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Diastereo- and Enantiomerically Pure Zwitterionic Spirocyclic λ^5*Si*-[(Ammonio)methyl]silicates with an *Si*O_2N_2C Skeleton Containing Two Bidentate Chelate Ligands Derived from α-Amino Acids[§]

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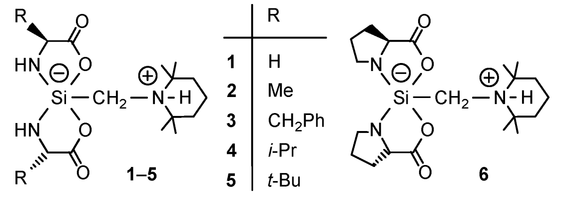
The zwitterionic λ^5*Si*-silicates (Λ,*S*,*S*)-**4**·CH_2Cl_2, (Λ,*S*,*S*)-**5**·CH_2Cl_2, (Λ,*S*,*S*)-**6**·2CH_2Cl_2, and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2, with a (2,2,6,6-tetramethylpiperidinio)methyl group and two identical bidentate chelate ligands derived from (*S*)-valine, (*S*)-*tert*-leucine, or (*S*)-proline bound to the silicon(IV) coordination center, were synthesized and structurally characterized (solution and solid-state NMR spectroscopy; single-crystal X-ray diffraction). All compounds were isolated as diastereo- and enantiomerically pure crystalline solids, and the λ^5*Si*-silicates (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** were demonstrated to exist as diastereo- and enantiomerically pure zwitterions in solution as well (CD_2Cl_2, temperature range −100 to 23 °C). The experimental investigations were complemented by computational studies of related model species.

Introduction

Recently, we have reported on the synthesis and structural characterization of the zwitterionic λ^5*Si*-silicates *rac*-**1**, (Δ,*S*,*S*)-**2**, and (Λ,*S*,*S*)-**3**·CH_2Cl_2.[1] In these neutral pentacoordinate silicon compounds, one (2,2,6,6-tetramethylpiperidinio)methyl group and two bidentate chelate ligands derived from the α-amino acids glycine (**1**), (*S*)-alanine (**2**), or (*S*)-phenylalanine (**3**·CH_2Cl_2) are bound to the silicon(IV) coordination center. Upon dissolution in dichloromethane, the diastereo- and enantiomerically pure compounds (Δ,*S*,*S*)-**2** and (Λ,*S*,*S*)-**3**·CH_2Cl_2 undergo a (Λ)/(Δ)-epimerization to give an equilibrium mixture of the respective (Λ,*S*,*S*)- and (Δ,*S*,*S*)-diastereomers. Compound (Δ,*S*,*S*)-**2** was found to be configurationally stable in dichloromethane at −40 °C over a period of 24 h; however, at 23 °C a (Λ)/(Δ)-epimerization was observed, with an equilibration time of ca. 2 h. In the case of (Λ,*S*,*S*)-**3**·CH_2Cl_2, the equilibration time was ca. 3 h. The molar (Λ)/(Δ)-equilibration ratios were 0.71:0.29 (**2**) and 0.73:0.27 (**3**), the respective (Λ)-isomers being thermodynamically more stable than the (Δ)-isomers.

We have now succeeded in synthesizing the structurally related zwitterionic λ^5*Si*-silicates (Λ,*S*,*S*)-**4**·CH_2Cl_2, (Λ,*S*,*S*)-**5**·CH_2Cl_2, (Λ,*S*,*S*)-**6**·2CH_2Cl_2, and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2, which were all isolated as diastereo- and enantiomerically pure crystalline solids. In these compounds, one (2,2,6,6-tetramethylpiperidinio)methyl group and two bidentate chelate ligands derived from the α-amino acid (*S*)-valine (**4**), (*S*)-*tert*-leucine (**5**), or (*S*)-proline (**6**) are bound to the silicon(IV) coordination center. These bidentate ligands are sterically more demanding than those derived from (*S*)-alanine and (*S*)-phenylalanine (compounds (Δ,*S*,*S*)-**2** and (Λ,*S*,*S*)-**3**·CH_2Cl_2, respectively). Most surprisingly, the λ^5*Si*-silicates (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** were demonstrated to exist as diastereo- and enantiomerically pure zwitterions in solution as well (dichloromethane, temperature range −100 to 23 °C).



1–5

	R
1	H
2	Me
3	CH_2Ph
4	*i*-Pr
5	*t*-Bu

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We report here on the synthesis and stereochemistry of the zwitterionic λ^5*Si*-silicates (Λ,*S*,*S*)-**4**·CH_2Cl_2, (Λ,*S*,*S*)-**5**·CH_2Cl_2, (Λ,*S*,*S*)-**6**·2CH_2Cl_2, and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2. All compounds were structurally characterized in the solid state (crystal structure analyses; ^{15}N and ^{29}Si VACP/MAS NMR experiments) and in solution (^1H, ^{13}C, ^{15}N, and ^{29}Si NMR experiments, including studies of the stereodynamics). The protonated lipophilic (2,2,6,6-tetramethylpiperidinio)methyl group of the zwitterions (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** increases the solubility of these compounds in dichloromethane and, hence, allowed their structural characterization by low-temperature solution NMR studies. These experimental investigations were complemented by computational studies (RI-MP2 geometry optimizations of the related model species **7**−**9**).

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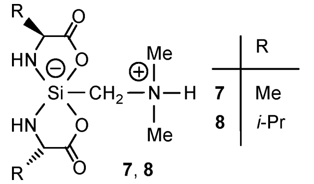
[§] Dedicated to Professor Hans Heinz Karsch on the occasion of his 60th birthday.

(1) Tacke, R.; Bertermann, R.; Burschka, C.; Dragota, S.; Penka, M.; Richter, I. *J. Am. Chem. Soc.* **2004**, *126*, 14493−14505.

10.1021/om050381v CCC: $30.25



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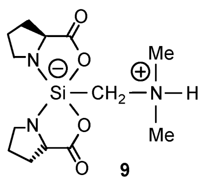

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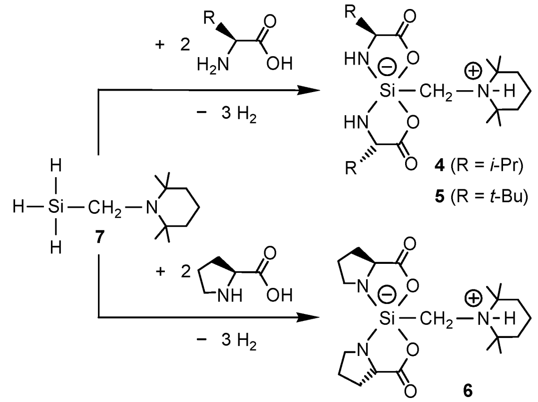
The studies presented in this paper have been performed as part of our systematic investigations on zwitterionic λ^5*Si*-silicates,[2] with a special emphasis on their stereochemistry (for reviews dealing with higher-coordinate silicon compounds, see ref 3).

Results and Discussion

Syntheses. The zwitterionic λ^5*Si*-silicates (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** were synthesized according to Scheme 1 by treatment of [(2,2,6,6-tetramethylpiperidino)methyl]silane (**7**)[4] with 2 molar equivs of (*S*)-valine, (*S*)-*tert*-leucine, or (*S*)-proline. The syntheses were performed in dichloromethane at 20 °C, and compounds (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ were isolated as colorless crystalline solids (yields: (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, 72%; (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, 78%; (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, 83%; (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$, 81%). For the preparation of the solvates **6**·2CH$_2$Cl$_2$ and **6**·1/2CH$_2$Cl$_2$, different synthetic methods were developed (for details, see Experimental Section).

Scheme 1



The identities of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ were established by elemental analyses (C, H, N), single-crystal X-ray diffraction studies, VACP/MAS NMR experiments (^{15}N, ^{29}Si), and solution NMR studies (^{1}H, ^{13}C, ^{15}N, ^{29}Si).

In principle, the formation of the crystalline diastereo- and enantiomerically pure dichloromethane solvates of (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** could occur by kinetic or thermodynamic control (kinetic control: selective formation of the (Λ,*S*,*S*)-diastereomers of **4**–**6** in solution, followed by crystallization of the respective solvates without change of absolute configuration of the zwitterionic λ^5*Si*-silicates; thermodynamic control: selective formation of one of the two diastereomers or formation of both diastereomers of **4**–**6**, followed by (Λ)/(Δ)-epimerization and crystallization of the thermodynamically more stable solvates).

Crystal Structure Analyses. The crystal data and the experimental parameters used for the crystal structure analyses of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ are summarized in Table 1. The molecular structures of the zwitterions in the crystals of the respective dichloromethane solvates are depicted in Figures 1–3; selected bond distances and angles are listed in Table 2.

Compounds (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ crystallize in chiral space groups. In the case of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, no crystallographic symmetry was found; the unit cell contains four symmetrically independent zwitterions (*Molecules I–IV*) with very similar structures and four additional disordered dichloromethane molecules.[5] The asymmetric unit of (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$ contains one zwitterion and one dichloromethane molecule, and in the case of (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, one zwitterion and two dichloromethane molecules are found in the asymmetric

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(2) Recent original publications dealing with zwitterionic λ^5*Si*-silicates: (a) Kost, D.; Kalikhman, I.; Krivonos, S.; Bertermann, R.; Burschka, C.; Neugebauer, R. E.; Pülm, M.; Willeke, R.; Tacke, R. *Organometallics* **2000**, *19*, 1083–1095. (b) Tacke, R.; Bertermann, R.; Biller, A.; Dannappel, O.; Penka, M.; Pülm, M.; Willeke, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1159–1173. (c) Tacke, R.; Ulmer, B.; Wagner, B.; Arlt, M. *Organometallics* **2000**, *19*, 5297–5309. (d) Tacke, R.; Mallak, M.; Willeke, R. *Angew. Chem.* **2001**, *113*, 2401–2403; *Angew. Chem., Int. Ed.* **2001**, *40*, 2339–2341. (e) Willeke, R.; Tacke, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1537–1541. (f) Tacke, R.; Bertermann, R.; Dannappel, O.; Neugebauer, R. E.; Pülm, M.; Willeke, R.; Tacke, R. *Inorg. Chem.* **2001**, *40*, 2520–2527. (g) Richter, I.; Burschka, C.; Tacke, R. *J. Organomet. Chem.* **2002**, *646*, 200–203. (h) Richter, I.; Penka, M.; Tacke, R. *Organometallics* **2002**, *21*, 3050–3053. (i) Dragota, S.; Bertermann, R.; Burschka, C.; Heermann, J.; Penka, M.; Richter, I.; Wagner, B.; Tacke, R. *Silicon Chem.* **2002**, *1*, 291–297. (j) Tacke, R.; Bertermann, R.; Biller, A.; Burschka, C.; Penka, M. *Can. J. Chem.* **2003**, *81*, 1315–1325. (k) Bertermann, R.; Biller, A.; Kaupp, M.; Penka, M.; Seiler, O.; Tacke, R. *Organometallics* **2003**, *22*, 4104–4110. (l) Tacke, R.; Bertermann, R.; Burschka, C.; Dragota, S. *Angew. Chem.* **2005**, *117*, 5426–5429; *Angew. Chem., Int. Ed.* **2005**, *44*, 5292–5295.

(3) Selected reviews dealing with higher-coordinate silicon compounds: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99–189. (b) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 227–303. (c) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 839–892. (d) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 2, pp 1241–1288. (e) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17–31. (f) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448. (g) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1–8. (h) Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175–241. (i) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233–295. (j) Tacke, R.; Dannappel, O. In *Tailor-made Silicon–Oxygen Compounds–From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Vieweg: Braunschweig, Wiesbaden, Germany, 1996; pp 75–86. (k) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1996**, *32*, 1381–1418. (l) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927–950. (m) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1339–1445. (n) Pestunovich, V.; Kirpichenko, S.; Voronkov, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1447–1537. (o) Chuit, C.; Corriu, R. J. P.; Reye, C. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley-VCH: New York, 1999; pp 81–146. (p) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221–273. (q) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; pp 97–114. (r) Tacke, R.; Seiler, O. In *Silicon Chemistry: From the Atom to Extended Systems*; Jutzi, P., Schubert, U., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 324–337. (s) Kost, D.; Kalikhman, I. *Adv. Organomet. Chem.* **2004**, *50*, 1–106.

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(5) Comparing the orientation of *Molecules I* and *IV* (−178.2°) and that of *Molecules II* and *III* (178.4°), a nearly 180° rotation about [1 0 0] is observed. Furthermore, *Molecules I* and *II*, and in the same sense Molecules *III* and *IV*, are connected to pairs via intermolecular hydrogen bonds (Table 3).

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of (Λ,*S*,*S*)-4·CH$_2$Cl$_2$, (Λ,*S*,*S*)-5·CH$_2$Cl$_2$, (Λ,*S*,*S*)-6·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-6·1/2CH$_2$Cl$_2$

	(Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$	(Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$	(Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$	(Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$
empirical formula	$C_{21}H_{41}Cl_2N_3O_4Si$	$C_{23}H_{45}Cl_2N_3O_4Si$	$C_{22}H_{39}Cl_4N_3O_4Si$	$C_{20.5}H_{36}ClN_3O_4Si$
formula mass, g mol^{-1}	498.56	526.61	579.45	452.07
collection *T*, K	173(2)	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	orthorhombic	orthorhombic	monoclinic
space group (no.)	$P1$ (1)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$C2$ (5)
a, Å	11.4543(11)	10.0371(6)	10.2471(9)	23.911(2)
b, Å	11.8958(11)	12.1617(7)	14.7908(12)	8.2717(4)
c, Å	19.7436(19)	22.9076(17)	18.635(2)	24.4908(19)
α, deg	85.224(11)	90	90	90
β, deg	82.253(11)	90	90	109.231(10)
γ, deg	89.398(11)	90	90	90
V, Å^3	2656.4(4)	2796.3(3)	2824.3(5)	4573.6(6)
Z	4	4	4	8
D(calcd), g cm^{-3}	1.247	1.251	1.363	1.313
μ (mm^{-1})	0.320	0.307	0.494	0.251
F(000)	1072	1136	1224	1944
cryst dimens, mm	0.5 × 0.3 × 0.2	0.5 × 0.3 × 0.2	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3
2θ range, deg	3.88−51.80	4.44−53.90	4.84−53.84	4.12−53.84
index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-24 \le l \le 24$	$-12 \le h \le 11$, $-14 \le k \le 15$, $-29 \le l \le 29$	$-12 \le h \le 13$, $-18 \le k \le 18$, $-23 \le l \le 23$	$-30 \le h \le 30$, $-10 \le k \le 10$, $-31 \le l \le 30$
no. of collected reflns	37 911	17 499	16 044	21 747
no. of indep reflns	19 168	6021	6026	9699
R_{int}	0.0286	0.0431	0.0352	0.0283
no. of reflns used	19168	6021	6026	9699
no. of restraints	450	0	14	20
no. of params	1333	317	340	565
S^a	0.925	1.017	1.049	1.058
weight params *a*/*b*^{b}	0.0368/0.0000	0.0509/0.0000	0.0576/0.1732	0.0487/1.3340
$R1^c$ [$I > 2\sigma(I)$]	0.0302	0.0347	0.0329	0.0355
$wR2^d$ (all data)	0.0666	0.0856	0.0893	0.0890
abs structure param	0.00(3)	0.05(5)	0.01(5)	0.03(5)
extinction coeff	0.0023(3)			
max./min. residual electron density, e Å^{-3}	+0.203/−0.220	+0.511/−0.476	+0.284/−0.254	+0.535/−0.375

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

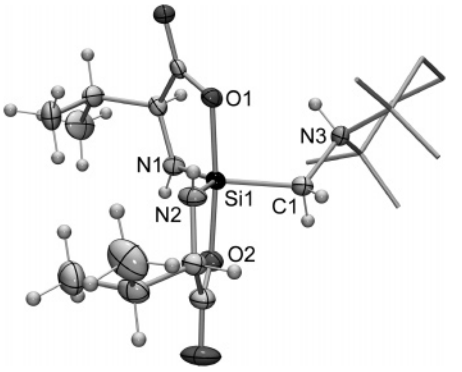

Figure 1. Molecular structure of (Λ,*S*,*S*)-**4** (*Molecule I*) in the crystal of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$ (probability level of displacement ellipsoids 50%; CH$_2$ and C(CH$_3$)$_2$ moieties of the 2,2,6,6-tetramethylpiperidinio group represented as stick model for clarity). The structures of *Molecules II−IV* are very similar.

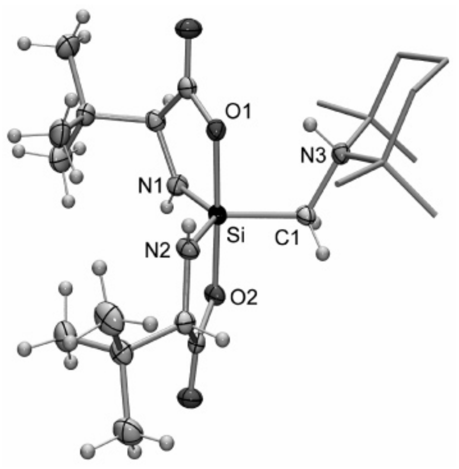

Figure 2. Molecular structure of (Λ,*S*,*S*)-**5** in the crystal of (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$ (probability level of displacement ellipsoids 50%; CH$_2$ and C(CH$_3$)$_2$ moieties of the 2,2,6,6-tetramethylpiperidinio group represented as stick model for clarity).

unit. The asymmetric unit of (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ contains two zwitterions (*Molecules I* and *II*) and one dichloromethane molecule.

The Si-coordination polyhedra of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ are distorted trigonal bipyramids, with the oxygen ligand atoms in the axial positions and the nitrogen and carbon ligand atoms in the equatorial sites. The Si−O distances range from 1.8058(14) to 1.8524(13) Å, the Si−C bond lengths are in the range 1.9142(18)−1.9274(19) Å, and the Si−N distances range from 1.7087(17) to 1.740(2) Å. These values are similar to those observed for the respective Si−O, Si−N, and Si−C distances of compounds *rac*-**1**, (Δ,*S*,*S*)-**2**, and (Λ,*S*,*S*)-**3**·CH$_2$Cl$_2$ (in this context, see ref 1).

In the crystals of all compounds studied, N−H···O hydrogen bonds between the NH groups of the ammonium moieties and one of the two axial oxygen ligand

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for (Λ,*S*,*S*)-4·CH$_2$Cl$_2$, (Λ,*S*,*S*)-5·CH$_2$Cl$_2$, (Λ,*S*,*S*)-6·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-6·1/2CH$_2$Cl$_2$

	(Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$[a]				(Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$	(Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$	(Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$[b]	
	Molecule I	*Molecule II*	*Molecule III*	*Molecule IV*			*Molecule I*	*Molecule II*
Si−O1	1.8275(13)	1.8116(12)	1.8122(13)	1.8267(13)	1.8258(14)	1.8524(13)	1.8322(14)	1.8227(14)
Si−O2	1.8098(13)	1.8242(13)	1.8251(14)	1.8144(14)	1.8058(14)	1.8105(13)	1.8169(14)	1.8279(15)
Si−N1	1.7146(17)	1.7133(18)	1.7151(18)	1.7162(18)	1.7087(17)	1.7287(17)	1.7378(18)	1.740(2)
Si−N2	1.718(2)	1.7168(17)	1.7135(19)	1.7184(17)	1.7124(16)	1.7381(17)	1.7387(18)	1.7285(19)
Si−C1	1.915(2)	1.918(2)	1.923(2)	1.922(2)	1.9274(19)	1.9142(18)	1.9228(19)	1.919(2)
O1−Si−O2	173.89(7)	174.37(7)	174.47(7)	173.13(7)	176.83(7)	179.25(7)	177.60(7)	178.26(7)
O1−Si−N1	86.23(7)	86.81(7)	86.91(7)	86.33(7)	85.98(7)	86.48(7)	87.27(8)	87.58(8)
O1−Si−N2	90.67(7)	90.13(7)	90.28(8)	90.33(7)	93.25(7)	91.60(7)	93.43(8)	91.51(8)
O1−Si−C1	97.27(7)	97.85(7)	98.09(7)	97.35(7)	92.71(7)	92.74(7)	91.64(7)	95.96(8)
O2−Si−N1	91.26(7)	91.83(7)	91.58(7)	91.02(7)	91.23(8)	92.78(7)	93.38(7)	91.58(8)
O2−Si−N2	86.69(7)	86.38(7)	86.44(8)	86.59(7)	87.24(7)	88.82(7)	88.12(7)	87.79(8)
O2−Si−C1	88.83(7)	87.63(8)	87.33(7)	89.50(8)	89.93(7)	87.64(7)	86.03(7)	85.77(8)
N1−Si−N2	130.18(9)	127.76(9)	127.75(9)	130.73(9)	127.24(9)	126.26(8)	124.24(8)	127.44(9)
N1−Si−C1	117.52(10)	117.41(9)	117.42(10)	116.97(9)	118.17(9)	117.82(8)	119.12(9)	118.54(10)
N2−Si−C1	112.20(9)	114.67(9)	114.63(9)	112.22(9)	114.56(9)	115.92(8)	116.59(8)	113.82(10)

[a] Atoms of *Molecule I*, Si1, O1, O2, N1, N2, and C1; atoms of *Molecule II*, Si21, O21, O22, N21, N22, and C21; atoms of *Molecule III*, Si41, O41, O42, N41, N42, and C41; atoms of *Molecule IV*, Si61, O61, O62, N61, N62, and C61. [b] Atoms of *Molecule I*, Si1, O1, O2, N1, N2, and C1; atoms of *Molecule II*, Si21, O21, O22, N21, N22, and C22.

Table 3. Hydrogen-Bonding Geometries for (Λ,*S*,*S*)-4·CH$_2$Cl$_2$, (Λ,*S*,*S*)-5·CH$_2$Cl$_2$, (Λ,*S*,*S*)-6·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-6·1/2CH$_2$Cl$_2$[a]

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
(Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$	N3−H3···O23 (inter)	0.88(2)	2.07(2)	2.922(2)	163.0(18)
	N23−H23···O3 (inter)	0.876(17)	2.035(18)	2.866(2)	158(2)
	N23−H23···O21 (intra)[b]	0.876(17)	2.57(2)	3.110(2)	121.1(18)
	N43−H43···O63 (inter)	0.858(17)	2.052(17)	2.879(2)	161.7(18)
	N63−H63···O43 (inter)	0.89(2)	2.08(2)	2.931(2)	161.8(18)
(Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$	N3−H3···O1 (intra)	0.92(2)	2.01(2)	2.742(2)	134.9(17)
(Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$	N3−H3···O1 (intra)	0.90(2)	2.14(2)	2.7884(18)	128.4(19)
(Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$	N3−H3···O1 (intra)	0.88(2)	2.06(2)	2.737(2)	134(2)
	N23−H23···O21 (intra)[c]	0.87(3)	2.55(2)	3.044(2)	116.9(19)
	N23−H23···O23 (inter)	0.87(3)	2.11(3)	2.947(2)	161(2)

[a] Data calculated by using the program *PLATON*.[6] [b] Bifurcate N23−H23···O21/O3 interaction; O21···H23···O3 = 78.7(6)°. [c] Bifurcate N23−H23···O21/O23 interaction; O21···H23···O23 = 80.4 (9)°.

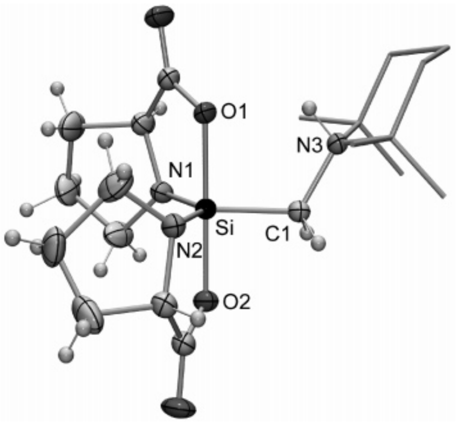

Figure 3. Molecular structure of (Λ,*S*,*S*)-**6** in the crystal of (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$ (probability level of displacement ellipsoids 50%; CH$_2$ and C(CH$_3$)$_2$ moieties of the 2,2,6,6-tetramethylpiperidinio group represented as stick model for clarity). The structure of the zwitterion in the crystal of (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ is very similar.

Table 4. ^{29}Si NMR Data for (Λ,*S*,*S*)-4·CH$_2$Cl$_2$, (Λ,*S*,*S*)-5·CH$_2$Cl$_2$, (Λ,*S*,*S*)-6·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-6·1/2CH$_2$Cl$_2$ in the Crystal and in Solution[a]

	δ (crystal)[b]	δ (CD$_2$Cl$_2$)
(Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$	−98.8 to −95.6 (m)	−98.0
(Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$	−101.2 to −99.1 (m)	−100.3
(Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$	−97.5 to −95.0 (m)	−97.8
(Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$	−97.0 to −93.0 (m)	−97.8

[a] Spectra recorded at 22 °C (solid state) or 23 °C (solution); chemical shifts in ppm. [b] Isotropic chemical shifts obtained by solid-state ^{29}Si VACP/MAS NMR experiments.

atoms (except for the intermolecular hydrogen bond formed by *Molecule II* of **6**·1/2CH$_2$Cl$_2$, where a carbonyl oxygen atom acts as the proton acceptor) were observed (Table 3).[6] In the case of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, the two zwitterions of each pair (*Molecule I*/*Molecule II* and *Molecule III*/*Molecule IV*, respectively) are connected via intermolecular N−H···O interactions; *Molecule II* is involved in a bifurcate hydrogen-bonding interaction, with one additional intramolecular N−H···O hydrogen bond. As can be seen from Table 3, the zwitterions of (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ (*Molecule I*) form an intramolecular N−H···O hydrogen bond, and *Molecule II* of (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ is involved in an additional intermolecular N−H···O interaction with its symmetry equivalent (bifurcate N−H···O/O interaction).

NMR Studies. Compounds (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ were characterized at 22 °C by solid-state ^{29}Si VACP/MAS NMR spectroscopy (Table 4). The isotropic ^{29}Si chemical shifts obtained clearly characterize the ^{29}Si resonance signals as arising from pentacoordinate silicon atoms. These chemical shifts are very similar to those obtained in the solution ^{29}Si NMR studies (Table 4), indicating that the λ^5*Si*-silicate skeletons exist in

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

solution as well. The solid-state ^{29}Si NMR spectra are characterized by slightly structured resonance signals that are split or broad due to $^{1}J(^{14}N,^{29}Si)$ couplings. We were not able to simulate these spectra and to extract the $^{1}J(^{14}N,^{29}Si)$ coupling constants because these couplings were poorly resolved. The line width of the ^{29}Si signals depends on the magnitude of $^{1}J(^{14}N,^{29}Si)$ and the quadrupole relaxation time of the ^{14}N nucleus $T_q(^{14}N)$. When $T_q(^{14}N)$ becomes comparable with $1/^{1}J(^{14}N,^{29}Si)$, splitting of the ^{29}Si resonance signals due to ^{14}N,^{29}Si coupling can be observed directly.[7]

Compounds (Λ,*S*,*S*)-**4**·CH_2Cl_2, (Λ,*S*,*S*)-**5**·CH_2Cl_2, (Λ,*S*,*S*)-**6**·2CH_2Cl_2, and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 were also characterized at 22 °C by solid-state ^{15}N VACP/MAS NMR spectroscopy. The spectra obtained (see Experimental Section) were compatible with the crystal structures of these compounds and demonstrated their diastereomeric and enantiomeric purity. The isotropic ^{15}N chemical shifts were very similar to those obtained in the solution ^{15}N NMR studies, again indicating that the zwitterions exist in solution as well.

Compounds (Λ,*S*,*S*)-**4**·CH_2Cl_2, (Λ,*S*,*S*)-**5**·CH_2Cl_2, (Λ,*S*,*S*)-**6**·2CH_2Cl_2, and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 were additionally characterized by solution ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Furthermore, 2D ^{15}N,^{1}H HMQC NMR spectra were recorded. These solution NMR studies were performed at 23 °C using CD_2Cl_2 as the solvent. In all cases, only one single diastereomer could be detected.

As can be seen from Table 4, the ^{29}Si chemical shifts are very similar to the isotropic ^{29}Si chemical shifts obtained in the solid-state NMR experiments. In contrast to the solid-state ^{29}Si NMR spectra with their slightly structured resonance signals, the solution ^{29}Si NMR spectra of the zwitterions (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** are characterized by sharp resonance signals (full-width at half-height ca. 15−25 Hz). When the spin−lattice relaxation time of the ^{14}N nucleus $T_q(^{14}N)$ is much shorter than $^{1}J(^{14}N,^{29}Si)$, the splitting of the ^{29}Si resonance signals due to the ^{14}N,^{29}Si coupling cannot be observed. In this case, the ^{14}N nucleus has a strong quadrupolar interaction with a strong EFG (electric field gradient).

The ^{1}H chemical shifts observed for the $SiCH_2NH$ protons of the zwitterions (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** (δ = 5.8−6.0 ppm) indicate the presence of the ammonium moieties. Thus, the solution ^{1}H NMR data are also compatible with the existence of the zwitterionic λ^5Si-silicates in solution (for further details, see Experimental Section). The chiral nature of the zwitterions is reflected by the ABX spin systems observed for the $SiCH_AH_BNH_X$ protons in the ^{1}H NMR spectra.

As the trigonal-bipyramidal Si-coordination polyhedron, with the carboxylato oxygen atoms in the axial sites, is the energetically most favorable one for all the zwitterionic λ^5Si-silicates studied (see Crystal Structure Analyses and ref 1), it is likely that this particular structure is also dominant in solution.

To learn more about the behavior of the zwitterionic compounds in solution, ^{1}H, ^{13}C, and ^{29}Si NMR cross-experiments at 300.1 MHz were carried out. For this purpose, *rac*-**1** (76 μmol) and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 (44 μmol) were dissolved in CD_2Cl_2 (750 μL). The NMR spectra, recorded at 23 °C and supported by correlation experiments, indicated that the zwitterions of *rac*-**1** and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 undergo an intermolecular ligand exchange, leading to the formation of a new zwitterionic λ^5Si-silicate containing one glycinato(2−) ligand and one prolinato(2−) ligand. Figure 4 shows a representative partial spectrum obtained in a ^{29}Si,^{1}H HMQC experiment. Related cross-experiments with (Λ,*S*,*S*)-**4**·CH_2Cl_2/(Λ,*S*,*S*)-**6**·1/2CH_2Cl_2, (Δ,*S*,*S*)-**2**/(Λ,*S*,*S*)-**3**·CH_2Cl_2, and (Λ,*S*,*S*)-**5**·CH_2Cl_2/(Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 demonstrated an intermolecular ligand exchange between the respective zwitterions as well.

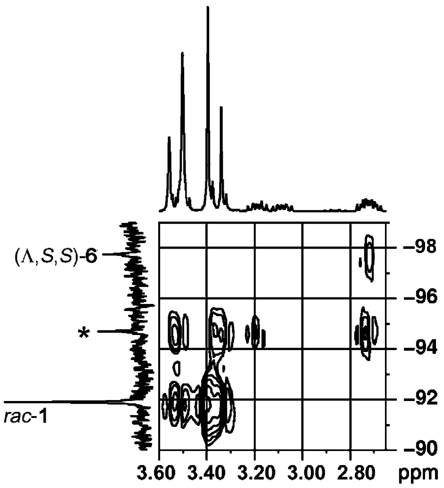

Figure 4. Partial spectrum obtained in a ^{29}Si,^{1}H HMQC experiment (23 °C, 300.1 MHz) with a solution of *rac*-**1** (76 μmol) and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 (44 μmol) in CD_2Cl_2 (750 μL). The spectrum was recorded ca. 2 h after dissolution of *rac*-**1** and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2. Top: ^{1}H NMR resonance signals. Left: ^{29}Si NMR resonance signals; the signal marked with an asterisk corresponds to the cross-product.

Additionally, low-temperature ^{1}H NMR experiments at 300.1 MHz with solutions of (Λ,*S*,*S*)-**4**·CH_2Cl_2 (20 mM), (Λ,*S*,*S*)-**5**·CH_2Cl_2 (32 mM), and (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 (44 mM) in CD_2Cl_2 were performed at −100 °C. The ^{1}H NMR spectra were recorded every 300 s; the first spectra were obtained ca. 6 min after dissolution of the zwitterionic λ^5Si-silicates. In all cases, only one single diastereomer could be detected, and no changes of the NMR spectra were observed over a period of 1 h. Compared to the ^{1}H NMR spectra obtained at 23 °C, no line-broadening was observed at −100 °C.

Furthermore, VT ^{1}H NMR experiments with a 12 mM solution of (Λ,*S*,*S*)-**6**·1/2CH_2Cl_2 in CD_2Cl_2 were carried out in the temperature range −60 to 23 °C. For this purpose, five ^{1}H NMR spectra were recorded every 180 s at this temperature (the first spectrum was recorded ca. 5 min after dissolution of the compound), followed by measurement of a further five ^{1}H NMR spectra each every 180 s at −40, −20, and 0 °C. After the sample was kept undisturbed for a period of 3 days at 23 °C, and ^{1}H, ^{13}C, and 2D ^{29}Si,^{1}H HMQC NMR spectra were recorded every 24 h, further ^{1}H NMR spectra were measured upon cooling to 0, −20, −40, and −60 °C. No changes of the ^{1}H NMR spectra were observed in all these NMR experiments; that is, only one single diastereomer could be detected in the temperature range and over the time period studied (see Figure 5). Attempts to perform VT NMR experiments with (Λ,*S*,*S*)-

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[7] Kupče, Ē.; Lukevics, E. *J. Magn. Reson.* **1988**, *76*, 63−73.

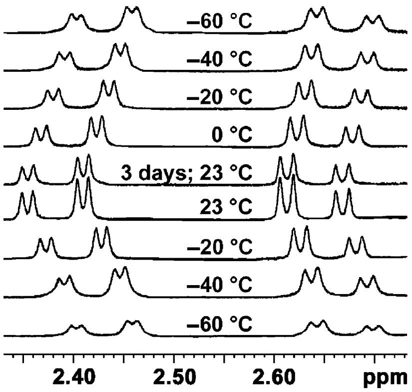

Figure 5. Partial ^{1}H NMR spectra (resonance signals of the SiCH$_2$N protons) of a 12 mM solution of (Λ,*S*,*S*)-$\mathbf{6}\cdot$1/2CH$_2$Cl$_2$ in CD$_2$Cl$_2$ at 300.1 MHz in the temperature range −60 to 23 °C (warming from −60 to 23 °C and subsequent cooling to −60 °C).

4, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** at higher temperatures failed because these zwitterions decompose at temperatures above 27 °C. Thus, no information about a potential (Λ)/(Δ)-epimerization of these compounds at higher temperatures could be obtained by NMR spectroscopy.

The presence of only one data set in all the solution NMR spectra of (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** could be interpreted in terms of a rapid (Λ)/(Δ)-epimerization that is very fast on the NMR time scale. However, no coalescence phenomena (line broadening) were observed upon cooling to −100 °C. As the derivatives (Δ,*S*,*S*)-**2** and (Λ,*S*,*S*)-**3** (compounds with sterically less demanding bidentate ligands) were demonstrated to undergo a relatively slow (Λ)/(Δ)-epimerization at 23 °C (equilibration times: **2**, ca. 2 h; **3**, ca. 3 h),[1] a rapid (Λ)/(Δ)-epimerization of (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** at 23 °C, and especially at −100 °C, is very unlikely.

The presence of only one data set in all the solution NMR spectra of (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** could be alternatively interpreted in terms of (Λ)/(Δ)-equilibrium ratios that do not allow the detection of both diastereoisomers. In the case of **2** and **3**, molar (Λ)/(Δ)-equilibrium ratios of 0.7:0.3 were determined at 23 °C (solvent, CD$_2$Cl$_2$), with the (Λ)-isomer being the thermodynamically more stable one.[1] This ratio corresponds to an energy difference between the respective (Λ)- and (Δ)-isomers of ca. 2.1 kJ mol^{-1}. This value matches with the calculated energy differences obtained for the respective (Λ)- and (Δ)-isomers of the model species **7** (2.3 kJ mol^{-1}) and **8** (2.1 kJ mol^{-1}) (see Computational Studies). Thus, it is unlikely that the molar (Λ)/(Δ)-equilibrium ratios of **4** and **5** differ totally from those of **2** and **3**; that is, the (Δ,*S*,*S*)-isomers of **4** and **5** should also be detectable at 23 °C. However, it is unlikely that the derivative (Δ,*S*,*S*)-**6**, with its two more rigid prolinato(2−) ligands, can be detected by ^{1}H NMR spectroscopy in solution at 23 °C: Geometry optimizations for the model species **9** demonstrated the (Λ)-isomer to be more stable than the (Δ)-isomer by 12.3 kJ mol^{-1} (see Computational Studies). This energy difference corresponds to a theoretical molar (Λ)/(Δ)-equilibrium ratio of 0.993:0.007.

Computational Studies. Geometry optimizations for the (Λ,*S*,*S*)- and (Δ,*S*,*S*)-isomers of **7**−**9** (model systems with the (dimethylammonio)methyl group instead of the (2,2,6,6-tetramethylpiperidinio)methyl moiety) were performed at the RI-MP2 level[8] using a TZP basis set[9] and a TZVP auxiliary basis for the fit of the charge density.[10] The calculations were performed using the *TURBOMOLE* program system.[11] The structures of the calculated minima are shown in Figures 6−8, with selected calculated distances and angles in Table 5. As can be seen from Figures 1, 3, 7, and 8 and Tables 2 and 5, the calculated structures of (Λ,*S*,*S*)-**8** and (Λ,*S*,*S*)-**9** and the respective experimentally established structures of (Λ,*S*,*S*)-$\mathbf{4}\cdot$CH$_2$Cl$_2$ and (Λ,*S*,*S*)-$\mathbf{6}\cdot$2CH$_2$Cl$_2$ are in reasonable agreement.[12] The Si-coordination polyhedra of all local minimum structures are slightly distorted trigonal bipyramids, with the oxygen ligand atoms in the axial positions and the nitrogen and carbon ligand atoms occupying the equatorial sites.

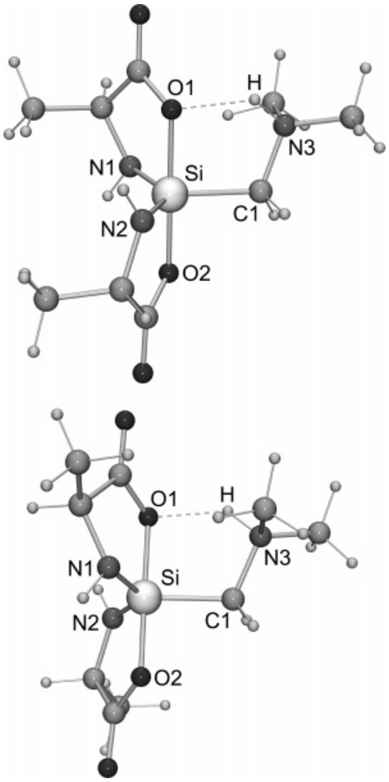

Figure 6. Calculated structures of (Λ,*S*,*S*)-**7** (above) and (Δ,*S*,*S*)-**7** (below). The dashed lines indicate intramolecular N3−H···O1 hydrogen bonds.

The calculated energy differences between the respective (Λ,*S*,*S*)- and (Δ,*S*,*S*)-isomers amount to 2.3 kJ mol^{-1} (**7**), 2.1 kJ mol^{-1} (**8**), and 12.3 kJ mol^{-1} (**9**), with the (Λ)-isomers being energetically more stable than the (Δ)-isomers. In the case of a (Λ)/(Δ)-epimerization, these energy differences would result in molar (Λ)/(Δ)-equilibrium ratios of 0.72:0.28 (**7**), 0.70:0.30 (**8**), and 0.993:0.007 (**9**) at 23 °C.

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[8] (a) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331−340. (b) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143−152.

[9] Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571−2577.

[10] Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829−5835.

[11] Program system *TURBOMOLE*: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

[12] A perfect agreement between the calculated and experimentally established structures cannot be expected since the latter are influenced by intermolecular interactions in the crystal.

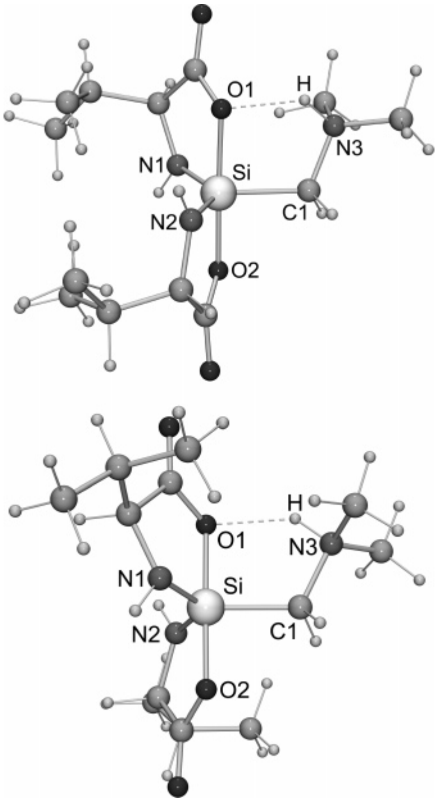

Figure 7. Calculated structures of (Λ,*S*,*S*)-**8** (above) and (Δ,*S*,*S*)-**8** (below). The dashed lines indicate intramolecular N3−H···O1 hydrogen bonds.

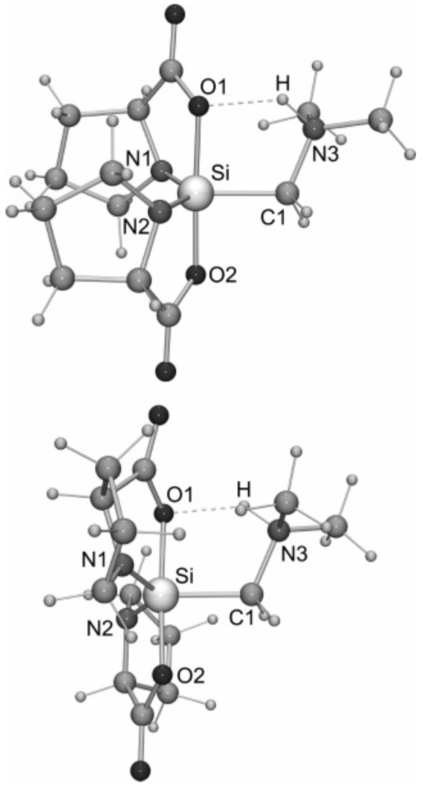

Figure 8. Calculated structures of (Λ,*S*,*S*)-**9** (above) and (Δ,*S*,*S*)-**9** (below). The dashed lines indicate intramolecular N3−H···O1 hydrogen bonds.

Conclusions

With the synthesis of the diastereo- and enantiomerically pure compounds (Λ,*S*,*S*)-**4**·CH_2Cl_2, (Λ,*S*,*S*)-**5**·CH_2Cl_2, (Λ,*S*,*S*)-**6**·$2CH_2Cl_2$, and (Λ,*S*,*S*)-**6**·$1/2CH_2Cl_2$, a series of new spirocyclic zwitterionic λ^5Si-silicates with an SiO_2N_2C skeleton were synthesized. In these zwitterions, a (2,2,6,6-tetramethylpiperidinio)methyl group and two identical bidentate ligands derived from the optically active α-amino acid (*S*)-valine, (*S*)-*tert*-leucine, or (*S*)-proline are bound to the silicon(IV) coordination center. All compounds were structurally characterized in the solid state (crystal structure analyses; solid-state ^{13}C, ^{15}N, and ^{29}Si NMR studies) and in solution (^1H, ^{13}C, ^{15}N, and ^{29}Si NMR studies, including VT NMR and cross-experiments). Most surprisingly, as demonstrated by solution NMR studies (solvent, CD_2Cl_2) in the temperature range −100 to 23 °C, the λ^5Si-silicates (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** exist as diastereo- and enantiomerically pure zwitterions in solution as well, whereas the structurally related zwitterionic λ^5Si-silicates **2** and **3** were found to undergo a (Λ)/(Δ)-epimerization in solution (solvent, CD_2Cl_2) at 23 °C, leading to equilibrium mixtures of the respective (Λ)- and (Δ)-isomers, the (Λ)-isomers being thermodynamically more stable than the (Δ)-isomers.[1] As the bidentate ligands of (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6** are sterically more demanding than those of (Δ,*S*,*S*)-**2** and (Λ,*S*,*S*)-**3**, one could speculate that the steric bulkiness of the bidentate ligands controls the stereochemistry of these zwitterionic λ^5Si-silicates in solution. However, further studies are necessary to confirm this hypothesis. As the compounds studied were found to undergo an intermolecular ligand exchange between λ^5Si-silicates

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for the Calculated Structures of the (Λ,*S*,*S*)- and (Δ,*S*,*S*)-Isomers of 7−9

	(Λ,*S*,*S*)-**7**	(Δ,*S*,*S*)-**7**	(Λ,*S*,*S*)-**8**	(Δ,*S*,*S*)-**8**	(Λ,*S*,*S*)-**9**	(Δ,*S*,*S*)-**9**
Si−O1	1.871	1.871	1.872	1.870	1.874	1.882
Si−O2	1.788	1.788	1.789	1.790	1.792	1.788
Si−N1	1.750	1.751	1.739	1.753	1.765	1.734
Si−N2	1.734	1.731	1.729	1.735	1.749	1.742
Si−C1	1.939	1.940	1.948	1.936	1.939	1.955
O1−Si−O2	179.9	179.5	178.4	179.3	177.8	176.6
O1−Si−N1	85.4	85.4	85.4	85.4	86.0	85.1
O1−Si−N2	91.4	91.6	92.3	91.6	91.8	92.8
O1−Si−C1	88.9	88.7	88.6	89.0	88.2	87.4
O2−Si−N1	94.7	95.0	95.2	95.0	95.0	95.4
O2−Si−N2	88.6	88.5	88.5	88.6	88.9	89.7
O2−Si−C1	91.0	90.9	89.9	90.4	89.6	89.4
N1−Si−N2	130.7	129.9	129.1	128.4	130.3	126.1
N1−Si−C1	114.2	114.4	116.0	116.6	114.8	117.2
N2−Si−C1	114.9	115.5	114.8	114.8	114.8	116.5

with different bidentate ligands on the hours time scale (NMR cross-experiments), one could speculate about an intermolecular (Λ)/(Δ)-epimerization process of **3**−**6**; however, this kind of process could not be detected under the experimental conditions used. In all NMR experiments, only one single diastereomer could be detected in the temperature range −100 to 23 °C.

A large number of chiral tetracoordinate silicon compounds, with the silicon atom as the center of chirality, were reported to be configurationally stable at room temperature and even at higher temperatures, and this chirality can be used for stereochemically controlled reactions.[13] Chiral pentacoordinate λ^5*Si*-silicates (such as (Λ,*S*,*S*)-**4**, (Λ,*S*,*S*)-**5**, and (Λ,*S*,*S*)-**6**), which exist as diastereo- and enantiomerically pure compounds in solution, represent a challenging extension of the stereochemistry of chiral silicon compounds to be explored in future studies.

Experimental Section

General Procedures. The syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under argon or nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, ^{15}N, and ^{29}Si solution NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{15}N, 30.4 MHz; ^{29}Si, 59.6 MHz). CD_2Cl_2 (99.6% D, <0.01% H_2O) was used as the solvent (Euriso-top). Chemical shifts (ppm) were determined relative to internal $CDHCl_2$ (^{1}H, δ 5.32), internal CD_2Cl_2 (^{13}C, δ 53.8), external formamide (^{15}N, δ −268.0), or external TMS (^{29}Si, δ 0). Analysis and assignment of the ^{1}H NMR data were supported by ^{1}H,^{1}H COSY and ^{13}C,^{1}H, ^{15}N,^{1}H, and ^{29}Si,^{1}H correlation experiments, and the ^{1}H spin systems were analyzed by using the program *WIN-DAISY* 4.05.[14] The $^2J_{AB}$ coupling constants reported for the AB parts of the spin systems studied represent absolute values. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. The thermocouple used with the probe in the VT ^{1}H NMR experiments was calibrated for low temperatures according to ref 15 using a 4% solution of CH_3OH in CD_3OD. The VT ^{1}H NMR spectra were recorded in the temperature range −100 to 23 °C; the time required for temperature equilibration was 15 min. Solid-state ^{15}N and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter, 7 mm) containing ca. 300 mg of sample (^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz; external standard, glycine (^{15}N, δ = −342.0) or TMS (^{29}Si, δ = 0); spinning rate, 5−7 kHz; contact time, 3 ms (^{15}N) or 5 ms (^{29}Si); 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s).

Preparation of (Λ,*S*,*S*)-[(2,2,6,6-Tetramethylpiperidinio)methyl]bis[valinato(2−)-*N*,*O*]silicate−Dichloromethane (4·CH$_2$Cl$_2$). Compound **7** (500 mg, 2.70 mmol) was added at 20 °C to a stirred suspension of (*S*)-valine (633 mg, 5.40 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred at this temperature for 12 h (evolution of hydrogen). The remaining solid was separated by filtration and discarded, *n*-pentane (40 mL) was added to the filtrate, and the resulting solution was kept undisturbed at 20 °C for 12 h (formation of crystals). The precipitate was isolated by filtration and dried in an argon stream (20 °C, 15 min) to give **4**·CH_2Cl_2 in 72% yield as a colorless crystalline solid (967 mg, 1.94 mmol); mp 187 °C (dec). ^{15}N VACP/MAS NMR (22 °C, ν_{rot} = 5 kHz): δ −349.8 to −345.0 (m, Si*N*HC), −301.7 (br s, C$_3$*N*H). ^{29}Si VACP/MAS NMR (22 °C, ν_{rot} = 6.5 kHz): δ −98.8 to −95.6 (m). ^{1}H NMR (CD_2Cl_2, 23 °C): δ 0.86 (δ_A), 0.92 (δ_B), 1.32 (δ_F), 1.96 (δ_M), and 3.44 (δ_X) (A_3B_3FMX system, $^3J_{AM}$ = 6.7 Hz, $^3J_{BM}$ = 7.0 Hz, $^3J_{MX}$ = 3.2 Hz, $^3J_{FX}$ = 4.1 Hz, 18 H, C(*H*$_A$)$_3$C(*H*$_B$)$_3$C*H*$_M$C*H*$_X$N*H*$_F$), 1.32 (s, 3 H, CC*H*$_3$), 1.33 (s, 3 H, CC*H*$_3$), 1.49 (s, 3 H, CC*H*$_3$), 1.55 (s, 3 H, CC*H*$_3$), 1.54−1.90 (m, 6 H, CC*H*$_2$C), 2.31 (δ_A) and 2.61 (δ_B) (AB part of an ABX system, $^2J_{AB}$ = 16.4 Hz, $^3J_{AX}$ = 3.9 Hz, $^3J_{BX}$ = 3.4 Hz, 2 H, SiC*H*$_A$*H*$_B$NH$_X$), 5.8 (br s, 1 H, C$_3$N*H*). ^{13}C NMR (CD_2Cl_2, 23 °C): δ 16.1 (NCC*C*H$_2$C), 17.1 (CH*C*H$_3$), 19.7 (CH*C*H$_3$), 20.1 (C*C*H$_3$), 20.4 (C*C*H$_3$), 30.0 (C*C*H$_3$), 31.1 (C*C*H$_3$), 32.7 (C*C*HC$_2$), 39.6 (NC*C*H$_2$C), 39.8 (NC*C*H$_2$C), 40.9 (Si*C*H$_2$N), 62.6 (SiN*C*HC$_2$), 65.0 (N*C*C$_3$), 65.3 (N*C*C$_3$), 177.7 (*C*=O). ^{15}N NMR (CD_2Cl_2, 23 °C): δ −350.5 (Si*N*HC), −292.0 (C$_3$*N*H). ^{29}Si NMR (CD_2Cl_2, 23 °C): δ −98.0. Anal. Calcd for $C_{21}H_{41}Cl_2N_3O_4Si$: C, 50.59; H, 8.29; N, 8.43. Found: C, 50.6; H, 8.1; N, 8.2.

Preparation of (Λ,*S*,*S*)-Bis[*tert*-leucinato(2−)-*N*,*O*]-[(2,2,6,6-tetramethylpiperidinio)methyl]silicate−Dichloromethane (5·CH$_2$Cl$_2$). Compound **7** (500 mg, 2.70 mmol) was added at 20 °C to a stirred suspension of (*S*)-*tert*-leucine (708 mg, 5.40 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred at this temperature for 6 h (evolution of hydrogen). The remaining solid was separated by filtration and discarded, *n*-pentane (40 mL) was added to the filtrate, and the resulting solution was kept undisturbed at 20 °C for 12 h (formation of crystals). The precipitate was isolated by filtration and dried in an argon stream (20 °C, 15 min) to give **5**·CH_2Cl_2 in 78% yield as a colorless crystalline solid (1.11 g, 2.11 mmol); mp 168 °C (dec). ^{15}N VACP/MAS NMR (22 °C, ν_{rot} = 5 kHz): δ −341.4 (br s, Si*N*HC), −292.4 (br s, C$_3$*N*H). ^{29}Si VACP/MAS NMR (22 °C, ν_{rot} = 5 kHz): δ −101.2 to −99.1 (m). ^{1}H NMR (CD_2Cl_2, 23 °C): δ 0.97 (s, 18 H, CHCC*H*$_3$), 1.315 (s, 3 H, CC*H*$_3$), 1.320 (s, 6 H, CC*H*$_3$), 1.49 (s, 3 H, CC*H*$_3$), 1.49 (s, 2 H, SiN*H*C), 1.57−1.92 (m, 6 H, CCH$_2$C), 2.27 (δ_A) and 2.58 (δ_B) (AB part of an ABX system, $^2J_{AB}$ = 16.4 Hz, $^3J_{AX}$ = 3.8 Hz, $^3J_{BX}$ = 3.4 Hz, 2 H, SiC*H*$_A$*H*$_B$NH$_X$), 3.25 (d, $^3J_{HH}$ = 1.7 Hz, 2 H, SiNC*H*C$_2$), 5.9 (br s, 1 H, C$_3$N*H*). ^{13}C NMR (CD_2Cl_2, 23 °C): δ 16.1 (NCC*C*H$_2$C), 20.3 (C*C*H$_3$), 20.4 (C*C*H$_3$), 26.4 (C(*C*H$_3$)$_3$), 29.9 (C*C*H$_3$), 31.0 (C*C*H$_3$), 35.2 (SiN*C*HC$_2$), 39.66 (NC*C*H$_2$C), 39.72 (NC*C*H$_2$C), 41.0 (Si*C*H$_2$N), 64.9 (N*C*C$_3$), 65.3 (N*C*C$_3$), 66.4 (CH*C*C), 176.8 (*C*=O). ^{15}N NMR (CD_2Cl_2, 23 °C): δ −340.7 (Si*N*HC), −292.7 (C$_3$*N*H). ^{29}Si NMR (CD_2Cl_2, 23 °C): δ −100.3. Anal. Calcd for $C_{23}H_{45}Cl_2N_3O_4Si$: C, 52.46; H, 8.61; N, 7.98. Found: C, 52.7; H, 8.3; N, 8.0.

Preparation of (Λ,*S*,*S*)-Bis[prolinato(2−)-*N*,*O*][(2,2,6,6-tetramethylpiperidinio)methyl]silicate−Bis(dichloromethane) (6·2CH$_2$Cl$_2$). Compound **7** (1.00 g, 5.39 mmol) was added at 20 °C to a stirred suspension of (*S*)-proline (1.24 g, 10.8 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred at this temperature for 5 days (evolution of hydrogen). The remaining solid was separated by filtration and discarded, the solvent of the filtrate was partially removed under reduced pressure (→ ca. 7 mL), *n*-pentane (30 mL) was added, and the resulting solution was kept undisturbed at 20 °C for 2 days (formation of crystals). The precipitate was isolated by filtration and dried in an argon stream (20 °C, 15 min) to give **6**·2CH_2Cl_2 in 83% yield as a colorless crystalline solid (2.59 g, 4.47 mmol); mp 122 °C (dec). ^{15}N VACP/MAS NMR (22 °C, ν_{rot} = 7 kHz): δ −332.3 (Si*N*HC), −324.9

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(Si*N*HC), −293.3 (C$_3$*N*H). ^{29}Si VACP/MAS NMR (22 °C, ν_{rot} = 5 kHz): δ −97.5 to −95.0 (m). ^{1}H NMR (CD$_2$Cl$_2$, 23 °C): δ 1.28 (s, 3 H, CC*H*$_3$), 1.29 (s, 6 H, CC*H*$_3$), 1.37−1.51 and 1.91−2.04 (m, 4 H, SiNCHC*H*$_2$C), 1.43 (s, 3 H, CC*H*$_3$), 1.54−1.91 (m, 6 H, CC*H*$_2$C), 1.55−1.71 (m, 4 H, SiNCH$_2$C*H*$_2$C), 2.32 (δ_{A}) and 2.57 (δ_{B}) (AB part of an ABX system, $^2J_{\mathrm{AB}}$ = 16.6 Hz, $^3J_{\mathrm{AX}}$ = 4.0 Hz, $^3J_{\mathrm{BX}}$ = 3.2 Hz, 2 H, SiC$H_{\mathrm{A}}H_{\mathrm{B}}NH_{\mathrm{X}}$), 2.69−2.80 and 3.06−3.16 (m, 4 H, SiNC*H*$_2$C), 3.53 (m, 2 H, SiNC*H*C$_2$), 6.0 (br s, 1 H, C$_3$N*H*). ^{13}C NMR (CD$_2$Cl$_2$, 23 °C): δ 16.0 (NCC*C*H$_2$C), 20.1 (C*C*H$_3$), 20.3 (C*C*H$_3$), 27.1 (SiNCH$_2$*C*H$_2$C), 29.9 (C*C*H$_3$), 30.3 (C*C*H$_3$), 30.5 (SiNCH*C*H$_2$C), 39.5 (NC*C*H$_2$C), 39.6 (NC*C*H$_2$C), 40.6 (Si*C*H$_2$N), 46.7 (SiN*C*H$_2$C), 64.0 (SiN*C*HC$_2$), 64.8 (N*C*C$_3$), 65.3 (N*C*C$_3$), 177.3 (*C*=O). ^{15}N NMR (CD$_2$Cl$_2$, 23 °C): δ −332.0 (Si*N*HC), −298.5 (C$_3$*N*H). ^{29}Si NMR (CD$_2$Cl$_2$, 23 °C): δ −97.8. Anal. Calcd for $C_{22}H_{39}Cl_4N_3O_4Si$: C, 45.60; H, 6.78; N, 7.25. Found: C, 45.8; H, 7.0; N, 7.4.

Preparation of (Λ,*S*,*S*)-Bis[prolinato(2−)-*N*,*O*][(2,2,6,6-tetramethylpiperidinio)methyl]silicate−Hemi(dichloromethane) (6·1/2CH$_2$Cl$_2$). Compound **7** (1.00 g, 5.39 mmol) was added at 20 °C to a stirred suspension of (*S*)-proline (1.24 g, 10.8 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred at this temperature for 2 days (evolution of hydrogen). The remaining solid was separated by filtration and discarded, *n*-pentane (40 mL) was added to the filtrate, and the resulting solution was kept undisturbed at 20 °C for 12 h (formation of crystals). The precipitate was isolated by filtration and dried in an argon stream (20 °C, 5 min) to give **6**·1/2CH$_2$Cl$_2$ in 81% yield as a colorless crystalline product (1.98 g, 4.38 mmol); mp 122 °C (dec). ^{15}N VACP/MAS NMR (22 °C, ν_{rot} = 5 kHz): δ −328.1 (Si*N*HC), −324.4 (Si*N*HC), −322.0 (Si*N*HC), −321.3 (Si*N*HC), −301.3 (C$_3$*N*H), −290.1 (C$_3$*N*H). ^{29}Si VACP/MAS NMR (23 °C, ν_{rot} = 6.5 kHz): δ −97.0 to −93.0 (m). The solution ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR data were identical with those obtained for **6**·2CH$_2$Cl$_2$. Anal. Calcd for $C_{20.5}H_{36}ClN_3O_4Si$: C, 54.47; H, 8.03; N, 9.30. Found: C, 54.4; H, 8.1; N, 9.5.

Crystal Structure Analyses. Suitable single crystals of (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$ were isolated directly from the respective reaction mixtures (see Preparation). The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)). All structures were solved by direct methods.[16] A riding model was employed in the refinement[17] of the C*H* hydrogen atoms, whereas the N*H* and O*H* 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 nos. CCDC-281849 ((Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$), CCDC-281850 ((Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$), CCDC-281851 ((Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$), and CCDC-281852 ((Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Studies. RI-MP2[8] geometry optimizations of the (Λ,*S*,*S*)- and (Δ,*S*,*S*)-enantiomers of **7**−**9** were carried out at the TZP level (with a TZVP auxiliary basis for the fit of the charge density)[9,10] using the *TURBOMOLE* program system.[11] The optimized structures were characterized as minima on the potential energy surfaces by harmonic vibrational frequency analysis. The reported energy differences include the MP2 energies and zero-point vibrational energies obtained by HF calculations.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for (Λ,*S*,*S*)-**4**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**5**·CH$_2$Cl$_2$, (Λ,*S*,*S*)-**6**·2CH$_2$Cl$_2$, and (Λ,*S*,*S*)-**6**·1/2CH$_2$Cl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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