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[(Dimethylammonio)methyl]bis[*cis*-1,2-diphenylethene-1,2-diolato(2−)]silicate: The First Zwitterionic Spirocyclic λ^5*Si*-Silicate Containing *cis*-Ethene-1,2-diolato(2−) Ligands

Melanie Pülm and Reinhold Tacke*

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

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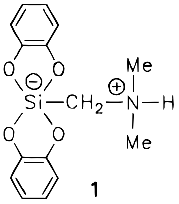
The zwitterionic spirocyclic λ^5*Si*-silicate [(dimethylammonio)methyl]bis[*cis*-1,2-diphenylethene-1,2-diolato(2−)]silicate (**3**) was synthesized by reaction of [(dimethylamino)methyl]trimethoxysilane with benzoin (molar ratio 1:2) in acetonitrile at room temperature and isolated as the crystalline hemiacetonitrile solvate **3**·$^1/_2CH_3CN$ (yield 73%). Compound **3** was characterized by spectroscopic methods (solid-state ^{29}Si CP/MAS NMR; solution-state ^1H and ^{13}C NMR, solvent [D$_6$]DMSO; FAB MS) and the solvate **3**·$^1/_2CH_3CN$ studied by single-crystal X-ray diffraction. Crystal data are as follows: $C_{32}H_{30.5}N_{1.5}O_4Si$, space group $P\bar{1}$, a = 9.3786(11) Å, b = 11.1090(12) Å, c = 14.0427(14) Å, α = 95.405(11)°, β = 107.61(2)°, γ = 97.106(11)°, V = 1370.3(3) Å^3, T = 193(2) K, Z = 2, and $R1$ = 0.0437. Compound **3** contains a pentacoordinate silicon atom (formally negatively charged) and a tetracoordinate nitrogen atom (formally positively charged). The coordination polyhedron around the silicon atom in the crystal of **3**·$^1/_2CH_3CN$ is best described as a slightly distorted trigonal bipyramid with the carbon atom in an equatorial position. In terms of the Berry pseudorotation coordinate, the geometry is displaced by 4.6% from the ideal trigonal bipyramid toward the ideal square pyramid. The experimental geometric parameters are in good agreement with the calculated data obtained for the related model species bis[*cis*-ethene-1,2-diolato(2−)]hydridosilicate(1−) (**4**) and [(dimethylammonio)methyl]bis[*cis*-ethene-1,2-diolato(2−)]silicate (**5**) by ab initio studies (geometry optimizations at the SCF/SVP level). According to NMR spectroscopic studies, the zwitterion **3** also exists in solution ([D$_6$]DMSO).

Introduction



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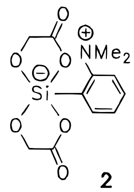

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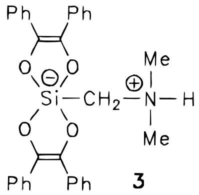

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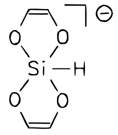

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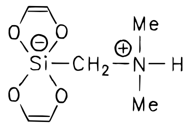

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The study of compounds with higher coordinate silicon is currently one of the main areas of research in silicon chemistry.[1] In a series of recent papers on zwitterionic spirocyclic λ^5*Si*-silicates, we have contributed to this topic.[1e−h,2] Compounds **1** and **2** are typical examples of the λ^5*Si*-silicates described in these publications. The spirocyclic zwitterions of this particular formula type contain bidentate diolato(2−) ligands of the benzene-1,2-diolato(2−) or glycolato(2−)-O^1,O^2 type. In this paper, we report on the synthesis and structural characterization of [(dimethylammonio)methyl]bis[*cis*-1,2-diphenylethene-1,2-diolato(2−)]silicate (**3**) (crystal structure of **3**·$^1/_2CH_3CN$), the first zwitterionic λ^5*Si*-silicate containing *cis*-ethene-1,2-diolato(2−) ligands. In addition, the results of ab initio studies concerning the structure of the related model species bis[*cis*-ethenyl-1,2-diolato(2−)]hydridosilicate(1−) (**4**) and [(dimethylammonio)methyl]bis[*cis*-ethene-1,2-diolato(2−)]silicate (**5**) are described and compared with the crystal structure of **3**·$^1/_2CH_3CN$. The studies presented here were carried out as a part of our systematic investigations on zwitterionic (molecular) λ^5*Si*-silicates (in this context, see refs 1e−h, 2, and 3).

Results and Discussion

Synthesis. The zwitterionic λ^5*Si*-silicate **3** was synthesized according to Scheme 1 by reaction of [(dimethylamino)methyl]trimethoxysilane (**6**) with benzoin

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* To whom correspondence should be addressed.

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Scheme 1

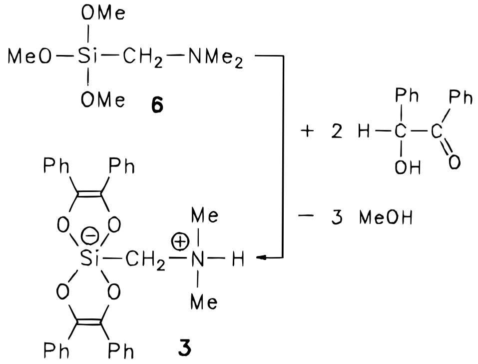


Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of $3 \cdot {}^1/_2CH_3CN$

empirical formula	$C_{32}H_{30.5}N_{1.5}O_4Si$
formula mass, g mol^{-1}	528.17
collection *T*, K	193(2)
λ(Mo Kα), Å	0.710 73
cryst syst	triclinic
space group (no.)	$P\bar{1}$ (2)
a, Å	9.3786(11)
b, Å	11.1090(12)
c, Å	14.0427(14)
α, deg	95.405(11)
β, deg	107.61(2)
γ, deg	97.106(11)
V, Å^3	1370.3(3)
Z	2
D(calcd), g cm^{-3}	1.280
μ, mm^{-1}	0.125
F(000)	558
cryst dimens, mm	0.4 × 0.4 × 0.3
2θ range, deg	4.50−45.94
index ranges	$-10 \le h \le 9$, $-12 \le k \le 12$, $0 \le l \le 15$
no. of coll reflns	4623
no. of indep reflns	3799
R_{int}	0.0317
no. of reflns used	3799
no. of params	368
no. of restraints	17
S^a	1.044
weight params *a*/*b*^{b}	0.0390/0.3931
$R1^c$ [$I > 2\sigma(I)$]	0.0437
$wR2^d$ (all data)	0.0984
extinction coeff	0.0062(11)
max/min res electron dens, e Å^{-3}	+0.172/−0.191

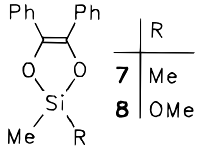
^{a} $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; *n* = no. of reflections; *p* = no. of parameters. ^{b} $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (F_o^2 + 2F_c^2)/3$. ^{c} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{d} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

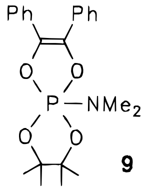
(molar ratio 1:2) in acetonitrile at room temperature and isolated in 73% yield as the crystalline hemiacetonitrile solvate $\mathbf{3}\cdot{}^1/_2CH_3CN$. The *cis*-1,2-diphenylethene-1,2-diolato(2−) ligands of **3** formally derive from the tautomeric benzoin species *cis*-HO(Ph)C═C(Ph)OH.

The acetonitrile of $\mathbf{3}\cdot{}^1/_2CH_3CN$ can be easily removed from the crystal lattice at room temperature in vacuo or by heating under normal pressure to yield the solvent-free crystalline product **3**. This observation is in accordance with the crystal structure of $\mathbf{3}\cdot{}^1/_2CH_3CN$, which indicates only van der Waals interactions between the zwitterions and the acetonitrile molecules (in this context, see Crystal Structure Analysis).

Compounds **3** and $\mathbf{3}\cdot{}^1/_2CH_3CN$ are almost insoluble in nonpolar organic solvents and also exhibit very poor solubilities in polar organic solvents. According to its zwitterionic nature, **3** is characterized by a high melting point (196 °C, dec). The identity of **3** was established by elemental analyses (C, H, N), solution-state NMR studies ([D$_6$]DMSO; ^{1}H, ^{13}C), and mass spectrometric investigations (FAB MS). In addition, **3** was studied by solid-state NMR spectroscopy (^{29}Si CP/MAS) and $\mathbf{3}\cdot{}^1/_2CH_3CN$ characterized by single-crystal X-ray diffraction. All these investigations unequivocally established the existence of **3** in the solid state and in solution.

To the best of our knowledge, the zwitterionic spirocyclic λ^5*Si*-silicate **3** is the first pentacoordinate silicon compound containing *cis*-ethene-1,2-diolato(2−) ligands, whereas monocyclic tetracoordinate silicon species containing this moiety have already been described in the literature.[4] The silanes **7**[4a] and **8**[4b] are examples of this





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type of compound. Related spirocyclic pentacoordinate phosphorus compounds are also known,[5] such as the phosphorane **9**.[5a] Compounds **7**−**9** were obtained by cycloaddition reactions of the α-diketone PhC(O)−C(O)-Ph with the corresponding silicon(II) and phosphorus(III) precursors.

Crystal Structure Analysis. Compound $\mathbf{3}\cdot{}^1/_2CH_3CN$ crystallizes in the space group $P\bar{1}$, the unit cell containing two enantiomeric zwitterions **3** and one disordered acetonitrile molecule. The crystal data and experimental parameters used for this study are given in Table 1 (for further details, see Experimental Section). The molecular structure of **3** in the crystal of **3**·

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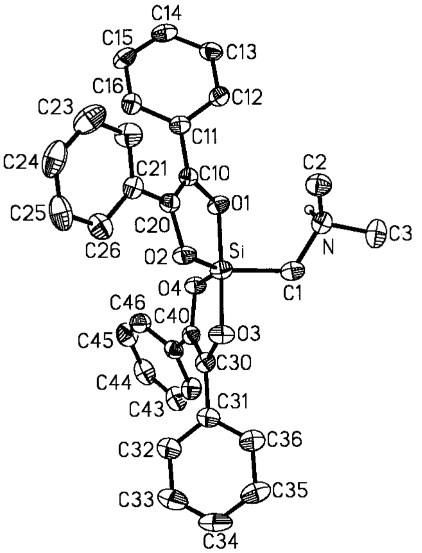


Figure 1. Molecular structure of **3** in the crystal of **3**·$^{1}/_{2}CH_3CN$ (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. The hydrogen atoms (except for NH) are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 3·$^{1}/_{2}CH_3CN$

Si−O1	1.788(2)	Si−O4	1.704(2)
Si−O2	1.680(2)	Si−C1	1.897(3)
Si−O3	1.763(2)		
O1−Si−O2	89.15(9)	O2−Si−O4	120.78(10)
O1−Si−O3	177.50(10)	O2−Si−C1	119.26(11)
O1−Si−O4	88.78(9)	O3−Si−O4	89.15(9)
O1−Si−C1	94.72(10)	O3−Si−C1	87.51(10)
O2−Si−O3	90.72(9)	O4−Si−C1	119.89(11)

$^{1}/_{2}CH_3CN$ is depicted in Figure 1. Selected interatomic distances and angles are listed in Table 2.

The coordination polyhedron around the silicon atom of **3** can be described as an only slightly distorted trigonal bipyramid, each bidentate *cis*-1,2-diphenylethene-1,2-diolato(2−) ligand spanning one axial (O1, O3) and one equatorial site (O2, O4). The axial Si−O distances are 0.06−0.11 Å longer than the equatorial ones. In terms of the Berry pseudorotation coordinate, the dihedral angle method[6] shows that the geometry of the coordination polyhedron is displaced by 4.6% from the ideal trigonal bipyramid toward the ideal square pyramid (pivot atom C1).

As expected from the presence of the NH group and the potential oxygen and nitrogen acceptor atoms, **3**·$^{1}/_{2}CH_3CN$ forms hydrogen bonds in the crystal. Bifurcate hydrogen bonds with an intramolecular N−H···O1 interaction [N···O1 = 2.833(3) Å, N−H = 0.89(3) Å, H···O1 = 2.49(3) Å, N−H···O1 = 103(2)°] and an intermolecular N−H···O1′ interaction [N···O1′ = 3.042(3) Å, N−H = 0.89(3) Å, H···O1′ = 2.22(3) Å, N−H···O1′ = 152(2)°] lead to the formation of centrosymmetric dimers in the crystal [O1···H···O1′ = 95.9(12)°].

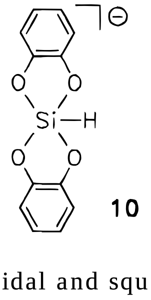
There exist only van der Waals interactions between the zwitterion **3** and the solvent molecule acetonitrile (C1A−C2A−N1A), which is found in channels between the stacks formed by the dimers of **3**. The shortest interatomic distance between the zwitterion **3** and the solvent molecule acetonitrile amounts to 2.52 Å (distance between the C26−*H* and C1A−*H* hydrogen atoms).

NMR Studies. Compound **3** was characterized by ^{29}Si CP/MAS NMR experiments in the solid state and by ^{1}H and ^{13}C NMR studies in solution ([D$_6$]DMSO). The isotropic ^{29}Si chemical shift (δ −87.6) observed in the CP/MAS NMR spectrum clearly characterizes this ^{29}Si resonance signal as arising from pentacoordinate silicon. Probably because of the very poor solubility of **3** and **3**·$^{1}/_{2}CH_3CN$ in [D$_6$]DMSO, solution-state ^{29}Si NMR experiments failed. Nevertheless, the ^{1}H and ^{13}C NMR data clearly indicate that the zwitterion **3** exists in solution as well. As would be expected for the bis[*cis*-1,2-diphenylethene-1,2-diolato(2−)]silicate framework, only one set of ^{13}C resonance signals for the Ph−C moieties is observed. On the other hand, the ^{1}H chemical shifts observed for the NCH$_3$ (δ 2.78) and NH group (δ 8.4) indicate the presence of an ammonium-type nitrogen atom. Furthermore, ^{1}H,^{1}H-COSY experiments gave evidence for a coupling of the SiCH$_2$N and NCH$_3$ hydrogen atoms with the NH hydrogen atom.

Theoretical Studies. The structure of the model species bis[*cis*-ethene-1,2-diolato(2−)]hydridosilicate(1−) (**4**) and [(dimethylammonio)methyl]bis[*cis*-ethene-1,2-diolato(2−)]silicate (**5**) were studied by quantum chemical methods. For this purpose, geometry optimizations at the SCF[7] level with an optimized SVP basis set[8] were performed using the TURBOMOLE[9] program system. Stationary geometries and transition states were characterized as local minima and saddle points, respectively, by calculation of the vibrational frequencies. The energies given include the single-point MP2 energy and the zero-point vibrational energy.

The SCF/SVP geometry optimizations of **4** demonstrated a slightly distorted trigonal bipyramid (**4a**, C_2 symmetry) to be the energetically preferred structure, whereas the alternative square-pyramidal geometry (**4b**, C_{2v} symmetry) was found to be energetically less favorable.[10] The calculated structures of **4a** and **4b** are depicted in Figure 2; selected interatomic distances and angles are listed in Table 3.

The square-pyramidal geometry **4b** represents a transition state for a Berry-type pseudorotation process (SiH hydrogen atom as the pivot ligand) which allows a conversion of the Λ- and Δ-enantiomer of **4a** (local minima) into each other. The energy barrier for this process is 6.90 kJ mol^{-1}. This value is very similar to that calculated for the bis[benzene-1,2-diolato(2−)]hydridosilicate(1−) ion (**10**), the energy difference between the trigonal-bipyramidal and square-pyramidal geometry of this species being 5.82 kJ mol^{-1}.[11] As the



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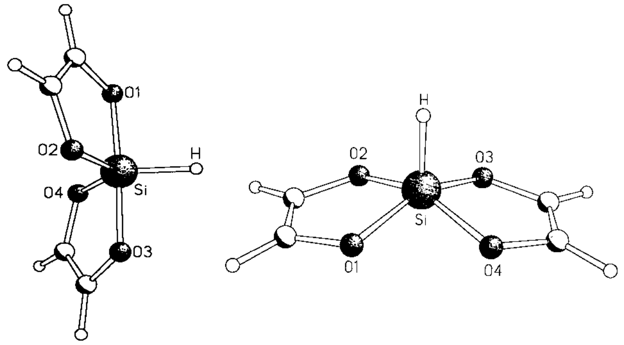

4a
C_2 Symmetry
(0 kJ mol^{-1})

4b
C_{2v} Symmetry
(6.90 kJ mol^{-1})

Figure 2. Calculated structures and relative energies of **4a** (local minimum) and **4b** (transition state) as obtained by SCF/SVP geometry optimizations.

Table 3. Selected Calculated Interatomic Distances (Å) and Angles (deg) for 4a and 4b

	4a	4b
Si–O1, Si–O3	1.787	1.740
Si–O2, Si–O4	1.696	1.740
Si–H	1.477	1.480
O1–Si–O2, O3–Si–O4	87.9	86.9
O1–Si–O3	176.8	152.5
O1–Si–O4, O2–Si–O3	90.5	86.6
O1–Si–H, O3–Si–H	91.6	103.8
O2–Si–O4	121.0	152.5
O2–Si–H, O4–Si–H	119.5	103.8

pseudorotation process for **4** and **10** needs only a small amount of energy, package effects in the crystal of related zwitterionic λ^5*Si*-silicates (such as **1** and **3**) are expected to determine the geometry of the respective *Si*-coordination polyhedron of these compounds. Indeed, crystal structure analyses of a series of derivatives of **1** have demonstrated that almost all transitions between a nearly ideal trigonal-bipyramidal and a nearly ideal square-pyramidal *Si*-coordination polyhedron are possible.[1e,2a–g,m] The same phenomenon is expected for related zwitterionic λ^5*Si*-silicates containing two cis-ethene-1,2-diolato(2–) ligands. Thus, the trigonal-bipyramidal geometry observed for the *Si*-coordination polyhedron of **3** in the crystal of **3**·$^1/_2$CH$_3$CN should be regarded as a specific characteristic of this particular compound rather than a general structural feature of compounds of this formula type. Nevertheless, the geometric parameters obtained for **3**·$^1/_2$CH$_3$CN by single-crystal X-ray diffraction are in good agreement with those obtained for **4a** by quantum chemical methods.

In addition, SCF/SVP geometry optimizations of **5** were performed and the resulting data compared with those obtained experimentally for **3**·$^1/_2$CH$_3$CN by single-crystal X-ray diffraction. The calculated structure of **5**[12] (local minimum) is depicted in Figure 3. Selected interatomic distances and angles for **5** as well as the differences between the geometric data of **5** and **3**·$^1/_2$CH$_3$CN are listed in Table 4.

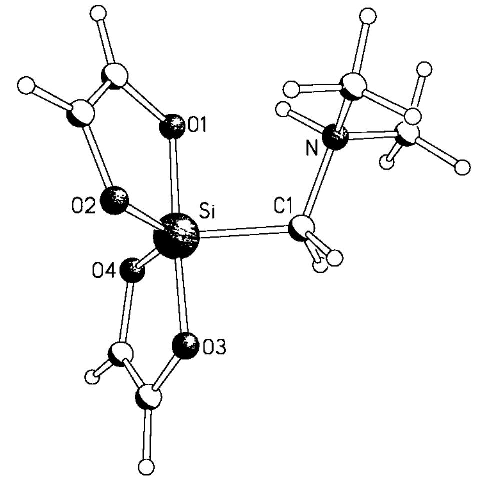

Figure 3. Calculated structure (local minimum) of **5** as obtained by SCF/SVP geometry optimization.

Table 4. Selected Calculated Interatomic Distances (Å) and Angles (deg) for 5 and the Differences between These Data and the Corresponding Experimental Data[a] for 3·$^1/_2$CH$_3$CN

	5	Δ(**5**, **3**·$^1/_2$CH$_3$CN)
Si–O1	1.808	+0.020
Si–O2	1.677	–0.003
Si–O3	1.737	–0.026
Si–O4	1.672	–0.032
Si–C1	1.939	+0.042
O1–Si–O2	87.3	–1.85
O1–Si–O3	177.5	0
O1–Si–O4	91.1	+2.32
O1–Si–C1	89.0	–5.72
O2–Si–O3	94.3	+3.58
O2–Si–O4	122.7	+1.92
O2–Si–C1	120.0	+0.74
O3–Si–O4	89.7	+0.55
O3–Si–C1	88.6	+1.09
O4–Si–C1	117.3	–2.59

[a] Experimental data taken from Table 2.

The geometries of the *Si*-coordination polyhedra of **3** and **5** are very similar. The relevant bond distances and angles deviate only slightly from each other (biggest deviations: Si–C1, 0.04 Å; O1–Si–C1, 5.72°). The Si–O1 distance of **5** is significantly longer than the Si–O3 distance (difference 0.071 Å), whereas the Si–O2 and Si–O4 distances of **5** are very similar (difference 0.005 Å). This result can be described in terms of an intramolecular N–H···O1 hydrogen bond [N···O1 = 2.587 Å, N–H = 1.024 Å, H···O1 = 1.780 Å, N–H···O1 = 132.8°].

Experimental Section

General Procedures. The synthesis of **3** was carried out under dry nitrogen; the acetonitrile used was dried and purified according to a standard procedure and stored under nitrogen. The melting point was determined with a DuPont Instruments differential scanning calorimeter type Thermal Analyzer 910. ^{1}H NMR [300.1 MHz; solvent [D$_6$]DMSO, internal standard [D$_5$]DMSO (δ 2.49)] and ^{13}C NMR spectra [75.5 MHz; solvent [D$_6$]DMSO, internal standard [D$_6$]DMSO (δ 39.50)] were recorded at room temperature on a Bruker DRX-300 spectrometer. Assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C,^{1}H long-range COSY experiments. The ^{29}Si CP/MAS NMR spectrum was recorded on a Bruker DSX-500 spectrometer at 11.74 T with double air

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[8] SVP basis set used: Si, (10s7p1d)/[4s3p1d]; C, N, and O, (7s4p1d)/[3s2p1d]; H, (4s1p)/[2s1p]. For details of the SVP basis set optimization, see ref 3d.

[9] (a) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kömel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169. (b) Computational results obtained by using software programs from Biosym/MSI of San Diego.

[10] Calculated SCF energies (Hartree): **4a** (C_2 symmetry), –743.683157; **4b** (C_{2v} symmetry), –743.680529.

[11] Dannappel, O.; Tacke, R. In *Organosilicon Chemistry II—From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996; pp 453–458.

[12] Calculated SCF energy (Hartree): **5** (C_1 symmetry), –916.708638.

bearing rotors of ZrO_2 (diameter 7 mm) [99.36 MHz; external standard TMS (δ 0)]. Mass spectra were obtained with a Finnigan MAT-8430 mass spectrometer (FAB MS; 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source). The selected *m/z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, and ^{28}Si. The starting material [(dimethylamino)methyl]trimethoxysilane (**6**) was prepared according to a published procedure.[2f]

Preparation of [(Dimethylammonio)methyl]bis[*cis*-1,2-diphenylethene-1,2-diolato(2−)]silicate (3). A solution of **6** (717 mg, 4.00 mmol) in acetonitrile (10 mL) was added dropwise over 5 min at room temperature to a stirred solution of benzoin (1.70 g, 8.01 mmol) in acetonitrile (100 mL) (spontaneous formation of a precipitate). After the reaction mixture was stirred at room temperature for 24 h, the precipitate was filtered off, washed with acetonitrile (2 × 10 mL), recrystallized from acetonitrile, and then dried in vacuo (0.01 Torr, 20 °C, 7 h) to give **3** in 73% yield as a crystalline solid (1.49 g, 2.94 mmol); mp 196 °C (dec). ^{1}H NMR ([D$_6$]DMSO): δ 2.67 (d, $^3J_{HH} = 5.3$ Hz, 2 H, $SiCH_2N$), 2.78 (d, $^3J_{HH} = 4.9$ Hz, 6 H, NCH_3), 7.08−7.27 and 7.34−7.44 (m, 20 H, CC_6H_5), 8.4 (br s, 1 H, NH). ^{13}C NMR ([D$_6$]DMSO): δ 45.9 (NCH_3), 49.5 ($SiCH_2N$), 126.0 (C4, C_6H_5), 126.4 (C3/C5, C_6H_5), 127.8 (C2/C6, C_6H_5), 135.3 (C1, C_6H_5), 135.7 (OC). ^{29}Si CP/MAS NMR (spinning rate 4105 Hz, 348 transients, contact time 7 ms, 90° ^{1}H transmitter pulse length 6.8 μs, repetition time 25 s): δ −87.6. FAB MS (negative ions): *m/z* 506 [2%, M − H$^+$], 153 [100%, matrix]. FAB MS (positive ions): *m/z* 508 [6%, M + H$^+$], 154 [100%, matrix]. Anal. Calcd for $C_{31}H_{29}NO_4Si$: C, 73.34; H, 5.76; N, 2.76. Found: C, 73.5; H, 5.8; N, 2.8.

Crystal Structure Analysis of 3. A suitable single crystal of $\mathbf{3}\cdot{}^1/_2CH_3CN$ was obtained by crystallization of **3** from acetonitrile at room temperature. The crystal was mounted in inert oil (RS 3000, Riedel-deHaën) on a glass fiber and transferred to the cold gas stream of the diffractometer (Enraf-Nonius four-circle diffractometer; graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å)).[13] Cell parameters were obtained from least-squares fits to the settings of 25 reflections in the range 20° ≤ 2θ ≤ 25°. No significant deviations in intensity were registered for two monitor reflections recorded at regular intervals. The structure was solved by direct methods.[14] All non-hydrogen atoms were refined anisotropically.[15] A riding model was employed in the refinement of the CH hydrogen atom positions. The position of the NH hydrogen atom was localized in difference Fourier syntheses and refined freely. The acetonitrile molecule (numbering scheme, C1A−C2A−N1A) resides close to a center of inversion; it was refined with a special position constraint suppressed.

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Supporting Information Available: Tables of atomic coordinates, additional interatomic distances and angles, and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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