Three-Membered Ring Formation by Si···N Interactions in Aminosulfenylsilanes

Norbert W. Mitzel

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)25183360 07.
E-mail: mitzel@uni-muenster.de

Z. Naturforsch. **58b**, 369–374 (2003); received February 24, 2003

The reaction of dimethylaminosulfenylchloride Me_2NSCl with trichlorosilane $HSiCl_3$ and triethylamine gives elemental sulphur and Me_2NSiCl_3. The aminosulfenylsilane $Me_2NSSiCl_3$ is postulated to be an intermediate of this reaction. *Ab initio* calculations (MP2/6–311G(d,p)) on Me_2N-S-SiH_3, Me_2N-S-SiH_2Cl, Me_2N-S-SiH_2F, and Me_2N-S-$SiCl_3$ have been carried out, demonstrating the occurrence of acute valence angles at sulphur and short Si···N distances, which are indicative of NSSi three-membered rings. The strength of the Si···N interactions depends on the electronegativity of the substituent at silicon in *anti*-position to the nitrogen atom and is strongest in the *anti* conformer of Me_2N-S-SiH_2F (< NSSi 68°, Si···N 2.208 Å). The coordination spheres of the nitrogen atoms in the Me_2N-S-SiR_3 molecules are steeply pyramidal, which is in contrast to the planarised N atoms in other $SNMe_2$ compounds, such as Me_2NSCl. The crystal structure of this compound has been determined, as well as that of the product of the above reaction, Me_2NSiCl_3. Both have planar coordination geometries at the nitrogen atoms.

Key words: Sulfur, Silicon, Crystal Structure

Introduction

Aminoxysilanes R'_2N-O-SiR_3 have been shown to possess attractive interactions between the silicon and nitrogen atoms, which lead to hypercoordinate Si centres and three-membered ring systems in some extreme cases [1]. Such non-classical bonding was observed to be most pronounced for O-silylhydroxylamines with electronegative substituents bonded to the silicon atoms. SiON triangular structures with acute angles at oxygen have been found in Me_2NOSiF_3 with a short Si···N distance of 1.963(1) Å and a valence angle of 77.1(1)° in the polar surrounding of the solid state [2]. Weaker interactions are present in isolated molecules in the gas phase (Si···N 2.273(17) Å, < SiON 94.4(9)°). The strength of these Si···N interactions depends also on the position of the electronegative substituent at silicon relative to the donor centre. The vapour of Me_2NOSiH_2Cl comprises two conformers, *anti* with an NOSiCl torsional angle of 180° having strong Si···N interactions and *gauche* with an NOSiCl torsional angle of 73° having a 0.308 Å wider Si···N distance and a 17° wider SiON angle [3].

Systems with linking atoms between the Si acceptor and the N donor centres different from oxygen are structurally much less well established. Silylhydrazines have been investigated and similar effects as described above have been found to be structure-determining in SiNN units [4]. However, in studies on aminomethylsilanes $R''_2NCR'_2SiR_3$ we could so far not find experimental proof for Si···N interactions, although earlier reports postulated them on the basis of reduced basicities of compounds $R''_2NCR'_2SiR_3$ as compared to carbon analogues $R''_2NCR'_2CR_3$ [5].

The aim of this contribution was initially to investigate compounds of the R'_2NSSiR_3 type, *i.e.* aminosulfenylsilanes (silylthiohydroxylamines), as we expected stronger Si···N interactions in such compounds due to the lower bending potential at the sulphur centres. We can show now on a theoretical basis that the Si···N interactions in NSSi systems depend on the same parameters as they do in NOSi systems.

To our knowledge the only Si-S-N compounds reported in the literature are $Me_2NSO_2SiMe_3$ and $Me_2NSSiMe_3$ [6], but no synthesis has been published for the latter.

Results

In an attempt to prepare a compound with an Si-S-N linkage which can serve as starting material

0932–0776/03/0500–0369 $06.00

for a series of derivatives, we tried to obtain $Me_2NSSiCl_3$ from the readily available dimethylaminosulfenylchloride under the conditions of a Benkeser type reaction [7], *i.e.* treatment with trichlorosilane and triethylamine. However, the reaction product consisted of elemental sulphur and a colourless liquid, which turned out to be free of sulphur and to contain a direct N-Si bond: Me_2NSiCl_3.

$$Me_2N\text{-}S\text{-}Cl + HSiCl_3 + NEt_3 \xrightarrow{-//\rightarrow} Me_2N\text{-}S\text{-}SiCl_3 \xrightarrow{} Me_2N\text{-}SiCl_3 + S$$

As it seems unlikely that the reactive intermediate of a trichlorosilane/triethylamine mixture (either the anionic Cl_3Si^- or the silylene Cl_2Si:) attacks the nitrogen centre of Me_2N-S-Cl, we propose that an intermediate Me_2N-S-$SiCl_3$ was formed, which decomposed with sulphur extrusion to give Me_2NSiCl_3.

In addition to the spectroscopic identification of the product mixture, the educt Me_2NSCl and the product Me_2NSiCl_3 were characterised structurally by means of X-ray diffraction on single crystals grown from these low melting liquids by in-situ methods. These structures will be discussed in the next paragraphs followed by a theoretical study of some model compounds containing NSSi units.

Crystal structure of Me_2NSCl. The molecular structure of Me_2NSCl in the crystal is shown in Fig. 1, selected structural parameters are listed in Table 1 together with those calculated *ab initio* (MP2/6–311G(d,p)) for a monomeric Me_2SNCl unit and a weakly bound dimer in the gas-phase. It is the first experimental structural study on an aminosulfenylchloride in the solid state. The fluorinated $(F_3C)_2NSCl$ was studied by electron diffraction in the gas phase by Oberhammer and co workers [8] and the structural parameters of this study are also given in Table 1. Me_2NSCl crystallises as a weakly bonded dimer with a centre of inversion in the S_2N_2 ring. The N···S contacts are 3.174(1) Å long, which is slightly shorter than the sum of the van-der-Waals radii of 3.39 Å [9]. In the calculated dimer, these weak contacts are predicted to be 2.992 Å, *i.e.* even shorter than found in the solid state. Otherwise the geometries of the calculated and experimentally examined dimers are very similar, as is obvious from the contents of Table 1.

Unexpectedly, the NSCl angle of 107.1(1)° is relatively wide, as compared to $(Me_2N)SO_2Cl$

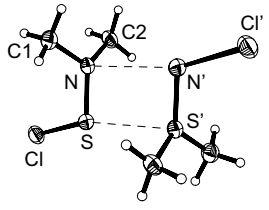

Fig. 1. Molecular structure of Me_2NSCl as obtained by low-temperature single crystal X-ray diffraction.

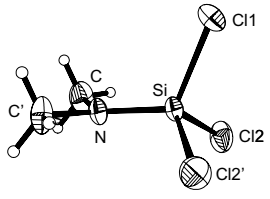

Fig. 2. Molecular structure of Me_2NSiCl_3 as obtained by low-temperature single crystal X-ray diffraction.

Table 1. Geometrical parameters (Å/°) of $(Me_2NSCl)_2$ as determined by low-temperature X-ray crystallography and by *ab initio* calculations of the monomer and dimer on the MP2/6–311G(d,p) level of theory. The last column shows values from the gas-phase electron diffraction (GED) structure determination of $(F_3C)_2NSCl$ for comparison.

	$(Me_2NSCl)_2$ XRD	Me_2NSCl MP2/6–311G(d,p)	$(Me_2NSCl)_2$ MP2/6–311G(d,p)	$(F_3C)_2NSCl$ GED
S-N	1.604(1)	1.630	1.636	1.667(7)
S-Cl	2.171(1)	2.163	2.154	2.090(8)
N-C(1/2)	1.462(1)/1.466(1)	1.465	1.464	1.453(5)
N-S-Cl	107.1(1)	106.1	105.1	98.3(13)
S-N-C(1/2)	120.0(1)/120.0(1)	117.9	117.8	121.5(6)
C-N-C	115.0(1)	113.5	113.6	116.4(18)
S···N	3.174(1)	–	2.992	–
N-S···N	86.9(1)	–	83.0	–

Table 2. Geometrical parameters (Å/°) of Me_2NSiCl_3 as determined by low-temperature X-ray crystallography (XRD) and gas-phase electron diffraction (GED) [12].

	XRD	GED
Si-N	1.665(3)	1.657(12)
Si-Cl(1)	2.020(1)	2.023(5)
Si-Cl(2)	2.043(1)	
N-C	1.459(3)	1.446(12)
Si-N-C	123.0(2)	123.1(8)
C-N-C	112.6(3)	113.1(18)
N-Si-Cl(1)	116.7(1)	111.3(1)
N-Si-Cl(2)	109.9(1)	

(103.0°) [10], $(F_3C)_2NSCl$ (98.2(13)°) [8] or the ClSCl angle in SCl_2 (102.71°) [11]. With 1.604(1) Å the S-N bond is shorter than the sum of the covalent radii of sulphur and nitrogen (1.74 Å) [9], but also shorter than in $(F_3C)_2NSCl$ with 1.667(7) Å [8]. This points to some multiple bond character of the S-N bond, resulting in an almost planar coordination geometry at the nitrogen atom, with the sum of angles about it being 354.9(1)°, which was also found in $(F_3C)_2NSCl$ [8]. It also parallels the situation in compounds with the nitrogen atom bonded to silicon (see below) or phosphorus [12]. Expectedly, the differences between the calculated dimer and monomer are very small. The largest difference is an elongation of the S-N bond by as little as 0.006 Å and a compression of the NSCl angle by 1.0°. An estimate of the interaction energy between the two monomers is given by the calculated difference between the energies of dimer and monomer, which is 4.4 kJ/mol at the B3LYP/6–311G(d,p) level of theory and based on fully geometry optimised structures at this level.

Crystal structure of Me_2NSiCl_3. The molecular structure of Me_2NSiCl_3 was determined earlier in the gas-phase by electron diffraction [13] and we shall refer to this structure of the free molecule in comparison to our new solid state structure. The molecules of Me_2NSiCl_3 lie on a crystallographic mirror plane bisecting the CNC angle and containing one of the chlorine atoms, Cl(1). The molecule has thus C_S symmetry, but no local C_3 symmetry for the $NSiCl_3$ group, as was assumed in the gas phase structure determination. This is manifested by the two different NSiCl angles of 116.7(1)° for NSiCl(1) and 109.9(1)° for NSiCl(2). Their mean of 112.2° is reasonably close to the reported gas phase value of 111.3°. The same applies to the different lengths of the Si-Cl bonds of 2.020(1) for SiCl(1) and 2.043(1) Å for SiCl(2), which compares to 2.023(5) Å in the gas phase. The coordination sphere of nitrogen is planar as is indicated by the sum of angles about this atom: 358.6° (gas phase 359.3°). Wide SiNC angles of 123.0(1)° and a smaller CNC angle of 112.6(3)° are observed in the solid state structure. The Si-N distance of 1.665(3) Å represents a short Si-N bond, as is expected for a silylamine with electronegative substituents at the silicon atom.

Including the two structure determinations reported in this paper, structures of the whole series of amino derivatives of chlorinated second octet period element compounds Me_2NSiCl_3, Me_2NPCl_2 [14] and Me_2NSCl are now available and consistently show planar environments of the nitrogen atoms.

Calculations on Si-S-N model compounds. A reaction of Me_2NSCl with $HSiCl_3/NEt_3$ could involve a Si-S-N three-membered ring intermediate with an Si···N interaction. In order to get an estimate of whether the formation of Si···N interactions is a possibility for the sulphur compounds of this type, $Me_2N\text{-}S\text{-}SiX_3$, we calculated the structures of four examples by *ab initio* methods: $Me_2N\text{-}S\text{-}SiH_3$, $Me_2N\text{-}S\text{-}SiH_2Cl$, $Me_2N\text{-}S\text{-}SiH_2F$ and $Me_2N\text{-}S\text{-}SiCl_3$. The calculations were performed up to the MP2/6–311G(d,p) level of theory, which turned out to give results closest to experimental gas phase structures for Me_2NOSiF_3. DFT calculations on Me_2NOSiF_3 did not reproduce the experimental gas-phase values and were therefore not applied to the new SiSN systems [2].

The results of the calculations are shown in Fig. 3, and some key parameters are compiled in Table 3. Coordinates of the calculated structures are listed in Table 4.

The calculations show strong deformations of the valence angles at the sulphur atoms in Me_2NSSiH_3, Me_2NSSiH_2F, Me_2NSSiH_2Cl and $Me_2NSSiCl_3$. Expectedly, the weakest Si···N interaction is found in Me_2NSSiH_3, with a Si···N distance of 2.774 Å, which is still below the sum of the vander-Waals radii of 3.54 Å. The angle at sulphur (90.2°) has to be compared with the angle at oxygen in the homologous compound Me_2NOSiH_3, which was determined in a crystal structure to be

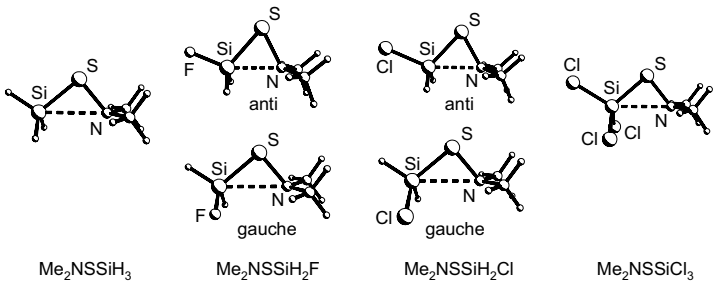

Fig. 3. Molecular structures of Me_2NSSiH_3, Me_2NSSiH_2F, Me_2NSSiH_2Cl and $Me_2NSSiCl_3$ as obtained by *ab initio* calculations on the MP2/6–311G(d,p) level.

Table 3. Selected geometric parameters (Å/°) and dipole moments [D] for Me_2NSSiH_3, Me_2NSSiH_2F, Me_2NSSiH_2Cl and $Me_2NSSiCl_3$ as obtained by *ab initio* calculations on the MP2/6–311G(d,p) level. For Me_2NSSiH_2F and Me_2NSSiH_2Cl only the *anti*-conformers are reported.

	Me_2NSSiH_3	**Me_2NSSiH_2F**		**Me_2NSSiH_2Cl**		**$Me_2NSSiCl_3$**
		anti	*gauche*	*anti*	*gauche*	
Si-S	2.134	2.129	2.112	2.120	2.116	2.098
S-N	1.766	1.790	1.766	1.784	1.764	1.762
Si···N	**2.774**	**2.208**	**2.750**	**2.315**	**2.762**	**2.675**
Si-S-N	90.2	68.0	89.9	72.2	90.3	87.3
S-N-C	110.5	112.2	110.4/110.5	111.9	110.5/110.6	110.9
C-N-C	110.8	112.3	111.0	112.0	110.0	111.3
μ	1.33	4.40	1.88	4.73	2.20	3.42

102.6(1)° [15], bearing in mind that valence angles at sulphur are generally smaller in homologous compounds.

As found experimentally for the SiON compounds Me_2NOSiF_3 [2] and Me_2NOSiH_2Cl [3] and predicted theoretically for Me_2NOSiH_2F [16], substitution of the silicon bound hydrogen atoms for electronegative substituents leads to a drastic decrease of the SiON angle. Our new calculations predict a similar behaviour for the thiohydroxylamines. The valence angle at the sulphur atoms in the *anti* conformers of Me_2NSSiH_2F and Me_2NSSiH_2Cl are calculated to be as small as 68.0 and 72.2°, corresponding to Si···N distances of 2.208 and 2.315 Å, respectively. The calculated values for the oxygen analogues *anti*-Me_2NOSiH_2F and *anti*-Me_2NOSiH_2Cl are 2.229 and 2.259 Å, *i.e.* very similar. Note that all these are gas-phase values and even stronger interactions have to be anticipated for solution, in particular for polar solvents or the solid state, as was shown to be the case for Me_2NOSiF_3 (<SiON gas phase 94.4(9), solid state 77.1(1)°) [2] and Me_2NOSiH_2Cl (<SiON gas phase 104.7(10), solid state 79.7(1)°) [3].

In the *gauche* conformers of Me_2NSSiH_2F and Me_2NSSiH_2Cl the corresponding NSSi angles are much larger than in the *anti* conformers (89.9 and 90.3°), which represents a widening of 21.9 and 18.1°, respectively. Similar behaviour was also observed for Me_2NOSiH_2Cl, which has an SiON angle 17° wider in the *gauche*- than in the *anti*-conformer. Despite these large structural differences between the conformers, their energies are surprisingly similar. In both cases, Me_2NSSiH_2F and Me_2NSSiH_2Cl, the *anti*-conformers represent the ground state, but the *gauche*-conformers are only 4 and 5 kJ mol^{-1} higher in energy.

The SiSN angle in $Me_2NSSiCl_3$ is predicted to be as much as 15° larger than in Me_2NSSiH_2Cl, an effect which was found earlier for the pair of hydroxylamines $Me_2NOSiCl_3$ [17] and Me_2NOSiH_2Cl [3]. It is probably due to the steric requirement of the comparably large Cl atoms at the silicon centre, which make an increase of the coordination number less favourable.

The molecular dipole moments have also been calculated and are strongly dependent on the substituents at silicon. The highest dipole moment of 4.73 D is found for Me_2NSSiH_2Cl, the smallest of 1.33 D for Me_2NSSiH_3.

The Si···N interactions in SiSN compounds lead to a distortion of the coordination geometries at

Table 4. Coordinates for Me_2NSSiH_3, Me_2NSSiH_2F, Me_2NSSiH_2Cl and $Me_2NSSiCl_3$ as obtained by *ab initio* calculations on the MP2/6–311G(d,p) level.

	Me_2NSSiH_3			***anti*-Me_2NSSiH_2F**			***anti*-Me_2NSSiH_2Cl**			***$Me_2NSSiCl_3$***		
Si1	0.000	0.000	0.000	0.788	– 0.990	0.000	0.000	0.000	0.000	0.000	0.749	0.000
S2	0.000	0.000	2.134	– 1.207	– 0.248	0.000	0.000	0.000	2.120	1.396	– 0.817	0.000
N3	1.766	0.000	2.139	0.000	1.073	0.000	1.699	0.000	1.573	0.026	– 1.926	0.000
H/F/Cl4	– 1.411	0.000	– 0.439	0.733	– 2.617	0.000	– 1.962	0.000	– 0.706	1.041	2.502	0.000
H/Cl5	0.679	– 1.207	– 0.501	1.482	– 0.658	1.250	0.576	– 1.240	– 0.527	– 1.191	0.716	1.647
H/Cl6	0.679	1.207	– 0.501	1.482	– 0.658	– 1.250	0.576	1.240	– 0.527	–1.191	0.716	– 1.647
C7	2.277	1.205	2.795	– 0.068	1.887	– 1.216	2.406	1.215	1.986	0.022	– 2.753	– 1.210
C8	2.277	– 1.205	2.795	– 0.068	1.887	1.216	2.406	– 1.215	1.986	0.022	– 2.753	1.210
H9	1.907	2.087	2.271	0.032	1.238	– 2.087	1.866	2.088	1.618	– 0.011	– 2.110	– 2.090
H10	3.369	1.189	2.736	0.760	2.602	– 1.200	3.406	1.197	1.543	– 0.880	– 3.371	– 1.190
H11	1.977	1.271	3.853	– 1.021	2.429	– 1.283	2.492	1.284	3.079	0.905	– 3.406	– 1.275
H12	1.907	– 2.087	2.271	0.033	1.238	2.087	1.866	– 2.088	1.618	– 0.011	– 2.110	2.090
H13	3.369	– 1.189	2.737	0.760	2.602	1.200	3.406	– 1.197	1.543	–0.880	– 3.371	1.190
H14	1.977	– 1.271	3.853	– 1.021	2.429	1.283	2.492	– 1.284	3.079	0.905	– 3.406	1.275

	***gauche*-Me_2NSSiH_2F**			***gauche*-Me_2NSSiH_2Cl**		
Si1	– 1.611	– 0.377	0.297	– 1.183	– 0.903	0.274
S2	0.126	– 0.796	– 0.828	0.630	– 0.904	– 0.817
N3	1.077	0.200	0.278	1.292	0.323	0.263
H4	– 2.717	– 1.144	– 0.298	– 2.044	– 1.948	– 0.300
F5/Cl5	– 1.989	1.191	0.200	– 2.198	0.878	0.104
H6	– 1.389	– 0.699	1.709	– 0.912	– 1.117	1.698
C7	2.180	– 0.578	0.845	2.490	– 0.179	0.939
C8	1.575	1.396	– 0.408	1.583	1.555	– 0.473
H9	1.778	– 1.436	1.386	2.236	– 1.073	1.512
H10	2.720	0.063	1.548	2.840	0.596	1.627
H11	2.883	– 0.938	0.078	3.300	– 0.427	0.236
H12	0.729	1.970	– 0.788	0.669	1.922	– 0.940
H13	2.116	2.003	0.324	1.938	2.301	0.244
H14	2.250	1.155	– 1.244	2.350	1.412	– 1.251

the nitrogen and silicon atoms. The nitrogen atoms in all calculated compounds adopt steeply pyramidal coordination geometries with sums of angles between 331.8 (Me_2NSSiH_3) and 336.5° (*anti*-Me_2NSSiH_2F), which is clearly at variance with the strongly planarised nitrogen atom in Me_2NSCl (sum of angles 355°) and other Me_2NS-compounds.

The pre-coordination of the Si···N type in the SiSN compounds makes the process of sulphur extrusion from the compound $Me_2NSSiCl_3$ quite likely, if a process exists in which the sulphur atom can be transferred. Insertion into an existing S-S chain could be such a possibility, but much more experimental and theoretical work has to follow to verify such a working hypothesis. However, it would be a possible explanation for our experimental observation that Me_2NSCl reacts with H_3SiCl and NEt_3 to give Me_2NSiCl_3 and sulphur with $Me_2NSSiCl_3$ as a transient species.

Experimental Section

Aminosulfenylchloride was prepared as described in the literature [18].

Reaction of Me_2NSCl with ClH_3Si and NEt_3: Under rigorous inert gas conditions triethylamine (9.6 mL, 70 mmol) and Me_2NSCl (6.7 g, 70 mmol) were dissolved in diethyl ether (150 mL) and cooled to – 10 °C. $HSiCl_3$ (7.8 ml) was added dropwise, whereupon a colourless precipitate formed and the yellow-orange solution became pale yellow. The mixture was filtered and the residue washed with two times 10 ml of ether. The solvent was removed from the ether phase by distillation over a 10 cm Vigreux column. The distillation residue, a yellowish liquid containing some solid, was

condensed into a cold trap in vacuum. It was identified by ^{1}H NMR, ^{29}Si NMR, GC-MS and X-ray crystallography as Cl_3SiNMe_2.

Crystal structure determination of Me_2NSCl and Me_2NSiCl_3. Single crystals of Me_2NSCl and Me_2NSiCl_3 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 Turbo-CAD4 diffractometer.

Crystal data Me_2NSCl, C_2H_6NSCl, M_r = 111.59, crystal system monoclinic, space group $P2_1/c$, Z = 4, a = 5.8213(3), b = 10.7705(7), c = 8.3786(6) Å, β = 101.419(5)°, V = 514.93(6) Å^3 at 133(2) K, μ = 0.976 mm^{-1}. $2\theta_{max.}$ = 70°, ω-scan, 8741 scattering intensities collected of which 2244 were unique [R_{int} = 0.1072], 70 parameters, R_1 = 0.0332 for 2038 reflections with $F_o > 4\ \sigma(F_o)$ and wR_2 = 0.0880 for all 2244 data.

Crystal data Me_2NSiCl_3, $C_2H_6NSiCl_3$, M_r = 178.52, crystal system monoclinic, space group P_1/m, Z = 2, a = 6.086(1), b = 10.450(2), c = 6.334(1) Å, β = 111.86(1)°, V = 373.90(6) Å^3 at 143(2) K, μ = 1.279 mm^{-1}. $2\theta_{max.}$ = 54°, ω-scan, 862 scattering intensities collected of which 793 were unique [R_{int} = 0.0345], 49 parameters, R_1 = 0.0456 for 740 reflections with $F_o > 4\ \sigma(F_o)$ and wR_2 = 0.1268 for all 793 data.

Structure solutions and refinements were undertaken with the program SHELXTL 5.01 [19]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-204077 (Me_2NSCl) and CCDC-204078 (Me_2NSiCl_3). 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. Mrs. Daniela Arnold is thanked for part of the preparative work.

[1] N. W. Mitzel, U. Losehand, Angew. Chem. **109**, 2897 (1997); Angew. Chem. Int. Ed. **24**, 2807 (1997).
[2] N. W. Mitzel, U. Losehand, A. Wu, D. Cremer, D. W. H. Rankin, J. Am. Chem. Soc. **112**, 4471 (2000).
[3] N. W. Mitzel, U. Losehand, J. Am. Chem. Soc. **120**, 7320 (1998).
[4] N. W. Mitzel, C. Kiener, D. W. H. Rankin, Organometallics **18**, 3437 (1999).
[5] V. P. Feshin, M. G. Voronkov, J. Mol. Struct. **83**, 317 (1982); F. G. Wilkinson, F. G. A. Stone, E. W. Abel, Comprehenshive Organometallic Chemistry, 1st Ed. Pergamon Press: Oxford, 1982, Board 2, p. 412; R. G. Kostyanovskii, A. K. Prokof'ev, Dokl. Akad. Nauk SSSR **164**, 1054 (1965); V. F. Mironov, A. L. Kravchenko, Izv. Akad. Nauk SSSR, Ser. Khim. **9**, 1563 (1963); M. G. Vorkonkov, V. P. Feshin, V. F. Mironov, S. A. Mikahilyants, T. K. Gar, Zh. Obshch. Khim. **41**, 2211 (1971).
[6] N. Wiberg, G. Hübler, Z. Naturforsch. **32b**, 1003 (1977); K. Barlos, G. Hübler, H. Nöth, P. Wanninger, N. Wiberg, B. Wrackmeyer, J. Magn. Reson. **31**, 363 (1978).
[7] R. A. Benkeser, J. M. Gaul, W. E. Smith, J. Am. Chem. Soc. **83**, 1000 (1961).
[8] M. Korn, H.-G. Mack, W. Meckstroth, R. Minkwitz, H. Oberhammer, J. Mol. Struct. **471**, 79 (1998).
[9] J. Emsley, The Elements, 2nd Edition, Clarendon Press, Oxford (1991).
[10] I. Hargittai, J. Brunvoll, Acta Chem. Scand. A **30**, 634, (1976).
[11] L. Bizzocchi, L. Cludi, C. Degli Espoti, A. Giorni, J. Mol. Spectrosc. **275**, 204 (2000).
[12] N. W. Mitzel, J. Chem. Soc., Dalton Trans. 3239 (1998).
[13] W. Airey, C. Glidewell, A. G. Robiette, G. M. Sheldrick, J. M. Freeman, J. Mol. Struct. **8**, 423 (1971).
[14] N. W. Mitzel, J. Chem. Soc., Dalton Trans. 3239 (1998).
[15] U. Losehand, N. W. Mitzel, Inorg. Chem. **37**, 3175 (1998).
[16] N. W. Mitzel, A. J. Blake, D. W. H. Rankin, J. Am. Chem. Soc. **119**, 4143 (1997).
[17] N. W. Mitzel, U. Losehand, D. W. H. Rankin, J. Chem. Soc., Dalton Trans. 4291 (1999).
[18] W. H. Mueller, P. E. Butler, J. Org. Chem. **33**, 2111 (1968).
[19] SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc. Madison, WI (1995).