

## The Crystal Structures of Chlorodimethyl(dimethylamino)silane and Dimethyl-bis-(dimethylamino)silane

Norbert W. Mitzel and Krunoslav Vojinović

Westfälische Wilhelms-Universität Münster, Institut für Anorganische und Analytische Chemie, Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany

Reprint requests to Prof. Dr. N. W. Mitzel.  
Fax (+49)251 83 36007. E-mail: mitzel@uni-muenster.de

Z. Naturforsch. **58b**, 708–710 (2003);  
received April 2, 2003

Single crystals of chlorodimethyl(dimethylamino)silane,  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ , and dimethyl-bis-(dimethylamino)silane,  $(\text{Me}_2\text{N})_2\text{SiMe}_2$ , have been grown *in situ* from the melt at low temperatures and their structures determined by X-ray diffraction. Important structural parameters ( $\text{Å}/^\circ$ ):  $\text{Me}_2\text{NSiMe}_2\text{Cl}$  ( $C2/m$ ) Si-N 1.686(2), Si-C 1.851(1), Si-Cl 2.109(1), N-Si-Cl 111.7(1), C-Si-Cl 105.1(1), C-N-C 112.8(2), Si-N-C 123.4(1);  $(\text{Me}_2\text{N})_2\text{SiMe}_2$  ( $P2_1/c$ ) Si-N(1) 1.725(1), Si-C(1) 1.868(1), N(1)-Si-N(2) 105.7(1), C(3)-N(1)-C(4) 111.6(1), Si-N(1)-C(3) 122.4(1), Si-N(1)-C(4) 120.0(1).

**Key words:** Silicon, Crystal Structure, Hypercoordination

The finding of a planar  $\text{Si}_3\text{N}$  skeleton in trisilylamine,  $(\text{H}_3\text{Si})_3\text{N}$ , by Hedberg in 1955 [1] was followed by numerous investigations on the structure of Si/N compounds. In the course of these studies it became evident, that even a single silicon substituent at nitrogen is capable of flattening the nitrogen coordination sphere [2]. Only in a minority of cases, a significant deviation from a planar surrounding of the nitrogen substituents was found, including  $\text{Me}_2\text{NSiH}_3$  [3],  $\text{Me}_2\text{HSiNMe}_2$  [4] and  $\text{Ph}_3\text{SiNH}_2$  [5].

The first examples of clearly pyramidal nitrogen atoms with silicon substituents were found in the hydroxylamine derivatives (*p*-TolSiH<sub>2</sub>)<sub>2</sub>NOMe [6],  $(\text{H}_3\text{Si})_2\text{NOMe}$  [7] and  $(\text{H}_3\text{Si})\text{MeNOMe}$  [8], which have deviations of the N-O vector from the  $\text{NSi}_2$  and  $\text{NSiC}$  planes of 38.7(1), 31.3(2) (solid) and 33.2(25)° (gaseous), respectively.

Recently we have reported the crystal structure of  $\text{Me}_2\text{NSiCl}_3$  [9], but there are still structurally unexplored silylamines bearing only the simple substituents  $\text{Me}_2\text{N}$ , H, Cl and Me. Here we report the structures of two of them:  $\text{Me}_2\text{NSiMe}_2\text{Cl}$  and  $(\text{Me}_2\text{N})_2\text{SiMe}_2$ .

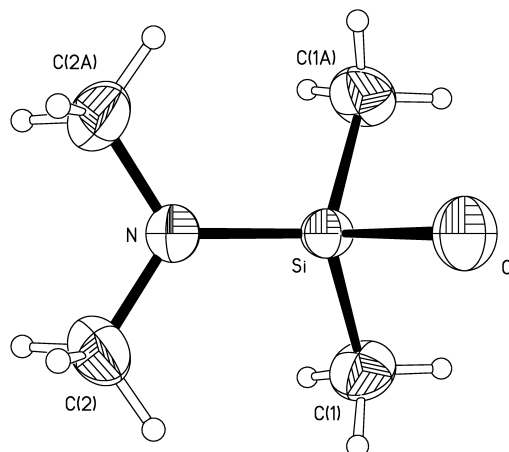


Fig. 1. Molecular structure of  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ . Selected bond lengths and angles ( $\text{Å}/^\circ$ ): Si-N 1.686(2), Si-C 1.851(1), Si-Cl 2.109(1), N-C 1.446(2), C-Si-C 112.3(1), N-Si-Cl 111.7(1), C-Si-Cl 105.1(1), C-N-C 112.8(2), Si-N-C 123.4(1).

Dimethyl-bis-(dimethylamino)silane,  $(\text{Me}_2\text{N})_2\text{SiMe}_2$ , was prepared from dimethylamine and dichlorodimethylsilane, and chlorodimethyl(dimethylamino)silane,  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ , was obtained from the latter by equilibration with dichlorodimethylsilane. Both syntheses are established literature procedures [10]. The distilled compounds, sealed in thin-walled glass capillaries, were used for *in situ* crystallisation experiments, which afforded single crystals suitable for single crystal X-ray diffraction.

Chlorodimethyl(dimethylamino)silane,  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ , crystallises in the monoclinic space group  $C2/m$ . The molecular structure is shown in Fig. 1, selected bond lengths and angles are listed in the figure caption. The molecules of  $\text{Me}_2\text{NSiMe}_2\text{Cl}$  have  $C_s$  symmetry. The nitrogen atom's coordination sphere is planar with the  $\text{C}_2\text{N}$  plane being perpendicular to the mirror plane of the molecule. Expectedly, the Si-N-C angles ( $123.4(1)^\circ$ ) are larger than the C-N-C angle ( $112.8(2)^\circ$ ). The Si-N bond length is 1.686(2) Å which is longer than in  $\text{Me}_2\text{NSiCl}_3$  (1.665(3) Å) [9], but shorter than in  $\text{Me}_2\text{NSiMe}_3$  (1.719(1) Å) [11]. This demonstrates its dependence on the number of electronegative substituents at the silicon atom. The Si-Cl and Si-C distances are of standard lengths. The coordination geometry about the silicon atom deviates slightly from a tetrahedral surrounding. Only the angles Cl-Si-C at  $105.1(1)^\circ$  are smaller than the tetra-

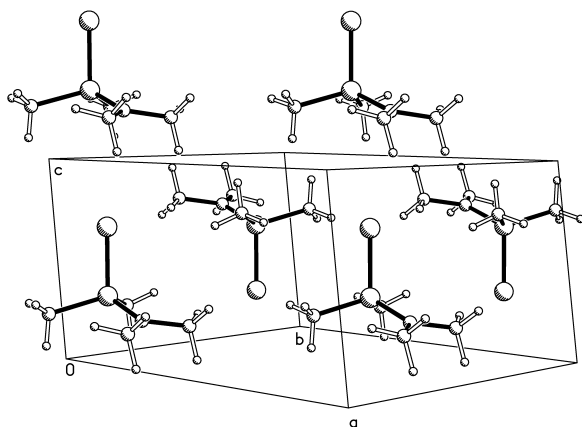


Fig. 2. Packing diagram of  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ .

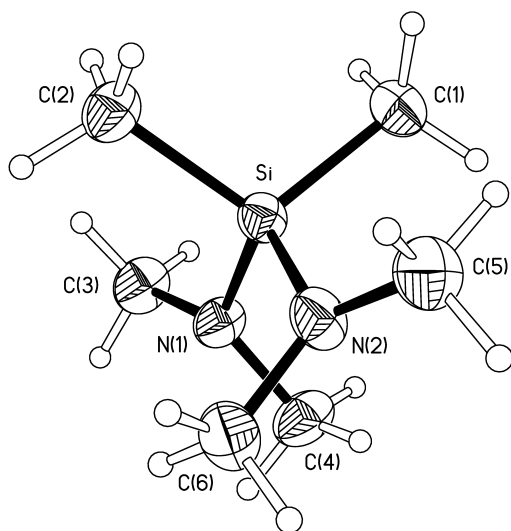


Fig. 3. Molecular structure of  $(\text{Me}_2\text{N})_2\text{SiMe}_2$ . Selected bond lengths and angles ( $\text{\AA}/^\circ$ ): Si-N(1) 1.725(1), Si-N(2) 1.719(1), Si-C(1) 1.868(1), Si-C(2) 1.867(1), N(1)-C(3) 1.447(1), N(1)-C(4) 1.451(2), N(1)-Si-N(2) 105.7(1), N(1)-Si-C(1) 113.6(1), N(1)-Si-C(2) 107.4(1), N(2)-Si-C(1) 108.0(1), N(2)-Si-C(2) 113.9(1), C(3)-N(1)-C(4) 111.6(1), Si-N(1)-C(3) 122.4(1), Si-N(1)-C(4) 120.0(1).

hedral angle, whereas all other angles are larger than  $109.5^\circ$ : N-Si-Cl ( $111.7(1)^\circ$ ), N-Si-C ( $111.2(1)^\circ$ ) and C-Si-C ( $112.3(1)^\circ$ ).

Figure 2 shows the packing diagram of  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ . The molecules are arranged in the crystal so that one Si-Cl bond points to the silicon atom of the next molecule in order to maximize dipole-dipole interactions. The intermolecular Cl $\cdots$ Si distance is  $4.220(1) \text{\AA}$  and thus far too large to be discussed as a bonding or van-der-Waals interaction.

Dimethylbis(dimethylamino)silane,  $(\text{Me}_2\text{N})_2\text{SiMe}_2$ , crystallises in the monoclinic space group  $P2_1/c$ . There are no intermolecular contacts of exceptional shortness. The molecular structure is shown in Fig. 3, selected bond lengths and angles are listed in the figure caption. The molecules of  $(\text{Me}_2\text{N})_2\text{SiMe}_2$  have approximate  $C_2$  symmetry. The coordination sphere of the nitrogen atoms is not completely but almost planar with the sum of angles about these atoms being  $354.0$  and  $355.8^\circ$ . As in  $\text{Me}_2\text{NSiMe}_2\text{Cl}$  and many other dialkylaminosilanes, the Si-N-C angles [ $120.0(1)$  to  $123.5(1)^\circ$ ] are larger than the CNC angles [ $111.6(1)$  and  $111.9(1)^\circ$ ]. The Si-N bond lengths are  $1.719(1)$  and  $1.725(1) \text{\AA}$  and thus longer than in  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ , which bears a Cl substituent at the silicon atom. The Si-C distances [ $1.868(1)$  and  $1.869(1) \text{\AA}$ ] are slightly longer than in  $\text{Me}_2\text{NSiMe}_2\text{Cl}$  at  $1.851(1) \text{\AA}$ . The silicon atom has a distorted tetrahedral coordination geometry with the smallest angle being N-Si-N at  $105.7(1)^\circ$ , a C-Si-C angle of  $108.4(1)^\circ$  and the N-Si-C angles falling over a range between  $107.4(1)$  and  $113.9(1)^\circ$ .

### Experimental Section

#### Crystal structure determination of $\text{Me}_2\text{NSiMe}_2\text{Cl}$ and $(\text{Me}_2\text{N})_2\text{SiMe}_2$

Single crystals of  $\text{Me}_2\text{NSiMe}_2\text{Cl}$  and  $(\text{Me}_2\text{N})_2\text{SiMe}_2$  were grown *in situ* on the diffractometer by slowly cooling the melt in a sealed capillary below the melting point after generation of a suitable seed crystal. Data collection was undertaken with a Nonius DIP2020 diffractometer. Crystal data for  $\text{Me}_2\text{NSiMe}_2\text{Cl}$ ,  $\text{C}_4\text{H}_{12}\text{NSiCl}$ ,  $M_r = 137.69$ , crystal system monoclinic, space group  $C2/m$ ,  $Z = 4$ ,  $a = 11.8892(3)$ ,  $b = 10.6304(3)$ ,  $c = 6.3063(3) \text{\AA}$ ,  $\beta = 97.3629(17)^\circ$ ,  $V = 790.46(5) \text{\AA}^3$  at  $143(2) \text{K}$ ,  $\mu = 0.537 \text{mm}^{-1}$ .  $2\theta_{\text{max}} = 63.86^\circ$ , 16340 scattering intensities collected of which 1309 were unique ( $R_{\text{int}} = 0.030$ ), 61 parameters,  $R_1 = 0.0449$  for 1263 reflections with  $F_o > 4 \sigma(F_o)$  and  $wR_2 = 0.1297$  for all 1309 data. Crystal data for  $(\text{Me}_2\text{N})_2\text{SiMe}_2$ ,  $\text{C}_6\text{H}_{18}\text{N}_2\text{Si}$ ,  $M_r = 146.31$ , crystal system monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 9.5583(2)$ ,  $b = 7.7879(1)$ ,  $c = 13.4111(3) \text{\AA}$ ,  $\beta = 103.4749(8)^\circ$ ,  $V = 970.83(3) \text{\AA}^3$  at  $138(2) \text{K}$ ,  $\mu = 0.177 \text{mm}^{-1}$ .  $2\theta_{\text{max}} = 63.96^\circ$ , 44227 scattering intensities collected of which 3209 were unique ( $R_{\text{int}} = 0.037$ ), 155 parameters,  $R_1 = 0.0445$  for 2988 reflections with  $F_o > 4 \sigma(F_o)$  and  $wR_2 = 0.1285$  for all 3209 data. Structure solutions and refinements were undertaken with the program SHELXTL 5.01 [12]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publica-

tion no. CCDC-206824 and CCDC-206825 ( $\text{Me}_2\text{NSiMe}_2\text{Cl}$ ) ( $(\text{Me}_2\text{N})_2\text{SiMe}_2$ ). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

#### Acknowledgements

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

- 
- [1] K. Hedberg, *J. Am. Chem. Soc.* **77**, 6491 (1955).  
[2] N. W. Mitzel, J. Riede, A. Schier, M. Paul, H. Schmidbaur, *Chem. Ber.* **126**, 2027 (1993).  
[3] C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, *J. Mol. Struct.* **6**, 231 (1970).  
[4] G. Gundersen, R. A. Mayo, D. W. H. Rankin, *Acta Chem. Scand.* **38**, 579 (1984).  
[5] K. Ruhlandt-Senge, R. A. Bartlett, M. M. Olmstead, P. P. Power, *Angew. Chem.* **105**, 459 (1993); *Angew. Chem. Int. Ed.* **32**, 425 (1993).  
[6] N. W. Mitzel, K. Angermaier, H. Schmidbaur, *Organometallics* **13**, 1762 (1994).  
[7] N. W. Mitzel, E. Breuning, A. J. Blake, H. E. Robertson, D. W. H. Rankin, B. A. Smart, *J. Am. Chem. Soc.* **118**, 2664 (1996).  
[8] N. W. Mitzel, H. Oberhammer, *Inorg. Chem.* **37**, 3593 (1998).  
[9] N. W. Mitzel, *Z. Naturforsch.* **58b**, 369 (2003).  
[10] S. S. Washburne, W. R. Peterson, *J. Organomet. Chem.* **21**, 59 (1970).  
[11] A. J. Blake, E. A. V. Ebsworth, D. W. H. Rankin, H. E. Robertson, D. E. Smitj, A. J. Welch, *J. Chem. Soc. Dalton Trans.* 91 (1986).  
[12] SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc. Madison, WI (1995).