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Notes

[Benzene-1,2-diolato(2−)][benzene-1,2-diolato(1−)]methyl[(2,2,6,6-tetramethylpiperidinio)methyl]silicate: Isolation, Structural Characterization, and Thermally Induced Methane Elimination

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*Summary: A novel zwitterionic pentacoordinate silicon(IV) complex with an SiO_3C_2 skeleton was synthesized, [benzene-1,2-diolato(2−)][benzene-1,2-diolato(1−)]methyl[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**11**). It contains one bidentate benzene-1,2-diolato(2−) ligand and one monodentate benzene-1,2-diolato(1−) ligand, a new structural motive in silicon(IV) coordination chemistry. Compound **11** was obtained by treatment of dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane (**10**) with 2 molar equiv of 1,2-dihydroxybenzene and was structurally characterized in solution (^1H, ^{13}C, and ^{29}Si NMR) and in the solid state (^{29}Si VACP/MAS NMR; crystal structure analysis of the solvate $\mathbf{11}\cdot 2CH_2Cl_2$). Upon heating in acetonitrile, **11** undergoes a methane elimination to afford the zwitterionic spirocyclic pentacoordinate silicon(IV) complex bis[benzene-1,2-diolato(2−)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**12**). The reaction sequence **10** → **11** (isolated intermediate) → **12** gives some insight into the mechanism of the reaction of dialkoxy(aminoorganyl)organylsilanes with organic diols to yield zwitterionic pentacoordinate silicon(IV) complexes of the (ammonioorganyl)bis[diolato(2−)]silicate type.*

Introduction

In context with our studies on zwitterionic λ^5Si-silicates,[1] we have discovered a series of remarkable Si−C bond cleavage reactions mediated by organic dihydroxy compounds, such as benzene-1,2-diols,[2] α-hydroxycarboxylic acids,[2h,3] salicylic acid,[4] and ethane-1,2-diol.[5] Dialkoxy(aminoorganyl)organylsilanes (SiO_2C_2 skeleton), and in some cases even alkoxy(aminoorganyl)diorganylsilanes ($SiOC_3$ skeleton), were found to react with these dihydroxy compounds via Si−O and Si−C bond cleavage to afford spirocyclic λ^5Si-silicates with an SiO_4C framework. In most cases, these reactions were performed in acetonitrile at room temperature. The transformations **1** → **3**,[2d] **2** → **3**,[2h] **4** → **5**,[2d] **6** → **7**,[3a] and **8** → **9**[3b] are typical examples (Scheme 1). Recently, such Si−C cleavage reactions were applied to a novel silicon-based linkage and cleavage strategy for solid-phase synthesis of aromatic organic compounds.[2h,6]

Almost nothing is known about the reaction mechanism of these cleavage reactions. We have now succeeded in isolating an intermediate in the transformation of the silane **10** into the zwitterionic λ^5Si-silicate **12**, compound **11** (Scheme 2). We report here on the isolation and structural characterization of **11** (solution and solid-state NMR spectroscopy; crystal structure analysis of the solvate $\mathbf{11}\cdot 2CH_2Cl_2$) and its further thermally induced conversion into **12**. The zwitterionic λ^5Si-silicate **11** contains one bidentate benzene-1,2-diolato(2−) ligand and one monodentate benzene-1,2-diolato(1−) ligand, a new structural motive in silicon(IV) coordination chemistry and also scarcely found in the coordination chemistry of other elements (for an example in niobium(V) chemistry, see ref 7). Compound **11** is the first example of a zwitterionic pentacoordinate silicon(IV) complex with an SiO_3C_2 skeleton (for reviews dealing with higher coordinate silicon, see ref 8).

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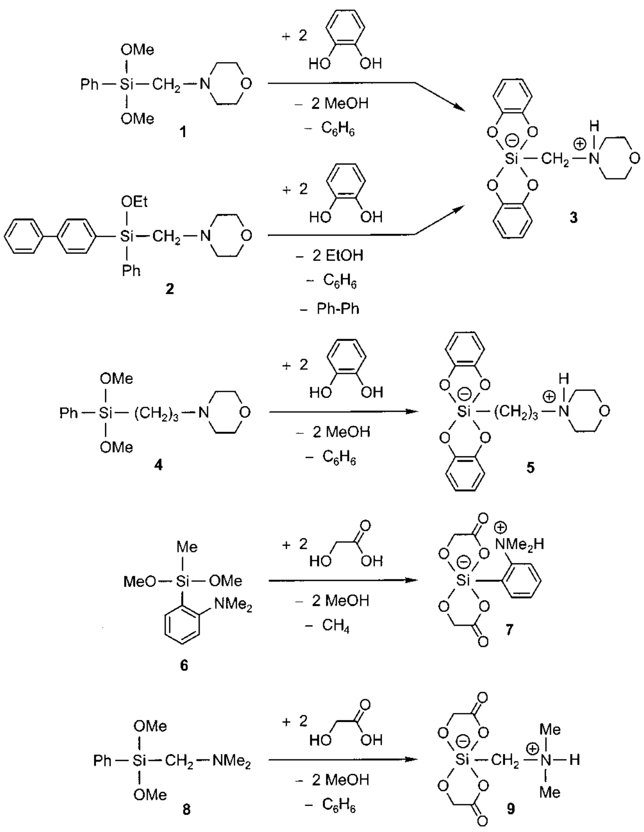
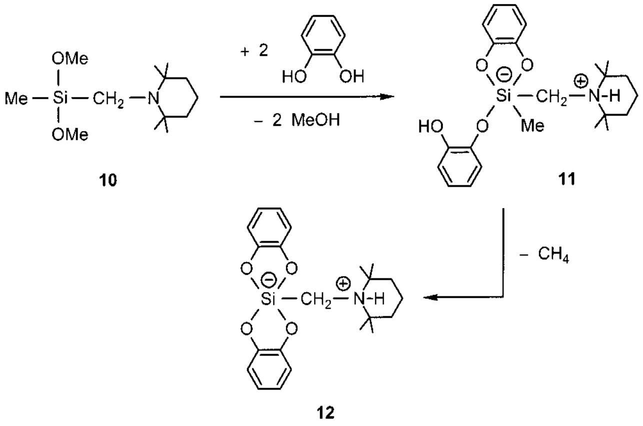
Scheme 1



Scheme 2



Results and Discussion

Syntheses. [Benzene-1,2-diolato(2−)][benzene-1,2-diolato(1−)]methyl[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**11**) was prepared according to Scheme 2 by treatment of dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane (**10**)[9] with 2 molar equiv of 1,2-dihydroxybenzene in acetonitrile at 0 °C. Crystallization of the crude product from dichloromethane/*n*-pentane afforded the crystalline solvate $\mathbf{11}\cdot 2CH_2Cl_2$, which was dried in vacuo to give analytically pure **11** in 88% yield as a colorless powder. This product was found to be surprisingly stable in acetonitrile at room temperature. Upon heating of the solution under reflux, the zwitterionic spirocyclic λ^5*Si*-silicate bis[benzene-1,2-diolato(2−)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**12**) was formed, along with methane (Scheme 2). This compound (for an alternative synthesis, see ref 10) was formed quantitatively and isolated as a colorless solid.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of $\mathbf{11}\cdot 2CH_2Cl_2$

empirical formula	$C_{25}H_{37}Cl_4NO_4Si$
formula mass, g mol^{-1}	585.45
collection *T*, K	173(2)
λ(Mo Kα), Å	0.71073
cryst syst	monoclinic
space group (No.)	$P2_1/c$ (14)
a, Å	11.440(2)
b, Å	15.188(3)
c, Å	17.037(3)
β, deg	100.20(3)
V, Å^3	2913.1(10)
Z	4
D(calcd), g cm^{-3}	1.335
μ, mm^{-1}	0.478
F(000)	1232
cryst dimens, mm	0.5 × 0.4 × 0.3
2θ range, deg	4.50−52.74
index ranges	$-14 \le h \le 14$, $-18 \le k \le 18$, $-21 \le l \le 21$
no. of collected reflns	42961
no. of ind reflns	5952
R_{int}	0.0533
no. of reflns used	5952
no. of params	384
no. of restraints	26
S^a	1.049
weight params *a*/*b* [b]	0.0526/0.5145
$R1^c$ ($I > 2\sigma(I)$)	0.0342
$wR2^d$ (all data)	0.0940
max./min. residual electron density, e Å^{-3}	+0.285/−0.161

[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 $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

The identities of **11** and **12** were established by elemental analyses (C, H, N), solution NMR studies (^{1}H, ^{13}C, ^{29}Si), and solid-state ^{29}Si VACP/MAS NMR experiments. In addition, compound $\mathbf{11}\cdot 2CH_2Cl_2$ was structurally characterized by single-crystal X-ray diffraction.

Crystal Structure Analysis. The crystal data and experimental parameters used for the crystal structure analysis of $\mathbf{11}\cdot 2CH_2Cl_2$ are summarized in Table 1. The structure of the zwitterion in the crystal is depicted in Figure 1; selected interatomic distances and angles are listed in Table 2.

The zwitterion **11** is chiral (C_1 symmetry), and the crystal of racemic $\mathbf{11}\cdot 2CH_2Cl_2$ (space group $P2_1/c$) is built up by (*A*)- and (*C*)-enantiomers.[11] The coordination polyhedron around the silicon atom is best described as

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(11) The stereodescriptors (*A*) and (*C*) are used according to *Nomenclature of Inorganic Chemistry, Recommendations 1990*; International Union of Pure and Applied Chemistry (Ed.); Blackwell Scientific Publications: Boston, MA, 1990; I-10.7.3.2.

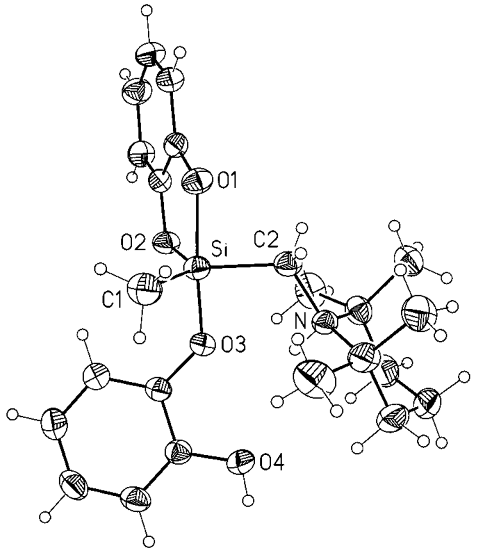


Figure 1. Structure of the zwitterion ((*C*)-enantiomer) in the crystal of **11**·2CH$_2$Cl$_2$ (probability level of displacement ellipsoids 50%).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 11·2CH$_2$Cl$_2$

Si−O1	1.8771(11)	O1−Si−C1	89.12(6)
Si−O2	1.7095(10)	O1−Si−C2	86.01(5)
Si−O3	1.7549(10)	O2−Si−O3	90.40(5)
Si−C1	1.8720(17)	O2−Si−C1	122.62(7)
Si−C2	1.9114(16)	O2−Si−C2	116.92(6)
		O3−Si−C1	97.41(6)
O1−Si−O2	86.52(5)	O3−Si−C2	90.24(5)
O1−Si−O3	173.44(5)	C1−Si−C2	119.78(8)

Table 3. Hydrogen-Bonding Geometries for 11·2CH$_2$Cl$_2$[a]

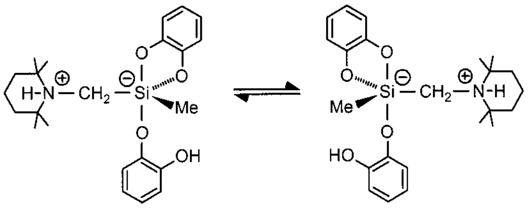
D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
N−H···O3 (intra)	0.884(18)	1.974(18)	2.6619(17)	133.6(15)
O4−H···O1 (inter)	0.83(2)	1.83(2)	2.6607(15)	172(2)

[a] Data calculated by using the program *PLATON*.[12]

a distorted trigonal bipyramid, the bidentate benzene-1,2-diolato(2−) ligand spanning one axial and one equatorial site. The benzene-1,2-diolato(1−) ligand occupies the second axial position. The axial Si−O distances [1.7549(10) and 1.8771(11) Å] are longer than the equatorial one [1.7095(10) Å]. The methyl and the (2,2,6,6-tetramethylpiperidinio)methyl ligand occupy equatorial positions, with Si−C distances of 1.8720(17) and 1.9114(16) Å, respectively.

As would be expected from the presence of the potential OH and NH donor functions and the potential oxygen acceptor atoms, O−H···O and N−H···O hydrogen bonds were observed in the crystal of **11**·2CH$_2$Cl$_2$ (Table 3). Besides an intramolecular N−H···O3 interaction, the existence of an intermolecular O4−H···O1 hydrogen bond can be assumed, leading to the formation of infinite chains along the base vector [0 1 0].[12]

NMR Studies. The isotropic ^{29}Si chemical shift of **11** ($\delta = -75.4$ ppm) obtained in a solid-state ^{29}Si VACP/MAS NMR experiment clearly characterizes the ^{29}Si resonance signal as arising from a pentacoordinate



(*A*)-**11** (*C*)-**11**

Figure 2. Enantiomerization of the zwitterionic λ^5*Si*-silicate **11** in solution. This process is based on the inversion of absolute configuration of the chiral trigonal-bipyramidal *Si*O$_3$C$_2$ skeleton ((*A*)-configuration ⇌ (*C*)-configuration).

silicon atom and is very similar to the ^{29}Si NMR shift determined in solution ($\delta = -75.7$ ppm; solvent CDCl$_3$). The ^{1}H and ^{13}C NMR data (see Experimental Section) also suggest the existence of the zwitterion **11** in solution (CDCl$_3$).

The (*A*)- and (*C*)-enantiomers of **11** are configurationally stable on the NMR time scale at room temperature, as is evident from the ^{1}H NMR spectrum. The chiral nature of the λ^5*Si*-silicate skeleton of **11** is reflected by the ABX spin system observed for the SiCH$_A$H$_B$NH$_X$ moiety (diastereotopic SiCH$_2$N protons). This chirality can also be deduced from the ^{13}C NMR spectrum (−16 °C), which shows separate resonance signals for all pairs of diastereotopic nuclei. It is interesting to note that 22 resonance signals were observed for the 23 different ^{13}C nuclei of **11** (two nuclei accidentally isochronous). Enantiomerization at the silicon atom ((*A*)/(*C*)-enantiomerization, Figure 2) was observed by coalescence of the SiCH$_A$H$_B$N spin system in the ^{1}H NMR spectrum at 55 °C. The activation free enthalpy for this process was estimated to be $\Delta G^{\ddagger} = 68.0(5)$ kJ mol^{-1}.

Conclusion

With the isolation and structural characterization of compound **11** we got some insight into the mechanism of the reaction of dialkoxy(aminoorganyl)organylsilanes with organic diols to yield zwitterionic pentacoordinate (ammonioorganyl)bis[diolato(2−)]silicates. Further studies are planned to get more information about this remarkable type of reaction. These investigations will also include related Si−C bond cleavage reactions mediated by aceto- and benzohydroxamic acid[13] and by benzoin.[1]

Experimental Section

General Procedures. The 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 DuPont Instruments differential scanning calorimeter, type Thermal Analyzer 910. The ^{1}H, ^{13}C, 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; ^{29}Si, 59.6 MHz). CDCl$_3$ was used as solvent. Chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H, δ 7.24), internal CDCl$_3$ (^{13}C, δ 77.0), and external TMS (^{29}Si, δ 0). Analysis and assignment of the NMR data were supported by ^{1}H,^{13}C correlation experiments and DEPT 135 experiments. Solid-state ^{29}Si VACP/MAS NMR

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

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spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer at 79.5 MHz with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample (external standard, TMS (δ 0); spinning rate, 5 kHz; contact time, 5 ms; 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s).

Preparation of Dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane (10). This compound was synthesized according to ref 9.

Preparation of [Benzene-1,2-diolato(2−)][benzene-1,2-diolato(1−)]methyl[(2,2,6,6-tetramethylpiperidinio)methyl]silicate (11). Compound **10** (1.00 g, 3.85 mmol) was added to a stirred solution of benzene-1,2-diol (849 mg, 7.71 mmol) in acetonitrile (1 mL) at 0 °C and the mixture stirred for 5 min at the same temperature (formation of a solid). The volatile components were removed in vacuo (0.01 Torr, 20 °C, 1 h), and the solid residue was recrystallized from dichloromethane/*n*-pentane (1:2 (v/v); addition of *n*-pentane to a solution of **11** in dichloromethane) at 20 °C. The resulting colorless crystalline solvate **11**·$2CH_2Cl_2$ was isolated by filtration and dried in vacuo (0.01 Torr, 20 °C, 3 h; loss of CH_2Cl_2) to give solvent-free **11** in 88% yield as a colorless powder (1.40 g, 3.38 mmol); mp 139 °C dec (loss of CH_4). ^{1}H NMR ($CDCl_3$, 22 °C): δ 0.30 (s, 3 H, $SiCH_3$), 1.28−1.79 (m, 18 H, CCH_3, CCH_2C), 2.60 (δ_A), 2.73 (δ_B), and 7.9 (br s, δ_X) (ABX system, $^2J_{AB} = 17.0$ Hz, $^3J_{AX} = 2.1$ Hz, $^3J_{BX} = 3.1$ Hz, 3 H, $SiCH_AH_BNH_X$), 6.52−6.93 (m, 8 H, ArH), 8.8 (br s, 1 H, OH). ^{13}C NMR ($CDCl_3$, −16 °C): δ 0.9 ($SiCH_3$), 15.7 (NCC*C*H_2C), 20.3 (C*C*H_3), 20.4 (C*C*H_3), 30.0 (C*C*H_3), 30.3 (C*C*H_3), 38.1 ($SiCH_2N$), 38.5 (NC*C*H_2C), 38.8 (NC*C*H_2C), 63.2 (N*C*C_3), 64.0 (N*C*C_3), 110.7, 111.6, 116.5, and 117.0 (C-4 and C-5; $C_6H_4O_2$, $C_6H_4(OH)O$), 120.0, 120.6, and 121.0 (2 C) (C-3 and C-6; $C_6H_4O_2$, $C_6H_4(OH)O$), 145.4, 146.3, 149.0, and 151.1 (C-1 and C-2; $C_6H_4O_2$, $C_6H_4(OH)O$). ^{29}Si NMR ($CDCl_3$, 22 °C): δ −75.7. ^{29}Si VACP/MAS NMR: δ −75.4. Anal. Found: C, 66.4; H, 8.1; N, 3.4. Calcd for $C_{23}H_{33}NO_4Si$: C, 66.47; H, 8.00; N, 3.37.

Preparation of Bis[benzene-1,2-diolato(2−)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (12). A solution of **11** (1.00 g, 2.41 mmol) in acetonitrile (10 mL) was heated under reflux for 12 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the resulting product dried in vacuo (0.01 Torr, 20 °C, 1 h) to give **12** in quantitative yield as a colorless solid (961 mg, 2.41 mmol); mp 280 °C dec. The NMR data of the product were identical with those reported in ref 10. Anal. Found: C, 65.7; H, 7.3; N, 3.5. Calcd for $C_{22}H_{29}NO_4Si$: C, 66.13; H, 7.32; N, 3.51.

Crystal Structure Analysis of 11·$2CH_2Cl_2$. A suitable single crystal of **11**·$2CH_2Cl_2$ was isolated after recrystallization of **11** from dichloromethane/*n*-pentane (see Preparation). The crystal was 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 ($\lambda = 0.71073$ Å)). The structure was solved by direct methods.[14a] Except for the disordered CH_2Cl_2 molecules, all non-hydrogen atoms were refined anisotropically.[14b] A riding model was employed in the refinement of the CH hydrogen atom positions. The NH and OH hydrogen atoms were localized in difference Fourier syntheses and refined freely.

VT ^{1}H NMR Sudies. The VT ^{1}H NMR experiments with **11** were carried out analogously to the standard ^{1}H NMR measurements using a Bruker DRX-300 NMR spectrometer. $CDCl_3$ was used as the solvent. The thermocouple used with the probe was calibrated for higher temperatures according to ref 15 using a 80% solution of ethane-1,2-diol in [D_6]DMSO. Spectra were recorded in the temperature range 296−333 K. The time required for temperature equilibration was 15 min. The NMR data obtained were fitted and simulated using the Bruker software program WIN-DYNA 32 1.01 (line-shape analysis).[16] The coupling of the protons A and B with the X proton ($SiCH_AH_BNH_X$ spin system) was not resolved above 313 K but was considered for the line-shape analysis. From the simulated spectra the coalescence temperature T_C and the exchange rate k_C at the coalescence point were extracted, and the value for the activation free enthalphy $\Delta G^{\ddagger}$ for the exchange process was calculated by using the Eyring equation:[17]

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

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **11**·$2CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-178677. 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).

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