


[6] Crystallographic data (excluding structure factors) for the structures have not been structurally characterized. Single crystals of (MeSi3)2(NH)3 (1) [8] 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 NH4Cl hinders the growth of single crystals and is difficult to remove.

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 Si3N3 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 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 Si3N3 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
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 and the need for bulk ligands bonded to the silicon centers. It should also be possible to use this route without this 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, 23.5 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 I (0.3 g, 23%) suitable for X-ray structure analysis were formed.

Decomposition temperature: 60 °C; 1H NMR (200 MHz, CD3CN, TMS): δ = 0.04 (s, 18H; CH2); 0.2−1.2 (s 9H, NH); 29Si NMR (79 MHz, CD3CN, TMS): δ = −21.98 (s); IR (KBr, Nujol): ν = 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+−CH3). Satisfactory elemental analysis for CH3;N4Si6.

Structure analysis of 1

A glassy network was formed on the silicon with perfluoropolyether and shock frozen. The glass collection was performed at 133 K on a Stoë-Siemens-Huber four-circle diffractometer connected with a Siemens CCD surface detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å) performing q and ω scans. The structure was solved by direct methods using SHEXL-97 and refined by using SHEXLX-97 with the full-matrix least-squares method against F2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to nitrogen were localized in the difference density 0.840−0.550 e Å−3.

The crystal was removed from the Schlenk tube under inert gas, mounted on a glass fiber with perfluoropolyether and shock frozen. 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 MoKα radiation (λ = 0.71073 Å) performing q and ω scans. The structure was solved by direct methods using SHEXL-97 and refined by using SHEXLX-97 with the full-matrix least-squares method against F2. 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-1005995. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EIZ, UK (fax: (+44) 1223-36-033; e-mail: deposit@ccdc.cam.ac.uk).

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