12** by treating (chloromethyl)dimethoxy(phenyl)silane (synthesis according to ref.[12]) (12.3 g, 56.8 mmol) with an excess of dimethylamine (6.92 g, 153 mmol). Compound **14** was isolated in 81% yield (10.4 g) as a colorless liquid. Bp 115°C/6 Torr. − ^1H NMR (C_6D_6, 300.1 MHz): δ = 2.31 (s, 2 H, $SiCH_2N$), 2.31 (s, 6 H, NCH_3), 3.61 (s, 6 H, OCH_3), 7.3−7.4 and 7.9−8.1 (m, 5 H, SiC_6H_5). − $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ = 47.7 ($SiCH_2N$), 49.7 (NCH_3), 50.5 (OCH_3), 128.1 (C-3/C-5, SiC_6H_5), 130.4 (C-4, SiC_6H_5), 133.7 (C-1, SiC_6H_5), 134.9 (C-2/C-6, SiC_6H_5). − $^{29}Si\{^1H\}$ (C_6D_6, 59.6 MHz): δ = −23.1. − EI MS: *m/z* (%) = 225 (2) [M^+], 210 (6) [$M^+ - CH_3$], 167 (8) [$M^+ - CH_2N(CH_3)_2$] 58 (100) [$CH_2{=}N(CH_3)_2^+$]. − $C_{11}H_{19}NO_2Si$ (225.4): calcd C 58.63, H 8.50, N 6.22; found C 59.0, H 8.6, N 6.0.

[(Dimethylammonio)methyl]tetrafluorosilicate (**15**): Synthesis according to ref.[2k]

(Trimethylsilyloxy)acetic Acid Trimethylsilyl Ester (**16**): Synthesis according to ref.[13]

2-Methyl-2-(trimethylsilyloxy)propionic Acid Trimethylsilyl Ester (**17**): Synthesis according to ref.[14]

Crystal Structure Analyses: Suitable single crystals of **5**$\cdot H_2O$ and **9**$\cdot H_2O$ were obtained by crystallization of **5** and **9** from water (slow evaporation of the solvent at room temperature), single crystals of **7** and **8** were obtained by crystallization from acetonitrile (slow cooling of a boiling saturated solution to room temperature). A suitable single crystal of **9**$\cdot 2CH_3CN$ was isolated directly from the reaction mixture (synthesis according to *method b*). The crystals were mounted on a glass fiber and then transferred to the cold gas stream of the diffractometer [**5**$\cdot H_2O$, **9**$\cdot H_2O$: Syntex-R3 diffractometer; **7**: Stoe STADI-4 diffractometer; **8**: Enraf-Nonius CAD4 diffractometer; **9**$\cdot 2CH_3CN$: Stoe IPDS; monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å)]. For compound **7** a semiempirical absorption correction (ψ scans) was applied. All structures were solved by direct methods.[15] All non-hydrogen atoms were refined anisotropically.[16] For the structures of **7**, **8**, **9**$\cdot H_2O$, and **9**$\cdot 2CH_3CN$ a riding model was employed in the refinement of the CH hydrogen atom positions; for the structure of **5**$\cdot H_2O$ the CH hydrogen atoms were localized in difference Fourier syntheses and

Table 6. Crystal data and experimental parameters for the crystal structure analyses of **5**·H_2O, **7**, **8**, **9**·H_2O, and **9**·$2CH_3CN$

Compound	**5**·H_2O	**7**	**8**	**9**·H_2O	**9**·$2CH_3CN$
empirical formula	$C_9H_{19}NO_7Si$	$C_{10}H_{19}NO_6Si$	$C_7H_{13}NO_6Si$	$C_{11}H_{23}NO_7Si$	$C_{15}H_{27}N_3O_6Si$
formula mass [g mol^{-1}]	281.34	277.35	235.27	309.39	373.49
collection T [K]	203(2)	203(2)	173(2)	203(2)	173(2)
λ(Mo Kα) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$Pbca$ (61)	$P2_1/c$ (14)	$Pbca$ (61)
a [Å]	9.050(3)	8.943(5)	7.7606(9)	9.0530(11)	13.207(3)
b [Å]	12.917(4)	12.993(9)	12.734(3)	12.286(2)	14.367(3)
c [Å]	13.122(4)	13.111(9)	20.372(7)	13.927(2)	21.097(4)
β [deg]	106.56(2)	106.92(5)	90	96.526(12)	90
V [Å^3]	1470.3(8)	1458(2)	2013.3(8)	1539.0(4)	4003.1(14)
Z	4	4	8	4	8
D(calcd) [g cm^{-3}]	1.271	1.264	1.552	1.335	1.239
μ [mm^{-1}]	0.183	0.179	0.244	0.181	0.151
F(000)	600	592	992	664	1600
crystal dimens [mm]	0.4×0.4×0.2	0.6×0.3×0.3	0.7×0.5×0.4	0.8×0.6×0.6	0.3×0.3×0.2
2θ range [deg]	5.66−60.00	4.52−54.00	4.00−49.94	4.44−58.02	4.62−49.52
index ranges	$-12 \leq h \leq 12$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$	$0 \leq h \leq 11$, $0 \leq k \leq 16$, $-16 \leq l \leq 16$	$-2 \leq h \leq 9$, $0 \leq k \leq 15$, $-24 \leq l \leq 24$	$-12 \leq h \leq 12$, $-11 \leq k \leq 16$, $0 \leq l \leq 19$	$-15 \leq h \leq 15$, $-14 \leq k \leq 16$, $-22 \leq l \leq 24$
no. of coll reflns	16726	3160	4018	4422	12253
no. of indep reflns	4288	2961	1766	4091	3416
R_{int}	0.0570	0.0317	0.0278	0.0212	0.0789
no. of reflns used	4288	2961	1766	4091	3416
no. of parameters	239	177	143	200	238
S[a]	1.045	1.049	1.036	1.046	0.907
weight params a/b[b]	0.0540/0.4089	0.0845/0.1256	0.0353/0.9794	0.0415/0.4621	0.0661/0
$R1$[c] [$I > 2\sigma(I)$]	0.0462	0.0401	0.0330	0.0296	0.0431
$wR2$[d] (all data)	0.1138	0.1188	0.0802	0.0847	0.1094
extinction coefficient	−	0.005(2)	0.0019(5)	0.0213(13)	−
max/min res electron density [e Å^{-3}]	+0.552/−0.580	+0.442/−0.402	+0.254/−0.323	+0.357/−0.261	+0.264/−0.381

[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] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

refined freely. In all cases, the positions of the NH and OH hydrogen atoms were localized in difference Fourier syntheses and refined freely.

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-101620 (**5**·H_2O), CCDC-101621 (**7**), CCDC-101622 (**8**), CCDC-101623 (**9**·H_2O), and CCDC-101624 (**9**·$2CH_3CN$). 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].

Computational Methods: Geometry optimizations at the SCF/SVP level for the anionic model species **10** and the zwitterion **8** were performed using the TURBOMOLE program system.[17] 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 **10** include the single point MP2 energy (SVP basis set) and the zero point vibrational energy.

VT ^{1}H-NMR Studies of 9: The experiments were carried out analogously to the standard ^{1}H-NMR measurements using a Bruker DRX-300 NMR spectrometer. [D$_6$]DMSO, CD_3CN, and $CDCl_3$ were used as solvents. The thermocouple used with the probe was calibrated for high temperatures according to ref.[18] using a 80% solution of 1,2-ethanediol in [D$_6$]DMSO. Spectra were recorded in the temperature range of 21−118°C ([D$_6$]DMSO), 22−94°C (CD_3CN), and 24−83°C ($CDCl_3$). 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:

$$\Delta G^{\neq} = 19.14\ T_C\ [10.32 + \log(T_C/k_C)]\ [\text{J mol}^{-1}]^{[19]}$$

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[5] Calculated energies (SCF + single point MP2 + E(vib0) energies [Hartree]): **10a**, −893.70429 (C_2 symmetry); **10b**, −893.69580 (C_1 symmetry); **10c**, −893.68806 (C_2 symmetry); **10d**, −893.69303 (C_2 symmetry); **10e**, −893.69233 (C_S symmetry).

[6] Calculated SCF energy [Hartree]: **8**, −1064.66653.

[7] As the equipotential surface around the local minimum **10c** is quite flat and the energy difference between **10c** and the transition state **10**$^{\ddagger 2}$ is rather small, further calculations with a larger basis set have to be performed in order to differentiate more precisely between the relative energies of **10c** and **10**$^{\ddagger 2}$.

[8] The calculated transition state **10d** is not needed to realize the Λ/Δ-isomerization according to Figure 9.

[9] Calculated energies (SCF + single point MP2 + E(vib0) energies [Hartree]): **10**$^{\ddagger 1}$, −893.69233 (C_S symmetry); **10**$^{\ddagger 2}$, −893.68635 (C_2 symmetry); **10**$^{\ddagger 3}$, −893.67732 (C_1 symmetry).

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