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[7] Crystal data for **1**: $[(C_4H_9)_4N][C_{11}H_{17}O_2B_3BrW]$, $M = 719.9$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.958(2)$, $b = 16.665(2)$, $c = 15.924(2)$ Å, $\beta = 101.07(1)^\circ$, $V = 3375.0(7)$ Å^3, $Z = 4$, $\rho_c = 1.42$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 46.3$ cm^{-1}, $F(000) = 1448$. An orange prism of dimensions $0.77 \times 0.70 \times 0.70$ mm was used. For **7**: $[(C_4H_9)_4N]_2[B_{12}H_{12}] \cdot 2\,CH_2Cl_2$, $M = 796.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.504(1)$, $b = 16.262(1)$, $c = 16.581(2)$ Å, $\beta = 99.67(1)^\circ$, $V = 2526.1(4)$ Å^3, $Z = 2$, $\rho_c = 1.05$ g cm^{-3}, $\mu(\mathrm{Cu_{K\alpha}}) = 22.9$ cm^{-1}, $F(000) = 868$. A clear rhomb of dimensions $0.43 \times 0.33 \times 0.20$ mm was used. Independent reflections: 5887 (3749); Siemens P4 diffractometers; graphite-monochromated $\mathrm{Mo_{K\alpha}}$ (**1**) and $\mathrm{Cu_{K\alpha}}$ radiation (**7**); ω scans. The structures were solved by the heavy atom and direct methods for **1** and **7**, respectively, and all the major occupancy non-hydrogen atoms were refined anisotropically (there being slight disorder in one of the butyl chains of the cation in **1**) with absorption corrected data using full-matrix least-squares based on F^2 to give $R_1 = 0.059$ (0.069), $wR_2 = 0.133$ (0.178) for 3734 (2555) independent observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leq 50^\circ\ (120^\circ)]$ and 325 (236) parameters for **1** and **7**, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101158. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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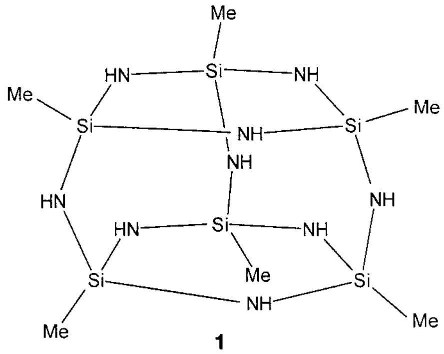
Synthesis and Structure of $(CH_3Si)_6(NH)_9$: A Si–N Cage Made from Methyltrichlorosilane and Ammonia

Bodo Räke, Herbert W. Roesky,* Isabel Usón, and Peter Müller

Dedicated to Professor Hans Bock on the occasion of his 70th birthday

Silicon–nitrogen compounds are being increasingly used for industrial purposes. Silicon nitride, for example, forms an integral part of many materials due to its high mechanical stability.[1] In recent years there has been an increasing effort to study nitridosilicates. These compounds consist of a highly polymeric three-dimensional silicon–nitrogen framework with incorporated cations.[2] We recently reported on cagelike silicon–nitrogen compounds with covalently bonded heteroatoms.[3, 4] Cyclopolyalkylsilazanes and alkylsilsesquiazanes have been known for a long time,[5] however these compounds have not been structurally characterized. Single crystals of $(MeSi)_6(NH)_9$ (**1**)[6] have now been investigated by X-ray structure analysis for the first time. They were obtained by developing a synthetic route in which no ammonium chloride is formed; our experience has shown that NH_4Cl hinders the growth of single crystals and is difficult to remove.



1

Ammonia was condensed onto elemental sodium at −78 °C, and methyltrichlorosilane was added. This led to NaCl (which can be easily removed) and **1,** which was characterized by NMR and IR spectroscopy, mass spectrometry, and elemental analysis [Eq. (a)]. We assume that in the course of the reaction sodium amide is initially formed, which then reacts with methyltrichlorosilane under formation of sodium chloride. According to the single-crystal X-ray structure analysis, **1** consists of two six-membered Si_3N_3 rings in the chair conformation with alternating silicon and nitrogen atoms. The rings are linked to one another by bridging NH groups connected to the Si centers, resulting in a prismatic

$$6\,\mathrm{MeSiCl_3} + 18\,\mathrm{Na} \xrightarrow[-\,18\,\mathrm{NaCl}]{\mathrm{NH_3\ liq.}} (\mathrm{MeSi})_6(\mathrm{NH})_9\ \mathbf{1} \tag{a}$$

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cagelike structure (Figure 1). One methyl group is bonded to each of the silicon centers. Two groups of nitrogen centers can be differentiated: six are part of the two six-membered rings (av Si–N distance: 1.720(3) Å) and three bridge the rings (av Si–N distance: 1.736(3) Å). The differences in bond length can be explained by the ring strain that is present in this cage.

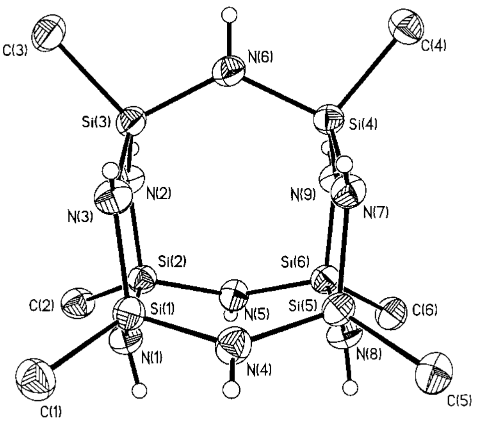

Figure 1. Structure of **1** in the crystal. Selected bond lengths [Å] and angles [°]: Si(1)–N(1) 1.729, Si(1)–N(3) 1.718, Si(1)–N(4) 1.733, Si(1)–C(1) 1.870; N(3)-Si(1)-N(1) 106, N(4)-Si(1)-N(1) 111, N(4)-Si(1)-N(3) 111, C(1)-Si(1)-N(1) 112, C(1)-Si(1)-N(3) 112, C(1)-Si(1)-N(4) 106.

The silicon centers all have slightly distorted tetrahedral coordination, and four groups of angles can be distinguished: the N-Si-N angle within the six-membered rings (av 111.1(2)°); the somewhat smaller angle between a nitrogen center of one of the six-membered rings and a bridging nitrogen atom (av 105.5(2)°); the N-Si-N angle between carbon centers and one nitrogen of a six-membered ring (av 111.8(2)°); and the somewhat smaller angle between carbon and bridging nitrogen centers (av 105.7(2)°). The nitrogen centers in the six-membered rings exhibit almost planar coordination (average sum of angles = 356.9(2)°), as do the bridging nitrogen centers—within the limits of experimental precision—with an average sum of angles of 359.8(2)°. The average Si–C bond length of 1.864(3) Å lies in the range typical for Si–C single bonds. A comparison of this structure with the isoelectronic oxygen compound was not possible as its structure is still unknown according to a search of the literature.

The ^{1}H NMR spectrum shows a signal for the methyl protons ($\delta = 0.04$) and a very broad singlet from the NH protons ($\delta = 0.20-1.20$), and the ^{29}Si NMR spectrum contains as expected just one signal ($\delta = -21.98$). The molecular ion ($m/z = 393$) is clearly apparent in the mass spectrum. Signals from other fragments resulting from the cleavage of methyl groups are also present. The results of the elemental analysis for carbon and silicon deviate somewhat from the calculated values because small amounts of silicon carbide are formed on decomposition of the compound. The bands of the N–H vibration (3393 cm^{-1}) and the Si–N vibrations (949, 1166, 1196 cm^{-1}) in the IR spectrum were assigned by experiment.

The unproblematic workup of the methyl derivative illustrates that the use of metallic sodium in liquid ammonia provides a facile route to cagelike Si–NH compounds without the need for bulky ligands bonded to the silicon centers. It should also be possible to use this synthetic route with other element halides.

Experimental Section

An excess of ammonia was condensed onto sodium (1.38 g, 60 mmol) at −78 °C. A solution of methyltrichlorosilane (2.99 g, 2.35 mL, 20 mmol) and *n*-hexane (60 mL) cooled to −78 °C was carefully added dropwise over a period of 1 h. The residue was filtered off and the volatile components were removed under vacuum. The residue was then taken up in diethyl ether. The solution was stored at −25 °C whereupon single crystals of **1** (0.3 g, 23 %) suitable for X-ray structure analysis were formed.

Decomposition temperature: 60 °C; ^{1}H NMR (200 MHz, C_6D_6, TMS): $\delta = 0.04$ (s, 18 H; CH_3), 0.2–1.2 (s, 9 H; NH); ^{29}Si NMR (79 MHz, C_6D_6, TMS): $\delta = -21.98$ (s); IR (KBr, Nujol): $\tilde{\nu} = 3462$, 3393, 3314, 2980, 1546, 1410, 1257, 1196, 1166, 1095, 1020, 949, 801, 723, 625 cm^{-1}; MS (EI): m/z (%): 393 (42, M^+), 378 (100, $M^+ - CH_3$). Satisfactory elemental analysis for $C_6H_{27}N_9Si_6$.

Structure analysis of **1**: $M_r = 393.91$, crystal dimensions $0.40 \times 0.30 \times 0.20$ mm^3, triclinic space group, $P\bar{1}$, $a = 8.722(2)$, $b = 9.876(2)$, $c = 11.411(2)$ Å, $\alpha = 76.25(3)$, $\beta = 83.14(3)$, $\gamma = 87.50(3)°$, $V = 947.8(3)$ Å^3, $\rho_{calcd} = 1.380$ g cm^{-3}, $Z = 2$, absorption coefficient: $\mu = 0.448$ mm^{-1}, max. resolution: $2\theta = 55°$, 18769 reflections measured of which 4330 ($R_{int} = 0.0391$) independent. Data/restraints/parameter ratio: 4330/9/223, $R1 = 0.0545$, $wR2 = 0.1420$ ($I > 2\sigma(I)$), $R1 = 0.0786$, $wR2 = 0.1628$ (all data), GOF = 1.163; ($R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2}$); weighting scheme: $w^{-1} = \sigma^2(F_o)^2 + (0.085\,P)^2 + 0.815\,P$; $P = [F_o^2 + 2F_c^2]/3$; max./min. residual electron density 0.840/−0.550 e Å^{-3}.

The crystal was removed from the Schlenk tube under inert gas, mounted onto a glass fiber with perfluoropolyether and shock frozen.[7] The data collection was performed at 133 K on a Stoe-Siemens-Huber four-circle diffractometer connected with a Siemens CCD surface detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) performing φ and ω scans. The structure was solved by direct methods using SHELXS-97[8] and refined by using SHELXL-97[9] by the full-matrix least-squares method against F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to nitrogen were localized in the difference Fourier synthesis and refined freely with the aid of distance restraints. The methyl hydrogen atoms were added to geometrically calculated positions and refined with a riding model. 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-100995. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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