Chalcogen Transfer to Bis[2-(dimethylaminomethyl)phenyl]silanediyl by Isocyanates and Isothiocyanates☆

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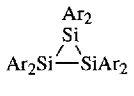
Reaction of hexakis[2-(dimethylaminomethyl)phenyl]cyclotrisilane (**1**) with isocyanates results in the clean formation of cyclic di- or trisiloxanes **3** and **4a** and the corresponding isonitrile. Single-crystal X-ray analysis of tetrakis[2-(dimethylaminomethyl)phenyl]cyclodisiloxane (**4a**) reveals each silicon center to interact with two amino groups forming Si···N distances, which differ significantly in length. Phenyl isothiocyanate reacts with **1** with transfer of sulfur to yield pentacoordinated bis[2-(dimethylaminomethyl)phenyl]silanethione (**11**).

The oxidation of silanediyls by oxygen transfer reagents such as dimethyl sulfoxide[1], tertiary amine oxides[1] or epoxides[2] in the presence of trapping agents usually yields products, whose formation may be explained by capture of initially generated silanones; in the absence of trapping reagents, oligomerization products of silanones are obtained, albeit in low yield. Accordingly, unstable silanones are frequently postulated as intermediates in these reactions; however, the involvement of free silanones in these oxidation reactions is still questionable[3]. In contrast, when silanediyls were treated in argon matrices with oxidants such as N_2O[4] or molecular oxygen[5], the formation of silanones as oxidation products of silanediyls was proven unambiguously by IR spectroscopy.

In this paper we report on the transfer of oxygen from isocyanates to silanediyl **2**[6], which is thermally generated from cyclotrisilane **1**[7]; evidences for the involvement of silanones or "silanonoids" in these reactions will be presented. In addition, we describe an extension of this chalcogen transfer reaction to isothiocyanate providing a new access to stable silanethiones[8].



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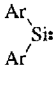

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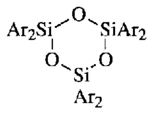

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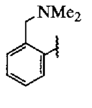
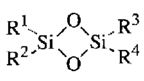


Stirring of a solution of **1** and 3 equiv. of cyclohexyl isocyanate in toluene (350 mmol/l, based on **1**) for 2 h at 70 °C resulted in the formation of cyclotrisiloxane **3**, which was isolated in 71% yield; cyclohexyl isonitrile was identified as another main product in the reaction mixture by ^{13}C-NMR spectroscopy[9]. The structure of **3** was confirmed by elemental analysis and mass spectrometry as well as by ^{29}Si-NMR spectroscopy: The shift of $\delta = -39.9$ resembles that found by Corriu for a structurally similar cyclotrisiloxane[10]. Careful examination of the crude reaction product by ^1H-NMR spectroscopy revealed, that almost quantitatively formed **3** was contaminated with small amounts of a second compound to which we assign the structure of cyclodisiloxane **4a** (vide infra). When the reaction of **1** with cyclohexyl isocyanate was repeated by starting with a concentration of 75 mmol **1**/l, the four-membered ring compound **4a** now was formed in a larger amount (**3**/**4a** = 1:1). An analogous dependence on the reaction conditions was observed for the reaction of **1** with *tert*-butyl isocyanate: The lower the starting concentration of cyclotrisilane, the more **4a** was formed at the expense of **3** (Table 1). In any of these oxidation reactions the formation of **4a** as well as **3** was totally suppressed in the presence of hexamethylcyclotrisiloxane (D_3); instead, quantitative conversion of **1** into **5**, the formal insertion product of a silanone **6** into the Si−O bond of D_3, occurred. A control experiment excluded **3** or **4a** to be the precursor of **5**: Neither cyclotrisiloxane **3** nor cyclodisiloxane **4a** did react with D_3 under the conditions employed.



4a: $R^1, R^2, R^3, R^4 = 2\text{-}(Me_2NCH_2)C_6H_4$ (= Ar)
4b: $R^1, R^2, R^3, R^4 = 2,4,6\text{-}Me_3C_6H_2$
4c: $R^1, R^2 = 2,4,6\text{-}Me_3C_6H_2$; $R^3, R^4 = 2,6\text{-}Me_2C_6H_3$

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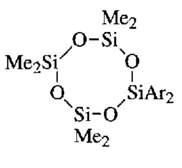

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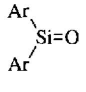

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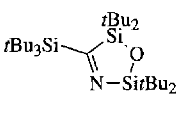

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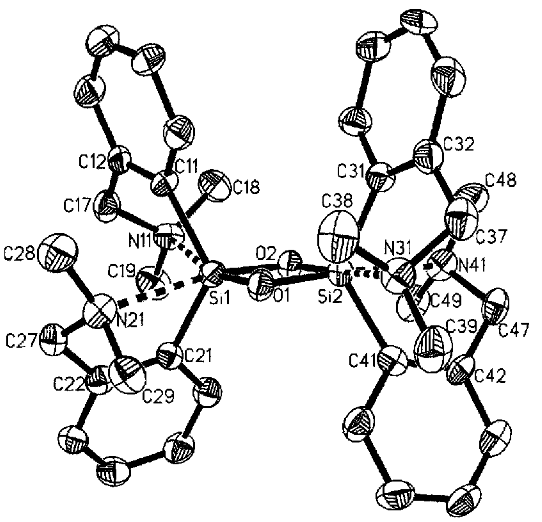
Whereas the oxidation of **1** with cyclohexyl and *tert*-butyl isocyanate proceeded with exclusive formation of **3** and **4a** as silicon-containing compounds, the reaction of phenyl isocyanate and **1** resulted in the formation of a complex product mixture, from which **4a** was isolated as main product in 23% yield. In the presence of D_3 a mixture of **5** and **4a** in a ratio of 5:1 was formed besides unidentified byproducts. The ^{29}Si-NMR signal of **4a** is significantly shifted to high field ($\delta = -45.4$) in comparison with other cyclodisiloxanes such as **4b** ($\delta = -3.4$) or **4c** ($\delta = -3.6, -2.3$)[11]. This high-field shift may be due to the shielding of the silicon nucleus by coordination of the amino groups to the silicon center[12].

Figure 1. Molecular structure of **4a** in the crystal; hydrogen atoms are omitted for clarity, displacement ellipsoids are at the 50% probability level[a]



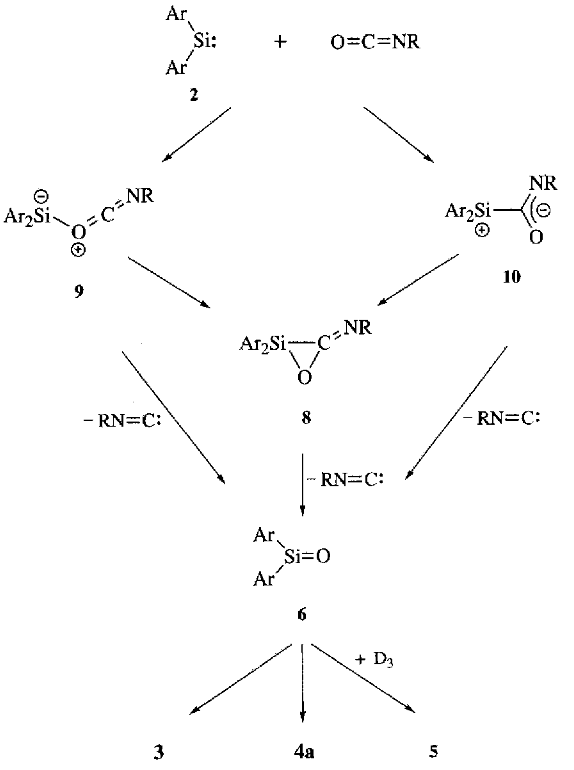
[a] Selected distances [pm] and angles [°] (the values separated by a slash are those for the chemically equivalent parameters in the second, crystallographically independent molecule): Si(1)−O(1) 166.0(4)/167.6(4), Si(1)−O(2) 169.2(4)/168.4(4), Si(1)···N(11) 297.2(5)/292.2(5), Si(1)···N(21) 266.5(5)/268.2(5), Si(1)−C(11) 188.7(5)/187.1(6), Si(1)−C(21) 186.9(5)/187.6(5), Si(2)−O(1) 169.0(4)/169.2(4), Si(2)−O(2) 166.8(4)/166.5(4), Si(2)···N(31) 291.7(5)/285.6(5), Si(2)···N(41) 269.6(5)/276.6(5), Si(2)−C(31) 187.5(5)/186.8(5), Si(2)−C(41) 187.1(6)/185.5(5), Si(1)−Si(2) 242.8(2)/242.6(2), O(1)−O(2) 231.6(5)/232.3(5); O(1)−Si(1)−C(11) 109.8(2)/109.1(2), O(1)−Si(1)−C(21) 116.5(2)/114.7(2), O(1)−Si(1)−O(2) 87.4(2)/87.4(2), O(1)−Si(1)···N(11) 164.6(2)/166.1(2), O(1)−Si(1)···N(21) 79.8(2)/79.7(2), O(2)−Si(1)−C(11) 109.8(2)/110.3(2), O(2)−Si(1)−C(21) 106.5(2)/107.3(2), O(2)−Si(1)···N(11) 78.8(2)/80.0(2), O(2)−Si(1)···N(21) 165.4(2)/165.7(2), C(11)−Si(1)−C(21) 121.3(2)/122.4(2), C(11)−Si(1)···N(11) 69.6(2)/70.4(2), C(11)−Si(1)···N(21) 81.3(2)/80.2(2), C(21)−Si(1)···N(11) 74.4(2)/75.2(2), C(21)−Si(1)···N(21) 73.7(2)/73.0(2), N(11)···Si(1)···N(21) 114.73(14)/113.45(14), O(1)−Si(2)−C(31) 109.0(2)/109.9(2), O(1)−Si(2)−C(41) 106.7(2)/107.4(2), O(1)−Si(2)−O(2) 87.2(2)/87.6(2), O(1)−Si(2)···N(31) 77.5(2)/79.9(2), O(1)−Si(2)···N(41) 168.0(2)/169.0(2), O(2)−Si(2)−C(31) 109.2(2)/109.0(2), O(2)−Si(2)−C(41) 114.8(2)/112.1(2), O(2)−Si(2)···N(31) 163.7(2)/166.6(2), O(2)−Si(2)···N(41) 82.2(2)/82.4(2), C(31)−Si(2)−C(41) 123.6(2)/124.7(2), C(31)−Si(2)···N(31) 71.3(2)/71.5(2), C(31)−Si(2)···N(41) 80.1(2)/77.7(2), C(41)−Si(2)···N(31) 75.6(2)/76.6(2), C(41)−Si(2)···N(41) 72.9(2)/72.7(2), N(31)···Si(2)···N(41) 113.5(2)/110.47(14), Si(1)−O(1)−Si(2) 92.9(2)/92.1(2), Si(1)−O(2)−Si(2) 92.5(2)/92.9(2).

Single-crystal X-ray analysis[13] revealed that **4a** crystallizes with two independent molecules in the asymmetric unit; both molecules, which have quite similar geometries, adopt an approximate C_2 symmetry in the solid state. In the following we will refer to the molecule shown in Figure 1. In agreement with the structures reported for other cyclodisiloxanes the four-membered ring of **4a** is nearly planar; the deviation from planarity does not exceed 1.46 pm. The transannular Si−Si distance (242.8 pm) is just slightly longer than a normal Si−Si single bond (233−237 pm[14]), a phenomenon typical of this class of compounds[15]. Both amino groups of each Ar_2Si unit are oriented towards the silicon center, which may explain the high-field shift observed in the ^{29}Si-NMR spectrum. If we take the Si···N distances as a rough measure of the strength of coordinative interaction, one amino group at each silicon atom is coordinated stronger to silicon than the other one [Si(1)···N(21) 266.5 vs. Si(1)···N(11) 297.2 pm; Si(2)···N(41) 269.6 vs. Si(2)···N(31) 291.7 pm]. This inequivalence of both nucleophilic interactions between silicon and nitrogen atoms is reflected by different endocyclic bond lengths: The Si(1)−O(2) and Si(2)−O(1) bonds (169.2 and 169.0 pm, resp.), which are located opposite to the stronger coordinating amino group, are slightly, but significantly elongated in comparison with the Si(1)−O(1) and Si(2)−O(2) bonds (166.0 and 166.8 pm, resp.). Thus, the Si_2O_2 ring, which is diamond-shaped in other cyclodisiloxanes[16], is distorted into a parallelogram in **4a**. The incorporation of two amino groups into the coordination sphere of the central silicon atom is made possible by the large exocyclic C−Si−C angles [C(11)−Si(1)−C(21) 121.3°; C(31)−Si(2)−C(41) 123.6°] which are significantly widened in comparison with the corresponding angles found in cyclodisiloxane **4b** (115.5°), although the latter bears the bulkier mesityl substituents.

All in all, with regard to its molecular structure, **4a** differs from known cyclodisiloxanes mainly by the presence of two silicon centers which are subject to a twofold, nonsynchronous nucleophilic attack of nitrogen. The possibility of such a process at silicon, in which a second nucleophile approaches the silicon center before detachment of the first leaving group was suggested by Corriu in order to explain the stereochemical results of nucleophilic attack on tetracoordinated silicon compounds[17]. In addition, based on an extensive structure correlation study by Dunitz and Britton, it was shown, that this mechanistic pathway might work for organotin compounds as well, and the term $(S_N2)^2$ reaction was coined for it[18].

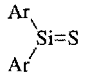
The reaction of **1** with isocyanates thus takes a different course than the photolysis of hexa-*tert*-butylcyclotrisilane in the presence of tri-*tert*-butylsilyl isocyanate, which was reported by Weidenbruch[19] to yield the five-membered ring **7**. The formation of cyclic siloxanes **3** and **4a** from cyclotrisilane **1** and isocyanates may be explained by oligomerization of an intermediate silanone **6**. A high concentration of **6** favors trimerization to **3**, whereas in diluted solutions dimerization product **4a** is formed preferentially. The latter reaction is surprising in view of the fact that up to now only one silanone bearing the very bulky 2,4,6-triisopropylphenyl substituent was reported to undergo dimerization[20]; less hindered silanones are known to form cyclic tri- and tetramers[3,21]. Various pathways to silanone **6** as crucial intermediate may be discussed (Scheme 1). It is well-known that silanediyls react with ketones with formation of siloxiranes; the characterization of these compounds is hampered severely by their inherent reactivity allowing up to now the isolation of only two stable siloxiranes[22]. The reaction of **2** with isocyanates may proceed analogously building up the framework of imino siloxirane **8**; subsequent cycloreversion with elimination of isonitrile would give rise to the formation of **6**. Alternatively, the initially formed sila ylide **9** may be converted directly to **6** without involvement of three-membered ring **8**. Eventually, having in mind the ambiphilic character of divalent group 14 species[23], nucleophilic addition of **2** to the carbon center of the isocyanate seems to be a feasible process, too. The resulting zwitterion **10** could either undergo ring closure to **8** or form **6** directly via a silicon shift to the oxygen center and subsequent or simultaneous cleavage of the carbon−oxygen bond; an analogous mechanism was proposed by Baldwin for the deoxygenation of isocyanates by silyl lithium compounds[24].

Scheme 1



D_3: hexamethylcyclotrisiloxane.

The successful trapping experiments with D_3 are in good agreement with the assumption of a silanone **6** as reactive intermediate in the reaction of **1** with isocyanates. However, although D_3 commonly is regarded as a trapping reagent for silanones, it cannot be excluded that actually the possible initial reaction products **8** or **9** are the reactive species, which with elimination of isonitriles either react with D_3 to yield **5** or oligomerize to form cyclic siloxanes **3** and **4a**. Thus, the structure of the precursors of the cyclic siloxanes which are formed in these oxidation reactions of **2** still has to be proven, and further experiments need to be undertaken in order to identify this intermediate unambiguously. At this point, it should be pointed out, that the oxidation of **1** with *tert*-butyl or cyclohexyl isocyanate appears to use other reaction channels than the reaction with phenyl isocyanate, because the presence of D_3 in this latter reaction did not totally suppress the formation of dimerization product **4a** as observed in the aforementioned trapping experiments.



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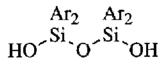

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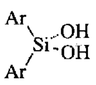

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The assumption that the conversion of **1** with isocyanates to cyclic siloxanes may proceed via silanone **6** as a reactive intermediate gains support by the reaction of **1** with phenyl isothiocyanate in toluene, which yielded smoothly silanethione **11**[25] as single product; in the presence of D_3, no insertion of **11** in a Si−O-bond was observed. Mass spectrometrical and elemental analytical data confirmed the structure of silanethione **11**, which is insoluble in ether and hexane, but moderately soluble in toluene and benzene. The ^{29}Si-NMR signal ($\delta = -21.0$) of **11** is appreciably high-field to that reported recently by Okazki[26] for the non-coordinated, "true" silanethione ($\delta = +166.6$), but is also found at significantly higher field than that of the tetracoordinated silanethiones reported by Corriu[27,8a] ($\delta = +22.3$, $+34.2$ and $+41.1$, resp.); accordingly, the silicon center of **11** is assumed to be pentacoordinated due to its intramolecular interaction with both amino groups. This kind of twofold coordination of the nucleophilic side arm of the 2-(dimethylaminomethyl)phenyl substituent to a coordinatively unsaturated silicon center has recently been proven to be effective in the stabilization of silyl cations as well[28].

Hydrolysis of **3** as well as **4a** yielded disiloxanediol **12** which, on exposure to moist C_6D_6, was transformed into silanediol **13**[29] after several days; both products may be obtained independently by hydrolysis of bis[2-(dimethylaminomethyl)phenyl]dichlorosilane[7,30] or **1**[29]. Attempts to close the four-membered ring **4a** by intramolecular condensation of disiloxanediol **12** failed. Whereas in solution dehydration with P_4O_{10} did not result in loss of water[31], heating of a solid sample of **12** at 200 °C in vacuo yielded cyclotrisiloxane **3**. Under the same conditions, silanediol **13** was also transformed into cyclotrisiloxane **3**, and primary formation of **12** was established by means of ^{1}H-NMR spectroscopy. In addition, heating of an isolated sample of **4a** without solvent for 8 h at 150 °C gave **3** quantitatively. Thus, cyclodisiloxane **4a** has to be considered as an intermediate in the condensation reactions of **12** and **13**, respectively, which undergoes subsequent reaction to **3** under the harsh conditions employed.

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Experimental

^{1}H NMR and ^{13}C NMR: Bruker AM 250 (^{1}H NMR: 250 MHz; ^{13}C NMR: 62.9 MHz). C_q, CH, CH_2, and CH_3 were determined by using the DEPT pulse sequence. – ^{29}Si NMR: Bruker AMX 300 (59.6 MHz), refocused INEPT pulse sequence, internal standard TMS. – Mass spectra: Varian MAT CH7 and MAT 731; HRMS: Varian MAT 311 A, preselected ion peak matching at R ~ 10 000 (±2 ppm of the exact mass). – Melting points are uncorrected. – Elemental analyses were performed at Mikroanalytisches Labor der Georg-August-Universität Göttingen.

Cyclotrisilane **1** was prepared according to a published procedure[7]. All manipulations were carried out under argon by using carefully dried glassware. Solvents used were dried by refluxing over sodium and distilled immediately before use.

1,1,3,3,5,5-Hexakis[2-(dimethylaminomethyl)phenyl]cyclotrisiloxane (**3**): A solution of 123 mg (0.14 mmol) of **1** and 53 µl (0.41 mmol) of cyclohexyl isocyanate in 0.4 ml of toluene was stirred at 70 °C for 2 h. After removal of solvent, excess isocyanate and cyclohexyl isonitrile a colorless oil was obtained. Crystallization from *n*-hexane at 0 °C gave 90 mg (71%) of **3** as a white solid; m. p. 222 °C. – Alternatively, a solution of 68 mg (0.08 mmol) of **1** and 0.1 ml of *tert*-butyl isocyanate in 0.4 ml C_6D_6 was heated at 60 °C for 1 h, forming **3** and **4a** in a 1.7:1 ratio (determined by ^{1}H-NMR spectroscopy). After evaporation of all volatile compounds, the remaining solid was recrystallized from *n*-hexane to yield 32 mg (38%) of **3** as a white solid. – ^{1}H NMR (C_6D_6): δ = 1.96 (s; 36H, NMe_2), 3.54 (s; 12H, CH_2N), 6.91 (dd, ^3J = 7 Hz, ^3J = 7 Hz; 6H, ar-H), 7.20 (dd, ^3J = 8 Hz, ^3J = 8 Hz; 6H, ar-H), 7.57 (d, ^3J = 8 Hz; 6H, ar-H), 7.77 (d, ^3J = 7 Hz; 6H, ar-H). – ^{13}C NMR (C_6D_6): δ = 45.5 (NMe_2), 64.4 (CH_2N), 126.4 (ar-CH), 128.0 (ar-CH), 129.9 (ar-CH), 136.1 (ar-CH), 136.6 (ar-C_q), 145.5 (ar-C_q). – ^{29}Si NMR (C_6D_6): δ = −39.9. – MS (70 eV); *m/z* (%): 936 (100) [M^+], 802 (13) [M^+ − Ar]. – $C_{54}H_{72}N_6O_3Si_3$ (939.5): calcd. C 69.19, H 7.74, N 8.96; found C 69.28, H 7.77, N 8.85.

1,1,3,3-Tetrakis[2-(dimethylaminomethyl)phenyl]cyclodisiloxane (**4a**): To a solution of 589 mg (0.66 mmol) of **1** in 20 ml of toluene was added 0.22 ml (2.0 mmol) of phenyl isocyanate. The solution was stirred at 50 °C for 2 h. After toluene and phenyl isonitrile had been evaporated in vacuo, the remaining brown oil was dissolved in ether and crystallized at −4 °C to give 145 mg (23%) of **4a** as colorless crystals; m. p. 163 °C. – ^{1}H NMR (C_6D_6): δ = 1.93 (s; 24H, NMe_2), 3.27 (s; 8H, CH_2N), 6.89–7.27 (m; 12H, ar-H), 8.07 (d, ^3J = 7 Hz; 4H, ar-H). – ^{13}C NMR (C_6D_6): δ = 45.7 (NMe_2), 64.1 (CH_2N), 126.3 (ar-CH), 126.8 (ar-CH), 128.9 (ar-CH), 137.2 (ar-CH), 138.8 (ar-C_q), 144.4 (ar-C_q). – ^{29}Si NMR (C_6D_6): δ = −45.4. – MS (70 eV); *m/z* (%): 624 (14) [M^+], 490 (7) [M^+ − Ar], 298 (10) [$SiAr_2^+$], 119 (100) [Ar^+ − Me]. – $C_{36}H_{48}N_4O_2Si_2$: calcd. 624.3315, found 624.3315 (HRMS).

1,1-Bis[2-(dimethylaminomethyl)phenyl]-3,3,5,5,7,7-hexamethylcyclotetrasiloxane (**5**): To a solution of 713 mg (0.80 mmol) of **1** in 20 ml of toluene were added 0.31 ml (2.4 mmol) of cyclohexyl isocyanate and 533 mg (2.40 mmol) of hexamethylcyclotrisiloxane. The solution was stirred at 60 °C for 2 h. After evaporation of the solvent in vacuo, the remaining, spectroscopically pure, colorless oil was distilled in a kugelrohr apparatus at 120 °C/10^{-3} Torr to afford 788 mg (61%) of **5** as a white solid; m. p. 69–70 °C. – ^{1}H NMR (C_6D_6): δ = 0.19 (s; 12H, $SiMe_2$), 0.22 (s; 6H, $SiMe_2$), 1.88 (s; 12H, NMe_2), 3.44 (s; 4H, CH_2N), 7.22–7.26 (m; 4H, ar-H), 7.43–7.47 (m; 2H, ar-H), 8.18–8.21 (m; 2H, ar-H). – ^{13}C NMR (C_6D_6): δ = 1.03 (3 × $SiMe_2$), 45.1 (NMe_2), 64.3 (CH_2N), 126.3 (ar-CH), 128.3 (ar-CH), 129.8 (ar-CH), 135.8 (ar-CH), 137.0 (ar-C_q), 145.4 (ar-C_q). – ^{29}Si NMR (C_6D_6): δ = −18.1 ($SiMe_2$), −18.6 ($SiMe_2$), −45.5 ($SiAr_2$). – MS (70 eV), *m/z* (%): 534 (13) [M^+], 519 (15) [M^+ − Me], 476 (9) [M^+ − Me_2NCH_2], 400 (100) [M^+ − Ar], 58 (20) [$Me_2NCH_2^+$]. – $C_{24}H_{42}N_2O_4Si_4$: calcd. 534.2222, found 534.2221 (HRMS).

Reaction of **1** *with Isocyanates at Different Concentrations:* In different runs a solution of **1** and 3 equiv. isocyanate in 0.4 ml of C_6D_6 was heated in an NMR tube for 2 h at 55–60 °C. After this period, **1** was transformed quantitatively into a mixture of **3** and **4a**; the product ratio was determined by means of ^{1}H-NMR spectroscopy (Table 1).

Table 1. Concentration dependence of the reaction of **1** with isocyanates

RNCO	c [mol/l][a]	**3**:**4a**
R = C_6H_{11}	0.350	>10:1
R = C_6H_{11}	0.200	2 : 1
R = C_6H_{11}	0.075	1 : 1
R = tC_4H_9	0.240	2 : 1
R = tC_4H_9	0.100	1 : 2
R = tC_4H_9	0.050	1 : 4

[a] Based on **1**.

Thermolysis of **4a**: A sample of 29 mg (0.05 mmol) of **4a** in 0.4 ml of C_6D_6 was heated at 45 °C for 3 d. After this period the ^{1}H-NMR spectrum showed besides small amounts of unidentified decomposition products only signals of unchanged **4a**. No signals corresponding to **3** were observed.

Thermolysis of **3** *and* **4a** *in the Presence of D_3:* To a solution of 53 mg (0.06 mmol) of **1** in 0.4 ml of C_6D_6 was added 0.1 ml of *tert*-butyl isocyanate. The solution was heated for 2 h at 60 °C to give a mixture of **3** and **4a** in a ratio 1.4:1. To this mixture was added an excess of D_3. Heating of the solution at 60 °C for 16 h did not change the composition of the mixture; no cyclotetrasiloxane **5** was formed.

Reaction of **1** *with Phenyl Isocyanate in the Presence of D_3:* A solution of 60 mg (0.07 mmol) of **1** and 0.02 ml (0.20 mmol) of phenyl isocyanate in 0.4 ml of C_6D_6 was heated to 70 °C in the presence of an excess of D_3 for 2 h. A complex mixture was obtained, which contained 0.09 mmol (43%) of **5** and 0.02 mmol (19%) of **4a** as determined by ^{1}H-NMR spectroscopy using the SiH signal of bis[2-(dimethylaminomethyl)phenyl]silane as internal integration standard.

Bis[2-(dimethylaminomethyl)phenyl]silanethione (**11**): A solution of 195 mg (0.21 mmol) of **1** and 80 µl (0.66 mmol) of phenyl isothiocyanate in 10 ml of toluene was stirred at 60 °C for 2 h. The ^{1}H-NMR-spectroscopically pure reaction product was crystallized from toluene to give 102 mg (49%) of **11** as a white powder; m. p. 215 °C (dec.). – ^{1}H NMR (C_6D_6): δ = 1.78 (s; 12H, NMe_2), 3.16 (s; 4H, CH_2N), 7.06–7.23 (m; 6H, ar-H), 8.78 (d, ^3J = 7 Hz; 2H, ar-H). – ^{13}C NMR (C_6D_6): δ = 45.5 (NMe_2), 64.9 (CH_2N), 126.9 (ar-CH), 127.8 (ar-CH), 128.1 (ar-CH), 137.3 (ar-CH), 138.4 (ar-C_q), 144.5 (ar-C_q). – ^{29}Si NMR (C_6D_6): δ = −21.0. – MS (FAB, 3-NBA); *m/z* (%): 480 (100) [M^+ + 3-NBA − 1], 329 (12) [M^+ + 1]. – $C_{18}H_{24}N_2SSi$ (328.6): calcd. C 65.80, H 7.36, N 8.53; found C 65.62, H 7.36, N 8.41.

1,1,3,3-Tetrakis[2-(dimethylaminomethyl)phenyl]-1,3-dihydroxydisiloxane (**12**) *and Bis[2-(dimethylaminomethyl)phenyl]silanediol* (**13**): A solution of 105 mg (0.11 mmol) of **3** in C_6D_6 was cooled to 0 °C in an open flask in order to condense moisture into the solution. After 30 min **12**[7] had formed quantitatively. The solution was stirred at room temp. for 4 d; **12** was transformed into silanediol **13**, which was crystallized from *n*-pentane to give 73 mg (67%) of **13** as white crystals, m. p. 81–106°C. – ^{1}H NMR (CDCl$_3$): δ = 2.26 (s, 12H, NMe$_2$), 3.52 (s, 4H, CH$_2$N), 7.12–7.20 (m, 2H, ar-H), 7.23–7.39 (m, 4H, ar-H), 7.70–7.79 (m, 2H, ar-H), 9.5 (br. s, 2H, OH). – ^{13}C NMR (CDCl$_3$): δ = 44.2 (NMe$_2$), 65.1 (CH$_2$N), 127.2 (ar-CH), 129.5 (ar-CH), 131.0 (ar-CH), 136.2 (ar-CH), 138.4 (ar-C$_q$), 142.3 (ar-C$_q$). – ^{29}Si NMR (CDCl$_3$): δ = −27.5. – MS (DCI, NH$_3$); *m/z* (%): 331 (100) [M$^+$ + 1], 313 [M$^+$ − OH] (7), 297 (1) [HSiAr$_2{}^+$]. – $C_{18}H_{26}N_2O_2Si$ (330.5): calcd. C 65.42, H 7.93, N 8.48; found C 65.18, H 8.04, N 8.49.

Thermolysis of Siloxanediol **12** *and Silanediol* **13**: 136 mg (0.21 mmol) of **12** was heated for 8 h at 200°C in vacuo (5 × 10^{-2} Torr). The resulting crude product was crystallized from *n*-hexane to give 60 mg (45%) of **3**. In a similar experiment, **13** was heated at 180°C in vacuo for 10 h to give crude **3**, which was not further purified.

Thermolysis of **4a**: 41 mg (0.06 mmol) of **4a** was heated at 140°C in vacuo (5 × 10^{-2} Torr) for 6 h. ^{1}H-NMR spectroscopy showed that **3** had formed with traces of impurities. Crystallization from *n*-hexane gave 23 mg (56%) of **3**.

Crystal Structure of **4a**: $C_{36}H_{48}N_4O_2Si_2$ (624.96); orthorhombic; space group $Pca2_1$; $Z = 8$; $a = 1827.3(2)$, $b = 1790.4(2)$, $c = 2118.2(4)$ pm; $V = 6.930(2)$ nm^3; $\rho_{\text{calcd.}} = 1.198$ Mg m^{-3}; μ(Mo-K_α) = 0.139 mm^{-1}; crystal dimensions 0.6 × 0.5 × 0.5 mm; 14196 reflections (9081 unique) were measured with a STOE-Siemens four-circle diffractometer at 153 K by using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm); 2Θ range: 8–45°. The structure was solved by direct methods (SHELXS-90[32]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-93)[33]. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions by using a riding model. The absolute structure parameter[34] was refined to −0.1(2). R values: $R1 = \Sigma\,\|F_o| - |F_c\|/\Sigma\,|F_o|$, w$R2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. $R1 = 0.0583$ [for $F > 4\sigma(F)$], w$R2 = 0.1584$ (for all data) with 809 parameters and 1 restraint. $w = 1/[\sigma^2(F_o^2) + (0.0602 \cdot P)^2 + 5.9048 \cdot P]$, where $P = (F_o^2 + 2\,F_c{}^2)/3$. Largest difference peak 252 e nm^{-3}, largest difference hole −244 e nm^{-3}.

☆ Dedicated to Prof. Dr. *H. W. Roesky* on the occasion of his 60th birthday.

[1] H. S. D. Soysa, H. Okinoshima, W. P. Weber, *J. Organomet. Chem.* **1977**, *133*, C17–20.

[2] [2a] W. F. Gore, T. J. Barton, *J. Organomet. Chem.* **1980**, *199*, 33–41. – [2b] D. Tzeng, W. P. Weber, *J. Am. Chem. Soc.* **1980**, *102*, 1451–1451. – [2c] W. Ando, M. Ikeno, Y. Hamada, *J. Chem. Soc., Chem. Commun.* **1981**, 621–622.

[3] See e. g.: G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**, p. 1015–1142.

[4] C. A. Arrington, R. West, J. Michl, *J. Am. Chem. Soc.* **1983**, *105*, 6176–6177.

[5] A. Patyk, W. Sander, J. Gauss, D. Cremer, *Angew. Chem.* **1989**, *101*, 920–922; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 898.

[6] [6a] J. Belzner, H. Ihmels, *Tetrahedron Lett.* **1993**, *34*, 6541–6544. – [6b] J. Belzner, H. Ihmels, B. O. Kneisel, R. O. Gould, R. Herbst-Irmer, *Organometallics* **1995**, *14*, 305–311. – [6c] For a photochemical approach to silanediyl **2**, see: R. Corriu, G. Laneau, C. Priou, F. Soulairol, N. Auner, R. Probst, R. Conlin, C. Tan, *J. Organomet. Chem.* **1994**, *466*, 55–68. – [6d] The reactivity of silicon compounds bearing the 2-(dimethylaminomethyl)phenyl substituent and of highly coordinated silicon compounds in general was reviewed several times; see e. g.: R. J. P. Corriu, J. C. Young in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**, p. 1241–1288; R. J. P. Corriu, J. C. Young in *The Silicon Heteroatom Bond* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**, p. 49–66; C. Chuit, R. J. P. Corriu, C. Reyé, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448.

[7] J. Belzner, *J. Organomet. Chem.* **1992**, *430*, C51–55.

[8] [8a] Isocyanates and isothiocyanates serve as oxygen or sulfur transfer reagents towards diaminosilanes: R. J. P. Corriu, G. F. Lanneau, V. D. Mehta, *J. Organomet. Chem.* **1991**, *419*, 9–26. – [8b] Transfer of sulfur from isothiocyanate to decamethylsilicocene has been reported: P. Jutzi, A. Möhrke, *Angew. Chem.* **1989**, *101*, 769–770; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 762.

[9] The volatile components of the reaction mixture were analyzed by NMR-spectroscopy. Cyclohexyl isonitrile was identified by its characteristic ^{13}C-NMR signals at δ = 157.3 and δ = 51.4 ($^1J_{\mathrm{C-^{14}N}}$ = 6 Hz) as well as by comparison with an authentic sample.

[10] P. Arya, J. Boyer, R. J. P. Corriu, G. F. Lanneau, M. Perrot, *J. Organomet. Chem.* **1988**, *346*, C11–14.

[11] [11a] H. B. Yokelson, A. J. Millevolte, B. R. Adams, R. West, *J. Am. Chem. Soc.* **1987**, *109*, 4116–4118. – [11b] K. L. McKillop, G. P. Gillette, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1992**, *114*, 5203–5208.

[12] B. J. Helmer, R. West, R. J. P. Corriu, M. Poirier, G. Royo, A. de Saxcè, *J. Organomet. Chem.* **1983**, *251*, 295–298.

[13] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshaffen (Germany), on quoting the depository number CSD-404128.

[14] W. S. Sheldrick in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**, p. 227–303.

[15] For a discussion of the electronic situation in 1,3-disiladioxetanes, see: [15a] M. S. Gordon, T. J. Packwood, M. T. Carroll, J. O. Boatz, *J. Phys. Chem.* **1991**, *95*, 4332–4337. – [15b] R. S. Grev, H. F. Schaefer, III, *J. Am. Chem. Soc.* **1987**, *109*, 6577–6585. – [15c] C. Liang, L. C. Allen, *J. Am. Chem. Soc.* **1991**, *113*, 1878–1884.

[16] [16a] H. Sohn, R. P. Tan, D. R. Powell, R. West, *Organometallics* **1994**, *13*, 1390–1394 and references cited therein. – [16b] For structures of M_2O_2 ring systems of higher group 14 homologs, see: M. Lappert, *Main Group Metal Chemistry* **1994**, *17*, 183–207 and references cited therein.

[17] R. J. P. Corriu, G. Dabosi, M. Martineau, *J. Organomet. Chem.* **1977**, *186*, 25–37.

[18] D. Britton, J. D. Dunitz, *J. Am. Chem. Soc.* **1981**, *103*, 2971–2979.

[19] M. Weidenbruch, B. Flintjer, S. Pohl, W. Saak, *Angew. Chem.* **1989**, *101*, 89–90; *Angew. Chem. Int. Ed. Engl.* **1994**, *28*, 95.

[20] [20a] M. Drieß, H. Pritzkow, *Angew. Chem.* **1992**, *104*, 350–353; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 316. – [20b] For a theoretical study of the dimerization of silanones, see: T. Kudo, S. Nagase, *J. Am. Chem. Soc.* **1985**, *107*, 2589–2595.

[21] Compare e. g.: N. Wiberg, G. Preiner, K. Schurz, *Chem. Ber.* **1988**, *121*, 1407–1412.

[22] [22a] W. Ando, Y. Hamada, A. Sekiguchi, *Tetrahedron Lett.* **1982**, *23*, 5323–5326. – [22b] The addition of **2** to adamantanone yields the corresponding stable siloxirane: J. Belzner, H. Ihmels, paper to be published.

[23] [23a] For the nucleophilic addition of stable tin(II) amides to acid chlorides, see: M. F. Lappert, M. C. Misra, M. Onyszchuk, R. S. Rowe, P. P. Power, M. J. Slade, *J. Organomet. Chem.* **1987**, *330*, 31–46. – [23b] **2** acts towards alkynes as a nucleophile: J. Belzner, H. Ihmels, unpublished results.

[24] J. E. Baldwin, A. E. Derome, P. D. Riordan, *Tetrahedron* **1983**, *39*, 2989–2994.

[25] **11** was also synthesized independently by treatment of bis[2-(dimethylaminomethyl)phenyl]silane with sulfur in C_6D_6 at 50°C for 16 h. For the formation of silanethiones by reaction of sulfur with silanes, see ref.[27a].

[26] H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11578–11579.

[27] [27a] P. Arya, J. Boyer, F. Carre, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot, C. Priou, *Angew. Chem.* **1989**, *101*, 1069–1071; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1016. – [27b] For double bonds of sulfur to higher homologs of group 14, see: N. Tokitoh, Y. Matsuhashi, K. Shibata, T. Matsumoto, H. Suzuki, M. Saito, K. Manmaru, R. Okazaki, *Main Group Metal Chemistry* **1994**, *17*, 55–65.

[28] J. Belzner, D. Schär, B. O. Kneisel, R. Herbst-Irmer, *Organometallics* **1995**, *14*, 1840–1843.

[29] Initially, the structure of **13** was misinterpreted by one of us to be another modification of **12**: See ref.[7].

[30] The hydrolysis of this dichlorosilane, yielding an HCl adduct of

12, was investigated independently by Auner: N. Auner, R. Probst, C.-R. Heikenwälder, E. Herdtweck, S. Gamper, G. Müller, *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 1625–1634.

[31] Also attempts to dehydrate tetramesityldisiloxanediol with dicyclohexylcarbodiimide to the corresponding cyclodisiloxane **4b** failed: M. J. Michalczyk, M. J. Fink, K. J. Haller, R. West, J. Michl, *Organometallics* **1986**, *5*, 531–538.

[32] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found Crystallogr.* **1990**, *A46*, 467–473.

[33] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen, **1993**.

[34] H. D. Flack, *Acta Crystallogr., Sect. A.: Found. Crystallogr.* **1983**, *A39*, 876–881.

[95120]