Ammonolysis of Trichlorosilanes

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Dedicated to Professor Willi Keim on the occasion of his 65th birthday

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The ammonolysis of trichlorosilanes $RSiCl_3$ [R = $CH(SiMe_3)_2$ **(1a)**, Ph **(1b)**, Et **(1c)**] leads to a series of condensed products such as six-membered rings $[(Me_3Si)_2CHSi(OH)NH]_3$ **(2a)** and $[PhSi(NH_2)NH]_3$ **(2b)**, disilazane $[(Me_3Si)_2CHSi(NH_2)_2]_2NH$ **(3)** and the cage compound $(EtSi)_6(NH)_9$ **(4)**. The mixed Si–N–O compound **2a** was obtained when liquid ammonia was not dried over sodium prior to use. The reaction with sodium gives NaCl instead of NH_4Cl as a by-product which is easily removed by filtration.

Introduction

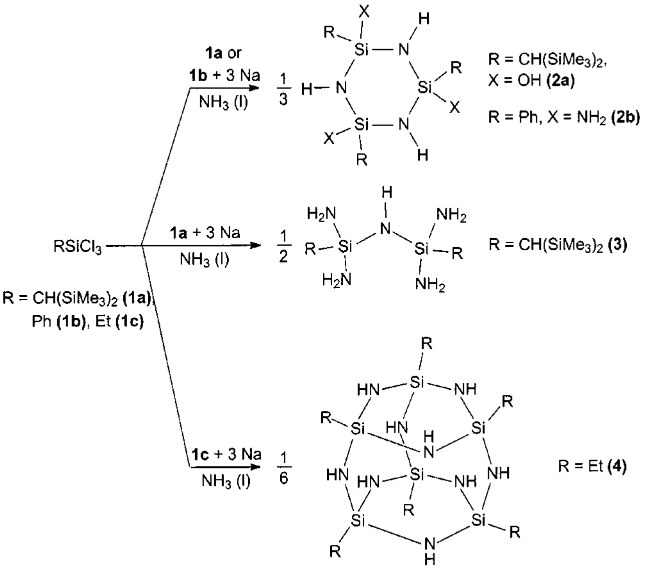
In recent years silicon−nitrogen compounds have gained more and more industrial importance due to the technical use of silicon nitride as a material which is mechanically stable and has a high resistance against heat.[1,2] Moreover, Schnick et al. reported on nitridosilicates, a class of compounds containing a highly polymeric three-dimensional silicon−nitrogen framework with incorporated cations.[3]

In 1993 Power et al. synthesized the first stable product with three NH_2 groups on one silicon atom by ammonolysis of the corresponding trichlorosilane. They used the 2,4,6-$Ph_3C_6H_2$ group as a bulky ligand for this reaction.[4] The chemistry of $RSi(NH_2)_3$ compounds was previously unknown. Consequently we became interested in this class of compounds after studying the isoelectronic compounds $RSi(OH)_3$.[5,6] In these systems R has to be a bulky ligand otherwise the formation of condensation products is observed.[7] Trichlorosilanes with ligands of medium size lead to cyclosilazanes, and trichlorosilanes with small ligands give condensed cage-like products from the reaction with ammonia.[8] Recently we reported the cage-like compound $(MeSi)_6(NH)_9$ using $MeSiCl_3$ in the presence of sodium in liquid ammonia.[9] The advantage of this method is the formation of NaCl instead of NH_4Cl which can be easily removed from the reaction mixture. Our experience has shown that NH_4Cl hinders to some extent the growth of X-ray quality single crystals. In a continuation of our work in liquid ammonia in the presence of sodium we report herein on the reaction using $RSiCl_3$ [R = $CH(SiMe_3)_2$ **(1a)**, Ph **(1b)**, Et **(1c)**] as starting material.

Results and Discussion

Synthesis and Spectra

We investigated the ammonolysis of $RSiCl_3$ compounds with and without sodium following two different routes. In the first approach the trichlorosilane $(Me_3Si)_2CHSiCl_3$ **(1a)** was stirred in liquid ammonia without sodium at −30 °C leading to a six-membered ring system with alternating silicon and nitrogen atoms and a hydroxy group at each ring-silicon atom $[RSi(OH)NH]_3$ [R = $(Me_3Si)_2CH$ **(2a)**] (Scheme 1).



Scheme 1. Reactions of $RSiCl_3$ compounds with ammonia in the presence of sodium

Single crystals suitable for an X-ray crystallographic measurement were isolated from an *n*-hexane solution. In the second route the trichlorosilane $RSiCl_3$ [R = $(Me_3Si)_2CH$ **(1a)**, Ph **(1b)**, Et **(1c)**] was dissolved in toluene

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and added to a solution of sodium in predried liquid ammonia to give various different types of condensation products (Scheme 1). From the reaction of **1b** we obtained the six-membered Si−N ring **2b**, similar to that of **2a**; however the OH groups at silicon are replaced by the isoelectronic NH_2 groups. In marked contrast is the reaction product using **1a** and liquid ammonia in the presence of sodium. Under these conditions the acyclic disilazane $[(Me_3Si)_2CHSi(NH_2)_2]_2NH$ **(3)** is formed. The reaction of $EtSiCl_3$ **(1c)** in liquid ammonia and sodium resulted in the formation of the cage compound $(EtSi)_6(NH)_9$ **(4)**. We assume that in all of the reactions employing liquid ammonia/sodium, sodium amide is initially formed in situ, and then reacts with the trichlorosilane with formation of sodium chloride. However, probably due to its low solubility, solid $NaNH_2$ in liquid ammonia does not react with the trichlorosilane. All ^1H NMR signals of the NH and NH_2 groups are in the range 0.25−1.80 ppm. The silicon atoms which are bonded to the nitrogen atoms give ^{29}Si NMR signals between −22.0 and −30.8 ppm. In the NMR spectra of product **3** the number of signals for the organic ligands, but not for the two central silicon atoms, are doubled. A possible explanation for this is, that there are two sterically different conformers of the molecule. In the IR spectra we see the typical signals of the NH vibrations between 3350 and 3500 cm^{-1}, and 1535 and 1545 cm^{-1}. The signals of the vibration of the Si−N−Si groups are in the range between 930 and 970 cm^{-1} for the cyclic products **2a**, **2b** and **4**, and at 1162 and 1014 cm^{-1} for the acyclic disilazane (**3**). The mass spectra show the molecular ion peak [M^+] or fragment peaks after elimination of one or two small groups such as Me, NH_2 or OH.

X-ray Structural Analysis

Compound **2a** crystallizes in the trigonal space group $P\bar{3}$ with one third of a molecule in the asymmetric unit. The rest of the molecule is generated by the $\bar{3}$ axis. The core of the structure is a six-membered Si_3N_3 ring showing 41% chair conformation[10] with N and Si atoms occupying alternating sites. To complete the tetrahedral coordination sphere each Si atom in the ring is connected to a hydroxy group and a bis(trimethylsilyl)methyl moiety. All OH groups are oriented in the same direction with respect to the ring plane (Figure 1). The endocyclic N−Si distance is 1.704(2) Å, the angles are 104.6(1)° for N−Si−N and 131.3(1)° for Si−N−Si. The distance between the Si in the ring and the connecting oxygen is 1.673(3) Å; the O−Si−C angle between the hydroxy group and the organic ligand is 106.9(1)°. In the crystal packing two molecules are always bridged by six hydrogen bonds (Figure 2). The distance between the connecting hydroxy groups was calculated to be 1.952 Å between the hydrogen and the accepting oxygen atom. The O−H−O arrangement is nearly linear with an angle of 173.6°.

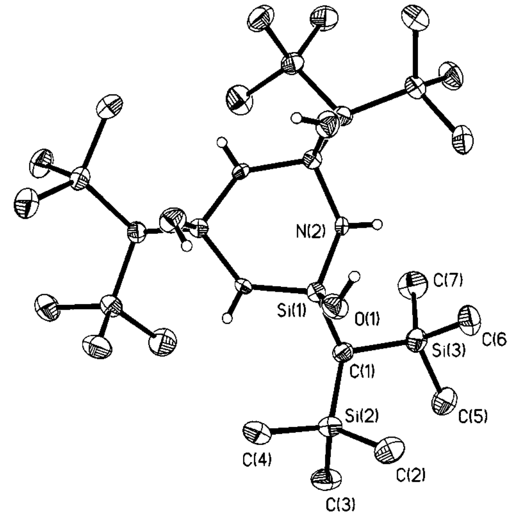

Figure 1. Molecule structure of **2a** in the crystal

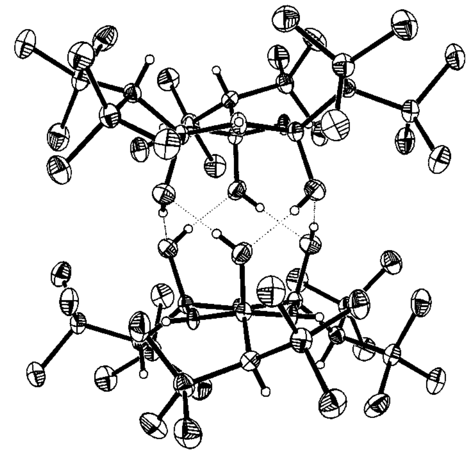

Figure 2. Molecule structure of **2a** with intermolecular hydrogen oxygen bridges

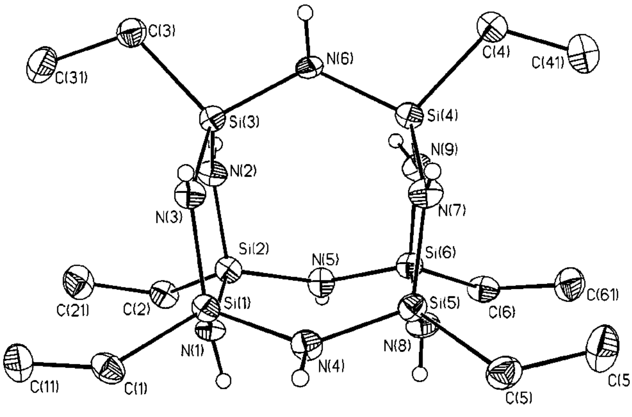

Figure 3. Molecule structure of **4** in the crystal

The single-crystal X-ray structure shows **4** to crystallize in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. The core of **4** consists of two six-membered Si_3N_3 rings in the chair conformation with alternating silicon and nitrogen atoms. The rings are linked by bridging NH groups connected to the Si centers. Thus, a prismatic cage-like structure results (Figure 3). One ethyl group is bonded to each of the silicon atoms. Two groups of nitrogen centers can be differentiated: six are part of the two six-membered rings (av. Si−N distance 1.714 Å) and three are located between the two rings in a bridging position (av. Si−N distance 1.734 Å), which are slightly longer. The silicon centers are all slightly distorted from an ideal tetrahedron. Three groups of angles can be distinguished: the endocyclic N−Si−N angle (av. 131.5°); the somewhat smaller angle between a nitrogen center of one of the rings and a bridging nitrogen center (av. 126.3°); and the C−Si−N angles (av. 109.8°). The nitrogen atoms in the six-membered rings show an almost planar coordination (av. sum of angles 356°). Within the experimental error the bridging N atoms are perfectly planar coordinated (av. sum of angles 360°). The average Si−C bond length of 1.865 Å lies in the range typical for Si−C single bonds.

Conclusion

The grade of condensation and thereby the structure of the aminosilanes is dependent on the size of the ligands. Triaminosilanes with bulky ligands are stable against condensation.[4,7] Small ligands such as methyl and ethyl lead to the formation of a cage.[9] When the ligands are of medium size, then six-membered rings or other low-condensed products are the most favorable configuration. The ammonolysis with sodium in ammonia is superior in handling due to the production of NaCl, rather than NH_4Cl, which can be easily removed from the reaction mixture. It is interesting to note that the ammonolysis of **1a** with ammonia which was not predried with sodium yielded the trihydroxycyclotrisilazane **2a** while the reaction with sodium in predried ammonia gave the acyclic tetraaminodisilazane **3**.

Experimental Section

General: All reactions were performed under dry nitrogen conditions using standard Schlenk and syringe techniques. − The solvents were dried according to literature methods[11] and freshly distilled and saturated with nitrogen prior to use. − Melting points were measured on a Bühler SPA-1 melting point apparatus (uncorrected). − IR spectra were recorded using a BIO-RAD FTS 7 spectrophotometer. − Mass spectra (MS) were obtained with a Finnigan MAT 8200 or a Finnigan MAT 95 spectrometer using the EI technique. − NMR spectra were recorded with a Bruker AM 200 or a Bruker AC 250 spectrometer, δ in ppm relative to external $SiMe_4$. − Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen.

Trichlorobis(trimethylsilyl)methylsilane (1a): To a suspension of $(SiMe_3)_2CHLi$ (7.4 g, 45 mmol) in toluene (100 mL) was added dropwise tetrachlorosilane (5.7 mL, 8.5 g, 50 mmol). The mixture was refluxed for 3 h, the generated LiCl was removed by filtration and the solvent was removed under vacuum. After distillation at 0.05 mbar, **1a** (10.9 g, 37 mmol, 83%) was obtained as a colorless liquid. − B.p. 45 °C (0.05 mbar). − ^1H NMR (C_6D_6): δ = 0.15 [s, $Si(CH_3)_3$]. (The signal from the *CH*-proton was not observed.) − ^{13}C NMR (C_6D_6): δ = 2.45 [$Si(CH_3)_3$], 15.75 ($CSiCl_3$). − ^{29}Si NMR (C_6D_6): δ = 0.37 ($SiMe_3$), 7.95 ($SiCl_3$). − IR (KBr): ṽ = 2976, 2955, 2901, 1406, 1269, 1257, 840, 772, 573, 561 cm^{-1}. − MS (EI): *m/z* (%) = 279 (100) [M^+ − Me]. − $C_7H_{19}Cl_3Si_3$ (293.8): calcd. C 28.6, H 6.5, Cl 36.2, Si 28.7; found C 28.8, H 6.5, Cl 35.7, Si 28.2.

1,3,5-Tris[bis(trimethylsilyl)methyl]-1,3,5-trihydroxycyclotrisilazane (2a): Ammonia (20 mL) was condensed at −78 °C onto **1a** (5.9 g, 20 mmol) and this mixture was stirred for 2 h under reflux. After warming to room temperature over 3 h, whereby the ammonia vaporized, *n*-hexane (50 mL) was added, the insoluble NH_4Cl was removed by filtration and the filtrate was concentrated in vacuo. A residue of **2a** (2.3 g, 3.5 mmol, 53%) was obtained as a white solid. Slow recrystallization from *n*-hexane (20 mL) resulted in colorless needles of **2a**. − M.p. 110 °C. − ^1H NMR (C_6D_6): δ = −0.39 [m, $CH(SiMe_3)_2$, 3 H], 0.29 [m, $Si(CH_3)_3$, 54 H], 0.50−1.00 (m, N*H*, 3 H), 1.25−1.40 (m, O*H*, 3 H). − ^{29}Si NMR (C_6D_6): δ = −25.1 [*Si*(NH)], −1.5 ($SiMe_3$). − IR (KBr): ṽ = 3398, 1541, 1262, 1250, 1204, 1015, 955, 854, 723, 678 cm^{-1}. − MS (EI): *m/z* (%) = 624 (100) [M^+ − 2 OH], 607 (81) [M^+ − 3 OH]. − $C_{21}H_{63}N_3O_3Si_9$ (658.6): calcd. C 38.3, H 9.6; found C 36.9, H 9.8.

1,3,5-Triamino-1,3,5-triphenylcyclotrisilazane (2b): To a solution of sodium (3.4 g, 147 mmol) in ammonia (20 mL) was added a solution of $PhSiCl_3$ (10.4 g, 49 mmol) in toluene (100 mL) at −78 °C. After warming to room temperature the mixture was stirred for 1 h. The white precipitate was filtered off and the solvent was removed under vacuum. The residue was washed with *n*-hexane (50 mL) to give **2b** (4.7 g, 11 mmol, 70%) as a white solid. − M.p. 64−68 °C. − ^1H NMR (C_6D_6): δ = 0.40−1.80 (m, N*H*, NH_2, 9 H), 7.15 (m, C_6H_5, 10 H), 7.75 (m, C_6H_5, 5 H). − ^{29}Si NMR (C_6D_6): δ = −30.80 [*Si*(NH)] − IR (KBr): ṽ = 3468, 3064, 1662, 1620, 1588, 1538, 1427, 1305, 1261, 1198, 1168, 1113, 1028, 936, 918, 892, 845, 727, 699, 611, 478 cm^{-1}. − MS (EI): *m/z* (%) = 408 (2) [M^+], 392 (3) [$M^+ - NH_2$], 376 (4) [$M^+ - 2\,NH_2$]. − $C_{18}H_{24}N_6Si_3$ (408.7): calcd. C 52.9, H 5.92, Si 20.6; found C 52.0, H 5.9, Si 20.6.

1,1,3,3-Tetraamino-1,3-bis[bis(trimethylsilyl)methyl]disilazane (3): Sodium (1.2 g, 52 mmol) was dissolved at −78 °C in liquid ammonia (20 mL). A solution of **1a** (4.6 g, 16 mmol) in toluene (100 mL) was then added dropwise over 30 min. The mixture was stirred for 2 h at −78 °C and, after heating to room temperature within 3 h, whereby the ammonia vaporized, the toluene was removed under vacuum, *n*-hexane (70 mL) was added and the insoluble solid was removed by filtration. After removing the *n*-hexane in vacuo, **3** (3.0 g, 6.6 mmol, 83%) was obtained as a colorless oil. − M.p. 10−15 °C. − ^1H NMR (C_6D_6): δ = −0.70 [s, $CH(SiMe_3)_2$, 1 H], −0.62 [s, $CH(SiMe_3)_2$, 1 H], 0.16 [s, $Si(CH_3)_3$, 18 H], 0.21 [s, $Si(CH_3)_3$, 18 H], 0.25−1.0 (br. m, N*H*, NH_2, 9 H). − ^{29}Si NMR (C_6D_6): δ = −23.20 [$Si(NH_2)_2$], −1.80 ($SiMe_3$), −1.68 ($SiMe_3$). − IR (KBr): ṽ = 3482, 3404, 2951, 2891, 1542, 1430, 1401, 1262, 1250, 1162, 1014, 837, 765, 678 cm^{-1}. − MS (EI): *m/z* (%) = 437 (40) [$M^+ - NH_2$], 405 (100) [$M^+ - 3\,NH_2$]. − $C_{14}H_{47}N_5Si_6$ (454.0): calcd. C 37.0, H 10.4; found C 37.0, H 10.4. The osmometric molecular mass determination in toluene gave a molecular weight of 449 Dalton.

Hexaethylsilsesquiazane (4): To a solution of sodium (1.4 g, 60 mmol) in ammonia (20 mL) was added a solution of $EtSiCl_3$ (3.7 g, 20 mmol) in toluene (40 mL) at −78 °C. After warming to room temperature the mixture was stirred for an additional 2 h. The crude product was extracted with *n*-hexane (100 mL). After removing the solvent under vacuum **4** (1.3 g, 78%) was obtained. Recrystallization from diethyl ether (10 mL) gave colorless crystals of **4**. − M.p. 130 °C. − ^1H NMR (C_6D_6): δ = 0.58 (m, CH_2, 12 H), 1.05 (m, CH_3, 18 H), 0.58−1.05 (m, N*H*, 9 H). − ^{29}Si NMR (C_6D_6): δ = −22.0 (Me*Si*). − IR (KBr): ṽ = 3388, 1304, 1260, 1238, 1196, 1160, 1081, 1011, 964, 935, 841, 794, 769, 722, 685, 640 cm^{-1}. − MS (EI): *m/z* (%) = 477 [M^+]. − $C_{12}H_{39}N_9Si_6$ (478.1): calcd. C 30.2, H 8.2; found C 29.6, H 8.2.

Table 1. X-ray structure analysis data of **2a** and **4**

Compound	**2a**	**4**
Formula	$C_{21}H_{63}N_3O_3Si_9$	$C_{12}H_{39}N_9Si_6$
Formula weight	658.55	478.06
Crystal size	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.1
Crystal system	Trigonal	Triclinic
Space group	$P\bar{3}$	$P\bar{1}$
Unit cell	$a = b = 13.51(1)$ Å	$a = 9.762(2)$ Å
	$c = 12.64(2)$ Å	$b = 11.515(2)$ Å
	$\alpha = \beta = 90°$	$c = 11.861(2)$ Å
	$\gamma = 120°$	$\alpha = 73.79(3)°$
		$\beta = 77.37(3)°$
		$\gamma = 76.69(3)°$
Volume	$V = 1997(3)$ Å^3	$V = 1228.7(4)$ Å^3
Z	2	2
Density	1.095 g/cm^3	1.292 g/cm^3
Absorption coefficient	0.323 mm^{-1}	0.358 mm^{-1}
$F(000)$	720	516
Reflections collected	37064	17087
Independent reflections	1917 ($R_{int} = 0.0771$)	4810 ($R_{int} = 0.0781$)
Data/Restr./Param.	1917/1/121	4810/9/277
Data collection range	$2.4 \leq \Theta \leq 23.3°$	$2.2 \leq \Theta \leq 26.0°$
Final R indices $[I > 2\sigma(I)]$[a]	$R1 = 0.0303$	$R1 = 0.0462$
	$wR2 = 0.0730$	$wR2 = 0.1088$
Final R indices (all data)	$R1 = 0.0510$	$R1 = 0.0817$
	$wR2 = 0.0780$	$wR2 = 0.1192$
Goodness-of-fit on F^2[b]	0.972	0.939
Largest diff. peak and hole	0.340 and −0.231 eÅ^{-3}	0.474 and −0.430 eÅ^{-3}

[a] $R1 = \Sigma|F_o - F_c| / \Sigma|F_o|$; $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma wF_o{}^4]^{1/2}$. – [b] Goodness of fit $S = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma (n\text{-}p)]^{1/2}$.

X-ray Crystal Structure Analysis:[12] The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[13] Diffraction data (see Table 1) were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), performing φ- and ω scans. The structures were solved by direct methods using SHELXS-97[14] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atoms bonded to nitrogen were localized in the difference Fourier synthesis and refined with the help of distance restraints and anisotropic displacement parameter restraints. The position of the hydrogen atom bonded to oxygen in **2a** was freely refined.

Acknowledgments

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[12] Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137377 **(2a)** and -137081 **(4)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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